MULTIFUNCTIONAL PLASMONIC METASURFACES FOR INVERTED ORGANIC PHOTOVOLTAICS

By

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Emerging next-generation photovoltaic devices are fabricated from thin-films, with devices having thicknesses of less than 1 µm, because of the reduced material waste, lower embodied energy, and propensity for forming flexible, light-weight devices. However, thin-film photovoltaics have limited absorption of light close to the absorption band edge of the semiconducting photoactive layer. In addition, thin-film photovoltaics fabricated from amorphous semiconductors, such as amorphous Si or organic semiconductors, typically require semiconductor thicknesses of ~100 nm due to their low charge carrier mobilities and correspondingly low charge diffusion lengths. However, by restricting the semiconducting active layer thickness in order to efficiently collect photogenerated charge carriers at the electrodes, incomplete light absorption occurs throughout the visible spectrum. To satisfy these competing constraints on the active layer thickness, light trapping techniques are required to increase the amount of light absorbed in physically-thin active layers. Conventional light trapping in thick, crystalline Si photovoltaics is typically achieved using micron-scale photonic structures that are not suitable for thin-film photovoltaics, which have active layers that are thinner than the height of these structures. Additionally, it is difficult to trap light in active layers with thicknesses below the diffraction limit (thicknesses less than half a wavelength in the material) using conventional photonic designs (e.g. total internal reflection of light scattered from a roughened surface). As such, nanophotonic designs, such as plasmonic nanostructures, are necessary to enhance the amount of light that can be absorbed by thin-film semiconductors.
Here, we propose the use of multifunctional plasmonic metasurfaces to enhance the light trapping and absorption within physically-thin semiconductor active layers. Plasmonic metasurfaces are two-dimensional artificial materials composed of arrays of sub-wavelength metallic nanostructures where the macroscopic electromagnetic properties of the surface arise from the collective response of the individual nanostructures. They support both localized and propagating surface plasmon polaritons, which are hybrid light-charge density waves that exist at metal-dielectric interfaces and have strongly enhanced electric fields near the metal surface. Use of plasmonic metasurfaces in thin-film photovoltaics leads to enhanced absorption via: increased generation of charge carriers by local electric field enhancements; or increased optical path length through the semiconducting active layer either through light scattering from the nanostructures or by coupling the light to an in-plane waveguiding plasmonic mode. As such, thin-films of semiconductors can be both physically and electrically thin (i.e., thinner than the carrier diffusion length), but optically thick when employing plasmonic metasurfaces as electrodes. We gain further control of the properties of the electrode through application of an ultrathin interfacial layer, with thicknesses of less than 5 nm, which allows for tailoring the electronic properties (e.g., surface workfunction) while minimizing the impact on the optical properties of the resulting multifunctional plasmonic metasurface.

In this thesis, we designed and fabricated multifunctional plasmonic metasurfaces with a focus on organic conjugated polymers as thin-film semiconductor active layers. Conjugated-polymer-based organic photovoltaics have shown great potential as alternative energy sources due to their propensity for solution-based processing, rendering devices with the fastest manufacture and energy payback times of all photovoltaic technologies. Conjugated polymers are organic semiconductors composed of primarily earth-abundant elements, and their optical, electronic, and morphological properties can be tuned synthetically. Due to the formation of tightly-bound Frenkel excitons upon photoexcitation, conjugated polymers have strong absorption coefficients, rendering them opaque at film thicknesses on the order of several hundred
nanometers. However, like other organic semiconductors, conjugated polymers have low charge mobilities, restricting their thicknesses to less than ~100 nm to minimize charge recombination, thus necessitating the use of nanophotonic light trapping techniques.

Improvements in the efficiency of photovoltaics predominantly arise from increases in the photocurrent or the open-circuit voltage of the device. We begin this work by predicting the optimal planar metal electrode structure by calculating the performance parameters for two types of organic photovoltaic devices (conventional and inverted) with a range of electrode surface workfunctions. We show that highly-efficient and stable inverted organic photovoltaics can be achieved by selecting metal electrodes with low parasitic absorption and high workfunctions, which maximizes the photocurrent and open-circuit voltage of the device, respectively. Based on our calculations, Ag electrodes with ultrathin (less than 5 nm) native AgOₓ surface layers lead to inverted organic photovoltaic devices with maximal efficiencies due to the low parasitic absorption and high workfunction of AgOₓ/Ag electrodes. This is the first reported theoretical study that systematically compares the performance parameters of conventional and inverted devices considering a range of different metal electrode types.

Having predicted the optimal metal electrode and photovoltaic device structure, we design and fabricate plasmonic metasurfaces comprised of Ag nanoparticle arrays on Ag films to increase the active layer absorption in thin-film photovoltaics. We demonstrate that plasmonic metasurfaces comprised of low aspect ratio (height-to-diameter fraction) Ag nanoparticles can lead to enhanced absorption in organic active layers. We show that, in addition to the localized surface plasmon resonances (LSPRs) and propagating surface plasmon polaritons (SPPs), absorber-coated plasmonic metasurfaces can support a previously unidentified optical mode type called absorption-induced scattering (AIS). Through our systematic experimental and computational studies, we show that AIS originates from the low energy mode of hybrid plasmon-exciton coupled states, and gives rise to many of the red-edge absorption enhancements frequently observed in plasmon-enhanced organic photovoltaics. We further demonstrate that
SPPs with energies less than the AIS mode are out-coupled from absorber-coated metasurfaces for amorphous absorber coatings, but are trapped for semi-crystalline absorber coatings.

In addition to developing a deep understanding of how Ag plasmonic metasurfaces can be employed to enhance sub-wavelength light-trapping and absorption in thin-film organic photovoltaic active layers, we further develop a method of controlling the surface workfunction of plasmonic metasurfaces. We fabricate multifunctional plasmonic metasurfaces comprised of Ag metasurfaces with ultrathin interfacial layers to simultaneously control the optical and electronic properties of the metasurface. We employ monolayer MoS$_2$ and AgO$_x$ as ultrathin interfacial layers to minimize changes to the optical properties of the plasmonic metasurfaces. We show that, unexpectedly, the MoS$_2$ interfacial layer contributed to the charge photogeneration process, resulting in the formation of a hybrid MoS$_2$-organic active layer. We demonstrate ultrafast charge transfer between MoS$_2$ and the organic layer, and show that the absorption and total charge generation is enhanced in the presence of the Ag plasmonic metasurface. AgO$_x$, on the other hand, serves as a passive interfacial layer, and does not impact the optical properties of the Ag plasmonic metasurface. Thus, these multifunctional plasmonic metasurfaces allow for control of the optical properties of the electrode through the metasurface designs and the electrical properties through selection of ultrathin interfacial layers, which are expected to give rise to enhanced photocurrent and open-circuit voltage, respectively, in thin-film photovoltaic devices.
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Figure 1.18. LSPRs from prolate AgNRs in water ($\varepsilon_d = 1.77$) with short axes $b = c = 25$ nm and varying long axis, $a$. (a) Transverse and (b) longitudinal LSPRs for AgNR with $a = 75$ nm, shown for $\lambda = 390$ nm and 760 nm, respectively. (c) Scattering from AgNRs for varying $a$, calculated using finite-difference time-domain (FDTD) simulations.

Figure 1.19. Scattering from metal NPs in water ($\varepsilon_d = 1.77$) with $r = 25$ nm for the metals supporting the lowest loss plasmons in the visible. Note that the scattering intensity was reduced by factors of 5 and 3 for Ag and Al, respectively.

Figure 1.20 Possible morphologies of conjugated polymer crystallites. (a-c) In general, there are 3 possible configurations for polymer chains to crystallize: (a) edge-on, with the polymer backbone parallel to the substrate and the side chains perpendicular; (b) face-on, with the polymer backbone and side chains parallel to the substrate; and (c) vertical, with the polymer chains perpendicular to the substrate and the side chains parallel.
Figure 2.1. (a), Schematic illustrating the different configurations for the BHJ-OPV devices studied here: conventional devices (left) and inverted devices (right) which may lead to improved BHJ-OPV device operational lifetime. A metal oxide/fluoride layer was present in 6 of the electrodes studied, but not present in the studies involving bare metal electrodes. (b)-(c), Energy level diagrams (flat-band conditions) for the corresponding (b), conventional and (c), inverted devices (magnitude of the energy levels is shown). The range of metals and metal oxides studied and their associated workfunctions are: LiF (2.6 eV); Ba (2.7 eV); Ca (2.87 eV); Mg (3.66 eV); ZnO (4.0 eV, see below); Ag (4.26 eV); Al (4.28 eV); Cu (4.65 eV); NiO (5.0 eV); Ag$_2$O (5.0 eV); Au (5.1 eV); Ni (5.15 eV); CuO (5.3 eV); MoO$_3$ (5.35 eV) (data is given for polycrystalline materials). Note that although the workfunction of ZnO is typically cited between 4.1-4.4 eV, it is known to form an ohmic contact to PCBM, potentially due to formation of an interface dipole. Other energy level data was obtained/averaged from the following references: ITO (4.7 eV); PEDOT:PSS (5.1 eV); P3HT HOMO (5.0 eV); PCBM LUMO (4.0 eV).

Figure 2.2. Graphical user interface (GUI) associated with simulation setup from Lumerical FDTD Solutions. (a) 3D perspective GUI associated with conventional devices simulated (Cu cathode shown here), showing entire simulation region including the source and monitors. (b) $x$-$z$ plane associated with device from (a), where the boundary conditions and mesh are shown (0.1 nm $dz$ mesh step size used here for comparison with transfer matrix method).

Figure 2.3. Calculated $J_{sc}$ from BHJ-OPV devices with varying the thicknesses of the P3HT:PCBM and PEDOT:PSS layers. The device structure was ITO (100 nm)/ PEDOT:PSS (varied from 10 nm to 50 nm, with 10 nm intervals) / P3HT:PCBM (varied from 20 nm to 240 nm, with 20 nm intervals) / Al (200 nm). The colorbar is for $J_{sc}$, calculated as described in Section 2.3.1.4.

Figure 2.4. Calculated $V_{oc}$ (top panel), $FF_0$ (middle panel) and $FF$ (bottom panel) as functions of increasing workfunction for the nine bare metal and six coated metal electrodes studied. For inverted devices, calculations were performed for both a slope parameter, $S_a$, of 1.0 (for all bare and coated metal anodes; solid symbols) and $S_a$ of 0.1 (for all bare metal and only $p$-type coated metal anodes; hollow symbols). For conventional devices, calculations were performed for both a slope parameter, $S_c$, of 1.0 (for all bare and coated metal cathodes; solid symbols) and $S_c$ of 0.1 (for all bare metal and only $n$-type coated metal cathodes; hollow symbols). Symbols with blue outlines denote values calculated for $p$-type metal oxides and symbols with green outlines denote values calculated for the $n$-type metal oxide and fluoride. Equivalent circuit values used for the $FF_0$ and $FF$ calculations are shown as insets in the middle and bottom panels, respectively. Note that for materials with identical workfunctions, their $V_{oc}$, $FF_0$, and $FF$ values are also identical.

Figure 2.5. Theoretical fractional absorption spectra in: (a),(b) the active layer and (c),(d) the metal for the conventional and inverted devices employing each bare metal cathode and anode studied, respectively. The fractional absorption spectra in the active layer and metal for the oxide- or fluoride-coated metals differed on average by $< 10\%$ across the visible spectrum (see Figure 2.6).

Figure 2.6. Fractional absorption in (a) the active layer and (b) the metal layer for inverted devices. (c,d) Corresponding percentage difference between the oxide-/fluoride-coated metal
electrodes and the bare metal electrodes for fractional absorption in c) the active layer and d) the metal layer. The metal oxide/fluoride thickness in all cases was 2 nm.

**Figure 2.7.** Reflection at P3HT:PCBM-metal interface (assuming no other interfaces present), calculated as:

\[ R = \frac{\tilde{n}_{\text{metal}} - \tilde{n}_{\text{P3HT:PCBM}}}{\tilde{n}_{\text{metal}} + \tilde{n}_{\text{P3HT:PCBM}}} \]

where \( \tilde{n} \) is the complex index of refraction for the respective layer (i.e., \( \tilde{n} = n + ik \)).

**Figure 2.8.** Integrated absorption in the active layer, electrode layer(s), metal oxide/fluoride layers (where present) and front interlayers (defined here as ZnO/ITO and PEDOT:PSS/ITO for inverted and conventional devices, respectively) for devices with a range of different bare or coated metal electrodes. The left (solid) bar in each column corresponds to inverted devices and the right (hatched) bar to conventional devices. Overlaid are data points for the calculated \( J_{sc} \) values for each device (inverted black triangles for inverted devices, orange triangles for conventional devices). The layers and thicknesses used for the simulations are described in Section 2.1; the thicknesses of each layer were kept constant between conventional and inverted devices to minimize the optical interference effects due to changing layer thickness.

**Figure 2.9.** Calculated power conversion efficiency for the nine bare metal and six coated metal electrodes studied for inverted (top) and conventional (bottom) configurations calculated using the data in Figure 2.4, and the \( J_{sc} \) values shown in Figure 2.5(e). The blue outlined bars refer to \( p \)-type metal oxide-coated metals and the green outlined bars refer to the \( n \)-type metal oxide- or fluoride-coated metals.

**Figure 2.10.** Solar spectral overlap with theoretical active layer and metal absorption. (a) AM1.5 spectrum overlain on the calculated fractional absorption spectra in the active layer for a conventional and an inverted device (both having Ag as the electrode). The region of maximal spectral overlap is highlighted. (b) Region of maximal spectral overlap for the active layer of several inverted devices simulated. (c) Region of maximal spectral overlap for the metal layer of several inverted devices simulated.

**Figure 2.11.** Generation rate of excitons in P3HT:PCBM for nine different metals studied for a) conventional and b) inverted orientations.

**Figure 2.12.** Generation rate of excitons in P3HT:PCBM for nine different metals studied for a) conventional and b) inverted orientations.

**Figure 3.1.** Schematics of planar and plasmonic inverted organic photovoltaic device structures. Typical device schematics shown for a planar inverted BHJ-OPV (left) and a plasmonic inverted BHJ-OPV (right), which has the potential to increase the efficiency of the device relative to its
planar counterpart.

**Figure 3.2.** Graphical user interface (GUI) associated with the simulation setup employed in Lumerical FDTD Solutions software to simulate the electromagnetic response of nanoparticle arrays studied in this chapter. a, x-y plane associated with a typical BHJ-OPV employing a plasmonic metasurface electrode; the simulation boundaries lie along the edges of one unit cell. Aspect ratios of 1.0, b, and 2.0, d, are shown in the 3D perspective view within one unit cell. e, x-z plane associated with the simulation from a. The axes in each figure depict the wave vector, \( k \), electric field vector, \( E \), and magnetic field vector, \( H \), as well as the x-y-z coordinates referred to throughout the text.

**Figure 3.3.** Tuning of \( J_{sc} \) by varying the aspect ratio of AgNPs on Ag. a, Calculated \( J_{sc} \) in the x-z plane as a function of y-position in inverted, Ag anode devices for both planar (100 nm active layer thickness) and plasmonic (100 nm active layer maximum thickness) configurations, varying AgNP aspect ratio (AR). Inset: electric field intensity contour plot in an x-y plane located at the base of the AgNPs for an AR of 1 at an excitation wavelength of 600 nm; the AgNPs are shown above the contour, with the black box denoting one simulated unit cell. Note that for this plot, the excitation source was depolarized for the \( J_{sc} \) versus y plot and the x-y electric field intensity contours. For b-j, the results are plotted under x-polarized excitation. b, Calculated average fractional absorption spectra in the active layer (top) and metal layer (bottom) for inverted, Ag anode devices for varying AgNP aspect ratio. For these plots, fractional absorption versus wavelength was calculated by averaging over ten x-z planes defined by y ranging from \( y = 0 \) to the maximum \( y \) value (refer to a and inset). c, Calculated fractional absorption spectra in the active layer in a single x-z plane for inverted, Ag anode devices. The x-z plane bisects the center of the AgNPs (yellow plane in inset) at the edge of the unit cell. d, Integrated fraction of light absorbed in the Ag anode for inverted devices, varying AgNP AR (left axis). Overlaid are calculated \( J_{sc} \) values (right axis). Note that an aspect ratio of 0 corresponds to the planar device. e - j, Total simulated electric field intensity profiles in an x-z plane bisecting the center of the AgNPs (see yellow plane in c, inset) for inverted, Ag anode devices in planar (e, h) and plasmonic configurations (aspect ratios of 5.0 (f, i) and 0.5 (g, j)), at 2 particular wavelengths: 640 nm (e - g) and 380 nm (h - j). The vertical scale bar in e is constant for all plots; the horizontal scale bars in e - g are constant for the corresponding shorter wavelength plots. The colour bar to the right of all the contours is the electric field intensity in normalized units and is used for all contours.

**Figure 3.4.** Polarization effects in plasmonic devices. a, (top) Calculated fractional absorption spectra in the active layer in a single x-z plane for inverted, Ag anode devices for both planar and plasmonic configurations, varying AgNP AR. The x-z plane bisects the center of the AgNPs at the edge of the unit cell (see Figure 3.3c and d). b, (bottom) Calculated fractional absorption spectra in the active layer for all x-z planes simulated for inverted, Ag anode plasmonic device having AR = 0.33. The planes in b correspond to the various spectra; beneath the nanoparticles in b is an electric field intensity contour in the x-y plane at a wavelength of 640 nm. Note that for these absorption spectra and the electric field intensity contour, the excitation source was depolarized. Electric field intensity contours in the x-y (c, d) and x-z (e, f) planes taken at maximum z or y values, respectively. In c, e, the excitation source is polarized along the x-direction (see Figure 3.2), whereas in d, f, the excitation source is depolarized.
Figure 3.5. Solar spectral overlap with theoretical active layer absorption. a, AM1.5 spectrum (obtained from the ASTM G173-03 standard, provided by the National Renewable Energy Laboratory) overlain on the imaginary part of the refractive index, $k$, of P3HT:PCBM (see Appendix A.1.2). b, AM1.5 spectrum overlain on the calculated fractional absorption spectra in the P3HT:PCBM active layer (100 nm thick) for the inverted, planar configuration for various anode materials. c, AM1.5 spectrum overlain on the calculated fractional absorption spectra in the P3HT:PCBM active layer for the inverted, plasmonic Ag anode devices with varying ARs, taken at an $x$-$z$ plane of high electric field intensity (cf. Figure 3.3c).

Figure 3.6. Absorption enhancement in P3HT:PCBM active layers for all metals and aspect ratios studied. Absorption enhancement is plotted relative to planar devices of the same metal for a-c low-loss metals (a, Ag; b, Au; c, Cu) and d-f lossy metals (d, Al; e, Ni; f, Ca). The white dashed line in each plot indicates where the absorption band edge wavelength for P3HT occurs.

Figure 3.7. Spectrally and spatially integrated fraction of light absorbed in active layer for each metal, AR, and contribution from each electric field component ($E_x$, $E_y$, and $E_z$). a, Schematic of ARs simulated. Note that fractional ARs are for oblate semi-spheroids whereas ARs greater than 1 are for prolate semi-spheroids. b-g Integrated (spectrally and spatially) fractional absorption in active layer, separated into contributions from the three components of the electric field ($A_x$, $A_y$, and $A_z$), for b-d low-loss (b, Ag; c, Au; d, Cu) and e-g lossy metals (e, Al; f, Ni; g, Ca). h-j Electric field intensity enhancements for the three electric field components for a AgNPA/Ag anode having nanoparticle AR = 0.5 at 640 nm (h, $|E_x|^2$; i, $|E_y|^2$; j, $|E_z|^2$). The electric field intensity plots in h-j are on the same length and intensity scales (length scale bars shown in i, and intensity scale shown in color bar).

Figure 3.8. Off-normal incidence excitation data. a, Fractional absorption in the active layer for Ag anode BHJ-OPVs excited at a wavelength of 650 nm for normal incidence (left) and at an angle of incidence of 15° (right). b-d, Percentage of total absorption for the contribution to the absorption from each electric field component at an AR = 1.0 for b, normal incidence, integrated broadband excitation; c, normal incidence, 650 nm excitation; d, 15° angled incidence, 650 nm excitation. e, Definition of normal incidence. f, Definition of angle of incidence.

Figure 4.1. Template-based fabrication of plasmonic metasurface using anodic aluminum oxide (AAO) nanotemplates. i) A handle consisting of AAO/Al/AAO is prepared using epoxy to prevent ~2 mm rim from being etched. The top layer of AAO and Al are then etched away using NaOH and FeCl$_3$, exposing the AAO barrier layer (a). ii) Barrier layer removal and pore-widening are performed to open and widen the AAO pores to a diameter of ~100 nm (b). iii) The epoxy is removed from the AAO nanotemplate, which is subsequently transferred to a metal film for additional metal to be thermally evaporated through the AAO pores. iv) The nanotemplate is removed, resulting in a metallic nanoparticle array on a metal surface (i.e., a plasmonic metasurface; c).

Figure 4.2. Particle diameter distribution analysis for AgNPs used in this study. The SEM images were taken from similar regions on the AgNPA/Ag where the DF spectra and AFM morphology were acquired, before the corresponding polymers or polymer:fullerene blends indicated in the top left corner of each SEM image were spin-coated onto the substrates. Inset in the top right
corner of each of SEM image is a true-color DF image (using Xe lamp illumination) of the AgNPA/Ag metasurface before a polymer or polymer:fullerene blend was spin-coated on top. Inset in the bottom left corner of each SEM image is a fast Fourier Transform of the representative SEM image. The diameter distributions were taken from a minimum of 4 different regions across the 3 AgNPA/Ag stripes for each sample, averaging over >1300 AgNPs for each sample. The mean and standard deviation values of the AgNP diameters are shown as insets in the diameter distribution plots. All of the DF images, SEM images, and FFT images are on the same respective scales (scale bars shown for the bare AgNPA/Ag).

Figure 4.3. Sample images and schematics. (a) Low-magnification SEM images of planar Ag and AgNPA/Ag stripes. The image is composed of 28 SEM images stitched together. Note that the dark circles in the SEM images were a result of the detector used (In-Lens) and the low magnification and always appeared in the center of each individual SEM image. The large-area coverage of AgNPAs was observed by the difference in contrast between the planar Ag and AgNPA/Ag regions, where the brighter regions indicated the presence of the AgNPAs (see Figure 4.2 for high magnification SEM images). (b-c) Cross-sectional schematics of planar Ag (b) and AgNPA/Ag metasurface (c) used in this study. (d) Top-down schematic of planar Ag and plasmonic metasurface sample layout used in this study. (e) Photograph of absorber-coated planar Ag and plasmonic metasurfaces used for all GIWAXS, DF scattered light spectroscopy, and AFM surface morphology measurements reported in the main text.

Figure 4.4. Polymer film thickness measurements and spin-coating conditions. (a) Representative AFM thickness measurement for a PCDTBT film. The left side of the measurement (0 to ~9 µm) was from a region where the polymer was removed with the edge of a tweezers prong. All thickness measurements were performed this way from a minimum of 2 separate regions, and ≥ 2 line scans were extracted from each image to determine the thicknesses. (b) Average thickness measurements determined from a minimum of 4 AFM line scans. Error bars represent standard deviation of 4 - 8 measurements. (c) Solution concentrations and spin-coating speeds used for each polymer, fullerene, or polymer:fullerene blend.

Figure 4.5. Screenshots of graphical user interface of Lumerical FDTD Solutions for the back-scattered simulation setup. (a) Overview of full simulation from x-z plane. (b) Schematic of hexagonal array of AgNPs, showing one unit cell from the x-y plane. (c) Magnified schematic of coated plasmonic metasurface from x-z plane, showing the TFSF source and its boundaries. (d) Perspective view of simulation.

Figure 4.6. Screenshots of graphical user interface of Lumerical FDTD Solutions for the transmittance through the vertical monitors simulation setup. (a) Overview of full simulation from x-z plane. (b) Schematic of hexagonal cluster of AgNPs from the x-y plane. (c) Magnified schematic of coated plasmonic metasurface from x-z plane, showing the TFSF source and its boundaries. (d) Perspective view of simulation.

Figure 4.7. Screenshots of graphical user interface of Lumerical FDTD Solutions for the absorption simulation setup. (a) Overview of full simulation from x-z plane. (b) Schematic of hexagonal array of AgNPs, showing one unit cell from the x-y plane. (c) Magnified schematic of coated plasmonic metasurface from x-z plane. (d) Perspective view of simulation.
Figure 4.8. Absorber-coated plasmonic metasurfaces a, Schematic of a plasmonic metasurface with an organic semiconductor thin-film coating (AgNPA - silver nanoparticle array; $h$ - nanoparticle height; $d$ - nanoparticle diameter; $\Lambda$ - nanoparticle period). b, Schematic of the dark-field (DF) scattered-light spectroscopy setup. c,d, Scanning electron microscope (SEM) images of a Ag film coated with a AgNPA (i.e., a plasmonic metasurface, e) and a planar Ag film (d). The scale bars are 500 nm. Insets are true-color DF images of the respective electrodes acquired under Xenon lamp illumination; the scale bars are 100 µm. e, Atomic force microscope (AFM) surface topography of a P3HT-coated AgNPA/Ag metasurface. The scale bar is 500 nm. f, DF scattered-light spectra for AgNPA/Ag metasurfaces and planar Ag films, with and without P3HT coatings. g,h, True-color DF images of a P3HT-coated AgNPA/Ag metasurface (g) and a P3HT-coated planar Ag film (h) acquired under Xenon lamp illumination. The scale bars are 100 µm.

Figure 4.9. Atomic force microscopy surface topography. AFM measurements of AgNPA/Ag metasurfaces coated with: (a) P3HT; (b) PCDTBT; (c) PTB7 (d) P3HT:PCBM; (e) PCDTBT:PC70BM; (f) PTB7:PC70BM; (g) PMMA; (h) PCBM; and (i) PC70BM; all images are on the same lateral scale [scale bar shown in (g)]. Height scale bars are shown at the right of each scan. (j) Average root-mean square (R.M.S.) surface roughness values determined from a minimum of 2 AFM topography measurements. Error bars represent standard deviation of 2 - 3 measurements. Inset in (j) shows the AFM surface topography of a bare (uncoated) AgNPA/Ag metasurface.

Figure 4.10. Mie-absorption-induced scattering in absorber-coated planar Ag films a, DF scattered-light spectra of various neat conjugated polymer (n, solid lines) and polymer:fullerene blend (b, dashed lines) coatings on planar Ag substrates. Insets are true-color DF images of the coatings on planar Ag substrates and were captured from regions where the DF spectra were acquired. All images are on the same length scale (scale bar is 100 µm, and is shown for PTB7:PC70BM/Ag). b, AFM surface topography of planar Ag substrates with neat polymer and polymer:fullerene blend coatings. Root-mean square (r.m.s.) surface roughness values are shown on each image; all images are on the same length scale (the scale bar is 500 nm, and is shown for neat PTB7) and same intensity scale, except for neat P3HT (intensity values are 2.5× the values on the intensity scale bar).

Figure 4.11. Single polymer nanoparticle on coating layer. Simulated scattered-light spectra of single polymer nanoparticles on the surface of the polymer coating, revealing the Mie-AIS peak for the P3HT nanostructured film. Note that the same simulation parameters and nanoparticle dimensions were used for these simulations as in the single metal NP simulations (see Figure 4.21).

Figure 4.12. Scattering from smooth absorber films. (a,b) DF scattered-light spectra of bare and organic-coated planar Ag substrates. Inset are true-color DF images of the coatings on planar Ag substrates and were captured from regions where the DF spectra were acquired. All images are on the same scale (scale bar shown for PMMA/Ag). (c-f) AFM surface topography of planar Ag substrates coated with: (c) PMMA; (d) nothing (bare Ag); (e) PCBM; (f) PC70BM. Root-mean square (r.m.s.) surface roughness values are shown on each image; all images are on the same scale.
lateral scale [scale bar shown in (c)], with the various corresponding height scales shown on the right of each topography image.

**Figure 4.13.** Back-scattered-light spectra for various absorber coatings. a, Experimental and simulated scattered-light spectra for: AgNPA/Ag metasurfaces with and without various absorber coatings (a) and dielectric-coated AgNPA/Ag metasurfaces (b). Solid lines represent empirical DF spectra, and dashed lines represent finite-difference time-domain (FDTD) simulations of the back-scattered spectra. Note that the experimental setup was limited to a wavelength range of approximately 380 nm - 860 nm. c-f, Schematic depictions of electric field lines and charge distributions (+ and - represent regions of positive and negative charge accumulation, respectively) for the various modes supported by a dielectric (n = 2.0)-coated AgNPA/Ag metasurface. Note that the schematics were created based on vector plots of the total electric field and the electric field amplitude profiles (shown to the right of the schematics). The Roman numerals in a and b refer to the mode types as referenced in c-f, and were assigned by analyzing the electric field vector plots and amplitude profiles for each peak. The modes occurred at the same or very similar wavelengths between neat conjugated polymers and polymer:fullerene blends and so were only labeled for the neat conjugated polymers. g, True-color DF images indicating the regions from which corresponding spectra were obtained (rectangular regions highlighted); all images are on the same length scale (scale bar is 50 μm, and is shown for the PC_{70}BM coating).

**Figure 4.14.** Excitation polarization (TE, TM), incident angle (0 - 35°), and refractive index (n)-dependent scattered light simulations. (a) Simulated scattered light spectra for bare AgNPA/Ag for TE (top panel) and TM (bottom panel) excitation polarizations. (b) Simulated scattered light spectra for PMMA/AgNPA/Ag for TE (top panel) and TM (bottom panel) excitation polarizations. (c) Simulated scattered light spectra for dielectric (n=2.0)/AgNPA/Ag for TE (top panel) and TM (bottom panel) excitation polarizations. Note that a course mesh (2.0 nm) was used for these particular simulations; all other parameters were the same as described in the Methods.

**Figure 4.15.** Simulated scattered-light spectra for dielectric-coated AgNPA/Ag with varying real part of the refractive index, n, for the dielectric coating. The imaginary part of the refractive index, k, was 0 for these simulations (i.e., no absorption in coating). The four mode types illustrated in Figure 3 are indicated on the plot in addition to a new mode (Mode VI) which appeared for only high-index dielectric coatings.

**Figure 4.16.** Scattered-light spectra for AgNPA/glass. (a) DF scattered-light spectra and FDTD simulations of AgNPA/glass substrates with various coatings. Solid lines represent empirical DF spectra, and dashed lines represent FDTD simulations of the back-scattered spectra. Note that the experimental spectroscopy setup was limited to a wavelength range of approximately 380 nm - 860 nm. (b) DF images of the corresponding spectra; all images are on the same scale (scale bar shown for the PC_{70}BM coating). Note that the scattering from the absorber-coated AgNPA/glass samples was inhomogeneous in some cases due to non-uniform pore widening of the anodic alumina nanotemplates (see Methods). The regions from where spectra were acquired are highlighted as red or blue rectangles on the images and were selected based on the most intense scattering (corresponding to regions where the AgNPA had diameters and periods similar to those shown in Figure 4.2).
Figure 4.17. Simulations for varying metal NPA material. Back-scattered simulations for various metal NPA/metal substrates coated with: (a) P3HT; (b) PMMA; (c) nothing (bare metal NPA/metal). Note that a course mesh (2.0 nm) was used for these simulations; all other parameters were the same as described in the Methods.

Figure 4.18. Simulations for varying spacer layer between absorber and scatterer. (a) Simulated scattered-light spectra for AgNPA/Ag metasurfaces coated with: thin (80 nm) and thick (150 nm) PMMA, and a 150-nm-thick PMMA spacer layer separating the top coatings from the AgNPA. (b) Simulated scattered-light spectra for P3HT:PCBM/PMMA-coated metasurfaces, for varying the PMMA spacer thickness. The dashed lines represent when the spacer thickness was ≥ the height of the AgNPs (i.e., ≥ 60 nm), whereas the solid lines represent when the AgNPs protruded through the PMMA spacer layer and made physical contact with the absorber. Note that a course mesh (2.0 nm) was used for these simulations; all other simulation parameters were the same as described in the Methods.

Figure 4.19. The effect of array period on scattered-light spectra. a, Normalized scattered-light spectra for P3HT/AgNPA/Ag metasurface, where the different scattering mode types are shown in addition to the plasmon-AIS mode. b,c, Normalized scattered-light spectra for bare (b) and PMMA-coated (c) AgNPA/Ag metasurfaces, revealing the localized and dispersive modes. (d) Normalized scattered-light spectra for P3HT/glass NPA/glass, where the Mie-AIS peak is labeled. Note that for (d), the absolute intensities of the scattering peaks are ≥ 1000 arb. units smaller than the scattering from (a-c) (see Appendix Figure A11 for absolute scattering intensity plots). Note that a course mesh (2.0 nm) was used for these simulations; all other simulation parameters were the same as described in the Methods.

Figure 4.20. Excitation polarization-dependent simulations for P3HT-coated metasurface. (a) Polarization-dependent simulated scattered-light spectra for P3HT/AgNPA/Ag, where the plasmon-AIS peak is still present under TE polarized excitation. (b-c) Electric field amplitudes under TE polarized excitation taken at 643 nm: (b) $E_z$; (c) $E_y$.

Figure 4.21. Single nanoparticle scattered-light simulations. (a-c) Single metal NP/metal films; (d-f) single metal NP/glass substrates.

Figure 4.22. Out-coupling of surface plasmon polaritons. a, Spectral in-plane ($E_x$) and out-of-plane ($E_z$) electric field distributions through the forward vertical monitor for P3HT:PCBM-coated AgNPA/Ag metasurface. b-d, Empirical and simulated scattered-light spectra (solid lines) and simulated transmission through the vertical monitors (dashed lines) for P3HT:PCBM (b), PTB7:PC$_{70}$BM (c), and PMMA (d) coatings. Note that the empirical spectra in (b,c) were obtained at an excitation/collection angle of 24°. Inset in (b) shows a schematic of a coated AgNPA/Ag metasurface in which the locations of the back-scattered power monitor (red dotted line) and vertical power monitor (purple dotted line) are indicated. e, Schematic depiction of electric field lines and charge distributions within the near-field of AgNPs that in-couple light to an SPP. Shown to the right of the schematic are real components of the electric field amplitude for the mode.
Figure 4.23. Angle-dependent DF scattered-light intensity at the longest wavelength scattering peak for various substrates coated with: P3HT ($\lambda = 663 \pm 18$ nm); PCDTBT ($\lambda = 715 \pm 11$ nm); and PTB7 ($\lambda = 757 \pm 3$ nm). The symbols with solid lines represent the empirical data, and the symbols with dashed lines correspond to single wavelength simulations. The Brewster angle ($\theta_B$) for the air-polymer interface is indicated on the simulated plots.

Figure 4.24. Wide-angle excitation polarization-dependent extinction measurements. (a) Polarization-dependent extinction spectra for an angle of incidence of 70° for planar Ag and AgNPA/Ag with neat conjugated polymer coatings. (b) Extinction enhancement factor for spectra shown in (a).

Figure 4.25. Grazing-incidence wide-angle X-ray scattering measurements. a-c, Molecular structures and expected physical distances of P3HT (5 monomer repeat units shown per chain segment in a), PCDTBT (2 monomer repeat units shown per chain segment in b), and PTB7 (2 monomer repeat units shown per chain segment in c). Two adjacent chain segments are shown for each polymer. Note that the [100] direction corresponds to the distance between adjacent backbone chains (i.e., intermolecular side-chain packing distance) and the [010] direction corresponds to the $\pi-\pi$ stacking distance. d-i, GIWAXS of polymer (d-f) and polymer:fullerene (g-i) thin film coatings on various substrates. d,g, Out-of-plane ($q_z$) line scans extracted at $q_z = 0$ for P3HT (d) and P3HT:PCBM (g) coatings, where the (100) reflections are shown. e,f,h,i, In-plane ($q_r$) line scans extracted at $q_z = 0$ for PCDTBT (e), PTB7 (f), PCDTBT:PC$_{70}$BM (h), and PTB7:PC$_{70}$BM (i) coatings, where the (100) reflections are shown.

Figure 4.26. Absorption measurements and simulations. a, Integrating sphere absorption measurements for polymer:fullerene films coated on optically-thick Ag and AgNPA/Ag films. Bottom panel of a shows the enhancement factor of the polymer:fullerene-coated AgNPA/Ag metasurface relative to the polymer:fullerene-coated Ag substrate on a reciprocal scale for the vertical axis. b, Simulated absorption enhancement in the coating for the polymer:fullerene-coated AgNPA/Ag or CuNPA/Cu metasurface relative to the polymer:fullerene-coated planar Ag or Cu substrates, respectively (solid lines). The simulated scattered-light spectra are shown as dashed lines for comparison. c, Integrated absorptance weighted by the AM1.5 solar spectrum for each layer. The solid bars represent the AgNPA/Ag substrates, and the cross-hatched bars represent the planar Ag substrates. The numbers over the planar polymer:fullerene bars indicate the total percent absorptance difference in the active layer for AgNPA/Ag substrates relative to planar Ag substrates, integrated over all wavelengths.

Figure 4.27. Scattering and absorption measurements and simulations for absorber-coated CuNPA/Cu metasurfaces. (a) DF scattered-light spectroscopy for bare, PMMA-, and P3HT:PCBM-coated planar Cu films and CuNPA/Cu metasurfaces.(b) True-color DF images of the coated Cu films and CuNPA/Cu metasurfaces from regions where the DF spectra were acquired. (c) Integrating-sphere UV-VIS absorptance measurements for the coated Cu films and CuNPA/Cu metasurfaces. (d,e) Simulated absorptance in (d) the P3HT:PCBM layer and (e) the CuNPA/Cu metasurface and Cu film. The absorptance enhancement factors are shown in the bottom panels of (d,e).
Figure 4.28. Summary of scattering modes supported by absorber-coated plasmonic metasurfaces. Scattering from the various optical modes are illustrated by the straight lines. 

- The organic semiconductor-coated planar Ag film has been shown to only support Mie-AIS for organic coatings exhibiting high degrees of nanoscale surface features. 
- The organic semiconductor-coated AgNPA/Ag metasurfaces have been shown to support various LSPRs, plasmon-AIS, and SPP modes. While the LSPRs and plasmon-AIS modes scatter for all absorber coatings, the SPP mode was trapped for semi-crystalline organic coatings and was only scattered to the far-field from the amorphous organic coated-metasurfaces.

Figure 5.1. (a) Core-shell nanoparticle structure used to investigate coupling between excitons in conjugated polymers (CPs) and localized surface plasmon resonances (LSPRs). The silver nanoparticle (AgNP) core radius is given by \( r \), and the CP shell thickness is given by \( h \). (b) Normalized absorption spectra of various conjugated polymers (MEH-PPV, P3HT, and PTB7) and a typical cyanine dye J-aggregate (TDBC-JA; see abbreviations section for full names of polymers and dye). (c) Real and imaginary parts of the relative permittivity for a single Lorentzian oscillator used as the basis for modeling J-aggregate optical properties. (d) Real and imaginary parts of the relative permittivity for a Lorentzian shell comprised of five oscillators used as the basis for modeling the CP optical properties. Symbols used: 0-\( v \) = absorption transition from the singlet exciton ground state, \( S_0 \), to the first-excited singlet exciton state, \( S_1 \), into the \( v \)th vibrational level; \( \lambda_0 \) = resonance wavelength; \( \lambda_{0-2} \) = resonance wavelength for 0-2 transition; \( f \) = oscillator strength; \( \hbar \gamma \) = resonance linewidth; \( \varepsilon_\infty \) = high-frequency relative permittivity; \( \Delta E \) = spacing between oscillators.

Figure 5.2. (a) Normalized scattering, (b) absorption, and (c) shell absorption enhancement from core-shell nanoparticles with shell relative permittivity described by a single Lorentzian oscillator. The AgNP radius and shell thickness were \( r = 25 \) nm and \( h = 5 \) nm, respectively, and the shell parameters used were: \( \lambda_0 = 420 \) nm; \( f = 0.05 \); \( \hbar \gamma = 0.10 \) eV; \( \varepsilon_\infty = 1.77 \). Note that \( \hbar \Omega \) represents the splitting energy between the exciton-plasmon hybrid modes, obtained from the scattering spectra, as shown in (a).

Figure 5.3. (a) Normalized scattering and (b) shell absorption enhancement for core-shell structures with a single Lorentzian oscillator shell for varying shell thicknesses, \( h \). 
- (c) Surface-averaged electric field intensity enhancement, \( |E/E_0|^2 \), for a bare AgNP and a core-shell structure with \( h = 5 \) nm. Inset is the \( |E/E_0|^2 \) enhancement profile taken from a plane parallel to the excitation polarization at \( \lambda = 420 \) nm. (d) Splitting energy for hybrid exciton-plasmon modes extracted from the scattering spectra. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon (\( \gamma_p \) - blue line), the exciton (\( \gamma_e \) - red line), and the relationship: \( \sqrt{\gamma_p \gamma_e} \) (purple line), given in Equation 5.3. The shell optical properties consisted of a single Lorentzian oscillator with \( \varepsilon_\infty = 1.77 \); \( \lambda_0 = 420 \) nm; \( f = 0.05 \); and \( \hbar \gamma = 0.10 \) eV.

Figure 5.4. Variation of resonance linewidth, \( \hbar \gamma \), for core-shell structures with a single Lorentzian oscillator shell for \( r = 25 \) nm and \( h = 40 \) nm. (a) Scattering; (b) total absorption; (c) peak splitting; and (d) shell absorption enhancement. The coupling regimes in (c) are defined by the linewidths of the surface plasmon (\( \gamma_p \) - blue line), the exciton (\( \gamma_e \) - red line), and the
relationship: \( \sqrt{\gamma_{sp}\gamma_{ex}} \) (purple line), as defined by Equation 5.3. The shell optical properties consisted of a single Lorentzian oscillator with \( \varepsilon_\infty = 1.77; \lambda_0 = 420 \) nm; and \( f = 0.05 \).

Figure 5.5. Variation of oscillator strength, \( f \), for core-shell structures with a single Lorentzian oscillator shell for \( h = 40 \) nm. (a) Normalized scattering; (b) shell absorption enhancement; and (c) splitting energy for hybrid exciton-plasmon modes. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon (\( \gamma_{sp} \)-blue line), the exciton (\( \gamma_{ex} \)-red line), and the relationship: \( \sqrt{\gamma_{sp}\gamma_{ex}} \) (purple line), given in Equation 5.3. The shell optical properties consisted of a single Lorentzian oscillator with \( \varepsilon_\infty = 1.77; \lambda_0 = 420 \) nm; and \( h\gamma = 0.30 \) eV.

Figure 5.6. Variation of oscillator strength, \( f \), for core-shell structures with a single Lorentzian oscillator shell for \( h = 40 \) nm. (a) Non-normalized scattering; and (b) shell absorption. The shell optical properties consisted of a single Lorentzian oscillator with \( \varepsilon_\infty = 1.77; \lambda_0 = 420 \) nm; and \( h\gamma = 0.30 \) eV.

Figure 5.7. a) Normalized scattering spectra for variation of high-frequency relative permittivity, \( \varepsilon_\infty \), for core-shell structures with a single Lorentzian oscillator shell for fixed \( \lambda_0 = 420 \) nm and \( h = 40 \) nm. The remaining shell optical properties were: \( f = 0.10; \) and \( h\gamma = 0.30 \) eV. b) Dispersion curve showing the peak energies of the hybrid states from the core-shell structures for varying \( \lambda_0 \) of the shell for \( r = 25 \) nm, \( h = 40 \) nm, \( f = 0.10; \) and \( h\gamma = 0.15 \) eV, and \( \varepsilon_\infty = 3.0 \). The uncoupled exciton resonance energies of the shell and the fitted LSPR energy are overlaid as solid lines.

Figure 5.8. (a) Normalized scattering spectra for core-shell structures with a single Lorentzian oscillator shell for varying high-frequency relative permittivity, \( \varepsilon_\infty \), with \( h = 40 \) nm, \( f = 0.10; \) and \( h\gamma = 0.30 \) eV. Note that \( \lambda_0 \) was selected as the LSPR wavelength of bare AgNPs in a background relative permittivity equal to \( \varepsilon_\infty \). (b) Splitting energy for hybrid exciton-plasmon modes extracted from the scattering spectra. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon (\( \gamma_{sp} \)-blue line), the exciton (\( \gamma_{ex} \)-red line), and the relationship: \( \sqrt{\gamma_{sp}\gamma_{ex}} \) (purple line), given in Equation 5.3. The peak splitting was obtained from the scattering spectra as the difference in energy between the highest and lowest energy hybrid

Figure 5.9. a) Normalized scattering spectra for variation of the number of oscillators for core-shell structures with \( h = 40 \) nm; \( f = 0.10; \) \( h\gamma = 0.15 \) eV; \( \Delta E = 0.15 \) eV; and \( \varepsilon_\infty = 3.0 \). The center oscillator (i.e., 0-0, 0-0, 0-1, 0-1, and 0-2 transitions for 1-5 oscillators, respectively) was resonant with the uncoupled LSPR of the AgNP (i.e., 500 nm), with additional vibrational modes either blue- or red-shifted from the uncoupled LSPR. b) Splitting energy for hybrid exciton-plasmon modes for variation of the number of oscillators. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon (\( \gamma_{sp} \)-blue line), the exciton (\( \gamma_{ex} \)-red line), and the relationship: \( \sqrt{\gamma_{sp}\gamma_{ex}} \) (purple line), given in Equation 5.3. The peak splitting was obtained from the scattering spectra as the difference in energy between the highest and lowest energy hybrid
modes.

**Figure 5.10.** (a-c) Normalized scattering and (d-f) shell absorption (left axis) and absorption enhancement (right axis) for prolate Ag nanorod core-shell structures with dispersive relative permittivities for common conjugated polymer materials used as the shells for $h = 40$ nm. The nanorod short axes were 25 nm and the long axes were: 28.2 nm (MEH-PPV); 33.2 nm (P3HT); and 37.2 nm (PTB7).

**Figure 5.11.** Non-normalized scattering spectra for prolate Ag nanorod core-shell structures with dispersive relative permittivities for common conjugated polymer materials used as the shells for $h = 40$ nm. The nanorod short axes were 25 nm and the long axes were: 28.2 nm (a; MEH-PPV); 33.2 nm (b; P3HT); and 37.2 nm (c; PTB7). Same data as shown in Figure 5.10a-c, except not normalized.

**Figure 6.1.** (a) Schematic of the hybrid P3HT:PCBM/MoS$_2$ heterojunction on a plasmonic metasurface. (b) Cross-sectional schematic of monolayer MoS$_2$. (c) True-color dark-field image of Ag nanoparticle array on Ag film plasmonic metasurface; scale bar value shown in (f). (d) SEM image of MoS$_2$ on the plasmonic metasurface prior to application of P3HT:PCBM. Inset is a magnified view of the MoS$_2$-coated metasurface. (e,f) Optical images for P3HT:PCBM/MoS$_2$ on a plasmonic metasurface. The bright-field image (e) is labeled with different regions near the edges of the MoS$_2$ film; the dark-field image (f) was acquired from the same area and helped to identify the different regions. Bright- and dark-field images are on the same scale (value shown in (f)). (g) Raman spectra of CVD-grown MoS$_2$ thin-films after being transferred onto the Ag and metasurface substrates. The two dominant vibrational modes are labeled.

**Figure 6.2.** Optical, scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of single-layer MoS$_2$ (light purple in the optical image) grown by chemical vapor deposition on SiO$_2$/Si wafer (pink in the optical image). MoS$_2$ crystals can be observed either isolated (a-c) or interconnected (d-f). At higher density of materials deposited, large-area polycrystalline MoS$_2$ film can form (g-i). The film was intentionally scratched in (g) to show the color contrast between MoS$_2$ and the substrate. Data acquired and figure prepared by Damien Voiry.

**Figure 6.3.** Photoluminescence (PL) spectral mapping and optical image of the planar MoS$_2$ film used in this study. (a) PL map; (b) optical image; (c) PL point spectra; and (d) Raman point spectra obtained from regions marked with ‘×’ or ‘o’ on the PL map and optical image.

**Figure 6.4.** SEM images of substrates employed for organic film deposition: a) Ag film (150 nm); b) polycrystalline MoS$_2$ film on Ag; c) plasmonic metasurface composed of a Ag nanoparticle array on a Ag film (AgNPA/Ag); d) polycrystalline MoS$_2$ film on plasmonic metasurface. Inset in each image are high-resolution SEM images taken from the same regions. All images and insets are on the same respective scales (scale bar values shown in (a)).

**Figure 6.5.** ps-scale transient pump-probe reflection measurements from P3HT:PCBM and the
hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurfaces using a pump wavelength of 400 nm and probe wavelengths of: a) 1000 nm (i.e., probing the polaron and exciton dynamics in P3HT); and b) 1150 nm (i.e., probing the exciton dynamics in P3HT).

Figure 6.6. Picosecond-scale transient pump-probe reflection measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurfaces using pump and probe wavelengths of 800 nm and 1000 nm, respectively (i.e., probing the polaron and exciton dynamics in P3HT).

Figure 6.7. Dark-field images of P3HT:PCBM coated on: a) planar Ag; b) MoS$_2$/Ag; c) metasurface; d) MoS$_2$-metasurface heterostructure. All images are on the same scale (scale bar shown in (a).)

Figure 6.8. Spatial distribution of the electric field intensity in the heterostructure for selected number of MoS$_2$ layers (from top to bottom: 0, 1, 5, 10, 25, and 70 layers), calculated using the transfer matrix method.

Figure 6.9. Nanosecond-scale transient pump-probe reflection measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurfaces using a pump wavelength of 400 nm and a probe wavelength of 1000 nm: a) magnitude of transient reflectometry; b) normalized data.

Figure 6.10. Photoluminescence (PL) spectra from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layer with and without the plasmonic metasurface. Spectra were acquired using a Nanofinder 30 spectrometer (Tokyo Instruments) under 532 nm laser excitation (0.05 mW initial power) directed through a 100× microscope objective (0.95 numerical aperture). The laser and PL signal from the sample were passed through a high-pass filter, then through a 500 µm pinhole prior to the CCD detector. Each spectrum shown was acquired using 1 s exposure time, 5 accumulations/spot, and between 5 (P3HT:PCBM only) to 17 (P3HT:PCBM and P3HT:PCBM/MoS$_2$ with metasurface) spots were averaged for each sample.

Figure 6.11. a) Microscope-coupled extinction measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurface. b) Simulated active layer absorbance, defined as the P3HT:PCBM absorbance plus the MoS$_2$ absorbance. c,d) Spatially-varying cross-sectional simulated absorption (calculated using Equation 4.3) in the heterostructure at two different wavelengths: c) 400 nm and d) 660 nm. The plots in (c,d) are on the same scale, and the scale bar is shown in (d).

Figure 6.12. a) Measured extinction enhancement factor (i.e., extinction from P3HT:PCBM/metasurface or P3HT:PCBM/MoS$_2$/metasurface divided by extinction from P3HT:PCBM/Ag). b) Simulated absorbance enhancement factor in the total active layer (P3HT:PCBM + MoS$_2$) for P3HT:PCBM/metasurface with and without the MoS$_2$ layer relative to P3HT:PCBM alone. c) Simulated absorbance enhancement factor in the MoS$_2$ layer for MoS$_2$/metasurface with and without the P3HT:PCBM layer relative to MoS$_2$ alone. d)
Normalized simulated scattered-light spectra for the metasurface with various coatings. Note that each of the scattering spectra is offset for clarity.

**Figure 6.13.** Energy level diagrams and photophysical processes for the different components of the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the plasmonic metasurface for two different time scales: a) instantaneously after photoexcitation, \textit{i.e.}, carriers are promoted to the first excited state and the plasmonic modes of the metasurface are excited; b) less than 100 fs after photoexcitation, when charge transfer processes occur. The black circles represent electrons, white circles represent holes; the orange arrow indicates the lowest energy absorption transition in P3HT; the red arrow indicates the lowest energy absorption transition in MoS\textsubscript{2}; the purple arrows indicate the direction of charge transfer. \[ E_F = \text{Fermi level}; \quad CB = \text{conduction band}; \quad VB = \text{valence band}; \quad LUMO = \text{lowest unoccupied molecular orbital}; \quad HOMO = \text{highest occupied molecular orbital} \] Note that due to the conformal nature of MoS\textsubscript{2} on the metasurface, the PL emission from MoS\textsubscript{2} shifted by 27 meV relative to planar MoS\textsubscript{2} (Figure 6.14). This relatively small shift represents the charge transfer between MoS\textsubscript{2} and P3HT.

**Figure 6.14.** Microscope-coupled PL spectra from MoS\textsubscript{2} with and without the plasmonic metasurface. Spectra were acquired from 10 spots on each sample, and the averaged and normalized spectra are shown.

**Figure 7.1:** XPS core level spectra for oxidized planar Ag surfaces: a) Ag3d\textsubscript{5/2} core electrons; b) magnified region of the Ag3d\textsubscript{5/2} plasmon arising from unoxidized Ag; c) O1s core electrons; d) C1s core electrons.

**Figure 7.2:** SEM micrographs of oxidized planar Ag surfaces for varying plasma exposure times: a) 0 s (untreated); b) 1 s; c) 5 s; d) 10 s; e) 20 s; f) 30 s. Inset in top left corner of each panel are photographs and in the top right corner are DF images of the Ag surfaces. All SEM and DF images are on the same respective scales (scale values indicated in (a)). Note that the bright features in ((a), right inset) are due to scattering from surface imperfections.

**Figure 7.3:** SEM micrographs of oxidized plasmonic Ag surfaces exposed to \textit{O\textsubscript{2}}/Ar plasma for either 0 s (untreated; (a) and (c)) or 1 s ((b) and (d)). The height of the nanoparticles on the plasmonic Ag surfaces is indicated in the images. Inset in the top right corner of each panel are DF images of the plasmonic Ag surfaces. All SEM and DF images are on the same respective scales (scale values indicated in (a)). Note that the bright spots observed in the insets are scattering from surface imperfections.

**Figure 7.4:** Transient pump-probe reflection measurements from P3HT:PCBM films coated onto planar (a) and plasmonic (b) Ag surfaces exposed to \textit{O\textsubscript{2}}/Ar plasma for various times. The pump wavelength was 400 nm, and the probe wavelength was 1000 nm (\textit{i.e.}, probing exciton and polaron dynamics in P3HT). (c) Peak ΔR/R signals from P3HT:PCBM coated onto planar and plasmonic Ag surfaces for different \textit{O\textsubscript{2}}/Ar plasma exposure times.
Figure A1. Optical constants of noble (low-loss) metals: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were obtained from: Burkardt et al. for Al; an online Refractive Index database for Au and Cu; and Lumerical FDTD Solutions (Handbook of Optical Constants, Palik) for Ag.

Figure A2. Optical constants of lossy metals: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were obtained from: Burkardt et al. for Ca; an online Refractive Index database for Ni, Pd, and Cr; Endiz et al. for Ba; and Machorro et al. for Mg.

Figure A3. Optical constants of neat conjugated polymers: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were obtained from: Tammer and Monkman for MEH-PPV; Lin et al. for PCDTBT; the thesis of Bernhauser for PTB7; for P3HT, the optical constants were taken from Morfa et al. and were averaged over the in-plane and out-of-plane anisotropic optical constants as effects of optical anisotropy were not considered in this thesis. Note that the tail in the $\varepsilon_2$ for P3HT arose from the out-of-plane optical axis; the in-plane $\varepsilon_2$ reported by Morfa et al. had a sharper cut-off at 660 nm.

Figure A4. Optical constants of polymer:fullerene blends: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Monestier et al. for P3HT:PCBM; Nickel et al. for PCDTBT:PC$_{70}$BM; and Hedley et al. for PTB7:PC$_{70}$BM.

Figure A5. Optical constants of neat fullerene derivatives: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Azimi et al. for PCBM; and Klein et al. for PC$_{70}$BM.

Figure A6. Optical constants of transparent polymers: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Burkhardt et al. for PEDOT:PSS; and an online Refractive Index database for PMMA.

Figure A7. Optical constants of $p$-type metal oxide interfacial layers: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Gao et al. for Ag$_2$O; an online Refractive Index database for CuO; Kumagai et al. for NiO; and May et al. for MoO$_3$.

Figure A8. Optical constants of $n$-type interfacial layers and ITO: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Burkhardt et al. for ITO; the Handbook of Chemistry and Physics for LiF; and Postava et al. for ZnO.
Figure A9. Optical constants of monolayer MoS$_2$: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from Liu et al..

Figure A10. Comparison of theoretical absorption spectra calculated using TMM (a,b) and FDTD (c,d) methods. Calculated fractional absorption spectra in the active layer for (a,c) conventional and (b,d) inverted device configurations for various electrode materials. FDTD method was performed using Lumerical FDTD Solutions. Devices studied here had a $dz$ stepsize of 0.1 nm in order to achieve < 1 % difference between TMM and FDTD methods.

Figure A11. Simulations for varying AgNPA period. Scattered-light simulations for varying AgNPA period for: AgNPA/Ag (a-c) with various coatings; AgNPA/glass with (f) and without (d) a P3HT coating; and glass NPA/glass with a P3HT coating (e). Spectra from (a,b,c,e) are the same data used for Figure 4.19 of the main text, except they have not been normalized or plotted as 2D contour plots.

Figure A12. $E_x$ and $E_z$ electric field amplitude profiles for the four modes described in Fig. 3 of the main text for five different periods, $\Lambda$, and for single AgNPs, with a dielectric coating having $n = 2.0$. The spectra and mode types are labeled in the top right panel.

Figure A13. Field profiles for surface plasmon polariton simulations. (a) Schematic of back-scattered simulation setup, showing location of the back-scattered monitor (green dashed line). (b) Schematic of transmitted SPP simulation setup, showing location of the vertical monitor (green dashed line). Spectral in-plane ($|E_x|$) and out-of-plane ($|E_z|$) electric field magnitudes through (c-h) the back-scattered monitor and (i-n) the vertical monitor for: (c,d,i,j) P3HT:PCBM; (e,f,k,l) PTB7:PC$_{70}$BM; and (g,h,m,n) PMMA coatings.

Figure A14. Surface plasmon polaritons in the scattered field. Surface plasmon polariton (SPP) mode for P3HT/AgNPA/Ag (at 767 nm). The box in the center of each image contains the total field amplitude, and outside of that box is the scattered field amplitude. These simulations included only a cluster of AgNPs (7, in a hexagonal packing arrangement) which coupled light into the propagating SPP at the Ag-P3HT interface. (a) charge distribution; (b) $H_y$; (c) $E_x$; (d) $E_z$.

Figure A15. Angle-dependent scattered-light spectra. Angle-dependent scattered-light spectra for all substrates coated with: (a) P3HT; (b) PCDTBT; (c) PTB7; (d) PMMA; (e) P3HT:PCBM; (f) PCDTBT:PC$_{70}$BM; (g) PTB7:PC$_{70}$BM; (h) nothing (bare substrates). The numerical aperture increased with increasing objective magnification, thus changing the angle of incidence and extending the collection cone of scattered light (see Methods).

Figure A16. 2D GIWAXS profiles for all coatings and substrates used in this study. Note that all measurements were acquired using the same incident angle and acquisition time (see Methods).

Figure A17. 2D GISAXS profiles for all coatings and substrates used in this study which were
useful for ensuring the AgNPA was being probed by the X-rays in the GIWAXS measurements (Appendix Figure A16). Note that all measurements were acquired using the same incident angle and acquisition time (see Methods).

**Figure A18.** Grazing-incidence wide-angle X-ray scattering line scans. 1D GIWAXS line scans extracted from the 2D data for the in-plane ($q_r$) direction (extracted at $q_z = 0$; top row for each panel) and the out-of-plane ($q_z$) direction (extracted at $q_r = 0$; bottom row for each panel) for: (a) P3HT; (b) PCDTBT; (c) PTB7; (d) P3HT:PCBM; (e) PCDTBT:PC$_{70}$BM; (f) PTB7:PC$_{70}$BM. Note that the arrows in each scattering profile represent the observed peaks: green - (100); violet - (010); orange - Ag (111); pink - PCBM. Three different plots were used for three different $q$ ranges to allow different intensity scales to be used so that the prominent peak(s) in that $q$ range could be clearly displayed.

**Figure A19.** Intensity of out-of-plane (100) peak for P3HT on various substrates for the raw data ($I_{100}$) and normalized to account for the volume of P3HT present in the region probed ($I_{100}^{norm}$).

**Figure A20.** Simulated absorptance enhancement factors. Simulated absorptance enhancement factors (solid lines) in (a) the coating layer and (b) the AgNPA/Ag metasurface for the polymer:fullerene coatings on AgNPA/Ag relative to polymer:fullerene-coated planar Ag substrates. Note that for the equivalent-volume planar simulations, the polymer:fullerene film thickness was 67.9 nm, whereas for the equivalent-thickness planar and AgNPA/Ag simulations, the polymer:fullerene film thickness was 80 nm. The simulated scattered-light spectra are overlaid for the coated AgNPA/Ag metasurfaces (dashed lines).

**Figure A21.** Examples of raw pump-probe signals from P3HT:PCBM coated on a Ag metasurface for a pump wavelength of 400 nm and probe wavelengths of a) 1000 nm and b) 1150 nm. The raw signal measured at the lock-in amplifier, in Volts, is the $\Delta R$, which is divided by the reflectance (R) at the probe wavelength in the ground state (i.e., without pumping). The signals each represent a single scan, with the color of the scans ranging from violet through red (following the visible spectrum) for increasing time of scan (i.e., first scan is purple, last scan taken is red). The thick black line shows the average of all measurements. This demonstrates the stability of the P3HT:PCBM film over the course of the measurements under photoexcitation.

**Figure A22.** ps-scale transient pump-probe reflection measurements from bare Ag and plasmonic metasurface and from MoS$_2$/Ag and MoS$_2$/metasurface using pump and probe wavelengths of 400 nm and 1000 nm, respectively. The $\Delta R$ value was the value obtained directly from the lock-in amplifier during the pump-probe measurement (i.e., not normalized to the reflection, R, from the probe alone). No signal was observed for all delay times.

**Figure A23.** Normalized ps-scale transient pump-probe reflection measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurfaces using: a) 400 nm pump, 1000 nm probe (i.e., probing the polaron and exciton dynamics in P3HT); b) 800 nm pump, 1000 nm probe; c) 400 nm pump, 1150 nm probe (i.e., probing the exciton dynamics in P3HT).
Figure A24. Fitting analysis for ns-scale transient pump-probe reflection measurements from a) P3HT:PCBM (constant fit); b) P3HT:PCBM with the metasurface (single exponential decay fit); c) the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer (single exponential decay fit); d) the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the metasurface (double exponential decay fit). The decay times and amplitudes are shown in Table 6.1.

Figure A25. Individual microscope-coupled extinction measurements from: a) P3HT:PCBM; b) P3HT:PCBM with the plasmonic metasurface; and c) the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the plasmonic metasurface. Although the spot size was roughly 5 \textmu m\textsuperscript{2}, the spectra acquired from these regions were quite reproducible, with the spot-to-spot variability within each sample being smaller than the difference between the three samples themselves. Note that the averages shown here are the same ones plotted in Figure 6.11a.
List of Table Captions

Table 1.1. Drude Parameters of Metals. Data obtained from Ordal et al. for $N$, $\tau$, and $\omega_p$, and West et al. for the $\omega$.

Table 1.2 Table of BHJ-OPV efficiency ($\eta$) enhancement factors for devices containing plasmonic metasurfaces as back electrodes relative to planar devices ($\eta_{\text{plasmonic}}/\eta_{\text{planar}}$) (actual $\eta_{\text{plasmonic}}$ values in brackets). Abbreviations used: EF = enhancement factor; $\lambda$ = wavelength; $d$ = diameter; $h$ = height; $\Lambda$ = period; Thry, $T$ = theory; Exp, $E$ = experiment; Conv = conventional; Inv = inverted; Coating = plasmonic metasurface coated with active layer (incomplete device); MIM = metal-insulator-metal; Ref = reference.*Denotes absorption EF occurring at the wavelength(s) specified in brackets; int = integrated absorption EF.

Table 2.1. Data tabulated from Figure 2.8 showing the differences in the total absorption fraction between conventional and inverted devices in each layer. PD = percentage difference (calculated as (Conv–Inv)/[(Conv+Inv)×2]×100 %). Positive PD indicates conventional device absorption was larger, whereas negative PD indicates inverted device absorption was larger.

Table 3.1. Comparison of short-circuit current density values for planar devices having different active layer thicknesses. Comparison of $J_{\text{sc}}$ values calculated for planar devices containing various metal electrodes for inverted and conventional configurations using the FDTD method for active layer thicknesses at constant volume ($t = 89.53$ nm) or constant thickness ($t = 100$ nm) compared to plasmonic devices. Negative percentage differences indicate larger $J_{\text{sc}}$ values for equivalent volume, whereas positive percentage differences indicate equivalent thickness values were larger. Note $t_{\text{AL}}$ refers to the active layer thickness.

Table 4.1. Intensity of the plasmon-AIS peak for absorber-coated AgNPA/Ag metasurfaces from FDTD simulations.

Table 4.2. Integrated absorptance increases in the various absorber coating layers and AgNPA/Ag for the metasurface substrate relative to the planar substrates separated into wavelength regimes of the various mode types.

Table 6.1. Decay parameters obtained from fitting the ns-scale $\Delta R/R$ curves to the following equation: $\Delta R/R = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + C$, where $t$ is the decay time, $A_1$ and $A_2$ are the amplitudes of the components of the decay, $\tau_1$ and $\tau_2$ are the lifetimes of the components of the decay, and $C$ is a constant for the excited states that did not decay within the time range (800 ps). The amplitude values are reported as actual $\Delta R/R$ percentages.

Table A1. Equivalent circuit parameters. Equivalent circuit parameters taken from the literature for similar device structures studied here. The average value was taken for the diode ideality factor.
Table A2. Comparison of short circuit current density ($J_{sc}$) values calculated for BHJ-OPV devices containing various metal electrodes for inverted and conventional configurations using the TMM and FDTD methods. In all cases, the $J_{sc}$ obtained from the TMM was larger than that obtained from the FDTD method, although by less than 1% in each case (calculated as ($\text{Conv} - \text{Inv}$) / ($\text{Conv} + \text{Inv}$) / 2 * 100%). The device configurations for these simulations were: ITO (100 nm)/ PEDOT:PSS (20 nm, conventional) or ZnO (20 nm, inverted)/ P3HT:PCBM (100 nm)/ Metal Oxide (20 nm, where appropriate)/ Metal (200 nm).

Table A3. Substrate (glass) correction methods. The TMM, which corrects for the glass substrate in the calculation, is compared to the FDTD method using different procedures to correct for substrate effects. The first procedure does not include glass at all, and uses a background index, $n_0$, of air (1.0). The second procedure uses $n_0 = 1.52$ (that of glass), such that reflections at the air-glass interface are ignored. The third procedure uses $n_0 = 1.52$, but includes a TM calculation of the identical device setup. The transmission coefficient through the glass-ITO interface is multiplied by the electric field intensity throughout the device in a similar way to how the TM method is computed.\(^4,5\) The fourth procedure uses an average value of this transmission coefficient, 0.8, which is averaged across the visible spectrum. The fifth procedure includes addition of a thin glass layer in the FDTD simulation, using $n_0 = 1.0$. In each simulation, the device structure was ITO (100 nm)/ PEDOT:PSS (20 nm)/ P3HT:PCBM (1:1, thickness indicated by tAL)/ Metal cathode (200 nm). \(d\lambda\) represents the wavelength spacing used in the simulations. The correction procedures were compared for varying metal electrode, tAL, addition of an electron transport layer (ETL) between the P3HT:PCBM and metal layers (thickness tETL), and \(d\lambda\). For each simulation, the correction procedure most closely matching the TM method is shown in bold. The blue highlighted cells indicate the control in each comparison (Al cathode, \(tAL = 100\) nm, \(d\lambda = 10\) nm, no ETL).

Tables A4-A7. The following tables show the numerical results of the $J_{sc}$, $V_{oc}$, FF, and $\eta_p$ calculations for conventional and inverted devices having $S$-parameters of 1.0 and 0.1 for each metal electrode studied.


Table A5. Performance Parameter Data. Conventional, $S_e = 0.1$.


Table A7. Performance Parameter Data. Inverted, $S_e = 0.1$.

Table A8. Performance parameters from literature. Performance parameters for BHJ-OPV devices reported in the literature for varying metal electrodes.

Table A9. Decay parameters obtained from fitting ps-scale $\Delta R/R$ curves to the following
equation: $\Delta R/R = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)} + C$, where $t$ is the decay time, $A_1$ and $A_2$ are the amplitudes of the components of the decay, $\tau_1$ and $\tau_2$ are the lifetimes of the components of the decay, and $C$ is a constant for the excited states that did not decay within the time range (12 ps). The amplitude values are reported as normalized percentages (i.e., $A_i/(A_1 + A_2 + C) \times 100\%$).
List of Acronyms

2D: two-dimensional
3D: three-dimensional
AAO: anodic aluminum oxide
AFM: atomic force microscopy
AgNPA/Ag: silver nanoparticle array on silver film
AIS: absorption-induced scattering
AM1.5: air mass 1.5
AR: aspect ratio
BF: bright-field
BHJ-OPV: bulk-heterojunction organic photovoltaic
CB: conduction band
CVD: chemical vapor deposition
DF: dark-field
E_F: Fermi level
ETL: electron transport layer
FDTD: finite-difference time-domain
FF: fill factor
FWHM: full-width, half-maximum
GISAXS: grazing-incidence small-angle X-ray scattering
GIWAXS: grazing-incidence wide-angle X-ray scattering
HOMO: highest occupied molecular orbital
HTL: hole transport layer
IFL: interfacial layer
ITO: tin-doped indium oxide
J_sc: short-circuit current density
LSPR: localized surface plasmon resonance
LUMO: lowest unoccupied molecular orbital
MEH-PPV: poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
MIM: metal-insulator-metal
NIR: near-infrared (portion of the electromagnetic spectrum)
NP: nanoparticle
NPA: nanoparticle array
OPA: optical parametric amplifier
P3HT: poly(3-hexylthiophene-2,5-diyi)
PC₆₀BM: [6,6]-phenyl-C₆₁-butyric acid methyl ester
PC₇₀BM: [6,6]-phenyl-C₇₁-butyric acid methyl ester
PCDTBT: poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)]
PEDOT:PSS: poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
PL: photoluminescence
PLED: polymer light-emitting diode
PML: perfectly matched layer
PMMA: poly(methyl methacrylate)
PTB7: poly([4,8-bis[(2-ethylhexyloxy)benzo[1,2-b:4,5-b’]dithiophene-2,6-diyi][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]])
SEM: scanning electron microscopy
SPP: surface plasmon polariton
TE: transverse electric
TFSF: total-field scattered-field
TM: transverse magnetic
TMM: transfer matrix method
UV-VIS: ultraviolet-visible (portion of the electromagnetic spectrum)

VB: valence band

$V_{oc}$: open-circuit voltage

XPS: X-ray photoelectron spectroscopy

$\eta_{EQE}$: external quantum efficiency

$\eta_p$: solar power conversion efficiency
List of Publications


Chapter 1. Background and Scope of Investigation

The primary aim of this thesis is to design and fabricate light-trapping techniques that can be used to enhance absorption in amorphous semiconducting films with thicknesses on the order of the wavelength of visible light. Amorphous semiconductors, such as organic materials, hybrid organic-inorganic perovskites, and amorphous Si, are emerging materials for photovoltaic applications and are of interest due to the reduction in the physical thickness and the low embodied energy achievable in these devices. However, due to the thickness of photovoltaics fabricated from amorphous semiconductors is comparable to the wavelength of visible light, traditional light trapping techniques cannot be used. As such, nanophotonic designs, such as plasmonic nanostructures, are necessary to enhance the amount of light that can be absorbed by these photovoltaic materials. In this thesis, we focus on designing plasmonic nanostructured surfaces to enhance absorption in organic semiconductors – particularly, conjugated polymers. Conjugated polymers are a particularly interesting class of amorphous semiconductor because they have strongly bound excitons that are stable at room-temperature, leasing to very strong absorption coefficients and intrinsically quantum-confined excitations. We introduce this thesis with a discussion of the properties of conjugated polymers in Section 1.1. In Section 1.2, we introduce the most common type of conjugated polymer solar cell, the bulk-heterojunction organic photovoltaic. In Section 1.3, we introduce the fundamentals of plasmonics, then describe how plasmonic metasurfaces can be used to improve the efficiency of bulk-heterojunction organic photovoltaics.

1.1. Conjugated Polymers

Conjugated polymers represent a fascinating class of materials because they exhibit the mechanical robustness of conventional polymers while having the electrical conductivity of semiconductors and metals. Conjugated polymers are organic polymers consisting of π-
conjugated backbones, imbuing the polymer with electrical conductivity. The simplest conjugated polymer is a linear hydrocarbon chain of alternating single and double bonds (i.e., polyacetylene, Figure 1.1a). The $sp^2$ bonding between adjacent carbon atoms in the repeat unit gives rise to the electrical conductivity in these polymers: out-of-plane $p_z$ orbitals interact to form the $\pi$-band, allowing for the delocalization of electrons along the polymer chain. The same concept applies for all conjugated polymers. The electrical conductivity of conjugated polymers can be tuned from insulating through semiconducting and even metallic-like conductivity through chemical doping. This has led to the implementation of conjugated polymers as the semiconducting active layers in optoelectronic devices, such as organic light-emitting diodes, organic-based lasers, and organic photovoltaics. Besides the mechanical advantages of organic semiconducting polymers, they also benefit from synthetic tunability and strong light-matter interactions. Small organic molecules are often insoluble in most common aqueous or organic solvents, requiring the use of vacuum deposition techniques to fabricate thin-film devices. The solubility of conjugated polymers in organic solvents can be controlled through chemical substituents as side groups, which enables solution-based thin-film deposition techniques such as spin-coating, blade-coating, and roll-to-roll printing. Conjugated polymers are also composed of predominantly earth-abundant elements (i.e., carbon, hydrogen, and oxygen), so scarcity of these semiconductors is not an issue as it is for the constituents of some inorganic compound semiconductors (e.g., tellurium, indium, and cadmium).
Figure 1.1. Molecular structure of common conjugated polymers. (a-c) Unsubstituted conjugated polymers: (a) polyacetylene; (b) poly(p-phenylene) (PPP); (c) poly(p-phenylenevinylene) (PPV). (d-g) Functionalized conjugated polymers: (d) P3HT; (e) PEDOT; (f) poly(9,9-dioctylfluorene) (PFO); (g) MEH-PPV. (h,i) Functionalized conjugated copolymers: (h) PCDTBT; (i) PTB7.

Through synthetic chemistry, the number of unique conjugated polymers is virtually limitless. However, certain classes of conjugated polymers have made a technological impact on the optoelectronics community, such as derivatives of polyacetylenes (Figure 1.1a), poly(p-phenylenes) (PPPs, Figure 1.1b), poly(p-phenylenevinylene) (PPVs, Figure 1.1c,g), polythiophenes (Figure 1.1d,e), and polyfluorenes (Figure 1.1f). PPPs, PPVs, and polyfluorenes are all highly emissive polymers and thus have been exploited for OLEDs and lasers. Polythiophene and its derivatives have been used extensively in technological applications because they are environmentally and thermally stable. They have been used as electrical conductors, OLEDs, optical modulators, organic field-effect transistors (OFETs), and artificial muscles, and they have been the most widely-studied polymer type employed in OPVs.
Unsubstituted conjugated polymers, such as the three polymers shown in Figure 1.1a-c are insoluble in most solvents and are thus challenging to form uniform thin-films. However, the solubility can be greatly increased by introducing functional groups to the side chains of these polymers, such as the polymers shown in Figure 1.1d-i. The length of the side chain (typically ranging from 1 carbon - 12 carbons) determines the solubility, morphology, and the optical and electronic properties of the polymer. For instance, poly(3-alkylthiophenes) (P3ATs), such as P3HT (Figure 1.1d), with alkyl groups shorter than butyl (4 carbons) are insoluble in most common organic solvents, but P3ATs with alkyl groups longer than butyl are readily soluble. In addition, P3ATs of varying alkyl lengths have shown to exhibit over 3 orders of magnitude variation in electrical conductivities of their thin-films, from as low as 1 Ω⁻¹ cm⁻¹ for poly(3-octylthiophene) to as large as 1000 Ω⁻¹ cm⁻¹ for poly(3-dodecylthiophene).

Three of the most widely employed conjugated polymers for OPV applications are P3HT (Figure 1.1d), PCDTBT (Figure 1.1h), and PTB7 (Figure 1.1i). P3HT was studied extensively in OPVs during the 00’s due to the high efficiencies achievable at that time resulting from a combination of the optical, electronic, and morphological properties of the active layer, which will be discussed in Section 1.2 in greater detail. The bandgap energy of P3HT is 2.0 eV, meaning it can absorb light having wavelengths less than 620 nm. However, to achieve higher efficiencies, lower bandgap polymers are required to absorb the red and near-infrared (NIR) parts of the visible spectrum. Frequently, these low bandgap polymers are copolymers with an A-B-A-B… chemical structure, where A and B are subunits such as the carbazole and dithienyl-benzothiadiazole (DTBT) subunits that comprise PCDTBT (Figure 1.1h). One of the subunits should be an electron rich donor (e.g., carbazole), whereas the other should be an electron deficient acceptor (e.g., DTBT). This promotes the highest occupied molecular orbital (HOMO) of the donor to have a high energy and the lowest unoccupied molecular orbital (LUMO) of the acceptor to have a low energy, resulting in a smaller band gap arising from
intrachain charge transfer.\textsuperscript{118} PCDTBT and PTB7 are two such examples of low bandgap co-polymers, with bandgap energies of 1.9 and 1.84 eV, respectively, and have led to high-efficiency OPV devices.\textsuperscript{27,115}

Another unique feature of conjugated polymers is that they exhibit strong electron-lattice interactions. Conjugated polymers can be chemically doped to increase their conductivities,

**Figure 1.2.** Polarons and excitons in polythiophene. (a) Ground state structure of polythiophene. (b,c) Lattice-relaxed structures of: (b) a positive polaron and (c) a negative polaron on a polythiophene chain. (d) Lattice-relaxed structure of a polaron-exciton on a polythiophene chain. (e-h) Energy level schematics for: (e) ground state; (f) positive polaron; (g) negative polaron; and (h) polaron-exciton. The green arrows represent possible absorption transitions in each state: P\textsubscript{1} and PE\textsubscript{1} are excitations from the HOMO band to the lowest lying polaron and polaron-exciton states, respectively; P\textsubscript{2} and PE\textsubscript{2} are excitations from the HOMO band to the highest lying polaron and polaron-exciton states, respectively; P\textsubscript{3} and PE\textsubscript{3} are excitations from the lower to higher polaron and polaron-exciton states, respectively; $E_{g}$ is the bandgap energy. The pink arrow in (h) represents radiative recombination of the polaron-exciton. (i) Hybridization between two charged polarons to form a neutral bipolaron (i.e., a polaron-exciton).
which is typically achieved using oxidizing agents (e.g., BF$_4^-$, Cl$, AsF$_6^-$, or I$_2$) for $p$-type doping or reducing agents (e.g., N(n-Bu)$_4^{+}$ or Na$^+$) for $n$-type doping.$^{74,76-78,120}$ Figure 1.2a shows the ground state molecular structure of a model conjugated polymer, polythiophene. This is the lowest energy configuration for polythiophene, when all the double bonds are localized on the thiophene subunits (i.e., the aromatic configuration), with single carbon-carbon bonds between each thiophene. When doped, $\pi$-electrons are added or removed to the polymer chain. However, the $\pi$-electron bond density directly determines the geometric structure of the molecular subunits due to the high polarizability of organic molecules.$^{74,75,121-123}$ For example, the carbon-carbon double bond length in thiophene is 1.42 Å, whereas the carbon-carbon single bond length is 1.50 Å. As such, when electrons are removed from the polymer chain (forming holes), there is a structural relaxation locally that extends over 1 ~ 4 repeat units (Figure 1.2b).$^{8,74,121}$ The local geometric distortion and hole migrate along the chain as one unit, forming a quasiparticle called a positive polaron. $^{8,74,120-122}$ This strong electron-lattice coupling is an intrinsic property of conjugated polymers (and, more generally, all organic semiconductors). When electrons are added to the polymer chain via reducing agents, negative polarons are formed in the same way (Figure 1.2c).$^{120}$

Importantly, these charged polarons are local electronic states, such that the energy levels associated with them do not coincide with the extended HOMO and LUMO bands of the polymer chain (Figure 1.2f,g).$^{8,122}$ The polaron states are relaxed to higher and lower energies from the HOMO and LUMO, respectively. Charge storage in conjugated polymers in these polaron states is always energetically favored over occupation in the extended band states. The polaron states allow for sub-band-gap optical absorption transitions in addition to the interband $S_0 \rightarrow S_1$ transition: absorption can occur from the HOMO band to either the lower or higher lying polaron states ($P_1$ and $P_2$, respectively), between the two polaron states ($P_3$), or from either polaron state to the LUMO band (degenerate to $P_1$ and $P_2$).
Similarly, when photoexcitation above the bandgap energy occurs in conjugated polymers (Figure 1.2e), electron-hole pairs are generated, which rapidly separate and locally relax the lattice (Figure 1.2d,h). The electron and hole are spatially separated by several repeat units (~1 nm in polythiophene), but are electrostatically bound to one another and move, along with the lattice distortion, as one quasiparticle, called a polaron-exciton. The polaron-exciton can be schematically represented as the hybridization between two charged polarons of opposite signs (Figure 1.2i). For clarity throughout the remainder of this thesis, polaron-excitons will simply be referred to as excitons, with the understanding that excitons in conjugated polymers always are accompanied by lattice distortions and occupy the polaron states. Conjugated polymers have low dielectric constants (~2-4) such that the screening of electric fields between the electron and hole is weak. This results in electron-hole pair binding energies in the range of 0.1 – 1 eV. The large binding energy and high degree of spatial confinement of excitons in conjugated polymers makes them of the Frenkel-type, unlike inorganic semiconductors which are Wannier-type (having binding energies on the order of 10 meV and spatial separations on the order of 2-10 nm). Because of their large binding energies, excitons in conjugated polymers are stable at room temperature. This leads to strong absorption coefficients ($10^5 – 10^6$ cm$^{-1}$) in conjugated polymers because the formation of excitons is energetically more favorable than the formation of free electrons and holes, increasing the absorption transition probability.

The charge photogeneration processes are shown schematically in Figure 1.3. Light having energy ($E_{\text{ex}}$) greater than $E_g$ of the polymer causes an interband $S_0 \rightarrow S_1$ transition, creating an electron-hole pair. Typically, intrachain excitons free of impurities will cause the lattice to relax rapidly, within 100 fs. These intrachain excitons then have four potential pathways: charge separation to form a polaron (discussed below); non-radiative recombination to the ground state; radiative recombination to the ground state (emitting a Stokes-shifted photon); or intersystem crossing to form a triplet exciton (not shown). Charge separation can either occur
before or after lattice relaxation, depending on the proximity of the photoexcitation to an interface. Charge separation occurs via interchain or impurity charge transfer, leaving only a single charge on the initial polymer chain, which then causes lattice distortions to form a polaron (e.g., a positive polaron).\(^8,75,122\) Charged polarons then diffuse along the polymer chain until either encountering another like-charged polaron (forming a doubly charged bipolaron), or recombining with an oppositely charged polaron.

Another effect of the strong electron-lattice coupling in conjugated polymers is that electronic transitions can also result in a change in the vibrational state of the molecule (Figure 1.4).\(^75,123,128\) These coupled vibrational-electronic transitions are referred to as **vibronic** transitions,
and are readily observed in the absorption and emission spectra of conjugated polymers, particularly the latter (Figure 1.4b). The electronic energy of a simple diatomic molecule plotted against the amplitude of structural distortion (e.g., the diatomic bond length) is shown as a model of vibronic coupling in Figure 1.4a. The energy curves are those of anharmonic oscillators, and the lowest vibrational levels are evenly spaced due to the approximation of the simple harmonic oscillator near the equilibrium positions. Electronic transitions from \( S_0 \rightarrow S_1 \) typically occur from the 0th vibrational level in \( S_0 \), and can be promoted to any of the vibrational levels, \( v \), in the \( S_1 \) state, depending on the displacement between the equilibria of the ground and excited states. Transitions are thus represented by both their electronic and vibrational configuration numbers: \( S_0 \rightarrow S_1 \, 0-v \) \((v = 0,1,2,\ldots)\) represents all possible absorption transitions between the ground and first excited vibronic states. These transitions are shown in the absorption spectra of a typical conjugated polymer, PFO (Figure 1.4b), but because of inhomogeneous broadening, the individual vibronic levels have significant overlap. Electrons in an excited vibrational state \((v > 0)\) rapidly relax to the lowest vibrational state, where they can eventually decay to any of the vibrational levels in the ground electronic state: \( S_1 \rightarrow S_0 \, 0-v \) \((v = 0,1,2,\ldots)\). The vibronic modes are typically more readily observed in emission spectra than in absorption spectra (Figure 1.4b). The differences arise from disorder in polymer chains leading to a distribution of effective conjugation lengths. Absorption can take place anywhere within the material and is thus characterized by a large degree of inhomogeneous broadening. The excitons and charged polarons, however, travel along and between the chains and can be trapped in chain segments with the longest conjugation lengths \((i.e., \, \text{the lowest energy})\), where emission occurs. This leads to both sharper and red-shifted emission peaks relative to the absorption peaks. Note that the \( S_0 \rightarrow S_1 \, 0-0 \) and \( S_1 \rightarrow S_0 \, 0-0 \) transitions are represented schematically as having the same energy in Figure 1.4a, but experimentally occur at different energies in Figure 1.4b. The difference between the lowest energy absorption transition and the highest energy emission transition is called the Stokes shift, and arises due to the polaronic nature of the exciton.
1.2. Bulk-Heterojunction Organic Photovoltaics

As mentioned in Section 1.1, semiconducting conjugated polymers have many distinct properties that make them more attractive than inorganic semiconductors for certain optoelectronic device applications. Unlike inorganic semiconductor devices, conjugated polymer-based devices can be fabricated using solution-based processing for each component of the device. Conjugated polymers are composed of primarily earth-abundant elements, and their optical, electronic, and morphological properties can be tuned synthetically. Devices fabricated from conjugated polymers can be flexible, lightweight, and can be woven into solar textiles for wearable electronics. Due to the formation of tightly-bound Frenkel excitons upon photoexcitation, conjugated polymers have very strong absorption coefficients, rendering...
Figure 1.5. Energy payback time (EPBT) for renewable energy technologies (i.e., wind, thermal, biomass, and solar PV). A range is given for most of the technologies, where the minimum EPBT is given by the solid bars and the maximum is given by the white striped bars. Adapted from Espinosa et al..

them opaque at film thicknesses of less than 300 nm. These properties make conjugated polymers compelling materials as the active layer in photovoltaic devices. Compared to other photovoltaic technologies, organic photovoltaics (OPVs) employing conjugated polymers benefit from having the fastest manufacture and energy payback times (Figure 1.5), which opens the potential for unique applications such as photovoltaic windows and greenhouses. Although the initial conjugated polymer-based OPVs were fabricated from neat conjugated polymers in a metal-semiconductor-metal configuration, by far the most successful device architecture for polymer-based OPVs has been the bulk-heterojunction organic photovoltaic (BHJ-OPV).

1.2.1. What is a bulk-heterojunction?

The initial metal-semiconductor-metal photovoltaics operated via the formation of a metal-semiconductor Schottky barriers (Figure 1.6a). In these devices, the strongly-bound photogenerated excitons within the conjugated polymers migrated to the metal electrodes, where
the change in potential energy at the metal-polymer interface was the driving factor for charge separation and collection. However, several problems existed with these photovoltaics: 1) excitons are neutral quasiparticles that are not influenced by drift currents; 2) excitons in conjugated polymers have very short diffusion lengths (< 20 nm); and 3) since Frenkel excitons have large binding energies, they can only be separated at interfaces (assuming no external stimulus). These types of OPVs had a maximum power conversion efficiency (PCE) of around 0.62 %.

Bilayer heterojunction OPVs, in which electron donor (i.e., the conjugated polymer) and acceptor materials are stacked between 2 metals with different workfunctions, were introduced to drive the separation of the exciton and provide some polarity to the device (Figure 1.6b). The bilayer device architecture offers the advantage that the electron and hole, once separated at the interface between the electron acceptor and donor, are separated into different materials; recombination predominantly occurs through traps after the exciton is separated into charged polarons. However, only excitons generated near the donor-acceptor interface can give rise to useful photocurrent, and all excitons generated in the bulk of the donor (at a distance from the donor-acceptor interface greater than the exciton diffusion length) recombine before they can contribute to useful photocurrent. Thinner donor regions are possible, but at the expense of less...
light absorption. Thus, there is a tradeoff between optimizing the thickness for maximal absorption or for minimal recombination losses of photogenerated excitons far from the donor-acceptor interface.

To minimize the distance between photogeneration sites and donor-acceptor interfaces, Yu et al. proposed blending together electron donor and acceptor materials, forming a dispersed, or bulk-heterojunction (BHJ; Figure 1.6c).⁸⁹ Soluble conjugated polymers are particularly suitable as the $p$-type electron donor in BHJ thin-films, and have been shown to form a bicontinuous, interpenetrating network, with nanoscale phase domains on the order of 10 nm, when blended with electron acceptors.⁹²,¹³⁵,¹⁵⁶-¹⁵⁹ The most widely studied electron acceptors in BHJ-OPVs have been fullerene ($C_{60}$) derivatives, since the initial demonstrations of ultrafast (<100 fs) photoinduced electron transfer from conjugated polymers to $C_{60}$ and subsequently to phenyl $C_{61}$ butyric acid methyl ester (PCBM),⁹²,¹⁵⁶,¹⁶⁴,¹⁶⁵ a soluble derivative of $C_{60}$. Fullerene derivatives have been the best acceptor materials to-date for conjugated polymer-based BHJ-OPVs due to their high electron affinities, reasonably large electron mobilities, three-dimensional electron transport, and their ability to form nanoscale phase domains on the order of the exciton diffusion length.¹⁶⁶ Ideally, BHJs should also be formed such that there is limited contact between the donor and cathode and between the acceptor and anode to minimize carrier recombination at the electrodes. However, typically both the donor and acceptor are in contact with both electrodes, necessitating the use of interfacial layers (as described in Section 1.2.2). BHJ-OPVs have achieved the highest power conversion efficiencies of all conjugated polymer-based OPVs (over 10 %).¹⁵²-¹⁵⁴

1.2.2. Conventional device architecture

A typical BHJ-OPV device stack is shown in Figure 1.6c. One of the electrodes needs to have high transmissivity to allow light to enter the device, as well as high conductivity; the most commonly used transparent electrode is indium tin oxide (ITO). The metallic electrode of a
conventional BHJ-OPV typically has a low workfunction (e.g., Ca, Ag, Al) such that electrons are collected at the metallic electrode (referred to as the cathode) and holes are collected at the transparent electrode (referred to as the anode). Since conjugated polymer and fullerene domains are both in contact with both electrodes, interfacial layers (IFLs) are required for high-efficiency BHJ-OPVs. An electron transport layer (ETL) is used between the metallic cathode and the polymer:fullerene active layer, and a hole transport layer (HTL) is used between the transparent anode and the active layer. Typical materials for the ETL in conventional BHJ-OPVs are LiF and thin films of Ca for the HTL, a conjugated polymer called poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, see Figure 1.1e for the PEDOT monomer) is used frequently. In addition to reducing recombination at the electrodes, IFLs also can help planarize rough surfaces (particularly for ITO), can reduce inter-diffusion between the electrode elements and the polymer active layer, and can act as optical spacers (see Section 1.2.5).

1.2.3. Inverted device architecture

A major limitation of BHJ-OPVs is their short device operational lifetimes - a
conventional BHJ-OPV degrades with a few days when left in air. The major cause of this low lifetime is due to the photodegradation of organic materials when left in ambient conditions - proper encapsulation techniques can be used to reduce photodegradation arising from oxygen or moisture, improving the lifetime to around 1 year. The other major contributor to the low lifetime of BHJ-OPVs arises from the interfaces, particularly between the organic layers and the electrodes. At the transparent electrode, PEDOT:PSS, which is widely used for its high hole conductivity and its solubility in water, is deposited onto ITO from aqueous solution; however, the acidic nature of solution-based PEDOT:PSS tends to corrode the ITO layer over time, making the ITO less conductive and lowering the power conversion efficiency of the device. At the metallic electrode, oxidation occurs when devices are left in air, which increases the workfunction of the metal. Since metals typically serve as cathodes in PVs, as the workfunction of the metal increases, the overall efficiency decreases.

To circumvent the instabilities associated with electrode degradation in conventional BHJ-OPVs, the inverted device architecture can be employed (Figure 1.7). In the inverted device geometry, the metallic electrode becomes the anode and the transparent electrode becomes the cathode through selection of metals with high workfunctions (e.g., Au, Ni, Cu) or proper IFLs (Figure 1.7). Because the polymer and fullerene are blended in BHJs, no changes are needed to the active layer. The inverted device geometry eliminates the use of corrosive PEDOT:PSS layers, leading to a more stable transparent electrode. Further, formation of a native oxide layer may increase the workfunction of the metal, resulting with, not only a more efficient device, but also a more stable electrode due to the inherent stability of higher workfunction metals. Lloyd et al. compared the stability of unencapsulated conventional and inverted BHJ-OPVs, and showed that conventional devices degraded to 80% of their maximum efficiency within 4 days, whereas inverted devices lasted up to 40 days in air before degrading to 80% of their initial value. However, although inverted devices are nearly always more stable than conventional devices, their efficiencies tend to be lower than their conventional counterparts. The average efficiencies
Figure 1.8. Performance parameters of photovoltaic cells. The red curve shows the illuminated current density-voltage characteristics of a typical PV. The blue curve shows the total output power of the PV, which is the product of the current and voltage. Ideally, the maximum peak of the power curve should occur at the $V_{oc}$, with a current density of $J_{sc}$; series and shunt resistances reduce this to a less than ideal value (which is related to the fill factor, see Section 2.4.2) (Reproduced from Kippelen\textsuperscript{11}).

of inverted BHJ-OPVs fabricated from P3HT:PCBM have ranged between $< 1$ to about 4 %,\textsuperscript{41,159,176-178} whereas conventional P3HT:PCBM-based devices have reached efficiencies ranging (on average) from 1 to around 6 %,\textsuperscript{107,113,114,159,178} The higher efficiency achievable in conventional devices is due in part to the differences in carrier mobilities for holes in P3HT and electrons in PCBM, as discussed in Section 2.4.7. However, inverted device efficiencies can outperform their conventional counterparts, as demonstrated by He et al. in a study comparing PTB7:PC$_{71}$BM-based BHJ-OPVs, where inverted devices achieved an efficiency of 9.15 %, compared to 8.24 % in the conventional configuration.\textsuperscript{42}

1.2.4. Efficiency and overview of performance parameters

The efficiencies of PV devices are quantified by their current-voltage ($I$-$V$) characteristics
(Figure 1.8). In the dark, PVs display $I$-$V$ behavior characteristic of diodes, as given by the non-ideal diode equation\textsuperscript{158,179}:

$$I_d = I_0 \left[ \exp\left(\frac{q(V - IR)}{k_B T}\right) - 1 \right] + \frac{V - IR}{R_{sh}}$$

(1.1)

where $I_d$ is the dark current, $I_0$ is the reverse saturation current, $q$ is the elementary charge, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $R_s$ and $R_{sh}$ are the series and shunt resistances, respectively. $R_s$ and $R_{sh}$ cause the $I$-$V$ characteristics to deviate from ideality, and arise from the resistance from all layers in the device stack and the resistance from short-circuited paths (e.g., pinholes) through the device, respectively.\textsuperscript{158} Thus, for an ideal diode, $R_s \to 0$ and $R_{sh} \to \infty$.

Under illumination, the total current is the summation of $I_d$ and the light current ($I_L$), arising from photogeneration of charge carriers:

$$I = I_d - I_L$$

(1.2)

Note that the current density, $J$, is simply $I$ divided by the illumination area, $S_{\text{illum}}$.

The critical performance parameters, which are the open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), and fill factor ($FF$), are all obtained from measurements of the current as a function of voltage (Figure 1.8).\textsuperscript{11,135} The efficiency is the output power ($P_o$) of the PV divided by the input power ($P_i$), or:

$$\eta_p = \frac{P_o}{P_i} = J_{sc} V_{oc} FF \frac{FF}{I_{\text{sol}}}$$

(1.3)

where $\eta_p$ is the power conversion efficiency of the device and $I_{\text{sol}}$ is the incident solar intensity (in units of W/m$^2$). The $FF$ is a measure of the ‘squareness’ of the $J$-$V$ curve, and depends on $R_s$ and $R_{sh}$. It is measured experimentally as the ratio of the maximum power to the product of the $J_{sc}$ and $V_{oc}$:

$$FF = \frac{J_{\text{max}} V_{\text{max}}}{J_{sc} V_{oc}}$$

(1.4)

The standard $I_{\text{sol}}$ value used is the AM 1.5 spectrum (air mass 1.5), which, under 1 sun
illumination, integrates to 1000 W/m². A detailed discussion on the origin of the performance parameters in BHJ-OPVs is given in Section 2.3.1.

1.2.5. **Optical interference effects in thin-film devices**

Because the thicknesses of each layer in BHJ-OPVs are on the same scale as the wavelength of visible light, when light is incident on devices, it undergoes a series of multiple reflections as it propagates through each layer. The coherent interference that arises from forward- and backward-traveling waves leads to spatial electric field intensity variations within each layer, as shown in Figure 1.9a. The transfer matrix method (TMM) is a useful technique for calculating the electric field intensity through a stack of thin-films.\textsuperscript{4,5,7} Matlab code provided by Burkhard \textit{et al.}\textsuperscript{2} has been used throughout this thesis to compute the electric field intensity in various planar thin-film stacks.

Due to the coherent interference effects within thin-film stacks, the thicknesses of each layer in BHJ-OPVs are critically important for achieving maximal absorption in the polymer:fullerene active layer.\textsuperscript{2,4,5} Two examples of the thickness-dependence of different layers

![Figure 1.9. Interference effects in thin-film BHJ-OPV devices. (a) Electric field intensity (at 500 nm) within inverted BHJ-OPV devices having varying HTL thicknesses, calculated using the TMM.\textsuperscript{2} Thicknesses of each layer are: ITO (100 nm) / ZnO (20 nm) / P3HT:PCBM (100 nm) / Ag\textsubscript{2}O (variable) / Ag (200 nm). (b) Spectrally integrated absorptance in P3HT:PCBM for BHJ-OPV devices having varying P3HT:PCBM thicknesses. The structure is identical to that of (a) without a Ag\textsubscript{2}O layer.](image-url)
are shown in Figure 1.9 for typical inverted BHJ-OPV devices. By varying the thickness of the HTL (Ag₂O) the peak electric field intensity shifts from the center of the P3HT:PCBM layer into the Ag₂O layer, resulting in a dip in the field strength within the P3HT:PCBM (Figure 1.9a). Since absorptance is directly proportional to the electric field intensity, the absorptance is reduced in the P3HT:PCBM as the electric field intensity peak shifts into the Ag₂O layer. In this particular configuration, minimizing the thickness of the Ag₂O is critical to avoid shifting the peak electric field intensity away from the center of the P3HT:PCBM. However, for certain polymer:fullerene film thicknesses, the peak electric field intensity is located closer to the ITO/ZnO layers. For those devices, it is useful to have a thicker HTL layer to shift the peak electric field intensity to the center of the polymer:fullerene active layer. When IFLs are used to modify the spatial position of the peak electric field intensity, they are called *optical spacers*.\(^6,18^0\) The influence of the P3HT:PCBM thickness on the spectrally integrated absorptance within P3HT:PCBM is shown in Figure 1.9b. Although P3HT:PCBM films > 400 nm in thickness could be used to maximize absorptance, thick films increase the $R_e$ of the device, and reduce the overall photocurrent due to an increase in charge carrier recombination because of the low charge carrier mobility of organic semiconductors (Figure 1.10). Minimizing the thickness of the polymer:fullerene layer is important to minimize recombination and $R_e$ of the device, so selecting

![Figure 1.10. Charge carrier mobilities in common inorganic and organic semiconductors. Data acquired from: Hummel for Si, Ge, and GaAs;\(^1^\) Mihailetechi *et al.* for P3HT and PCBM;\(^18^\) Clarke *et al.* for PCDTBT;\(^2^2^\) and Liang *et al.* for PTB7.\(^2^7^\) ](image-url)
Figure 1.11. Charge generation, separation, and transport processes in polymer:fullerene BHJ-OPVs. (a) Schematic of the exciton generation, diffusion, charge transfer, and polaron formation processes at the polymer:fullerene interface. (b) Energy level schematics for the photogeneration processes: (i) photon absorption by the polymer; (ii) exciton generation, including structural relaxation of the polymer chains; (iii) exciton diffusion to the polymer:fullerene interface; (iv) electron transfer from the polymer to the fullerene; (v) geminate pair dissociation, with both free charges relaxing to the polaron states; (vi) polaron transport via drift and diffusion to the respective electrodes; (vii) charge collection at the electrodes. The timescale, $\tau$, of each photophysical process is indicated, along with the efficiency, $\eta$, of each process, where the $i$ symbols are: absorption (a), generation (g), exciton diffusion (ED), charge transfer (CT), geminate dissociation (GD), transport (tr), and charge collection (cc). Other symbols used: $E_{ex}$ excitation energy, $E_g$ bandgap energy, $E_F$ Fermi energy.

either the first or second maxima (80 or 205 nm, respectively) in Figure 1.9b are good first approximations for ideal active layer film thicknesses for this device architecture.

1.2.6. Device photophysics and quantum efficiencies

The charge photogeneration process in polymer:fullerene BHJ-OPVs is similar to the process for neat conjugated polymers described in Section 1.1 (Figure 1.3), where the major difference is the fullerene acts as an impurity, promoting charge separation (Figure 1.11). The steps shown in Figure 1.11b show exciton generation, charge transport, and charge transfer;
however, each of these steps occur with a finite quantum efficiency, $\eta$. Recombination of the excited state species can occur at any step from the initial exciton generation through the charge collection at the respective electrodes. In the subsequent sections, we describe each step in the charge photogeneration process and their associated quantum efficiencies.

1.2.6.1. Exciton generation and diffusion

Although there are quantum efficiencies associated with each of the processes depicted in Figure 1.11, they are often grouped into two macroscopic quantum efficiencies: the external quantum efficiency, $\eta_{\text{EQE}}$, which is the ratio of the number of charge carriers collected at the electrodes to the number of photons incident on the device, and the internal quantum efficiency, $\eta_{\text{IQE}}$, which is the ratio of charge carriers collected at the electrodes to the initial number of excitons generated. Thus, $\eta_{\text{EQE}}$ is simply the product of the efficiency of photon absorption, $\eta_a$, and $\eta_{\text{IQE}}$. $\eta_{\text{IQE}}$ represents all of the internal electrical processes that occur after photon absorption, and is given by the product of the quantum efficiencies of each of those steps:

$$\eta_{\text{IQE}} = \eta_g \times \eta_{\text{ED}} \times \eta_{\text{CT}} \times \eta_{\text{GD}} \times \eta_{\text{tr}} \times \eta_{\text{cc}}$$  \hspace{1cm} (1.5)

where $\eta_i$ represent the efficiencies of exciton generation ($\eta_g$), exciton diffusion ($\eta_{\text{ED}}$), charge transfer ($\eta_{\text{CT}}$), geminate pair dissociation ($\eta_{\text{GD}}$), carrier transport through the active blend ($\eta_{\text{tr}}$), and charge collection at the respective electrodes ($\eta_{\text{cc}}$).\textsuperscript{159,181,182} Since $\eta_{\text{EQE}}$ is directly related to the $J_{\text{sc}}$ of PVs, as will be discussed in Section 2.3.1.4, we discuss the quantum efficiencies of each charge photogeneration process in detail below.

For a typical BHJ-OPV consisting of a polymer:fullerene active blend, $\eta_g$ is nearly 100 %,\textsuperscript{156} such that each photon absorbed by the conjugated polymer generates one exciton (Figure 1.11b(ii)). $\eta_{\text{ED}}$ through the conjugated polymer is the fraction of excitons that reach the polymer:fullerene interface out of the number of generated excitons (Figure 1.11b(iii)). The exciton diffusion length in organic materials is on the order of 10 nm,\textsuperscript{5,158,159} meaning that on average,
after diffusing for 10 nm, most of the excitons generated will recombine. As mentioned in Section 1.2.1, this was the motivation for the BHJ structure, in which the electron donor and acceptor are blended together to reduce the distance the exciton must diffuse. Thus, in BHJ-OPVs, $\eta_{ED}$ can be $\sim 100\%$, such that each exciton generated diffuses to a polymer:fullerene interface.$^{158}$

1.2.6.2. Charge transfer

It has been shown through photoluminescence quenching and femtosecond time-resolved pump-probe experiments that the transfer of an excited electron from $S_1$ of a conjugated polymer to the empty $S_1$ of a fullerene is an ultrafast process, occurring on the order of 10 fs (Figure 1.11biv).$^{156}$ This is primarily a result of the high electron affinity of the fullerene and the low ionization potential of the conjugated polymer.$^{156}$ Since this is the fastest process that can occur for the excited electron (cf. photoluminescence, which occurs on the nanosecond scale, and non-radiative recombination, which occurs on the picosecond scale$^{159}$), $\eta_{CT}$ is also very nearly 100%.$^5,156,159$ This means that for every exciton which reaches the polymer:fullerene interface, each excited electron from the polymer is transferred to $S_1$ of the fullerene. However, the electron, now residing in the fullerene, and hole, which is still in the positive polaron state of the polymer, are still electrostatically bound to one another, in a charge-transfer exciton state termed a geminate pair.$^{158}$ In order for the electron and hole to be completely separated from one another, the geminate pair binding energy must be overcome. There are 3 competing processes that the geminate pair may undergo: 1) the geminate pair may completely dissociate, forming free charged polarons; 2) the excited electron in $S_1$ of the fullerene may relax to $S_0$ of the fullerene; 3) the geminate pair may recombine by the electron from $S_1$ of the fullerene returning to $S_0$ of the polymer.$^{158}$ All of these processes limit the efficiency of geminate pair dissociation, rendering $\eta_{GD} < 100\%$, in general (Figure 1.11bv). The value of $\eta_{GD}$ depends primarily on the properties of the donor and acceptor blend, particularly the LUMO ($S_1$) offset energies.$^{158}$ For P3HT:PCBM,
the LUMO offset energy is close to 1 eV, which is sufficient to completely dissociate the geminate pair, so $\eta_{GD} \sim 100\%$.$^{158}$

1.2.6.3. Exciton separation and charge transport

$\eta_r$ of free charged polarons through the polymer:fullerene blend is determined by both the electron (negative polaron) transport through the fullerene and the hole (positive polaron) transport through the conjugated polymer (Figure 1.11bvi). $\eta_r$ is generally less than 100 % due to bimolecular recombination of negative polarons in the fullerene and positive polarons in the conjugated polymer. It is determined by simultaneously solving the drift-diffusion equations for the concentration of negative polarons in the fullerene as well as the concentration of positive polarons in the conjugated polymer, dividing each by the total number of electrons transferred to the fullerene (or, identically, the total number of positive polarons left in the conjugated polymer after charge transfer), then taking the lower value as $\eta_r$, since that value will limit the carrier transport efficiency. $\eta_r$ depends on the electronic properties of the photoactive blend, such as carrier mobility and trap densities within the fullerene and conjugated polymer regions.$^{158,159}$ The quantum efficiency of hole transport through the conjugated polymer will be lower than that of electron transport through the fullerene due to the lower mobility of holes in P3HT (see Figure 1.10), making them more likely to undergo bimolecular recombination before reaching the anode. $\eta_{cc}$ (Figure 1.11bvii) is dependent on the formation of Schottky barriers at the contacts; if ohmic contacts are selected, $\eta_{cc}$ is $\sim 100\%$.$^{183}$

1.2.7. Concluding remarks

We have now described the fundamentals of the architecture and photophysical processes involved in BHJ-OPVs, with an emphasis on the inverted configuration. Throughout this thesis, we will describe methods of increasing the efficiency of BHJ-OPVs by optimizing $V_{oc}$, $J_{sc}$,
Since the $J_{sc}$ is related to the $\eta_{EQE}$ by: $J_{sc} = \int \Phi_p(\lambda) \eta_{EQE}(\lambda) d\lambda$,\textsuperscript{157} where $\Phi_p$ is the incident photon flux, increasing the $J_{sc}$ fundamentally arises from increasing the $\eta_{EQE}$, particularly $\eta_a$, $\eta_r$, and $\eta_{sc}$, since all other processes are already nearly 100% efficient. We largely focus our attention on increasing $\eta_a$, the efficiency of photon absorption, by employing plasmonic nanostructures, as discussed in the following section.

1.3. **Plasmonic Metasurfaces for Bulk-Heterojunction Organic Photovoltaics**

In Section 1.2, we discussed the motivation for BHJ-OPV devices, particularly in the inverted configuration, and the photophysical processes that lead to the conversion of light to electricity. We also presented the contradictory constraints on the thickness of the polymer:fullerene active layer: organic semiconductors have low charge carrier mobilities (Figure 1.10), necessitating the use of physically thin active layers (less than ~100 nm); however, keeping the active layer physically thin reduces the total amount of light absorbed (Figure 1.9b). One approach to satisfy these two contradictory constraints is to employ light-trapping techniques that can increase the total amount of light absorbed in physically thin-films. In this section, we describe one such light-trapping technique that can be used to increase absorption in polymer:fullerene active layers: plasmonic metasurfaces.

Surface plasmon resonances that exist on the surface of highly conductive, nanostructured metals have been shown to be of benefit to thin-film, inorganic PVs\textsuperscript{184-192} as well as OPVs\textsuperscript{193-198} through light trapping or localization in the active layer. Metals that are efficiently able to support surface plasmons in the visible regime (e.g., Ag, Cu, and Au) tend to have high workfunctions (either for the pure metal or with a native surface oxide), making them ideal anodes for inverted BHJ-OPVs.\textsuperscript{178,199} Plasmonic nanostructures can be incorporated into BHJ-OPVs either by forming metallic nanostructured electrodes or interlayers, or by embedding metallic NPs into one of the layers of the device. In this section, we will review recent work on
Figure 1.12 Possible plasmonic metasurface architectures. (a) Plasmonic back electrodes consist of a nanostructured opaque metal electrode serving as the back reflector of the device. (b) Plasmonic front/transparent electrodes consist of metallic nanostructures forming a continuous transparent conductive network, such as silver nanowire meshes. (c) Plasmonic interlayers consist of continuous metallic nanostructures embedded in one of the interlayers (electron- or hole-transport layer), which, in some cases, can have a dual role as both an interlayer and a front/transparent electrode.

the incorporation of plasmonic metasurfaces, which are continuous metallic films composed of an array of metallic nanostructures, as electrodes into BHJ-OPV devices, with an emphasis on the inverted architecture. For a review of discrete metallic NPs distributed into BHJ-OPV layers, the reader is referred to several recent reviews. There are three primary ways in which plasmonic metasurfaces can be placed inside a PV: 1) on the back metallic electrode; 2) on the front/transparent electrode; or 3) as a charge transport interlayer inside of the device stack (see Figure 1.12). In this section, we focused on the optical, electrical, and morphological effects that plasmonic metasurfaces as back electrodes have on BHJ-OPVs; Table 1.2 shows the enhancement factors for BHJ-OPV devices incorporating plasmonic back electrodes from prior studies. We begin by reviewing the fundamentals of surface plasmons, including both localized surface plasmon resonances (LSPRs) and propagating surface plasmon polaritons (SPPs).

1.3.1. Surface plasmon fundamentals

Surface plasmon polaritons are hybridized light – charge density waves that exist at the
interface between materials with opposite real, relative permittivities, such as a metal and a dielectric. All metal-dielectric interfaces are capable of supporting SPPs, although they require special techniques to be excited, as discussed in Section 1.3.1.1. Discrete metal nanoparticles (NPs) support LSPRs, which are highly dependent on the size, shape, and material of the NPs and give rise to the vibrant color of some stained glasses. Nanostructured metallic electrodes (i.e., plasmonic metasurfaces), however, are capable of supporting both localized (LSPRs) and delocalized, propagating plasmonic modes (SPPs). This makes plasmonic metasurfaces particularly interesting for PV applications, since they are capable of localizing the electric fields near the surface of the metal while also coupling light into waveguided modes to increase the distance the light travels within the thin active layer.

We begin our discussion on surface plasmons with the fundamentals of SPPs, which form the theoretical basis of the field of plasmonics, then describe the properties of LSPRs to understand the importance of the size and shape of metallic nanostructures on the optical properties.

1.3.1.1. Surface plasmon polaritons

A single, planar metal-dielectric interface is the simplest geometry capable of supporting an SPP mode. The only requirement is that the metal and dielectric must have opposite signs for the real parts of their relative permittivities, $\varepsilon_d$ and $\varepsilon_m$ (Figure 1.13a), which is always achieved at frequencies below the bulk plasmon frequency, $\omega_p$, of the metal, where the real part of $\varepsilon_m$ is negative (see Appendix A.1). Solving Maxwell’s equations using the appropriate boundary conditions yields propagating wave solutions confined to the metal-dielectric interface with evanescent decay in the perpendicular z-direction. Solutions exist only under transverse magnetic (TM) excitation, where the electric field has a normal component to the interface (see Figure 1.13c, inset), which is required for generating the surface charge oscillations in the plane (Figure 1.13a). As the surface charges are generated, the field component perpendicular to
the surface is enhanced, and decays exponentially away from the surface. The SPP dispersion relation, which is the frequency-dependent SPP wavevector, $k_{\text{SPP}}$, is obtained from the TM solutions:

$$k_{\text{SPP}} = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$

(1.6)

where $k_0$ is the free space wavevector, and is equal to $2\pi / \lambda_0$, where $\lambda_0$ is the free space wavelength. The dispersion relation, Equation 1.6, is shown in Figure 1.13b for an air-Ag interface, using literature values of the relative permittivity of Ag (Appendix A.1). In Figure 1.13b, the normal dispersion for light in air is shown as the light line, which is given by the equation $\omega = ck_0$, where $\omega$ is the angular frequency, and $c$ is the speed of light in vacuum. For low frequencies, the SPP has similar wavevector as an unbound light wave and displays more light-like character. As the frequency increases, the SPP wavevector becomes larger than that of light, such that special phase-matching conditions are required for their excitation, as discussed.

**Figure 1.13.** Surface plasmon polaritons at a planar metal-dielectric interface. (a) Electric fields normal to the metal-dielectric interface can excite surface charges within the metal. The charge density oscillations cause enhancements of the electromagnetic near-field close to the interface. (b) Dispersion curve for a surface plasmon polariton mode at a Ag-air interface. The grey line is the dispersion for the light line, where the slope is given by the speed of light in air. The dashed pink line is the surface plasmon frequency. (c) Amplitude of the evanescent electric fields in the surface normal direction for 2 different SPP wavevectors (shown in (b)), reflecting SPPs with large and small penetration depths into the dielectric layer in $i$ and $ii$, respectively.
below. As the frequency approaches the surface plasmon frequency of the metal, the SPP wavevector continues to deviate from the light line, at which point the SPP behaves more like a surface plasmon, which has a fixed frequency for all wavevectors.\textsuperscript{210-212}

Two key characteristics that quantify SPP modes are the field penetration depth into the dielectric and metal layers, and the propagation length. The penetration depth into the dielectric and metal regimes, $\delta_d$ and $\delta_m$, respectively, determine the amount of mode confinement normal to the surface, and are calculated as $\delta_{d,m} = 1/k_{z,d,m}^2$, with $k_{z,d,m}^2 = \sqrt{k_{\text{SPP}}^2 - \varepsilon_{d,m}(\omega/c)^2}$. Figure 1.13c shows two normal electric field profiles for the decay into the dielectric and metal layers, calculated at low (i) and high (ii) frequencies (shown in Figure 1.13b). The penetration depth into the dielectric is very large at low frequencies, on the order of 1-10 $\mu$m.\textsuperscript{210-212} However, at frequencies approaching the surface plasmon frequency, the penetration depth into the dielectric is very low, $\sim$100 nm, meaning the fields are more tightly confined to the interface. The leakage into the metal film is roughly constant for all frequencies ($\sim$30 nm), except at the surface plasmon frequency,

![Figure 1.14. Methods of exciting SPPs: (a) Kretschmann configuration; (b) Otto configuration; (c) grating-coupling; (d) near-field excitation. Symbols used; $k_{\text{SPP}}$ SPP wavevector; $E_{\text{ev}}$ evanescent electric field; $\theta_{\text{SPP}}$ SPP excitation angle; $E$, $H$ incident electric and magnetic field vectors, respectively.](image-url)
where the penetration depth becomes very large. The propagation length, $L$, given by
\[ L = 1/(2\text{Im}k_{spp}), \]
has the opposite trend as the field confinement: at low frequencies, the confinement is weak, but $L$ is very large ($10 \text{–} 100 \mu\text{m}$); at frequencies near the surface plasmon frequency, the confinement is strong, but $L$ is very small ($100 \text{nm} \text{–} 1 \mu\text{m}$). Thus, there is a trade-off between having very tightly confined fields and long propagation lengths.\textsuperscript{210-212}

Because SPPs have a larger wavevector than light, phase-matching techniques are required to for their excitation (Figure 1.14). Excitation of SPPs requires out-of-plane electric field components to generate surface charges, so normal-incidence excitation (which have only in-plane field components) cannot be employed for planar metal-dielectric interfaces. Furthermore, off-normal incidence excitation at an angle $\theta$ onto a planar metal-dielectric interface always results in the photon momentum, $k_x = k_0 \sin \theta$, being smaller than $k_{spp}$, even at grazing-incidence.\textsuperscript{211} To increase the wavevector of the incident photon, three-layer systems, gratings, or near-field excitation can be used.\textsuperscript{211,212} Common types of three-layer systems are combinations of air, metal, and glass prisms. For these systems, when light passes through the prism, it undergoes total internal reflection (TIR), so only the evanescent field interacts with the metal film. Because the incident excitation passes through the glass prism with a relative permittivity, $\varepsilon_p$, larger than that of air ($\varepsilon_d = 1$), the incident photon momentum is increased to $k_x = k_0 \sqrt{\varepsilon_p} \sin \theta$, which is sufficient to excite SPPs at the metal-air interface (but not at the metal-prism interface). SPPs are observed experimentally as dips in angle-dependent reflectance spectra when $\theta = \theta_{spp}$. The two most common experimental setups for prism-coupled SPP excitation are the Kretschmann\textsuperscript{219} and Otto\textsuperscript{220} configurations. In the Kretschmann configuration (Figure 1.14a), a thin metal film is evaporated on top of a glass prism, and the evanescent field at the metal-prism interface tunnels through the metal film to excite SPPs at the top metal-air interface. In the Otto configuration, the prism is separated from the metal film by a thin air (or low index medium) gap. The evanescent
field from TIR occurs at the prism-air interface, and SPPs are excited at the top air-metal interface when the metal film lies within the penetration depth of the evanescent field. The major advantage of the Kretschmann configuration is that the metal film is easily contacted to the prism via thermal evaporation; in the Otto configuration, the major advantage is that any stand-alone metal film can be used, regardless of its thickness.

The use of prism excitation is not practical to generate SPPs in optoelectronic devices, such as BHJ-OPVs. Instead, addition of surface features to the metallic film can be employed to meet the phase-matching conditions. Metallic gratings or periodic hole arrays (with period, \( \Lambda \)) in the metal film can be used to increase the in-plane momentum to couple the incident light into SPPs.\(^{211,212} \) The phase-matching conditions are achieved at the diffraction modes of the grating:

\[
k_{\text{pp}} = k_\text{o} \sin \theta \pm mg
\]

where \( g = \frac{2\pi}{\Lambda} \) is the reciprocal vector of the grating and \( m = (1, 2, 3, \ldots) \) is the diffraction order. Note that excitation of SPPs is only achievable under TM polarized excitation, which was also the case for prism-coupling. In addition to a periodic arrangement of grooves or holes, random surface features on a metal film can also cause near-field excitation of SPPs.\(^{211,212} \) For randomly rough surfaces, SPPs are excited for all incident angles, since, in the near-field region, diffracted

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**Figure 1.15.** Displacement of the free electrons on a metallic nanoparticle while being driven by an external oscillating electromagnetic field. The charge density oscillation forms an oscillating electric dipole with a resonant frequency of \( \omega_{\text{sp}} \).
components contain all possible wavevectors. However, under non-resonant excitation, randomly rough surfaces have a low efficiency of light-to-SPP conversion, and control of the SPP direction is not possible (e.g., for waveguide applications). Under resonant excitation conditions, most of the incident light can be coupled into SPPs, leading to a much larger light-to-SPP conversion efficiency.\textsuperscript{212} Both the grating coupling and random metallic nanostructures can not only in-couple SPPs, but can out-couple them as well \textit{via} scattering to the far-field.

\subsection*{1.3.1.2. Localized surface plasmon resonances}

Discrete metallic nanostructures (\textit{i.e.}, isolated nanostructures not connected through a planar metal film) can support non-propagating, localized surface plasmon resonances (LSPRs). Gold and silver colloidal nanoparticles (NPs) are responsible for the vivid red and yellow colors observed in stained glass windows.\textsuperscript{213-215,217} The strong colors observed by colloidal NP suspensions arise from the strong response of the free electrons on the surface of metallic NPs to incident illumination. As the size of NPs gets smaller, the surface-to-volume ratio increases such that the free charge density on the surface of metal NPs dominates the charge density oscillations supported by the metal. The surface charges are highly polarizable and exhibit a strong response to a driving field. When metallic NPs with diameters small compared to the wavelength of visible

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig16.png}
\caption{Real and imaginary parts of the dipolar polarizability of a AgNP with $r = 25$ nm, calculated using Equation 1.9. The background relative permittivity of the surrounding dielectric medium is that of water ($\varepsilon_d = 1.77$).}
\end{figure}
light are illuminated, the oscillating incident electric field causes the surface charges to become displaced relative to the positive nuclei (Figure 1.15).\textsuperscript{214,215,221} The positive nuclei exhibit a restoring force on the displaced charges, resulting in oscillation of the surface charge density relative to the nuclear framework. This oscillatory behavior is equivalent to an oscillating electric dipole, and the frequency of this oscillation is called the dipolar LSPR. The oscillating electric dipole absorbs the incident light at the LSPR frequency, and re-radiates it in the form of elastic light scattering.\textsuperscript{222} Metal NPs thus have large absorption and scattering cross-sections at their dipolar LSPR frequencies.

To determine the absorption and scattering cross-sections for metal NPs small compared to the wavelength,\textsuperscript{211,214,223} it is necessary to solve LaPlace’s equation: $\nabla^2 \phi = 0$, where $\phi$ is the electric potential and is related to the field $\vec{E}$ by $\vec{E} = -\nabla \phi$. Using the appropriate boundary conditions, the spherical harmonic solutions to Laplace’s equation result in the field outside the sphere, $\vec{E}_{\text{out}}$:

$$
\vec{E}_{\text{out}} = E_0 \hat{x} - \alpha E_0 \left[ \frac{\hat{x}}{\rho^3} - \frac{3x}{\rho^3} (x\hat{x} + y\hat{y} + z\hat{z}) \right]
$$

where $E_0$ is the amplitude of the incident electric field, $\alpha$ is the dipolar polarizability of the sphere, $\rho$ is the radial spherical coordinate, $\rho = \sqrt{x^2 + y^2 + z^2}$, and $\hat{x}, \hat{y}, \hat{z}$ are the unit vectors. The first term in Equation 1.8 is the applied field, and the second is the induced dipolar field. The dipolar polarizability of a sphere is given by:

$$
\alpha = g_d \rho^3
$$

where $g_d$ is:

$$
g_d = \left( \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \right)
$$

which, since $\epsilon_m$ is complex, $\alpha$ is also complex; see Figure 1.16 for $\alpha$ for a AgNP in water with $r =$
Figure 1.17. LSPRs from AgNPs in water ($\varepsilon_d = 1.77$) of varying $r$. (a) Dipolar LSPR for AgNP with $r = 25$ nm, shown for $\lambda = 420$ nm. (b) Quadrupolar LSPR for AgNP with $r = 50$ nm, shown for $\lambda = 395$ nm. (c) Scattering from AgNPs for varying $r$, calculated using finite-difference time-domain (FDTD) simulations.

25 nm. The resonance condition for a sphere is achieved when $\varepsilon_m = -2\varepsilon_d$, which occurs at 390 nm for this AgNP. The extinction (i.e., absorption + scattering) and scattering cross-sections ($C_{\text{ext}}$ and $C_{\text{sca}}$, respectively) are calculated as:

$$C_{\text{ext}} = \pi r^2 4\chi \text{Im}(g_d)$$

$$C_{\text{sca}} = \pi r^2 \frac{8}{3} \overline{\chi}^4 |g_d|^2$$

where $\chi = 2\pi r(\varepsilon_d)^{1/2} / \lambda$. Note that these calculations are only valid when the NP is small compared to the wavelength ($\chi \ll 1$), when the NP is essentially embedded in a uniform static field; this is called the electrostatic approximation.$^{211,214,223}$

The induced dipolar field (second term in Equation 1.8) gives rise to an enhancement in the local electric field relative to the incident field, $E_0$, and typical enhancement values are around 100× for spheres.$^{214}$ The field enhancement is largest just at the metal-dielectric interface, and falls off as $1/\rho^3$ away from the NP surface (Figure 1.17a). Additionally, $C_{\text{sca}}$ scales with $r^6$, so
small changes in the NP radius can lead to large increases in the scattering intensity (Figure 1.17c). For slightly larger particles (but still within the limit $\chi << 1$), higher order LSPR modes are supported. In particular, the quadrupolar mode becomes significant as $r$ increases to ~40 nm for AgNPs. Including the quadrupolar modes in the solutions to Laplace’s equation yields:

$$\dot{E}_{\text{ext}} = E_0 \hat{x} + i k E_0 (x \hat{x} + z \hat{z}) - \alpha E_0 \left[ \frac{x}{\rho^3} - \frac{3x}{\rho^3} (x \hat{x} + y \hat{y} + z \hat{z}) \right] - \beta E_0 \left[ \frac{x \hat{x} + z \hat{z}}{\rho^3} - \frac{5z}{\rho^5} (x^2 \hat{x} + y^2 \hat{y} + xz \hat{z}) \right]$$

(1.13)

which now contains the incident field (first real and imaginary terms), the dipolar field (second real term), and the quadrupolar field (last term). The quadrupolar polarizability is given by:

$$\beta = g_q r^5$$

(1.14)

with

$$g_q = \left( \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + \frac{4}{3} \varepsilon_d} \right)$$

(1.15)

Thus, the quadrupolar resonance condition for a sphere is achieved when $\varepsilon_m = -\frac{1}{2} \varepsilon_d$. The extinction and scattering cross-sections are given by:

$$C_{\text{ext}} = 4 \pi r^2 \chi \left[ g_d + \frac{2}{15} g_q + \frac{2}{90} (\varepsilon_m - 1) \right]$$

(1.16)

$$C_{\text{scat}} = 2 \pi r^2 \left[ \frac{g_q}{240} + \frac{22}{900} (\varepsilon_m - 1) \right]$$

(1.17)

The 4 lobes of the quadrupolar fields are shown in Figure 1.17b for an AgNP in water with $r = 50$ nm, at $\lambda = 395$ nm. The quadrupolar and dipolar modes are observed at short and longer wavelengths, respectively, in the scattering spectra from AgNPs having $r = 40$ or 50 nm (Figure 1.17c). We note that the scattering spectra shown in Figure 1.17c were calculated numerically using finite-difference time-domain (FDTD) simulations, and so differ from the analytical Equations 1.12 and 1.17. The equations for $C_{\text{scat}}$ do not include finite wavelength effects, which become important as $r$ becomes large relative to the wavelength, when the electrostatic
approximation is no longer valid.\textsuperscript{211,214,223}

The shape of metal NPs is also important in determining the LSPR due to the shape-dependent polarizability of the free electrons.\textsuperscript{216,217,224} For example, nanorods having ellipsoidal geometry with one axis a different length from the other two support different resonances along each axis: transverse and longitudinal LSPRs along the short and long axes of the nanorod, respectively.\textsuperscript{214,221,225,226} This arises directly from the shape-dependent ellipsoid polarizability:

$$\alpha_i = (4\pi abc)g_i$$ \hspace{1cm} (1.18)

where $a$, $b$, and $c$ are the half-lengths of the ellipsoid along the three major axes, and $g_i$ is:

$$g_i = \frac{\varepsilon_m - \varepsilon_\delta}{3\varepsilon_\delta + 3L_i(\varepsilon_m - \varepsilon_\delta)}$$ \hspace{1cm} (1.19)

where $L_i$ is the depolarization factor along the $i^{th}$ direction. Metal nanorods (NRs) typically have prolate ellipsoidal structures resulting from their anisotropic growth along a preferential crystalline plane. The scattering from prolate AgNRs, which have $a > b = c$, for fixed short axes of $b = c = 25$ nm and varying long axis of $a$, are shown in Figure 1.18c. When all axes are the same length, the dipolar LSPR from the symmetric spherical geometry is observed at 420 nm. As $a$ increases in length, breaking the spherical symmetry results in splitting of the dipolar LSPR, with the transverse (short wavelength) LSPR blue-shifting slightly as $a$ increases, and the longitudinal (long wavelength) LSPR red-shifting to a much larger degree. Comparing the scattering from AgNRs to that from AgNPs, the AgNRs allow for greater wavelength tunability in the plasmonic modes without dramatically increasing the damping (\textit{i.e.}, the linewidth) of the mode. The electric field intensity profiles are shown in Figure 1.18a,b for AgNRs with $a = 75$ nm (\textit{i.e.}, an aspect ratio, $a/b = 3$) for the two peaks observed in the scattering spectra: 390 nm (a) and 760 nm (b). The electric field intensity profiles confirm the transverse and longitudinal nature of the two resonances. It should be noted that the electric fields from the longitudinal LSPR at 760 nm are enhanced to a significantly larger degree compared to those from the transverse LSPR at 390 nm.
Figure 1.18. LSPRs from prolate AgNRs in water ($\varepsilon_d = 1.77$) with short axes $b = c = 25$ nm and varying long axis, $a$. (a) Transverse and (b) longitudinal LSPRs for AgNR with $a = 75$ nm, shown for $\lambda = 390$ nm and 760 nm, respectively. (c) Scattering from AgNRs for varying $a$, calculated using finite-difference time-domain (FDTD) simulations.

Finally, the choice of metal is important in determining the plasmonic resonances of nanostructures (see Equation 1.10). The bulk plasma frequency, $\omega_p$, of a metal is given by:

$$\omega_p = \sqrt{\frac{N q^2}{\varepsilon_0 m_e}}$$

(1.20)

where $N$ is the number of free electrons, $q$ is the electrical charge, $\varepsilon_0$ is the vacuum permittivity, and $m_e$ is the electron mass. Thus, the number of free electrons is critical for determining $\omega_p$, and ultimately the LSPR and $\omega_{pp}$. The optical properties of a metal can be described by $\omega_p$ and the collision frequency of free electrons, $\gamma$, by the Drude-Lorentz equation:

$$\varepsilon_m(\omega) = \varepsilon_{int} - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}$$

(1.21)

where $\varepsilon_{int}$ is contribution due to interband transitions, and the real and imaginary parts of
Equation 1.21 are given by:

\[ \varepsilon_1(\omega) = \varepsilon_{1,\text{int}} - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \]  \hspace{1cm} (1.22a) 

\[ \varepsilon_2(\omega) = \varepsilon_{2,\text{int}} + \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} \]  \hspace{1cm} (1.22b) 

where \( \tau = 1/\gamma \) is the electron scattering time. For very conductive materials, \( N \) and \( \tau \) are large (see Table 1.1), meaning the most conductive metals have large carrier concentrations and long times between electron-electron scattering events. Based on the large values for \( N \), metals have \( \omega_p \) in the UV regime. For \( \omega < \omega_p \), \( \varepsilon_1 \) is negative and metals have metallic character (e.g., high reflectivity, can satisfy the resonance conditions for Equations 1.10 and 1.15). \(^{211}\) \( N \) and \( \tau \) effectively determine the plasmonic properties of the metal, such as the strength of the field enhancement and the SPP decay length. Larger \( N \) and \( \tau \) result in a more negative \( \varepsilon_1 \) and a smaller \( \varepsilon_2 \), which increases the field enhancement the SPP decay length. As \( \tau \) decreases, the loss increases, resulting in reduced SPP decay lengths. Thus, metals that support the lowest loss plasmons in the visible are Ag, Au, Cu, and Al (Table 1.1). Three examples of lossy metals are included in Table

<table>
<thead>
<tr>
<th>Metal</th>
<th>( N (\times 10^{22} \text{ cm}^{-3}) )</th>
<th>( \tau ) (fs)</th>
<th>( N\tau (\times 10^{22} \text{ fs/cm}^3) )</th>
<th>( \omega_{\text{int}} ) (eV)</th>
<th>( \omega_p ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>5.89</td>
<td>230.0</td>
<td>1355</td>
<td>3.9</td>
<td>9.01</td>
</tr>
<tr>
<td>Au</td>
<td>5.91</td>
<td>155.1</td>
<td>917</td>
<td>2.3</td>
<td>9.03</td>
</tr>
<tr>
<td>Cu</td>
<td>3.96</td>
<td>455.7</td>
<td>1805</td>
<td>2.1</td>
<td>7.39</td>
</tr>
<tr>
<td>Al</td>
<td>15.8</td>
<td>50.54</td>
<td>798</td>
<td>1.41</td>
<td>14.8</td>
</tr>
<tr>
<td>Pt</td>
<td>1.92</td>
<td>59.78</td>
<td>115</td>
<td>5.15</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.73</td>
<td>94.76</td>
<td>164</td>
<td>4.89</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>2.98</td>
<td>68.49</td>
<td>204</td>
<td>6.41</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.19. Scattering from metal NPs in water ($\varepsilon_d = 1.77$) with $r = 25$ nm for the metals supporting the lowest loss plasmons in the visible. Note that the scattering intensity was reduced by factors of 5 and 3 for Ag and Al, respectively.

1.1: Pt, Ni, and W. Appendix A1, Figures A1 and A2 show the optical constants (complex refractive index and $\varepsilon_m(\omega)$) of the 4 low-loss metals and several lossy metals. Note that the effect of interband transitions increases $\varepsilon_1$ and $\varepsilon_2$, resulting in a lossier metal within the range of interband transitions. Au and Cu have interband transitions in the visible regime, resulting in an increase in their lossiness compared to Ag and Al, which have interband transitions in the UV and NIR, respectively (Table 1.1).\textsuperscript{20,211,227} This is strongly evidenced in the LSPR from Ag, Au, Cu, and Al NPs in water (Figure 1.19). Ag and Al exhibit strong scattering throughout the visible because of their low loss, particularly for Ag. Au and Cu have significantly reduced scattering compared to Ag and Al, and their LSPRs occur at wavelengths near their interband transition wavelengths. For these reasons, Ag is often the metal of choice for low-loss surface plasmons in the visible regime.

1.3.2. Plasmonic metasurfaces as back electrodes in BHJ-OPVs

Having reviewed the fundamental properties of surface plasmon polaritons and localized surface plasmon resonances, we now discuss how plasmonic metasurfaces,\textsuperscript{228,229} which can support both LSPRs (Figure 1.17) and SPPs (Figure 1.13), can lead to improved efficiency in
Table 1.2 Table of BHJ-OPV efficiency (η) enhancement factors for devices containing plasmonic metasurfaces as back electrodes relative to planar devices (η_{plasmonic}/η_{planar}) (actual η_{plasmonic} values in brackets). Abbreviations used: EF = enhancement factor; λ = wavelength; d = diameter; h = height; Λ = period; Thry, T = theory; Exp, E = experiment; Conv = conventional; Inv = inverted; Coating = plasmonic metasurface coated with active layer (incomplete device); MIM = metal-insulator-metal; Ref = reference.*Denotes absorption EF occurring at the wavelength(s) specified in brackets; int = integrated absorption EF.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Active layer system</th>
<th>EF (η) or (Δ)</th>
<th>Thry / Exp</th>
<th>Device type</th>
<th>Mechanisms</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D Ag grating (Λ = 140 nm)</td>
<td>P3HT:PCBM</td>
<td>1.21 (int)*</td>
<td>T</td>
<td>Conv</td>
<td>Near-field enhancement</td>
<td>(9)</td>
</tr>
<tr>
<td>1D Al grating (Λ = 250 nm)</td>
<td>P3HT:PCBM</td>
<td>2.72 (618 nm)*</td>
<td>E</td>
<td>MIM</td>
<td>SPP</td>
<td>(2)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 300 nm)</td>
<td>PTB7:PCBM</td>
<td>1.04 (10.21%)</td>
<td>T</td>
<td>Inv</td>
<td>Improved absorption, reduced charge separation</td>
<td>(23)</td>
</tr>
<tr>
<td>1D Al grating (Λ = 350 nm)</td>
<td>P3HT:PCBM</td>
<td>0.89 (2.28%)</td>
<td>T</td>
<td>Conv</td>
<td>Increased generation rate, reduced charge separation</td>
<td>(24)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 500 nm)</td>
<td>PCDTBT:PCBM</td>
<td>1.102 (int)*</td>
<td>T</td>
<td>Coating</td>
<td>LSPR and SPP</td>
<td>(25)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 700 nm)</td>
<td>PTB7:PCBM</td>
<td>1.07 (7.73%)</td>
<td>E</td>
<td>Inv</td>
<td>Waveguide modes, Wood’s anomaly, and LSPR</td>
<td>(3)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 750 nm)</td>
<td>P3HT:PCBM</td>
<td>1.19 (3.68%)</td>
<td>E</td>
<td>Inv</td>
<td>Diffraction and SPP</td>
<td>(38)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 750 nm)</td>
<td>PBDTTT-C-T:PCBM</td>
<td>2.37 (1.73%)</td>
<td>E</td>
<td>Inv</td>
<td>Near-field enhancement, reduced recombination and space-charge accumulation</td>
<td>(4)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 750 nm)</td>
<td>P3HT:PCBM</td>
<td>1.10 (8.38%)</td>
<td>E</td>
<td>Inv</td>
<td>Increased interface area, reduced Rs, Wood’s anomaly, and SPP-Floquet mode hybridization</td>
<td>(6)</td>
</tr>
<tr>
<td>1D Ag grating (Λ = 1040 nm)</td>
<td>P3HT:PCBM</td>
<td>1.15-1.25 (int)*</td>
<td>T+E</td>
<td>Conv</td>
<td>SPP and Fabry-Pérot resonance hybridization and waveguide modes</td>
<td>(26)</td>
</tr>
<tr>
<td>2D Ag grating (Λ = 350 nm, h = 55 nm)</td>
<td>P3HT:PCBM</td>
<td>1.25 (3.85%)</td>
<td>E</td>
<td>Inv</td>
<td>Reduced Rs, polarization-insensitive LSPR</td>
<td>(6)</td>
</tr>
<tr>
<td>2D periodic Ag nanohole array (Λ = 320 nm)</td>
<td>PCPDTBT:PCBM</td>
<td>2.12</td>
<td>T</td>
<td>Conv</td>
<td>Short range SPP</td>
<td>(6)</td>
</tr>
<tr>
<td>2D periodic Ag granular structures (Λ = 420 nm)</td>
<td>PTPTB:PCBM</td>
<td>1.10 (3.15%)</td>
<td>E</td>
<td>Conv</td>
<td>Back-scattering and SPR</td>
<td>(6)</td>
</tr>
<tr>
<td>2D quasi-periodic Ag hole array</td>
<td>P3HT:PCBM</td>
<td>7 (700 nm)*</td>
<td>E</td>
<td>Coating</td>
<td>Near-field enhancement</td>
<td>(6)</td>
</tr>
<tr>
<td>Multi-periodic Ag triangular grating</td>
<td>P3HT:PCBM</td>
<td>1.207 (int)*</td>
<td>T</td>
<td>Coating</td>
<td>SPP resonances, waveguide mode resonances, Fabry-Pérot modes, and scattering</td>
<td>(6)</td>
</tr>
<tr>
<td>Corrugated Ag film</td>
<td>P3HT:ICBA</td>
<td>1.06 (5.56%)</td>
<td>E</td>
<td>Inv</td>
<td>LSPR</td>
<td>(6)</td>
</tr>
<tr>
<td>AgNP monolayer (d=45 nm; h=20 nm)</td>
<td>P3HT:PCBM</td>
<td>2.4 (0.11%)</td>
<td>E</td>
<td>Inv</td>
<td>Back-scattering</td>
<td>(6)</td>
</tr>
<tr>
<td>AgNP array/Ag film</td>
<td>P3HT:PCBM</td>
<td>11 (740 nm)*</td>
<td>E</td>
<td>Coating</td>
<td>LSPR</td>
<td>(2)</td>
</tr>
<tr>
<td>Gap waveguide mode with vertically-oriented polymer chains</td>
<td>P3HT</td>
<td>2.5 (int)*</td>
<td>T</td>
<td>Coating</td>
<td>Orientation-dependent SPP coupling</td>
<td>(2)</td>
</tr>
</tbody>
</table>

BHJ-OPV devices.

Nanostructuring the back electrode is a common method employed to increase light trapping in the active layer of BHJ-OPVs. Patterns can be fabricated using large-area, nanofabrication methods such as nanoimprint lithography (NIL), 38,54,65,230 nanosphere
Roll-to-roll processes that incorporate NIL are currently under development and could enable high-throughput integration of plasmonic back electrodes. We begin by discussing some of the fabrication methods for producing plasmonic back electrodes.

Metallic gratings have been extensively studied as the back electrodes of BHJ-OPVs for both inverted and conventional devices. One-dimensional (1D) gratings have the benefit of relatively simple fabrication (e.g., laser interference, NIL, or solution-based fabrication via NP-imprinting) and can couple light into both LSPR and propagating SPP modes. NIL is one of the most common approaches to fabricating metallic gratings as back electrodes as it is capable of fabricating large areas of nanoscale structures with great precision and low cost. NIL is carried out by the direct mechanical deformation of a resist by applying pressure at elevated temperatures or by exposure to UV light. It is considered a non-conventional lithography in that it can achieve higher resolution (sub-25 nm structures) than traditional photolithography techniques since it is not limited by the effects of light diffraction and beam scattering. 1D metallic grating back electrodes have been fabricated by imprinting directly into the BHJ active layer blend, where the active layer serves as the resist in the NIL process, followed by subsequent metal deposition. In some instances, where it would have been deleterious to the active layer to use thermal or photocurable NIL, Li et al. developed and employed a vacuum-assisted NIL process, in which NIL was conducted simply by applying the mold containing the nanostructures to the active layer and placing the set in a vacuum chamber at 10^{-2} Torr and room-temperature. Alternatively, metallic grating electrodes have also been fabricated by depositing the active layer on top of a pre-patterned grating. While directly imprinting the active layer can potentially change the molecular orientation or crystallinity of the active layer due to the application of pressure and/or high temperatures (see Section 1.3.2.3), this potential morphological impact on device performance is not often characterized or accounted
Two-dimensional (2D) plasmonic metasurfaces can have additional benefits over 1D grating electrodes, as discussed in the sections below, although they often require more fabrication steps than 1D plasmonic metasurfaces. One type of 2D nanostructured metallic back electrode employed in BHJ-OPVs is an array of nanoholes perforated into a metallic thin film. In one study, various periodic nanohole arrays were patterned by focused ion beam (FIB) milling into a 300-nm-thick Ag film (see Section 1.3.2.1). Although this type of study is very useful to gain an understanding of how periodicity affects absorption enhancements, the FIB nanofabrication route is not amenable to large-scale processing, which is a major drawback for incorporating these structures into real devices.

Another class of 2D nanostructured metallic electrodes explored for BHJ-OPVs are corrugated metal surfaces. In one example, wrinkles and folds were formed on an optical adhesive layer by biaxially-induced stress from UV exposure followed by corona discharge, and the device was constructed on the corrugated epoxy surface, giving each layer a textured corrugation. Variations of nanosphere lithography have also been used in creating corrugated surfaces. For example, one study employed hole-mask colloidal lithography, in which PS beads were drop cast onto the active layer, followed by deposition of MoO$_x$ and subsequent removal of the PS beads. This left behind an array of holes in the MoO$_x$; another 5 nm of MoO$_x$ was deposited as a buffer layer in the pits of the holes, followed by 200 nm of Ag, resulting in a corrugated Ag electrode. Another variation of nanosphere lithography first created a hole array by depositing PS spheres onto a Si substrate, partially etching the spheres using O$_2$ plasma, evaporating Ni onto the PS-coated substrate, removing the PS spheres, and inductively coupled plasma (ICP) etching into the holes left behind by the spheres. A negative copy of the hole array was formed using PDMS, which was then coated with P3HT:PCBM, and was finally transferred to the PEDOT:PSS/ITO substrate by stamping. This left a 2D, periodic hole array in the active layer, which was then coated with Al to form the corrugated metallic electrode by
filling in the holes of the active layer.\textsuperscript{67} Finally, thermal evaporation through a nanoporous anodic aluminum oxide (AAO) membrane onto a metallic film has been used to create a randomly-distributed 2D array of AgNPs on a Ag film, which was then coated by the active layer by spin-coating.\textsuperscript{72,201}

1.3.2.1. Optical effects of plasmonic metasurfaces as back electrodes

As described in Section 1.3.1.1, the phase-matching conditions to couple light to a SPP for a 1D metallic grating structures are achieved for the diffraction modes of the grating (Equation 1.7).\textsuperscript{211} The incident light should have a component polarized perpendicular to the grating lines in order to couple into a grating mode (\textit{i.e.}, either unpolarized or TM polarization).\textsuperscript{193} It has been shown that, compared to TM polarization, for light polarized parallel to the grating lines (\textit{i.e.}, TE polarization), there was considerably less absorption enhancement in an organic active layer-coated metallic grating relative to the same active layer material coated onto a planar metallic electrode.\textsuperscript{21,29,69,242} Therefore, the performance of a 1D metallic grating back electrode is highly sensitive to the polarization of incident light, and for unpolarized sunlight, the observed enhancement factors in BHJ-OPV devices are less than what can be achieved for purely TM-polarized incident light. This has been a large motivation for the use of 2D metallic nanostructured electrodes, which tend to be far less sensitive to the incident light polarization state.\textsuperscript{28,65,69} However, it is also possible to overcome polarization issues associated with 1D gratings by employing 1D gratings with large periods (> 1000 nm), which not only can couple SPPs with Bloch modes, but can also excite a photonic waveguide mode under TE polarized illumination, thereby allowing for both an in-plane propagating TM-polarized plasmonic mode and an in-plane propagating TE-polarized photonic mode to contribute to increased light trapping in the active layer.\textsuperscript{28}

The range of plasmonic and photonic modes that have been observed for 1D metallic gratings used in BHJ-OPVs are Bloch (\textit{i.e.}, Floquet) mode-coupled SPPs.\textsuperscript{21,37,38,54,64,69,242} Wood’s
anomaly,\textsuperscript{37,64} LSPRs,\textsuperscript{29,37} back-scattering,\textsuperscript{29,37} and Fabry-Pérot resonances for triangular\textsuperscript{69} and large-period gratings.\textsuperscript{28} For excitation of Bloch mode-coupled SPPs, TM-polarized incident light was used in order to observe the effect in BHJ-OPV devices. Incident angle-insensitive absorption enhancement has been observed theoretically for a 1D triangular grating structure.\textsuperscript{69} The non-dispersive absorption enhancement was achieved by tuning “bright” and “dark” SPP modes, \textit{i.e.}, modes that were present for $\theta_i = 0$ and those that required $\theta_i > 0$. Tuning the grating height and fill factor (base length of triangle divided by the period) were crucial to control the bright and dark modes.\textsuperscript{69} By extending the simulations to a 2D pyramid grating structure, the absorption enhancement became polarization-insensitive as well.\textsuperscript{69}

Lu \textit{et al.} integrated plasmonic 1D Ag grating structures fabricated using NIL on the back electrodes of BHJ-OPV devices incorporating an active layer of PCDTBT:PCBM with two different thicknesses (30 nm and 60 nm).\textsuperscript{29} They observed that the absorption enhancement factor decreased with increasing active layer thickness because a thinner active layer absorbs less light and, therefore, offers larger potential for absorption enhancement. Additionally, the origin of the absorption enhancements was attributed to a combination of broadband scattering from the grating, LSPR modes near the active layer absorption edge, and SPP modes at wavelengths longer than the absorption band edge. It was shown that SPP modes were particularly sensitive to active layer thickness and grating period due to requirements for phase matching. Parasitic absorption by the metallic gratings was also considered theoretically and was expected to account for a significant fraction of the experimentally measured absorption enhancement of the metallic grating and active layer composite structure,\textsuperscript{29} which is a common issue associated with reporting absorption enhancement factors from only experimental measurements.\textsuperscript{21,28,70,72,201}

Sefunc \textit{et al.} theoretically investigated the active layer optical absorption enhancement that occurred for a 1D Ag grating back electrode, having a period of 140 nm, integrated into a conventional P3HT:PCBM-based BHJ-OPV device.\textsuperscript{16} They compared the active layer absorption in a BHJ-OPV device incorporating the grating electrode to that of a planar BHJ-OPV for both
TE and TM polarizations and found that active layer absorption increased for both polarizations by up to ~21% relative to the planar device configuration. The authors also reported that the performance of such grating electrodes exceeded that of similar gratings embedded in the PEDOT:PSS hole transport layer (i.e., as a plasmonic interlayer).\textsuperscript{16}

Other plasmonic back electrode structures, such as 2D nanohole arrays in Ag, have resulted in broadband absorption enhancement in P3HT:PCBM films, particularly for thinner P3HT:PCBM films (~24 nm thickness).\textsuperscript{66,68,254} For thicker P3HT:PCBM films (150 nm), nanohole array back electrodes resulted in more modest absorption enhancement across the visible spectrum, with the strongest enhancement occurring for wavelengths longer than 600 nm, where the absorption coefficient of P3HT:PCBM is small.\textsuperscript{66,68,254} A heptadeca-grid quasi-periodic nanohole array was predicted to be polarization- and angle-insensitive due to the broad, diffuse diffraction rings occurring in the Fourier transform power spectrum of the nanohole array compared to the periodic points occurring in the Fourier transform power spectrum of a periodic nanohole array.\textsuperscript{68} The quasi-periodic nanohole array was also further optimized using a “cut and projection” algorithm in order to maximize the constructive interference between SPPs generated at each of the holes,\textsuperscript{254} leading to an absorption enhancement factor of ~6 at a wavelength of ~700 nm. Theoretical calculations of a periodic nanohole array in an Ag back electrode have shown that integrated absorption enhancement factors can reach 2.12 for an optimized period of 320 nm by coupling light into a broadband short-range SPP (SR-SPP).\textsuperscript{66}

Random arrays of AgNPs on Ag electrodes have been shown to enhance OPVs predominantly through LSPR hot spots and back-scattering into the active layer.\textsuperscript{67,70,72,201} Although these 2D corrugated metallic electrodes should theoretically be able to support SPPs at the interface between the polymer active layer and the metal films, this has not yet been demonstrated experimentally. P3HT:PCBM-based OPV device efficiency enhancement from corrugated metallic electrodes formed on wrinkles and folds was shown not to arise from plasmonic effects, but was attributed to refraction of light at each interface of the folded and
wrinkled device leading to improved light trapping and waveguiding within the photoactive layer.\textsuperscript{248} Interestingly, this study also demonstrated significant external quantum efficiency (EQE) enhancement at wavelengths longer than the absorption edge of the P3HT:PCBM system (greater than 600% enhancement at wavelengths longer than 650 nm), which the authors suggested was due to either charge-transfer complexes or tail states of the P3HT and/or PCBM.\textsuperscript{248} This type of electronic-state enhancement in the EQE beyond the bandgap wavelength of the polymer absorber can only be readily observed experimentally in functioning BHJ-OPV devices, and is challenging to predict using optical simulations alone. This highlights the need for more extensive EQE studies of BHJ-OPV devices incorporating plasmonic metasurfaces because optical/photonic effects may not be the only cause of enhancements in solar power conversion efficiency.

1.3.2.2. Electrical and electronic effects of plasmonic metasurfaces as back electrodes

Although optical effects of plasmonic metasurfaces have been studied thoroughly, both for back and front electrodes, studies on how plasmonic metasurfaces can improve the electrical or electronic properties of BHJ-OPVs have been limited, especially for plasmonic metasurfaces as back electrodes. Several studies employing 1D metallic gratings on the back electrode have shown improved fill factors ($FF$), which the authors attributed to the nanoimprinted active layer having a larger interfacial area than the planar one, as well as the lower series resistance ($R_s$) of the nanoimprinted device.\textsuperscript{38,64} While this could be due to the geometry of the grating structure alone, molecular orientation or crystallinity effects that may arise from directly imprinting the active layer were not considered in detail.\textsuperscript{243,244} Such effects could give rise to increased charge mobility in the active layer, thereby reducing bulk recombination and $R_s$ (see Section 1.3.2.3 on morphological effects).

However, a recent study has shown that the space-charge limit in OPVs can be overcome in devices incorporating metallic gratings.\textsuperscript{54} This was attributed to the grating structure causing a
redistribution of the local exciton generation in the active layer, thus giving a shortened transport path for positive charge carriers in inverted BHJ-OPV devices. The authors suggested the resulting faster collection of holes at the plasmonic metasurface reduced the bulk recombination and hole accumulation, as supported by photovoltage measurements.\textsuperscript{54} The grating structure was shown to be more useful for the inverted device architectures, where holes are collected at the metallic grating and electrons at the transparent, flat electrode.\textsuperscript{54} These experiments indicate that electrical effects play an important role in designing plasmonic metasurfaces as electrodes for BHJ-OPVs.

Coupled optical and electrical simulations have been performed for plasmonic-enhanced inorganic photovoltaics,\textsuperscript{255} but to date, relatively few such studies have been carried out for plasmonic-enhanced BHJ-OPVs. In some reports, coupled optical and electrical simulations of metallic grating back electrodes for BHJ-OPVs have shown that, in general, optical absorption enhancements tend to be canceled out by electrical charge separation reductions.\textsuperscript{25,200} However, it has been stressed that inverted OPVs can benefit more from grating electrodes because, in a planar OPV, the generation of excitons is highest towards the front electrode\textsuperscript{25,200} (anode in conventional device; cathode in inverted device; see Figure 1.7). Since holes typically have lower mobilities in polymers than electrons in the fullerenes, in the inverted configuration, the holes have a much further path to travel to reach the metallic anode, leading to increased hole recombination in inverted devices relative to conventional devices. The presence of the grating back electrode (or potentially any of the plasmonic back electrode structures discussed here) modifies the generation rate in the active layer, allowing for the holes to have a shortened path to the back plasmonic anode. The elimination of the space-charge limited region in the grating-inverted OPV was the first experimental evidence that these plasmonic metasurfaces can influence the charge carrier transport properties in BHJ-OPVs,\textsuperscript{54} highlighting the importance of coupled optical and electrical experiments and simulations for designing effective plasmonic metasurfaces for use in BHJ-OPVs.
Another unique electronic effect that has not yet been explored for plasmon-enhanced BHJ-OPV devices, but is, regardless, a very active area of research for plasmon-enhanced PVs, is hot carrier generation and extraction at a metal nanostructure-semiconductor interface.\textsuperscript{256-261} As mentioned in Section 1.3.2.1, parasitic absorption by the metal is often a common problem when employing metallic nanostructures for PV applications. Instead of losing the energy absorbed by the metal to heat, it is desirable to find an approach for generating electricity out of that energy. For a metal-semiconductor non-Ohmic interface, a Schottky barrier exists, which is typically a smaller energy compared to the bandgap of the semiconductor.\textsuperscript{256-261} When the metal absorbs light, an electron in the metal can be excited above the Fermi level (\textit{i.e.,} a ‘hot electron,’), leaving behind a ‘hot hole,’ and, if the energy of the incident light is greater than that of the Schottky barrier, the hot electron (hole) can be injected into the conduction (valence) band of the \textit{n}-type (\textit{p}-type) semiconductor, a process called internal photoemission.\textsuperscript{256-261} In this way, sub-bandgap light can be absorbed by the device. Although the process usually is very inefficient for a typical metal-semiconductor interface,\textsuperscript{258,260} employing the strong plasmonic absorption by metallic nanostructures can increase the hot carrier density, leading to greatly enhanced internal photoemission efficiencies.\textsuperscript{260} This phenomenon has been studied for Si\textsuperscript{258} and metal

\textbf{Figure 1.20} Possible morphologies of conjugated polymer crystallites. (a-c) In general, there are 3 possible configurations for polymer chains to crystallize: (a) edge-on, with the polymer backbone parallel to the substrate and the side chains perpendicular; (b) face-on, with the polymer backbone and side chains parallel to the substrate; and (c) vertical, with the polymer chains perpendicular to the substrate and the side chains parallel.
oxides, but has not yet been investigated for organic semiconductors. The generation and extraction of hot electrons or holes should be further investigated in BHJ-OPV devices employing plasmonic metasurfaces, as they can potentially help harness sub-bandgap incident light wavelengths or parasitic absorption by the metal that would otherwise be wasted.

1.3.2.3. Morphological effects of plasmonic metasurfaces as back electrodes

A recent theoretical study has addressed the important issue of polymer chain morphology in coupling highly anisotropic SPP waves into anisotropic polymer absorbers. Since single-interface SPPs have a strong out-of-plane component of the electric field, the largest absorption enhancement can be observed when the polymer chains align such that their transition dipole moment is oriented out-of-plane (i.e., in the ‘vertical’ orientation, Figure 1.20(c)). While most conjugated polymers tend to have optical transition dipole moments oriented along the polymer backbone chain direction (hence, transition dipoles are typically in-plane due to the edge-on and face-on orientations that most conjugated polymers take during the spin coating process, Figure 1.20(a,b)), polymers such as polycarbazole (PVK), with the conjugation occurring on the side group rather than the polymer backbone itself, satisfy the requirement for an out-of-plane transition dipole moment. Additionally, polymer chains may align in the out-of-plane direction under certain circumstances, such as electrodeposited polymerization of P3HT through an AAO membrane, as evidenced by photoluminescence anisotropy studies. Experimental studies of the effect of molecular orientation on SPPs generated at conjugated polymer-metal interfaces are currently lacking. Such studies could help to determine if control of molecular orientation can be used as an approach to further increase BHJ-OPV efficiency enhancement factors beyond those currently observed when incorporating electrodes that support surface plasmon modes.

As mentioned in the preceding sections, although the active layer is often imprinted directly prior to thermal evaporation to form a metallic grating, morphological studies (using, for
example, wide-angle X-ray scattering (WAXS)), have not often been conducted in order to rule out contributions of improved crystallinity or molecular orientation to device performance enhancements.\textsuperscript{37,38,64} However, it has been shown that by imprinting the active layer directly, the orientation of the polymer molecules will be affected.\textsuperscript{243,244} For example, imprinting a 1D grating from a hard Si mold into neat P3HT led to an increase in the face-on to edge-on ratio, with the polymer backbones aligning preferentially along the direction of the grating’s grooves.\textsuperscript{244} Such morphological effects can have significant implications for polymer solar cells, since the face-on orientation has been suggested to have improved charge transport across the polymer-electrode interface.\textsuperscript{244,270} Additionally, vertical polymer chain alignment was shown to occur in another study in which different mold materials were used for the pattern imprint (Figure 1.20(d,e)).\textsuperscript{243} As mentioned above, vertical chain alignment could be useful for gaining further active layer absorption enhancement through alignment of the transition dipole axis of the polymer chains to the TM-polarized SPP electric fields. Therefore, these types of molecular orientation effects should be explored when directly imprinting the active layer for subsequent plasmonic back electrode formation.

1.4. Thesis Objectives and Overview

The key objectives of this thesis are: (1) to predict the optimal planar metallic electrodes for conventional and inverted BHJ-OPVs; (2) to design and fabricate plasmonic metasurfaces that can lead to enhanced absorption and photocurrent within BHJ-OPVs; (3) to develop an understanding of the electromagnetic coupling between plasmons and excitons in broad spectral absorbers, and how this coupling can be used to enhance absorption in photovoltaics; and (4) to fabricate multifunctional plasmonic metasurfaces with ultrathin interfacial layers to simultaneously control the surface workfunction and the optical properties of the metasurface. As described in Section 1.3.2, plasmonic metasurfaces have been shown to lead to improvements in the efficiency of BHJ-OPVs through: enhancements in the active layer absorption via propagating
SPPs and LSPR field enhancements; reduction of the space-charge limit *via* spatial modification of the photogenerated excitons; and control of the molecular orientation of the conjugated polymer chains. Active layer absorption enhancement nearly always is maximal at wavelengths red-shifted from the absorption band edge of the active layer, regardless of the type of plasmonic nanostructure employed. In this thesis, we demonstrate that this red-edge absorption enhancement arises from a previously unidentified mode type called absorption-induced scattering, which we show is the low energy hybrid mode of plasmon-exciton coupled states. Further, while the effects described above for plasmonic metasurface-enhanced BHJ-OPVs have lead to improvements in the $J_{sc}$, they have had minimal impact on the $V_{oc}$. We show here that the application of ultrathin interfacial layers, specifically 2D MoS$_2$ and AgO$_x$, to Ag plasmonic metasurfaces has minimal impact on their optical properties, but are are expected to modify the metasurface workfunction. This is expected to allow for simultaneous enhancements in the $J_{sc}$ and $V_{oc}$ of BHJ-OPVs employing multifunctional plasmonic metasurfaces.

To predict the optimal planar metal electrodes for conventional and inverted devices in BHJ-OPVs, in Chapter 2, we compute the performance parameters ($J_{sc}$, $V_{oc}$, FF, and $\eta_p$) for devices employing 15 different metal electrode types covering a range of workfunctions. Due to the inherent stability of inverted devices, particularly with the formation of a native oxide layer, achieving comparable or higher efficiencies in inverted devices is highly desirable. We consider many of the most common electrode configurations employed in typical BHJ-OPVs, including bare metal electrodes (*i.e.*, Ni, Pd, Au, Cu, Ag, and Al), bare low workfunction metal bilayer electrodes (*i.e.*, Mg/Ag, Ca/Al, and Ba/Al), and coated metal electrodes (*i.e.*, MoO$_3$/Al, CuO/Cu, NiO/Ni, Ag$_2$O/Ag, ZnO/Al, and LiF/Al), where the coating thickness was 2 nm. We compute the absorption in the P3HT:PCBM active layer using FDTD simulations, and the $V_{oc}$ and FF using analytical equations considering realistic experimental values for the active layer – metal electrode interface, $R_s$, and $R_{shunt}$. We show that: (1) inverted devices can perform as well as, or superior to, conventional devices; (2) high workfunction bare metal electrodes (Au, Pd, Ni) are
ideal for high-efficiency inverted device performance; and (3) formation of a $p$-type native metal oxide layer (e.g., CuO/Cu, NiO/Ni, or Ag$_2$O/Ag) can result in high-efficiency inverted devices (up to 6.7%). We further demonstrate that the highest efficiencies for inverted devices can be achieved through minimizing the parasitic absorption from the metal while maximizing the workfunction, which is achieved for Ag$_2$O/Ag, which has the lowest parasitic absorption throughout the visible spectrum and has a workfunction of 5.0 eV. This work was an important advance over prior studies as it demonstrated the importance of considering both the optical and electronic properties of the electrode type, and predicted the electrode types that can lead to highly efficient and stable BHJ-OPVs.

Having predicted the optimal planar metal electrode type for inverted BHJ-OPVs, we next designed plasmonic metasurfaces that could be employed in BHJ-OPVs to lead to enhancements in the absorption and photocurrent. In Chapter 3, we demonstrate, using electromagnetic FDTD simulations, that the addition of square-packed paraboloidal Ag nanoparticle arrays to the Ag electrode of inverted BHJ-OPV devices can lead to active layer absorption enhancements up to 9.3% for nanoparticles with aspect ratios (height-to-diameter) of 0.33. We show that metasurfaces comprised of Ag nanoparticles having aspect ratios greater than or equal to 0.75 result in decreased active layer absorption due to an increase in parasitic absorption from the metal. Furthermore, we show that for all other metal metasurfaces investigated (i.e., Au, Cu, Al, Ni, and Ca), the parasitic absorption is too large, and, for all nanoparticle aspect ratios studied, resulted in decreased active layer absorption. We thus highlight the importance of minimizing parasitic absorption by the metal in designing plasmonic metasurfaces for BHJ-OPVs.

To gain a deeper understanding of how plasmonic metasurfaces can lead to improved BHJ-OPV device efficiency, we investigate the electromagnetic coupling between plasmons and excitons in broad spectral absorbers in Chapters 4 and 5. To do so, we focus our attention on the interaction between conjugated polymer absorbers and metallic nanostructures, without the full
BHJ-OPV device architecture. In Chapter 4, we demonstrate that scattering from Ag plasmonic metasurfaces couples to excitonic transitions in organic absorbers experimentally using dark-field scattered-light spectroscopy and computationally using FDTD simulations. We identify three distinct modes that absorber-coated plasmonic metasurfaces support: LSPRs, SPPs, and a previously unidentified optical mode type called absorption-induced scattering (AIS). We show that AIS originates from electromagnetic coupling between optical transitions of absorber materials and scattering modes, regardless of whether the scattering modes are plasmonic, localized, or collective in origin. Through our investigations of AIS, we also demonstrate that SPPs are back-scattered when the crystallinity of the absorber is low but are absorbed for more crystalline absorber coatings. This work showed that the red-edge absorption enhancement frequently observed in plasmon-enhanced BHJ-OPVs arises from plasmon-AIS, and led to a deeper understanding of plasmon-absorber interactions that can enable plasmonic metasurfaces be of benefit to BHJ-OPVs.

In Chapter 5, we further illucidate the electromagnetic coupling between plasmons and excitons in conjugated polymers using a Ag nanoparticle core – conjugated polymer shell structure, where we model the optical properties of the conjugated polymer shell using a summation of Lorentzian oscillators. Selection of single Ag nanoparticle cores allowed us to restrict our attention to the excitons in the conjugated polymers, since small Ag nanoparticles only support dipolar LSPRs, as opposed to Ag metasurfaces, which support multipolar LSPRs, SPPs, and collective resonances from the Ag nanoparticle arrays. Through this computational study, we show how tuning the optical and physical properties of the conjugated polymer shell can influence the Rabi splitting energy, which is the difference in energy between the hybridized plasmon-exciton states. We demonstrate that strong coupling can be achieved for these core-shell structures, despite the broad spectral linewidth of conjugated polymers. Using realistic material dispersive dielectric constant parameters, we predict Rabi splitting energies of over 1000 meV are achievable. We show that as the number of Lorentzian oscillators and their widths increase, the
high-energy hybrid plasmon-exciton modes become damped and have significant overlap, whereas the low-energy hybrid mode remains pronounced. We show that this low-energy hybrid mode is identical to the AIS observed from absorber-coated plasmonic metsurfaces, confirming that AIS arises from electromagnetic coupling between plasmons and excitons.

With a new understanding of the coupling between plasmons and absorbers, and the influence this has on absorption enhancement, and ultimately the photocurrent, in the active layer of BHJ-OPVs, in Chapters 6 and 7 we turn our attention towards the fabrication of multifunctional plasmonic metsurfaces with ultrathin interfacial layers to simultaneously control the surface workfunction and the optical properties of the metsurface. We investigate interfacial layers having thicknesses less than 5 nm, since the near-field enhancement from plasmonic metsurfaces decays exponentially away from the metal surface. In Chapters 6 and 7, we employ 2D semiconductors and partial oxidation of the Ag plasmonic metsurface, respectively, as ultrathin interfacial layers. We found unexpected results when employing MoS$_2$ as an interfacial layer: MoS$_2$ played an active role in the charge photogeneration process, resulting in the formation of a hybrid MoS$_2$-organic active layer. Although MoS$_2$-organic van der Waals heterostructures have previously been shown to act as $p$-$n$ heterojunctions, exhibiting the photovoltaic effect under illumination, this was the first study to experimentally demonstrate ultrafast charge transfer from the MoS$_2$ to the organic layer. We further show that, by employing plasmonic metsurfaces, the absorption was enhanced in both MoS$_2$ and organic layers, leading to a 6-fold increase in the positive polaron population in the organic layer in the presence of the MoS$_2$ and metsurface. While MoS$_2$ does not strongly influence the optical properties of the plasmonic metsurface, it serves as an active component in the charge photogeneration process. In Chapter 7, we controllably oxidize planar and plasmonic Ag surfaces to form a passive interfacial layer with minimal impact on the Ag optical properties. By exposing Ag surfaces to an O$_2$/Ar plasma for short times, we form ultrathin AgO$_x$ layers on both planar and plasmonic Ag surfaces, as confirmed using X-ray photoelectron spectroscopy. We show that this oxide layer
does not impact the optical properties of the Ag plasmonic metasurface using dark-field imaging. These oxidized planar and plasmonic Ag surfaces have laid the foundation for fully functional BHJ-OPV devices to be fabricated with control of the optical and electronic properties of the metallic electrode.

The knowledge developed throughout this thesis will benefit the organic optoelectronics and nanophotonics communities, and has laid the groundwork for fully functioning BHJ-OPV devices incorporating multifunctional plasmonic metasurfaces to be fabricated. Further, knowledge gained from the theoretical and experimental investigations of plasmon-exciton coupling has provided insight into the mechanism of absorption enhancement in plasmon-enhanced photovoltaics, and will be of benefit to other plasmon-enhanced optoelectronic devices, including LEDs and lasers.
Chapter 2. Computational Comparison of Conventional and Inverted Organic Photovoltaic Performance Parameters with Varying Metal Electrode Surface Workfunction

2.1. Abstract

Inverted polymer-based bulk-heterojunction organic photovoltaic (BHJ-OPV) device designs have enabled a breakthrough in operational lifetime through use of stable electrode materials. To date, there have not been systematic performance parameter comparisons between conventional and inverted devices that consider a range of different metal electrodes and presence of native metal oxides at the organic-metal interface. In this chapter, we systematically compute optical and electronic performance parameters for both conventional and inverted BHJ-OPV devices for 15 different electrode types covering a range of workfunctions. We quantitatively demonstrate that: (1) high-workfunction bare metal electrodes (Au, Pd, Ni) are ideal for high-efficiency inverted device performance; and (2) native metal oxide formation on metal electrodes (e.g., CuO/Cu, Ag₂O/Ag, NiO/Ni), which dramatically reduces conventional device efficiencies, can result in highly efficient inverted BHJ-OPV devices ($\eta_p$ of up to 6.7 % for the P3HT:PCBM system). This work is an important advance over prior studies as it predicts the electrode materials and configurations that would lead to both high efficiency and high stability BHJ-OPV devices.

2.2. Background

In conventional BHJ-OPV devices, the organic active layer is sandwiched between a low-workfunction metallic cathode (or electron collector) and a higher workfunction transparent anode (or hole collector, Figure 2.1a). In recent years, many studies have demonstrated that low-workfunction metallic cathodes are a primary contributor to device performance degradation for conventional BHJ-OPVs left in air.$^{171,173,271-273}$ In particular, degradation arises since, as metals oxidize or age, their workfunction increases (i.e., many have $p$-type semiconductor
Figure 2.1. (a), Schematic illustrating the different configurations for the BHJ-OPV devices studied here: conventional devices (left) and inverted devices (right) which may lead to improved BHJ-OPV device operational lifetime. A metal oxide/flouride layer was present in six of the electrodes studied, but not present in the studies involving bare metal electrodes. (b)-(c), Energy level diagrams (flat-band conditions) for the corresponding (b), conventional and (c), inverted devices (magnitude of the energy levels is shown). The range of metals and metal oxides studied and their associated workfunctions are: LiF (2.6 eV); Ba (2.7 eV); Ca (2.87 eV); Mg (3.66 eV); ZnO (4.0 eV, see below); Ag (4.26 eV); Al (4.28 eV); Cu (4.65 eV); NiO (5.0 eV); Ag$_2$O (5.0 eV); Au (5.15 eV); CuO (5.3 eV); MoO$_3$ (5.35 eV) (data is given for polycrystalline materials). Note that although the workfunction of ZnO is typically cited between 4.1 eV to 4.4 eV, it is known to form an ohmic contact to PCBM, potentially due to formation of an interface dipole. Other energy level data was obtained/averaged from the following references: ITO (4.7 eV); PEDOT:PSS (5.1 eV); P3HT HOMO (5.0 eV); PCBM LUMO (4.0 eV), making them less effective electron collectors, which results in a
marked reduction in the open-circuit voltage over time. In inverted BHJ-OPVs, the polarity of the device is reversed: the metal acts as the anode and the transparent electrode acts as the cathode (Figure 2.1a), usually through the use of high-workfunction metals and/or the incorporation of appropriate transport layers. Thus, device degradation due to electrode oxidation is circumvented in inverted devices using metals as anodes, where the formation of a $p$-type metal oxide can facilitate effective hole collection. While low-workfunction metals have conventionally been chosen to match the lowest unoccupied molecular orbital (LUMO) ($\sim 4$ eV) of the electron acceptor (typically a fullerene derivative such as phenyl-C$_{61}$-butyric acid methyl ester, PCBM), for inverted devices, the metal workfunction must match the highest occupied molecular orbital (HOMO) ($\sim 5$ eV) of the electron donor (typically, poly(3-hexylthiophene), P3HT). As a result, inverted device designs have been shown to be substantially more air-stable than their conventional counterparts. A secondary benefit of the inverted design is the elimination of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layers, which are widely used in organic optoelectronics to improve the electrical properties of the anode, but are known to be corrosive to the transparent electrode.

Although the operational lifetimes of inverted BHJ-OPVs have been dramatically improved over conventional BHJ-OPVs, especially when left in air, the power conversion efficiency ($\eta_p$) of inverted BHJ-OPVs has typically remained lower than that of comparable conventional devices: inverted devices based on a P3HT:PCBM blend typically reach $\eta_p$ values of $\sim 3\%$ to $4\%$, whereas $\eta_p$ of conventional devices based on the same blend can reach $4\%$ to $5\%$. Although there have been many studies focused on optimizing the device structure of conventional BHJ-OPVs, there have been fewer studies to date where the device structure of inverted BHJ-OPVs has been optimized. In one study by Schumann et al., inverted P3HT:PCBM devices
consisting of electrodeposited ZnO as the electron transport layer (ETL) and WO$_x$-coated Al as the hole transport layer (HTL)-coated anode reached an $\eta_p$ of $\sim$4.8%. In another study by Hau et al., the optimized thickness and blend ratio for an inverted device consisting of ZnO prepared by the sol-gel method resulted in an inverted device $\eta_p$ ($\sim$3.5 %) exceeding that of a similarly-fabricated conventional device ($\eta_p$ $\sim$2.4 %; consisting of PEDOT:PSS as the HTL and LiF/Al as the ETL-coated cathode). A similar type of blend optimization was performed for a different active layer morphology (a low bandgap polymer blended with PC$_{71}$BM), in which the ideal blend ratio for the inverted configuration was different from that of the conventional configuration. The $\eta_p$ of the optimized inverted device ($\eta_p$ = 5.97 %) exceeded that of a similarly-fabricated conventional device ($\eta_p$ = 5.41 %), but was still lower than that of the optimized conventional device ($\eta_p$ = 6.24 %). Further inverted BHJ-OPV device optimization is necessary in order to achieve device efficiencies that can perform as well as, or better than, comparable conventional devices.

There have been a number of studies comparing the performance of BHJ-OPVs using different metal cathodes in a conventional configuration and different metal anodes in an inverted configuration. Hadipour et al. recently compared, experimentally and computationally, the performance parameters of BHJ-OPVs incorporating different interfacial layers (IFLs), including the low-workfunction metal, Ca. In their study, the authors suggested that many low-workfunction metals have large parasitic optical absorption, and that their elimination can further improve device efficiency. However, while these studies considered a range of metal workfunctions, there has not yet been a systematic study comparing the performance parameters of BHJ-OPVs consisting of a range of metallic electrodes, both bare (no metal oxide) and coated with a native metal oxide, for both conventional and inverted devices. Furthermore, computational analysis of conventional BHJ-OPVs has greatly aided our understanding of the limits to device efficiency, and although there have
been many experimental studies showing that high-workfunction metals are beneficial for inverted BHJ-OPV device performance,\textsuperscript{47,171,174,175,278,282,299} this type of systematic study directly comparing inverted to conventional BHJ-OPVs for a variety of different bare and coated metal electrodes has not yet been explored computationally.

Here, we computationally compare the performance of nine different bare metal and six metal oxide-/fluoride-coated metal electrodes with a range of surface workfunctions in both inverted and conventional device configurations to identify the most suitable metal (either with or without an oxide/fluoride coating) in terms of both optical and electronic properties. We quantify the open-circuit voltage ($V_{oc}$) and fill factor ($FF$) for conventional and inverted devices for two different organic-metal interfacial interaction conditions: (1) assuming a large interface dipole between the metal and the organic layers (e.g., in the case of a strong interaction between the metal and organic layer, such as for chemisorption);\textsuperscript{276,300,301} and (2) assuming no interface dipole between the metal and the organic layers (e.g., in the case of a very weak interaction between the metal and organic layer, such as in physisorption).\textsuperscript{181,300} We show that the $V_{oc}$ of conventional devices is optimal for low-workfunction metals, while the $V_{oc}$ of inverted devices is optimal for more air-stable, high-workfunction metals. Additionally, we prove that inverted BHJ-OPVs can theoretically outperform conventional devices in terms of their short-circuit current densities ($J_{sc}$) due to the optical properties of the IFLs. The presence of an ultrathin metal oxide/fluoride coating does not significantly affect the $J_{sc}$ based on our optical calculations, but markedly improves $V_{oc}$ (electronic calculations). Finally, we demonstrate that native metal oxides are desirable for inverted device performance but detrimental to conventional device performance by calculating the total $\eta_p$ for all device configurations and electrode types studied here.
2.3. Methods

2.3.1. Performance parameter calculations

2.3.1.1. Device setup

Figure 2.1(a) shows general schematics of the different device configurations considered in this theoretical work. For typical conventional BHJ-OPV devices, indium-tin oxide (ITO) serves as the transparent anode, PEDOT:PSS serves as the HTL, and P3HT blended with PCBM is used as the active layer.\textsuperscript{107,113,114,289} Although more efficient active layer morphologies have been identified (e.g., PCDTBT:PC\textsubscript{70}BM,\textsuperscript{57} PTB7:PC\textsubscript{70}BM\textsuperscript{42}), the P3HT:PCBM blend system has been extensively studied\textsuperscript{23,30,107,113,114,181,276,289,291-294} and is used as a model system for studying changes to the BHJ-OPV device structure other than the active layer.\textsuperscript{49,171,279,291-293} A metal cathode, with or without a metal oxide or fluoride ETL, completes the device stack. For the inverted configuration, the bare or HTL-coated metal electrode serves as the anode and, typically, ZnO replaces PEDOT:PSS as the ETL,\textsuperscript{47-49} making ITO the cathode. In addition to the conventional and inverted device configurations defined above, we studied three possible cases at the metal electrodes defined as: (1) bare metal electrode (Figure 2.1(d)); (2) bare, low-workfunction metal bilayer electrode (Figure 2.1(e)); and (3) metal oxide-/fluoride-coated metal electrode (Figure 2.1(f)). The six bare metal electrodes studied were Ag, Al, Cu, Au, Pd, and Ni; the three bare low-workfunction metal bilayer electrodes studied were Ba/Al, Ca/Al, and Mg/Ag; all nine of these metal electrode types will be referred to as the bare metal electrodes unless otherwise noted. The six coated metal electrodes studied were LiF/Al and ZnO/Al as \textit{n}-type coatings; NiO/Ni, Ag\textsubscript{2}O/Ag, CuO/Cu as \textit{p}-type native metal oxide coatings, and MoO\textsubscript{3}/Al as a standard \textit{p}-type coating.

Figure 2.1(d)-(f) also shows the thicknesses of each of the layers employed in this computational study. For each electrode configuration, the thickness of the ITO was 100 nm,\textsuperscript{276} and the total metal electrode thickness was kept at 200 nm, ensuring that it was optically thick.\textsuperscript{302} The thickness of the front IFLs (here defined as the HTL PEDOT:PSS for the conventional
devices and the ETL ZnO for the inverted devices) and that of the P3HT:PCBM layers were optimized optically to be 10 nm and 240 nm, respectively (see Section 2.3.2.2). For bare metals, the metal thickness was 200 nm; for the bare low-workfunction bilayer metal electrodes, 25 nm of the low-workfunction metal was supported by 175 nm of Al (for Ba and Ca) or Ag (for Mg) in keeping with typical experiments involving these metals in BHJ-OPVs. For the coated metal electrodes, the thickness of the oxide/fluoride was 2 nm, and the metal was 198 nm. The thickness of the coating was chosen to modify the electrode workfunctions without significantly changing the optical properties of the electrode. It should be noted that the ideal thickness of LiF is typically around 0.6 nm based on empirical \( \eta_p \) measurements, but to minimize optical differences due to thickness changes, all of the oxide/fluoride coatings were kept at a constant thickness.

Figure 2.1(b),(c) shows energy level diagrams for both conventional and inverted device configurations, respectively. The labeled levels show the magnitude of the workfunction (i.e., the Fermi level) for the electrodes and transport layers; the HOMO and LUMO levels are both shown for the P3HT:PCBM active layer. Note that the Fermi level falls within the valence band for metals, whereas for the semiconducting metal oxides and fluorides, the Fermi level lies just above the valence band edge (for \( p \)-type semiconductors) or just below the conduction band edge (for \( n \)-type semiconductors). The bands have been omitted from the figure for clarity. It was assumed that ohmic contacts occurred at the anode of the conventional device and the cathode of the inverted device, i.e., PEDOT:PSS was used as the HTL and ZnO was used as the ETL of the conventional and inverted devices, respectively. For conventional devices, metals and \( n \)-type coatings with workfunctions equal to or smaller in magnitude than the LUMO energy of PCBM are expected to form ohmic contacts at the cathode (see Section 2.3.1.2). LiF and ZnO have been extensively studied for conventional BHJ-OPVs, and are known to form ohmic contacts to PCBM (see Section 2.3.1.2). Although the workfunction of ZnO is typically cited between 4.1 eV to 4.4 eV, it is expected to have a large interface dipole that
reduces the energetic offset between the LUMO of PCBM and the workfunction of ZnO to nearly zero; thus the workfunction of ZnO is taken to be equivalent to the LUMO of PCBM (4.0 eV). However, electrodes with workfunctions larger in magnitude than the LUMO energy of PCBM will reduce $V_{oc}$ due to electron energy loss, $\psi_e$. For inverted devices, metals and $p$-type metal oxides with workfunctions equal to or larger in magnitude than the HOMO energy of P3HT form ohmic contacts at the anode due to Fermi level alignment (see Section 2.3.1.2), whereas metals or metal oxides with workfunctions smaller in magnitude introduce an energy loss for holes, $\psi_h$, from P3HT, resulting in a lower $V_{oc}$. Native $p$-type metal oxide formation was studied for three different metals: Ag$_2$O/Ag, NiO/Ni, and CuO/Cu. Oxides of Ag, Cu, and Ni have been shown to be of benefit to organic light emitting diodes (OLEDs) as well as OPVs. CaO has been shown to be detrimental to device performance by creating voids in the electrode, and so insulating native metal oxides (BaO, CaO, MgO, Al$_2$O$_3$) are not considered here, but are expected to degrade device performance in all cases. Au and Pd are not expected to spontaneously oxidize in air, so oxides of Au and Pd were also not considered here. For comparison, MoO$_3$/Al, which is a common anode for inverted BHJ-OPVs, was studied. While the results presented here are purely computational, they can be used as design criteria for future electrode selection for inverted and conventional BHJ-OPVs and are relevant to various methods of electrode deposition.

2.3.1.2. Open-circuit voltage calculation

The maximum attainable $V_{oc}$ of a BHJ-OPV for a given donor-acceptor blend, $V_{oc,max}$, has been shown to be given by:

$$V_{oc,max} = \frac{1}{q} \left( E_{\text{HOMO}}^{\text{donor}} - E_{\text{LUMO}}^{\text{acceptor}} - \Delta E \right)$$  \hspace{1cm} (2.1)$$

where $q$ is the elementary charge (in units of C), $E_{\text{HOMO}}^{\text{donor}}$ is the HOMO energy level of the donor, $E_{\text{LUMO}}^{\text{acceptor}}$ is the LUMO energy level of the acceptor, and $\Delta E$ is an empirical factor equal to 0.3 eV
for P3HT:PCBM. The physical significance of $\Delta E$ arises from either reverse dark current of the photodiode;\textsuperscript{23} the exciton binding energy;\textsuperscript{311} non-radiative recombination of excited states in the active layer;\textsuperscript{312} or some combination thereof. For ohmic contacts at both the anode and cathode, the $V_{oc} = V_{oc,\text{max}}$ because there are no energy losses due to energy level mismatches. In the case of non-ohmic contacts, however, the $V_{oc}$ is reduced by an amount proportional to the energy loss for electrons and/or holes, $\psi_{e/h}$, at the respective electrodes:

$$V_{oc} = \frac{1}{q} \left( |E_{\text{HOMO}}^{\text{donor}}| - |E_{\text{LUMO}}^{\text{acceptor}}| - \Delta E - S_c \psi_e - S_a \psi_h \right)$$  \hspace{1cm} (2.2)$$

where $S_{c/a}$ are the slope parameters for the dependence of $V_{oc}$ on cathode/anode workfunction. The slope parameter, $S$, is a measure of the strength of the interaction between the organic layer and the electrode. A strong interaction between the organic layer and the electrode usually occurs due to the formation of an interface dipole between the two layers, which is highly dependent on the identity of the two materials, the properties of their interface, and the method of depositing one material on the other.\textsuperscript{276,300,301,313} For BHJ-OPV devices, the $S$-parameter typically represents the $V_{oc}$ dependence on metal workfunction; however, $S$-parameters have also been defined for organic films on varying substrates, where the $S$-parameter represents the dependence of the effective workfunction of the organic-coated substrate on the workfunction of the bare substrate.\textsuperscript{301,314,315} Both the $S$-parameter for devices and that for films are measures of the energy level alignment of the organic molecular orbital bands and the underlying substrate Fermi level. The stronger the interface dipole, the lower the $S$-parameter value, which has been shown to be as small as 0.1 for non-ohmic contacts.\textsuperscript{276,300,313} The typical metal-insulator-metal (MIM) model that has been used previously\textsuperscript{181,294} to calculate the $V_{oc}$ assumes that there is no interface dipole formed, and the $V_{oc}$ depends linearly on the metal workfunction, with an $S$-parameter of 1; this should occur in the case of vacuum-level alignment, or the Mott-Schottky limit.\textsuperscript{300,301,314,315} In the case of ohmic contacts, it has been shown that there is no dependence of $V_{oc}$ on metal workfunction, regardless of the workfunction of the metal,\textsuperscript{181,279,294} a process which has been referred to as
‘Fermi level pinning.’ Therefore, in the pinning regime, the \( S \)-parameter is zero.\(^{279,300,301,314,315}\) The \( S \)-parameter for non-ohmic contacts has been cited as 0.1,\(^{276}\) 0.26,\(^{294}\) 0.6,\(^{279}\) and 1.0.\(^{181,300,314,315}\) The \( V_{oc} \) was thus calculated for an \( S \)-parameter of 1.0, which assumed no interface dipole formation,\(^{181,300,314,315}\) as well as for an \( S \)-parameter of 0.1, which assumed formation of a strong interface dipole\(^{276,300,313}\) for non-ohmic contacts. For ohmic contacts, an \( S \)-parameter of 0 was used.

Ohmic contact occurs between the cathode and the \( n \)-type acceptor material when the magnitude of the workfunction of the cathode, \( \phi_c \), is less than or equal to \( E_{LUMO}^{\text{acceptor}} \), due to Fermi level pinning,\(^{279,300,301,314,315}\) and \( \psi_e = 0 \). For non-ohmic contact between the cathode and the acceptor, \( |\phi_c| > |E_{LUMO}^{\text{acceptor}}| \), there is an energy loss for electrons at the cathode defined as:

\[
\psi_e = |\phi_c| - |E_{LUMO}^{\text{acceptor}}| \tag{2.3}
\]

(see Figure 2.1(b)). For the case where the magnitude of the workfunction of the anode, \( \phi_a \), is greater than or equal to \( E_{HOMO}^{\text{donor}} \), an ohmic contact is formed to the \( p \)-type donor material due to Fermi level pinning\(^{279,300,301,314,315}\) and \( \psi_h = 0 \). For \( |\phi_a| < |E_{HOMO}^{\text{donor}}| \) there is an energy loss for holes at the anode, which we define as:

\[
\psi_h = |E_{HOMO}^{\text{donor}}| - |\phi_a| \tag{2.4}
\]

(see Figure 2.1(c)). The \( V_{oc} \) was then calculated assuming that \( E_{HOMO}^{\text{donor}} \) of P3HT is 5.0 eV, \( E_{LUMO}^{\text{acceptor}} \) of PCBM is 4.0 eV (see Figure 2.1 for references), and \( \Delta E \) for P3HT:PCBM is 0.3 eV.\(^{23}\)

### 2.3.1.3. Fill factor calculation

Analytical expressions for the fill factor have been proposed by Green\(^{316}\) in 1982 and applied to BHJ-OPVs by Servaites et al. in 2009.\(^{157}\) Briefly, the ideal fill factor (\( FF_0 \)) which
assumes ideal shunt and series resistances (i.e., shunt resistance → ∞; series resistance → 0), was calculated as follows: \(^{157, 316}\)

\[
FF_0 = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1}
\]  
(2.5)

where \(v_{oc}\) is the normalized open-circuit voltage defined as:

\[
v_{oc} = V_{oc} \left(\frac{q}{n_d k_B T}\right)
\]  
(2.6)

where \(n_d\) is the diode ideality factor, \(k_B\) is the Boltzmann constant, and \(T\) is temperature. If non-zero series resistances are present, the series fill factor \((FF_s)\) is calculated as:

\[
FF_s = FF_0 \left(1 - 1.1 r_s\right) + \frac{r_s^2}{5.4}
\]  
(2.7)

where \(r_s\) is the normalized series resistance defined as:

\[
r_s = \frac{R_s}{v_{oc} / J_{sc}}
\]  
(2.8)

where \(R_s\) is the specific series resistance (in units of \(\Omega\) \(\text{cm}^2\)). Finally, when finite shunt resistances are considered, the total fill factor \((FF)\) was calculated as:

\[
FF = FF_s \left(1 - \frac{v_{oc} + 0.7 FF_s}{v_{oc}} r_s\right)
\]  
(2.9)

where \(r_{sh}\) is the normalized shunt resistance defined as:

\[
r_{sh} = \frac{R_{sh}}{v_{oc} / J_{sc}}
\]  
(2.10)

where \(R_{sh}\) is the specific shunt resistance (in units of \(\Omega\) \(\text{cm}^2\)). Equation 2.5, 2.7, and 2.9 are accurate to greater than a few percent for \(v_{oc} > 10\) and \(r_s + 1/r_{sh} < 0.4^{316}\). Values of \(n_d\) for P3HT:PCBM BHJ-OPVs were taken from the literature and averaged (See Appendix Table A1). \(R_s\) values were obtained for both P3HT:PCBM BHJ-OPV devices containing PEDOT:PSS hole transport layers (conventional) and ZnO electron transport layers (inverted) (See Appendix Table A1). Here, \(n_d = 1.83, R_s = 4.51\ \Omega\ \text{cm}^2\) for conventional devices, \(R_s = 5.36\ \Omega\ \text{cm}^2\) for inverted
devices, and room temperature (300 K) operation was assumed. Shunt resistance values varied considerably in the literature, but according to Servaites et al., for well-optimized BHJ-OPVs, $R_{sh} = 1 \text{ M } \Omega \text{ cm}^2$ is a typical value.\textsuperscript{157} Tabulated values of $FF$, $FF_s$, $FF_0$, the normalized parameters, and literature values for the equivalent circuit parameters can be found in the Appendix, Section A.2.

### 2.3.1.4. Short-circuit current density calculation

The $J_{sc}$ is related to the efficiency of absorption of photons by the active layer (optical properties), as well as the efficiencies of separation and transport of the electrons and holes to their respective electrodes (electrical properties). The $J_{sc}$ depends on the external quantum efficiency, $\eta_{\text{EQE}}$, of the device as follows:\textsuperscript{5,182}

$$J_{sc} = q \int \eta_{\text{EQE}}(\lambda) N_{\text{ph}}(\lambda) d\lambda$$  \hspace{1cm} (2.11)

where $\lambda$ is the wavelength (in units of nm) and $N_{\text{ph}}$ is the photon flux density of the AM1.5 solar spectrum over the wavelength range of interest (in units of photons m$^{-2}$ nm$^{-1}$ s$^{-1}$).\textsuperscript{182} The $\eta_{\text{EQE}}$, which is defined as the ratio of the number of free carriers collected at the electrodes to the number of photons incident on the device, is determined by the product of the individual quantum efficiencies of each step of the conversion process of photons to electrons\textsuperscript{159,182,277} (see Section 1.2.6). Here, we approximate the $\eta_{\text{EQE}}$ to be given by:

$$\eta_{\text{EQE}}(\lambda) \approx \eta_a(\lambda)$$  \hspace{1cm} (2.12)

where $\eta_a(\lambda)$ is the wavelength-dependent efficiency of photon absorption (see Section 1.2.6 for details). By making this approximation, we have assumed that each photogenerated exciton has dissociated into its free charge carriers, each of which have been collected at the respective electrode. While this effectively neglects the electrical transport aspects of the devices, e.g., by assuming an internal quantum efficiency ($\eta_{\text{IQE}}$) value of 100% (see Sections 1.2.6 and 2.4.5 for
further discussion), there should not be much change in the efficiency of charge transport within the active layer between devices having different metallic electrodes, particularly since the exciton generation rate maxima are located in nearly the same regions for each electrode (see Section 2.4.7). Based on these assumptions, the $J_{sc}$ calculated here is expected to be the optimum value achievable. In reality $J_{sc}$ of a device fabricated using the same materials and thicknesses we describe will be less than that calculated due primarily to recombination mechanisms.

Further, since the calculations in this work were carried out on a discrete basis, the integral in Equation 2.11 becomes a summation:

$$J_{sc} = q \sum_{\lambda} (\eta_a(\lambda) N_{ph}(\lambda) d\lambda) = q \sum_{\lambda} \left( \eta_a(\lambda) \frac{I_{solar}(\lambda)}{h \nu} d\lambda \right)$$  \hspace{1cm} (2.13)

where the photon flux density has been evaluated as the wavelength-dependent power density of light from the AM1.5 solar spectrum, $I_{solar}(\lambda)$ (in units of W m$^{-2}$ nm$^{-1}$) divided by the energy per incident photon [$h \nu$, where $h$ is Planck’s constant (in units of J s photon$^{-1}$) and $\nu$ is the frequency of light (in units of s$^{-1}$)]. From Equation 2.13, it is clear that in order to calculate the $J_{sc}$ of BHJ-OPV devices (assuming good electrical transport through the active layer), it is necessary to calculate $\eta_a(\lambda)$, the wavelength-dependent efficiency of photon absorption by the active layer.

The $\eta_a(\lambda)$ is related to the power density absorbed in the active layer, $I_{active}(\lambda)$ (W m$^{-2}$ nm$^{-1}$), by dividing it by the incident power density, $I_{solar}(\lambda)$:

$$\eta_a(\lambda) = \frac{I_{active}(\lambda)}{I_{solar}(\lambda)}$$ \hspace{1cm} (2.14)

where $I_{active}(\lambda)$ is given by:

$$I_{active}(\lambda) = \sum_{z} Q(z, \lambda) \cdot dz = \sum_{z} \alpha(\lambda) n(\lambda) I_{solar}(\lambda) \frac{E(z, \lambda)}{E_0} \cdot dz$$ \hspace{1cm} (2.15)

where $Q(z,\lambda)$ is the thickness- and wavelength-dependent power absorbed by the active layer and is summed over the thickness of the active layer, $\alpha(\lambda)$ is the absorption coefficient of the active
layer (in units of cm$^{-1}$, see Equation 2.16), $n(\lambda)$ is the real part of the complex index of refraction, and $|E(z,\lambda)/E_0|^2$ is the normalized electric field intensity in the active layer. The absorption coefficient is related to the imaginary part of the complex wavelength-dependent index of refraction, $k(\lambda)$:

$$\alpha(\lambda) = \frac{4\pi k(\lambda)}{\lambda} \quad (2.16)$$

By inserting Equations 2.14 and 2.15 into 2.13, the $J_{sc}$ can be expressed as:

$$J_{sc} = q \sum_{\lambda} \sum_{z} \left( \alpha(\lambda) n(\lambda) \left|\frac{E(z,\lambda)}{E_0}\right|^2 \cdot \frac{I_{\text{solar}}(\lambda)}{h\nu} \cdot dq \cdot d\lambda \right) \quad (2.17)$$

which can be re-written as:

$$J_{sc} = q \sum_{\lambda} \sum_{z} \left( \frac{Q(z,\lambda)}{h\nu} \cdot dq \cdot d\lambda \right) \quad (2.18)$$

or:

$$J_{sc} = q \sum_{\lambda} \sum_{z} \left( G(z,\lambda) \cdot dq \cdot d\lambda \right) \quad (2.19)$$

where $G(z,\lambda)$ is the generation rate of excitons in the active layer and is equal to $Q(z,\lambda)/h\nu$. As seen from Equation 2.17, based on the assumptions made here, the $J_{sc}$ is primarily determined by the wavelength-dependent optical constants [$n(\lambda)$ and $k(\lambda)$] and the electric field intensity within the device. Due to the nature of thin-films, there is significant coherent interference of incident and reflected electromagnetic waves that occurs within each layer of the device, since the thickness of each layer is on the order of or less than the wavelength of light, so the electric field intensity will vary greatly with changing thickness of each layer (see Section 2.3.2.1 for method of calculating electric field intensity).

2.3.1.5. Efficiency calculation

The overall power conversion efficiency, $\eta_p$, was calculated using the following equation:
\[ \eta_p = \frac{J_{sc}V_{oc}FF}{I_{solar}} \times 100\% \]  

(2.20)

where \(V_{oc}, FF\), and \(J_{sc}\) are calculated as per Equations 2.2, 2.9, and 2.11, respectively, and \(I_{solar}\) is obtained by integrating the AM1.5 solar spectrum.

2.3.2 Computational methodology

2.3.2.1 Electric field calculations/simulation parameters

Full-field electromagnetic simulations were performed numerically using commercially-available finite-difference time domain (FDTD) software for all of the devices studied here (see Figure 2.2). The FDTD method was preferred over the traditional transfer matrix method (TMM) because, although the TMM is fast and accurate for studying planar thin films, it cannot be used to study effects such as non-homogenous active layer morphologies, scattering from rough surfaces, or confinement of the electric field from nanophotonic structures. This is not applicable in this chapter because the devices and interfaces are all planar, but is useful to compare the accuracy of FDTD to TMM for subsequent work where nanostructures are added (Chapters 3-6). In the FDTD simulations, plane wave excitation incident normal to the plane of

![Figure 2.2](image-url)

**Figure 2.2.** Graphical user interface (GUI) associated with simulation setup from Lumerical FDTD Solutions. (a) 3D perspective GUI associated with conventional devices simulated (Cu cathode shown here), showing entire simulation region including the source and monitors. (b) \(x-z\) plane associated with device from (a), where the boundary conditions and mesh are shown (0.1 nm \(dz\) mesh step size used here for comparison with transfer matrix method).
the device was employed in all cases. The FDTD method assumes that optical materials are non-magnetic (relative permeability, \( \mu_r = 1 \)) such that the only necessary data to input into the software are the optical constants, \( n \) and \( k \), of each material (see Appendix Section A.1), and the geometry of the structures. However, there are several simulation parameters that must be considered to ensure accurate results are achieved, e.g. the size of the mesh, the properties of the source, and the boundary conditions. To verify the accuracy of the FDTD simulations, initial simulations were compared to results obtained using the TMM calculations, which were shown to agree to within 1\% (see Table A2 and Figure A10).

The FDTD method cannot be used practically for nanometer-scale objects distributed on the macro or millimeter scale due to limited computational resources; it is primarily used for structures of nanometer or micrometer size. As such, the glass substrate was not included in the device, but the background index through which the electromagnetic source initially propagated was set to that of SiO\(_2\) glass (\( n = 1.52 \)). The final result was then corrected for reflective losses at the air-glass interface from multiple passes through the device stack by multiplying the numerically calculated electric field value by the transmission coefficient at the glass-ITO interface as calculated by the TMM (see Appendix Section A.2.4).

The thicknesses of the remaining layers were set to the values described in Section 2.3.1.1. Each layer had a cross-sectional area that was ‘infinite’ in extent by defining appropriate boundary conditions; see below. The FDTD simulation region cross-sectional area was set to 20 nm \( \times \) 20 nm (see Figure 2.2) with a depth of 1700 nm. The source was a plane wave pulse, with continuous wave normalization (CWN), a pulselength of 2.325 fs, wavelength range of 350 nm to 800 nm, and wavelength stepsize of 1 nm. The solar irradiance AM1.5 spectrum was taken into consideration during post-simulation processing (see Equation 2.17). As such, the source had an amplitude of 1, phase of 0°, and the polar and azimuthal angles were both also set to 0° (i.e., normal incidence). The source propagated in the direction normal to the device (\( z \)) with the electric field vector (\( \mathbf{E} \)) polarized along the \( x \) direction and the magnetic field vector (\( \mathbf{H} \))
polarized along the \( y \) direction. The source was 1000 nm from the first layer of the device. A 2D frequency-domain field and power monitor as well as a 2D refractive index monitor were included in the simulation (in the \( x-z \) plane at \( y = 0 \)). The geometries of these monitors were identical and chosen to agree with the polarization of the plane wave source; the monitors extended beyond the simulation region in the \( x \)- and \( z \)-directions. Figure 2.2 shows the graphical user interface (GUI) representation of the simulation setup.

The boundary conditions of the simulation were as follows: anti-symmetric boundary conditions along the polarization direction of the \( \mathbf{E} \)-field (\( x \)), symmetric boundary conditions along the polarization of the \( \mathbf{H} \)-field (\( y \)), and perfectly matched layer (PML) boundary conditions along the direction of propagation (\( z \)),\(^{317}\) with 12 PMLs. Symmetric boundary conditions can be used whenever the electromagnetic fields have a plane of symmetry through the middle of the simulation region, which allows the simulation volume and time to be reduced by up to a factor of eight.\(^{317}\) Since the devices simulated here are composed of planar thin-films, they can be considered infinite in extent for the in-plane (\( x,y \)) directions, since the area of a typical device (~1 mm\(^2\)) is many orders of magnitude greater than the device thickness (~500 nm). Symmetric (anti-symmetric) boundary conditions preserve the phase of the normal component of the magnetic (electric) field across the boundary, as well as the phase of the tangential component of the electric (magnetic) field across the boundary. As such, symmetric boundary conditions were selected for the boundaries parallel to the \( \mathbf{E} \)-field polarization (\( i.e. \), the \( x-z \) plane boundaries), and anti-symmetric boundaries conditions (see Figure 2.2b) were selected for the boundaries normal to the \( \mathbf{E} \)-field polarization (\( i.e. \), the \( y-z \) plane boundaries), such that the total phase of the incident excitation was preserved across all in-plane boundaries of the FDTD simulation. The use of symmetric or anti-symmetric boundary conditions on four of the boundaries reduced the total simulation time and volume by a factor of four. Symmetry was enabled on all boundaries, and the structure was extended through the PMLs. The simulation time was 1000 fs. The simulations had a mesh accuracy set to 8, with mesh refinement type set to conformal variant 1.\(^{317}\) A mesh
override of $dx = dy = dz = 0.9$ nm was set through the entire device which is a practical stepsize for simulations involving nanophotonic designs (nanoparticles, dielectric scatterers, etc. – which are explored in Chapters 3-6). This step size is also significantly smaller than the $x$- and $y$-dimensions of the thin-film devices, and small enough to provide at least a few spatial grid points in the $z$-direction for the thinnest films used (i.e., 2 nm for the metal oxide/fluoride coatings) and more than 100 grid points in the $z$-direction for the P3HT:PCBM active layer. The simulations automatically shut-off when the normalized field intensities decayed to less than $10^{-7}$.

2.3.2.2. Thickness optimization

The front interface layer (PEDOT:PSS) and the active layer (P3HT:PCBM) for a conventional BHJ-OPV device were optically optimized by fixing the thicknesses of the other layers (as described in Section 2.3.1.1), and using a bare Al cathode, then performing FDTD simulations for 5 different PEDOT:PSS thicknesses (ranging from 10 nm to 50 nm, in 10 nm intervals), each having 12 different P3HT:PCBM thicknesses (ranging from 20 nm to 240 nm, in 20 nm intervals; Figure 2.3). The $J_{sc}$ was calculated for each simulation and an oscillatory-type

![Figure 2.3](image.png)

**Figure 2.3.** Calculated $J_{sc}$ from BHJ-OPV devices with varying the thicknesses of the P3HT:PCBM and PEDOT:PSS layers. The device structure was ITO (100 nm)/ PEDOT:PSS (varied from 10 nm to 50 nm, with 10 nm intervals) / P3HT:PCBM (varied from 20 nm to 240 nm, with 20 nm intervals) / Al (200 nm). The colorbar is for $J_{sc}$, calculated as described in Section 2.3.1.4.
behavior was observed for changing P3HT:PCBM thickness, as observed for others in the literature.\cite{289,290,297,298} Note that for this optimization, only the optical properties were considered for the \( J_{sc} \); the electrical properties were not considered in this study.

2.4. Results and Discussion

2.4.1. Open-circuit voltage

Figure 2.4 (top panel) shows the results of the calculations of \( V_{oc} \) for the 15 different electrode types studied here. Note that in the case of a \( p \)-type coating on the cathode as well as an \( n \)-type coating on the anode, the \( V_{oc} \) was assumed to be zero, since they serve as effective electron and hole blocking layers, respectively.\cite{6,30} The presence of strong interface dipoles (\( S_c \) or \( S_a = 0.1 \) for conventional or inverted devices, respectively), which may form in the case of strongly interacting layers,\cite{300} reduced the energy loss for charge collection (\( \psi_e \) or \( \psi_h \)) at the respective electrodes, and increased \( V_{oc} \). With optimized workfunctions (\( i.e. \), ohmic contacts at both the cathode and anode), maximum attainable open-circuit voltage (\( V_{oc,max} \)) values of 0.7 V were calculated for both conventional and inverted P3HT:PCBM BHJ-OPV devices (which is in good agreement with the design rules developed by Scharber et al.,\cite{23} assuming a LUMO energy for PCBM of 4.0 eV and a HOMO energy of P3HT of 5.0 eV\cite{30,56}). For conventional devices, \( V_{oc} \) was negligible for \( S_c = 1 \) when \( |\phi_e| \geq \left| E_{\text{LUMO}}^{\text{excess}} \right| + qV_{oc,max} \), since the electron energy loss at the cathode exceeded the total \( V_{oc} \) (see Figure 2.1(b)). For inverted devices, \( V_{oc} \) was also negligible for \( S_a = 1 \) when \( |\phi_a| \leq \left| E_{\text{HOMO}}^{\text{donor}} \right| - qV_{oc,max} \) due to the hole energy loss at the anode (see Figure 2.1(c)) exceeding the total \( V_{oc} \). For conventional devices, with increasing metal electrode workfunction, the \( V_{oc} \) decreased from its maximum value to 0.585 V for \( S_c = 0.1 \) and to 0 V for \( S_c = 1 \) for the highest workfunction metals (\( i.e., \) Ni, Pd, Au). For inverted devices, with increasing bare/coated metal electrode workfunction, the \( V_{oc} \) increased to its maximum value from 0.47 V for \( S_a = 0.1 \) and from 0 for \( S_a = 1 \) for the lowest workfunction bare metals (\( i.e., \) Ba/Al, Ca/Al, Mg/Ag). The best
Figure 2.4. Calculated $V_{oc}$ (top panel), $FF_0$ (middle panel) and $FF$ (bottom panel) as functions of increasing workfunction for the nine bare metal and six coated metal electrodes studied. For inverted devices, calculations were performed for both a slope parameter, $S_a$, of 1.0 (for all bare and coated metal anodes; solid symbols) and $S_a$ of 0.1 (for all bare metal and only $p$-type coated metal anodes; hollow symbols). For conventional devices, calculations were performed for both a slope parameter, $S_c$, of 1.0 (for all bare and coated metal cathodes; solid symbols) and $S_c$ of 0.1 (for all bare metal and only $n$-type coated metal cathodes; hollow symbols). Symbols with blue outlines denote values calculated for $p$-type metal oxides and symbols with green outlines denote values calculated for the $n$-type metal oxide and fluoride. Equivalent circuit values used for the $FF_0$ and $FF$ calculations are shown as insets in the middle and bottom panels, respectively. Note that for materials with identical workfunctions, their $V_{oc}$, $FF_0$, and $FF$ values are also identical.

Performing cathodes for the conventional configuration were composed of the unstable low-workfunction metals (i.e., LiF/Al, Ba/Al, Ca/Al, and Mg/Al) and for the inverted configuration were anodes with native metal oxide coatings (i.e., Ag$_2$O/Ag, NiO/Ni, and CuO/Cu), the stable
high-workfunction metals (i.e., Au, Pd, and Ni) and the standard inverted BHJ-OPV anode (i.e., MoO$_3$/Al). Comparison of the $V_{oc}$ calculations to experimental data will be provided in Section 2.4.5.

2.4.2. Fill factor

The $FF$ showed the same trends as $V_{oc}$ for both device configurations and the range of electrode materials studied (Figure 2.4, middle and bottom panels), with maximum achievable values of 0.76 assuming no parasitic resistances (i.e., $R_s = 0$, $R_{sh} = \infty$). For $V_{oc} = 0$, the $FF_0$ according to Equation 2.5 resulted in a value of 0.33 due to the limited accuracy of the fill factor calculation for $v_{oc} < 10$ (see Section 2.3.1.3 and Tables A4-A7 for $v_{oc}$ values); however, a fill factor for $V_{oc} = 0$ has no physical significance, so the $FF_0$ was set to 0 in these cases. Assuming no parasitic resistances, the maximum $FF_0$ was identical for the conventional and inverted devices. However, the more meaningful calculation incorporating parasitic resistances resulted in reduced $FF$ values (Figure 2.4, bottom panel), giving a maximum value for the $FF$ of 0.70 for conventional devices and 0.68 for inverted devices. The main reason for this difference is the larger $R_s$ for ZnO-based BHJ-OPVs (5.36 $\Omega$ cm$^2$) compared to PEDOT:PSS-based devices (4.51 $\Omega$ cm$^2$). If the $R_s$ for inverted devices is set equal to or less than that of conventional devices, then the maximum $FF$ for inverted devices can exceed that of conventional devices. Comparison of the $FF$ calculations to experimental data will be provided in Section 2.4.5.

2.4.3. Optical absorption spectra and short-circuit current density

Calculations of the optical absorption and $J_{sc}$ in the devices as a function of bare and coated metal electrode materials were performed to identify the electrodes with the most desirable optical response (i.e., lowest parasitic absorption loss) for the BHJ-OPV devices studied here. Figure 2.5(a) and (b) show the calculated active layer absorption spectra for both conventional
Figure 2.5. Theoretical fractional absorption spectra in: (a),(b) the active layer and (c),(d) the metal for the conventional and inverted devices employing each bare metal cathode and anode studied, respectively. The fractional absorption spectra in the active layer and metal for the oxide- or fluoride-coated metals differed on average by < 10 % across the visible spectrum (see Figure 2.6).

and inverted device configurations, respectively, for each of the nine different bare metal electrodes. The coated metal electrodes showed very similar trends as their bare counterparts (within ~10 % on average across the spectrum; see Figure 2.6 for the inverted devices). It was observed that Ag and Al electrodes resulted in the largest overall absorption in the active layer, with ~90 % of light absorbed between 380 nm to 610 nm. For Au, Cu, Ba/Al, Pd, Ni, Ca/Al, and Mg/Ag electrodes, active layer absorption ranged from ~83 % to 90 % between 350 nm to 550 nm for the conventional configuration. Between 550 nm to 610 nm, devices with Au, Cu, and Ba/Al electrodes absorbed between 80 % to 85 % of light in the active layer, but for Pd, Ni and Ca/Al electrodes, active-layer absorption dropped to ~75 % to 78 %, and for Mg/Ag electrodes
active-layer absorption dropped further to ~65 % to 85 %. All active layer absorption dropped rapidly to ~10 % from 610 nm to 660 nm, then continued to drop towards 0 % at longer wavelengths. For all metals, the absorption onset in the active layer occurred at (655 ± 5) nm.

Conventional and inverted active layer absorption spectra showed similar trends, except for an additional dip in the inverted fractional absorption spectra in the range 350 nm to 380 nm arising from interband absorption from the ZnO ETL (Figure A8).

The fraction of light absorbed (i.e., parasitic absorption) by the metal electrode for both the conventional and inverted configurations is shown in Figure 2.5(c) and (d), respectively, for the nine different bare metal electrodes. The metals that were more absorptive in the visible part
Figure 2.7. Reflection at P3HT:PCBM-metal interface (assuming no other interfaces present), calculated as:

\[ R = \frac{\tilde{n}_{metal} - \tilde{n}_{P3HT:PCBM}}{\tilde{n}_{metal} + \tilde{n}_{P3HT:PCBM}} \]

where \( \tilde{n} \) is the complex index of refraction for the respective layer (i.e., \( \tilde{n} = n + ik \)).

of the spectrum tended to be poorer reflectors (Figure 2.7), which reduced the overall active layer absorption [Figure 2.5(a),(b)]. Ag and Al had the lowest absorption loss in the range of 350 nm to 600 nm (Ag absorbed between less than 1 % to 2 % and Al absorbed between less than 1 % to 5 %). Although Al became more absorptive at longer wavelengths, with absorption ranging from 5 % to 18 % between 600 nm to 800 nm, this did not significantly impact the amount of light absorbed by the active layer since P3HT does not absorb strongly beyond 650 nm. For lower bandgap polymers (such as PCDTBT, PBDTT, or PTB7), longer wavelength absorption in Al electrodes may substantially reduce active layer absorption. Ag absorbed less than 5 % of light beyond 600 nm, making it more ideal for lower bandgap polymer absorbers. Cu and Au were both slightly more absorptive at shorter wavelengths, absorbing ~ 7 % and 9 %, respectively, at 390 nm, and, overall, absorbing up to 7 % and 5 % of light between 350 nm to 600 nm, respectively. This was attributed to interband absorption by Cu and Au in the range of 500 nm to 600 nm. This region corresponded to the region of maximum absorption by P3HT:PCBM, which resulted in Au- or Cu- based electrodes reflecting less light (between 350 nm to 600 nm)
back into the active layer compared with Ag- or Al-based electrodes. Although Cu and Au were less absorptive beyond 600 nm (5% to 7% for Cu and 6% to 10% for Au), P3HT does not absorb strongly beyond 650 nm, so the lower loss at longer wavelengths did not compensate the high loss at shorter wavelengths.

The remaining metals all followed a similar trend of absorbing less incident light in the region of 350 nm to 600 nm (where most of the light was absorbed by P3HT:PCBM) and absorbing much more beyond 600 nm. At 390 nm, the total light absorbed in the metal was 4.4%, 6.0%, 6.6%, 8%, and 10% for Ba/Al, Pd, Ca/Al, Ni, and Mg/Ag, respectively. Beyond 600 nm, the absorption of these metals peaked near 650 nm, where the fraction of light absorbed by each metal was 31%, 40%, 48%, 53%, and 69% for Ba/Al, Pd, Ni, Ca/Al, and Mg/Ag, respectively. The low-workfunction metals, Ba, Ca, and Mg, all tended to have high absorption losses, and their absorption losses would have exceeded those from Pd and Ni if a comparable thickness was
Table 2.1. Data tabulated from Figure 2.8 showing the differences in the total absorption fraction between conventional and inverted devices in each layer. PD = percentage difference (calculated as (Conv−Inv)/[(Conv+Inv)×2]×100 %). Positive PD indicates conventional device absorption was larger, whereas negative PD indicates inverted device absorption was larger.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Active Layer</th>
<th>Metal</th>
<th>Oxide/Fluoride (A×10^3)</th>
<th>Front Interlayers</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Conv.</td>
<td>Inv.</td>
<td>PD (%)</td>
<td>Conv.</td>
</tr>
<tr>
<td>Mg/Ag</td>
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<td>0.527</td>
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<td>0.317</td>
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<td>0.542</td>
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<td>0.219</td>
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<tr>
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<td>0.545</td>
<td>0.547</td>
<td>-0.467</td>
<td>0.245</td>
</tr>
<tr>
<td>Ni</td>
<td>0.544</td>
<td>0.546</td>
<td>-0.394</td>
<td>0.220</td>
</tr>
<tr>
<td>Pd</td>
<td>0.554</td>
<td>0.556</td>
<td>-0.328</td>
<td>0.174</td>
</tr>
<tr>
<td>Ba/Al</td>
<td>0.560</td>
<td>0.562</td>
<td>-0.339</td>
<td>0.145</td>
</tr>
<tr>
<td>CuO/Cu</td>
<td>0.556</td>
<td>0.558</td>
<td>-0.354</td>
<td>0.057</td>
</tr>
<tr>
<td>Cu</td>
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<td>0.561</td>
<td>-0.309</td>
<td>0.056</td>
</tr>
<tr>
<td>Au</td>
<td>0.559</td>
<td>0.561</td>
<td>-0.325</td>
<td>0.048</td>
</tr>
<tr>
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<td>0.578</td>
<td>-0.137</td>
<td>0.075</td>
</tr>
<tr>
<td>MoO₃/Al</td>
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<td>0.578</td>
<td>-0.133</td>
<td>0.075</td>
</tr>
<tr>
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<td>0.579</td>
<td>-0.133</td>
<td>0.074</td>
</tr>
<tr>
<td>Al</td>
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<td>0.581</td>
<td>-0.138</td>
<td>0.072</td>
</tr>
<tr>
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<td>0.578</td>
<td>-0.249</td>
<td>0.022</td>
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<tr>
<td>Ag</td>
<td>0.580</td>
<td>0.581</td>
<td>-0.183</td>
<td>0.021</td>
</tr>
</tbody>
</table>

used for the low workfunction metals (i.e., 200 nm). It should be noted that thicknesses of Ca electrodes have been reported up to 50 nm\(^{291}\) or 80 nm\(^{276}\) which would result in even greater parasitic absorption. Fractional absorption in the metal layer was similar for both conventional and inverted device configurations, except for a dip in metal layer absorption between ~ 350 nm to 380 nm, as described above. Less than 1 % of the total (integrated) light was absorbed by each of the 2 nm thick metal oxide/fluoride layers (see Figure 2.8 and Table 2.1).

The fraction of light absorbed in the active layer, electrode layer(s) and front interlayers (defined here as ZnO/ITO and PEDOT:PSS/ITO for inverted and conventional devices, respectively) integrated over the 350 nm to 800 nm wavelength range is represented in Figure 2.8 for both inverted and conventional devices along with calculated \(J_{sc}\) values. The amount of light absorbed by the active layer generally increased with decreasing fraction of light absorbed by the metal (i.e., increasing reflectivity of the metal electrode; see Figure 2.7) except for NiO/Ni, Al and all metal oxide-/fluoride-coated Al electrodes. Inverted devices tended to absorb more light in
the active layer compared with conventional devices (see also Figure 2.10). It was observed that the $J_{sc}$ increased as the fraction of light absorbed in the active layer increased, but did not correlate with total absorbed light in the device (due to parasitic absorption in more absorptive metals such as Mg). In all cases, the $J_{sc}$ of inverted devices was larger than that of conventional devices by 0.12 mA/cm$^2$ to 0.19 mA/cm$^2$, with inverted devices reaching a maximum $J_{sc}$ of 14.26 mA/cm$^2$ for a Ag anode compared with 14.13 mA/cm$^2$ for a conventional device with a Ag cathode. Ag and Al electrodes, either bare or coated, resulted in the highest $J_{sc}$ values in both conventional or inverted configurations; devices employing the low-workfunction bilayer metal electrodes, Ni, and Pd resulted in the lowest $J_{sc}$ values, with Mg/Ag having the lowest $J_{sc}$ of 12.66 mA/cm$^2$ in the inverted configuration. Details of the simulation accuracy will be discussed in Section 2.4.5. The difference between 1 (i.e., total normalized incident light intensity) and the total integrated fraction of light absorbed in each device represents the fraction of light lost due to reflection; thus, if light trapping techniques, such as application of anti-reflection coatings, are employed, then BHJ-OPVs with the lowest total absorption (i.e., Ag, Au, Cu metal electrodes) have the most potential for improvement.

2.4.4. Power conversion efficiency

Figure 2.9 shows the theoretical $\eta_p$ for all the device and electrode types. Low-workfunction metals (bare or coated) (e.g., LiF/Al, Ba/Al, Ca/Al, Mg/Al) were necessary for high $\eta_p$ conventional devices (efficiencies of up to 6.77 % for LiF/Al); however, lower workfunction metals are typically not stable in air and are very likely to have relatively short operational lifetimes.\textsuperscript{6,173} Higher workfunction metal electrodes (e.g., Au, Pd, Ni), native metal oxide-coated metal electrodes (e.g., Ag$_2$O/Ag, CuO/Cu, NiO/Ni), or high workfunction $p$-type metal oxide-coated metal electrodes (e.g., MoO$_3$/Al) were necessary for high $\eta_p$ inverted devices ($\eta_p$ of up to 6.70 % for Ag$_2$O/Ag) and are expected to be more stable in ambient conditions.\textsuperscript{6,173} It is notable
that $p$-type native metal oxide formation, which is likely to occur for Ag, Cu, and Ni when exposed to air$^{32,33,171,271,274}$ or if oxygen permeates through the device, $^{171,173,272}$ can result in high $\eta_p$ inverted devices, but is detrimental to conventional device performance; therefore the performance of conventional devices is likely to degrade with aging or oxidation of the electrode.$^6,49,173$ Based on our computations, we believe that inverted BHJ-OPVs can theoretically outperform conventional BHJ-OPVs, and one possible limitation is the higher $R_s$ for inverted devices; develop of methods of reducing the $R_s$ of inverted devices (e.g., use of more conductive ETLs, doping ZnO to improve conductivity, etc.) will result in inverted device $\eta_p$ exceeding that of comparable conventional devices.

2.4.5. Simulation accuracy

The accuracy of the numerical results presented here was validated through a comparison

![Figure 2.9](image.png)

**Figure 2.9.** Calculated power conversion efficiency for the nine bare metal and six coated metal electrodes studied for inverted (top) and conventional (bottom) configurations calculated using the data in Figure 2.4, and the $J_{sc}$ values shown in Figure 2.5(e). The blue outlined bars refer to $p$-type metal oxide-coated metals and the green outlined bars refer to the $n$-type metal oxide- or fluoride-coated metals.
with experimental data from several different metal electrode-dependent studies (Table A8). Eo et al. studied conventional BHJ-OPVs based on P3HT:PCBM with varying metal cathode from LiF/Al, Ca/Al, Mg/Al, Al, and Au and found that the $J_{sc}$ was lowest for Ca and Mg based devices (8.21 mA/cm$^2$ and 9.17 mA/cm$^2$, respectively) and increased for less lossy electrodes (LiF/Al, Al, and Au had values of 9.74 mA/cm$^2$, 9.27 mA/cm$^2$, and 8.28 mA/cm$^2$). Apart from LiF, they observed similar trends in the $J_{sc}$ data as reported here (i.e., Al performed better than Au, which performed better than Ca and Mg). Mg had a higher $J_{sc}$ than Ca, but both were supported by Al (whereas in this study, we chose to support Mg by Ag). All the $J_{sc}$ values from that study are lower by ~5 mA/cm$^2$ compared to the values reported here (i.e., 60% to 70% of our calculated values), which we attribute to $\eta_{IQE} < 100\%$ due to recombination (typical $\eta_{IQE}$ values range from ~50% to 80% between 350 nm to 650 nm), exciton decay losses and different device layer geometries. However, as we report in the Section 2.4.7, since the generation rate profiles (Figure 2.11) were similar for each metal electrode, and the active layer thickness and material were kept constant, we expect our $J_{sc}$ to be an overestimate of the experimental $J_{sc}$ values and represent the maximum possible $J_{sc}$. The trends should still hold when a non-ideal $\eta_{IQE}$ is considered. Another possible factor that could result in a lowering of empirical $J_{sc}$ values relative to those calculated here is a very high series resistance for bare Al electrodes. This is presumably the reason why the LiF/Al electrode outperforms the Al electrode in the study by Eo et al., which could potentially protect the active layer from reactions with Al, potentially increasing the series resistance.

The $V_{oc,max}$ reported here (0.7 V) is also considered an upper limit for the P3HT:PCBM blend. In reality, the $V_{oc}$ for P3HT:PCBM BHJ-OPVs is typically around 0.5 V to 0.6 V max, although it has been reported as high as 0.67 V. The $FF_0$ values reported here are higher (~0.76) than most experimental values for $FF$ (typically in the range of 0.5 - 0.67), however when parasitic resistances were considered, values closer to the...
Figure 2.10. Solar spectral overlap with theoretical active layer and metal absorption. (a) AM1.5 spectrum overlain on the calculated fractional absorption spectra in the active layer for a conventional and an inverted device (both having Ag as the electrode). The region of maximal spectral overlap is highlighted. (b) Region of maximal spectral overlap for the active layer of several inverted devices simulated. (c) Region of maximal spectral overlap for the metal layer of several inverted devices simulated.

Experimental values were calculated (~0.69). Due to the high \( J_{sc} \) values reported here, the total \( \eta_p \) values are slightly higher (~6.7 %) than what is frequently observed experimentally (~5 %) for
P3HT:PCBM based devices. However, the purpose of these calculations is to compare and obtain insight into the trends in conventional and inverted device performance with electrode types, rather than directly predicting empirical performance parameters (particularly since there is uncertainty in the precise values of the energy levels, $\eta_{QE}$, $n_d$, $R_s$, $R_{sh}$, and the optical constants, and slight changes in any of these values can result in large changes in $J_{sc}$, $V_{oc}$ and $FF$).

2.4.6. Comparison between conventional and inverted devices

As stated in Section 2.4.3, the inverted BHJ-OPV devices tended to outperform the conventional devices in terms of $J_{sc}$, which can be attributed to maximizing the optical electric field in the active layer for the inverted devices compared to the conventional devices, particularly at the more useful wavelengths (450 nm to 650 nm, where the AM1.5 spectrum has its peak intensity and within the active layer’s absorption band, Figure 2.10a,b). This is a result of the interlayers in the conventional (PEDOT:PSS) and inverted (ZnO) devices having different optical constants (see Appendix, Figures A6 and A8, respectively). Figure 2.10 shows the importance of having large absorption in the active layer in the region with maximal spectral overlap with the AM1.5 spectrum. Higher absorption in the regions of high solar spectral intensity (450 nm to 600 nm) can compensate for greater loss at other wavelength regions, such as 350 nm to 380 nm for the inverted device (Figure 2.10a).

Additionally, in the region of maximal spectral overlap between the active layer and the solar spectrum, the metal absorption should be minimized (Figure 2.10b,c). When selecting metals as electrodes for photovoltaics, it is important to select metals that have the lowest parasitic absorption loss in the region of maximum overlap between the active layer and the solar spectrum (mostly between 450 nm and 600 nm in the case of P3HT:PCBM based BHJ-OPVs). This is largely the reason why Al electrode devices outperform Au and Cu, which are known to be less lossy than Al in general. Al is very lossy at wavelengths longer than 600 nm, but Au
Figure 2.11. Generation rate of excitons in P3HT:PCBM for nine different metals studied for a) conventional and b) inverted orientations.

and Cu are lossier than Al between 350 nm to 600 nm (see Figure 2.5c,d or Figure 2.10c).

2.4.7. Spatial dependence of exciton generation rate for different metal electrodes

The spatial dependence of the generation rate of excitons in P3HT:PCBM did not vary significantly for different metal electrodes in either the conventional or inverted configurations (Figure 2.11). This suggests that the transport properties of the excitons and free charge carriers in the active layer will not be significantly different for different metal electrodes, as described in Section 1.2.6.3. However, it was observed that the metals with the lowest parasitic loss (i.e., the largest reflectivity; Figure 2.7) resulted in the exciton generation rate extending to longer wavelengths. In general, the spatial dependence of the generation rate of excitons is partially responsible for the tendency of inverted devices to underperform relative to conventional devices, experimentally. As shown in Figure 2.12, the maximum of the generation rate profile, for all
metal electrodes, occurs closer to the transparent electrode. This means that most of the excitons will be formed closest to the transparent electrode (the anode for conventional devices; the cathode for inverted devices). Because electrons in PCBM have a higher mobility ($\sim 3 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) than holes in P3HT ($\sim 2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$; see Figure 1.10), this means that for inverted devices, the slower hole must be transported a longer distance than the faster electron, giving it more opportunities for recombination to occur. Thus, modifying the charge mobility or re-distributing the generation rate profile to make the peak occur closer to the center or to the metallic electrode are important steps towards improving inverted device efficiency relative to conventional devices.

### 2.5. Conclusions

In summary, we have calculated the electronic and optical performance parameters for various metal electrodes, with and without metal oxide/fluoride coatings for inverted and conventional bulk-heterojunction organic photovoltaic (BHJ-OPV) device configurations. We have quantified the open-circuit voltage and fill factor of inverted and conventional BHJ-OPVs for 2 extreme cases of: (1) strong interface dipole formation between the organic active layer and

![Figure 2.12.](image)

**Figure 2.12.** Generation rate of excitons in P3HT:PCBM for nine different metals studied for a) conventional and b) inverted orientations.
the metal; and (2) no interface dipole formation between the organic active layer and metal. This was the first reported computational study that systematically compared the performance parameters of conventional and inverted devices considering a range of different metal electrode types. We have quantitatively shown that inverted BHJ-OPVs can outperform conventional BHJ-OPVs in terms of their short-circuit current density values and that addition of an ultrathin metal oxide/fluoride interfacial layer does not significantly affect these values based on optical simulations. Based on our efficiency calculations, we have shown that: (1) high-workfunction metals are necessary for high-efficiency inverted device performance; and (2) native metal oxide formation on metal electrodes can result in high-efficiency inverted devices but can also degrade conventional device efficiency. We recommend that future BHJ-OPV research should focus on the inverted configuration, which is known to be more air-stable than its conventional counterpart, and can theoretically perform as well as, or superior to, conventional devices.

The results presented in this chapter have also highlighted another key feature regarding the selection of metal electrodes in BHJ-OPVs: metals that can support low-loss surface plasmon resonances in the visible regime (i.e., Ag, Au, Al, and Cu) can achieve high-efficiency inverted devices (with or without an oxide interlayer), but are detrimental to conventional device efficiency. Thus, it is expected that incorporating plasmonic nanostructures as electrodes for BHJ-OPVs, such as the plasmonic metasurfaces described in the subsequent chapters, should be of greater benefit to inverted devices due to the higher workfunction of noble metals. Additionally, devices employing metal electrodes with the lowest loss in the visible regime have the greatest potential to be enhanced using light-trapping techniques such as plasmonic nanostructures (most notably, Ag), since most of the light not absorbed by the active layer is lost to reflections rather than parasitic absorption by the metal.
Chapter 3. Computational Optimization of Plasmonic Metasurfaces for Bulk Heterojunction Organic Photovoltaics: Variation of Aspect Ratio and Metal

3.1. Abstract

In Chapter 2, we demonstrated that the selection of metal electrodes is critical to the performance of BHJ-OPVs, and that high-workfunction metals and native metal oxide formation on metals can lead to high-efficiency inverted devices. Metals having low absorption losses in the visible and high-workfunctions, such as Au, Ag, Al, and Cu, are the most suitable electrode materials for achieving both large $J_{sc}$ and $V_{oc}$ values. In addition, BHJ-OPVs employing these metals have the most potential to be improved by nanostructuring the metallic electrode, allowing light to couple into surface plasmon modes. In this chapter, we extend our investigation of the dependence of performance parameters of BHJ-OPVs on the metal electrode type when the metal electrode is nanostructured in such a way that it supports both localized surface plasmon resonances (LSPRs) and propagating surface plasmon polaritons (SPPs). We begin our investigation by studying plasmonic metasurfaces comprised of a Ag nanoparticle array (AgNPA) on a Ag thin-film (AgNPA/Ag) as anodes in inverted devices, since Ag is the metal with the lowest loss in the visible.

We choose to vary the aspect ratio (where aspect ratio is the nanoparticle height divided by the nanoparticle diameter) of the Ag nanoparticles (AgNPs) for a square-packed array with fixed interparticle spacing of 30 nm. We vary the aspect ratio by fixing the nanoparticle height to 60 nm and varying the nanoparticle diameter from 12 nm to 180 nm, allowing for tunability of the transverse LSPR and the intensity of the scattering (see Section 1.3.1.2). We show that AgNPs with aspect ratios less than or equal to 0.5 lead to enhanced $J_{sc}$ values for BHJ-OPVs containing plasmonic metasurfaces relative to equivalent devices with planar electrodes. We then vary the metal type of the plasmonic metasurface, ranging from Ag, Au, Cu, Al, Ni, and Ca to determine the impact of parasitic loss on the $J_{sc}$ of BHJ-OPVs containing plasmonic metasurfaces. In this
chapter, we focus our attention on the impact of plasmonic metasurfaces on the optical absorption in BHJ-OPVs, and thus on the $J_{sc}$. We do not calculate $V_{oc}$ and $FF$ here because: (1) it is not currently known how the workfunction of metal electrodes will change upon nanostructuring (see Section 8.2.1); and (2) proper computation of $V_{oc}$ and $FF$ for BHJ-OPVs with plasmonic metasurfaces require the use of 3D electrical simulations (see Section 8.3).

Lastly, we investigate off-normal angles of incidence for the incident electromagnetic radiation to excite SPP modes and to determine whether LSPRs or SPPs are more beneficial to enhancing absorption in the BHJ-OPV active layer. The computational results presented in this chapter are of benefit to the plasmon-enhanced photovoltaic community and demonstrate the importance of selecting an appropriate metal type to minimize parasitic loss while balancing the workfunction and absorption enhancement. This is an important advancement over prior work in the field as we demonstrate that plasmonic metasurfaces do not always yield beneficial absorption enhancements when incorporated into thin-film photovoltaics, and careful selection of the metasurface geometry and material is critical for enhancing active layer absorption.

3.2. Background

Surface plasmons are of interest for enhancing light absorption in thin-film photovoltaics by: increasing the generation rate of excitons through the strongly enhanced near-field; or increasing the optical path length through resonant scattering from nanostructures or by coupling light into an in-plane propagating plasmonic mode (see Section 1.3).$^{72,184,192,323}$ For visible plasmonic applications, Ag and Au are typically the preferred materials as they exhibit the lowest loss plasmonic resonances in the visible regime;$^{187}$ however, Al and Cu can also support low-loss surface plasmons in the visible and may be less expensive alternatives to Ag and Au for practical applications. Metals capable of supporting low-loss surface plasmons are expected to be of greater benefit as anodes in inverted BHJ-OPV devices, where electrode oxidation can be beneficial by increasing the workfunction of the metal, rather than cathodes in conventional
devices. As demonstrated in Chapter 2 (Figure 2.9), the metals that support the lowest-loss surface plasmons in the visible regime (i.e., Ag, Au, Cu, and Al) can all serve as efficient anodes in inverted BHJ-OPV devices, regardless of whether interfacial dipoles are formed, but can be detrimental to conventional devices when employed as cathodes. Therefore, the inverted device design, which has been shown to be substantially more air-stable than the conventional BHJ-OPV devices, also has greater potential for light-trapping by use of plasmonic metasurfaces as anodes.

In this chapter, we investigate the influence of plasmonic metasurfaces comprised of AgNPA/Ag as electrodes in BHJ-OPVs on the active layer absorption and $J_{sc}$. The plasmonic metasurfaces can support both localized and propagating surface plasmon modes, while the planar metal electrodes investigated in Chapter 2 do not support localized surface plasmon modes and do not efficiently enable coupling to propagating surface plasmon polaritons. We employ a square-packed AgNPA, which is a pattern that can be fabricated using large-area, high-throughput nanofabrication techniques, such as nanoimprint lithography (NIL), and we vary the diameter of the component NPs to control the fraction of light scattered from the AgNPA relative to the light absorbed by the AgNPAs (albedo) due to the localized plasmonic modes. We show that addition of paraboloidal AgNPs to the back electrode of inverted BHJ-OPV devices results in an enhancement in the $J_{sc}$ relative to the planar device for NP aspect ratios of 0.33 and 0.5 (enhancement of 9.27 % and 3.43 %, respectively). We compare the performance of six different metal types in the metal NPA/metal electrode configuration with a range of surface workfunctions in inverted BHJ-OPV devices, and demonstrate that plasmonic metasurfaces comprised of Ag, Au, or Cu can give rise to absorption enhancements at the red-edge of the P3HT:PCBM absorption band, whereas nanostructured electrodes comprised of Al, Ni, or Ca always lead to reduced absorption in P3HT:PCBM throughout the visible spectrum. Finally, we investigate the contributions of the different electric field components ($E_x$, $E_y$, and $E_z$) to the P3HT:PCBM absorption for all plasmonic metasurfaces to gain insight into the relative
contributions from propagating and localized plasmonic modes. We show that by varying the angle of incidence of the incident electromagnetic radiation, the largest enhancement in $J_{sc}$ can be achieved by maximizing the normal component ($E_z$) of the electric field intensity. This likely arises from coupling the incident light into propagating SPP modes and, hence, can convert a fraction of the incident light that is normally lost to reflection (up to 20 %) to useful in-plane absorption in the active layer.

3.3. Methods

3.3.1. Device setup

Figure 3.1 shows schematics of the different inverted device configurations considered in this work. For planar inverted devices (Figure 3.1a), the layers chosen were the same as those employed in Chapter 2 (Section 2.3.1.1). The thicknesses chosen were different only for the front IFL (ZnO, 20 nm)$^{47-49}$ and the P3HT:PCBM active layer (100 nm),$^{3,48,72}$ since layer thickness optimization was not conducted for BHJ-OPVs incorporating plasmonic metasurfaces. For the plasmonic BHJ-OPV devices (Figure 3.1b), we initially investigated a square-packed Ag nanoparticle array (AgNPA) on a Ag thin-film (AgNPA/Ag), since Ag is the metal with the lowest loss in the visible (see Section 3.3.2 for discussion of the AgNPA geometry). We

![Figure 3.1](image-url)  
**Figure 3.1.** Schematics of planar and plasmonic inverted organic photovoltaic device structures. Typical device schematics shown for a planar inverted BHJ-OPV (left) and a plasmonic inverted BHJ-OPV (right), which has the potential to increase the efficiency of the device relative to its planar counterpart.
calculated the absorption in each layer of the device and the $J_{sc}$ values from the active layer absorptance using the same methodology employed in Chapter 2 (Section 2.3.1.4).

### 3.3.2. FDTD simulations of BHJ-OPVs incorporating plasmonic metasurfaces

FDTD simulations\textsuperscript{317} were performed using the same parameters (e.g., mesh and wavelength step sizes, mesh accuracy, \textit{etc.}) as described in Section 2.3.2.1, making the following modifications to incorporate the plasmonic metasurfaces. The NP geometry employed was an array of square-packed paraboloids that were created using the equation:

$$z = \left(x^2 + y^2\right)^{\frac{4h}{d^2}}$$  \hspace{1cm} (3.1)

which was rotated about the $z$-axis, where $x$, $y$, and $z$ were the Cartesian coordinates corresponding to the spatial grid used in the simulations (Figure 3.2), $h$ was the maximum height of the paraboloids (fixed at 60 nm), and $d$ was the basal diameter of the paraboloids, which varied based on the aspect ratio (from 12 nm to 180 nm). The height was chosen based on previous work demonstrating that Ag plasmonic metasurfaces with nanoparticle heights of 60 nm led to maximal absorption enhancement in P3HT:PCBM absorber coatings with thicknesses of 90 nm, while keeping the nanoparticle heights less than the absorber coating thickness (to prevent short-circuiting).\textsuperscript{72,328} The inter-paraboloid spacing, or the minimum distance between the base of 2 adjacent nanoparticles, was fixed (30 nm)\textsuperscript{72} instead of fixing the period to eliminate restrictions on maximum nanoparticle diameter (e.g., if the period was fixed at 100 nm, then the maximum nanoparticle diameter could only be 100 nm; if a significantly larger period was chosen, then small-diameter nanoparticles would become less effective at enhancing absorption). Only one unit cell was simulated (see Figure 3.2), where the edges of the unit cell corresponded to the perpendicular bisectors of the paraboloids. Compared to the planar simulations from Chapter 2, the simulation region was larger in size and increased with decreasing aspect ratio, requiring more computational memory for the larger simulation regions. Further, since the planar devices
Figure 3.2. Graphical user interface (GUI) associated with the simulation setup employed in Lumerical FDTD Solutions software to simulate the electromagnetic response of nanoparticle arrays studied in this chapter. a, x-y plane associated with a typical BHJ-OPV employing a plasmonic metasurface electrode; the simulation boundaries lie along the edges of one unit cell. Aspect ratios of 1.0, b, and 2.0, d, are shown in the 3D perspective view within one unit cell. c, x-z plane associated with the simulation from a. The axes in each figure depict the wave vector, \( k \), electric field vector, \( E \), and magnetic field vector, \( H \), as well as the x-y-z coordinates referred to throughout the text.

do not have electric field intensities varying in the x-y plane, only one simulation was required per device. However, due to the presence of inhomogeneous electric fields in the x-y plane for the plasmonic devices, monitoring the electric field intensity along a single x-z plane does not give an accurate description of the total electric field intensities within the device. A fully 3D electric field monitor is ideal, but can be computationally intensive for tight spatial grids, so for the simulations reported in this chapter, the electric field intensity was monitored at 10 different x-z planes to approximate the fully 3D electric fields within the device (Figure 3.4b). Due to the symmetry of the structures, only half of the unit cell was monitored. The optical constants of all materials used in these simulations are reported in Appendix Section A.1.

3.3.3. Thickness considerations for active layer

In our simulations, we assumed that the P3HT:PCBM layer filled in the gaps between the
nanoparticles, and formed a planar interface above the nanoparticles. This resulted in thickness variations throughout the active layer. Since optical electric field interference patterns (arising from reflected electromagnetic waves at each interface in a multilayer device) are highly dependent on the thickness of each layer, care must be taken when comparing results from devices employing plasmonic metasurfaces to those of the planar devices. One option is to assume an equivalent maximum thickness of the active layer (100 nm in this study), which is the more practical method when fabricating these devices. However, it may be more accurate to make a comparison between plasmonic and planar devices having equivalent volume of the active layer. Therefore, both equivalent volume and equivalent thickness planar device calculations were performed and compared; however, the majority of results reported throughout this chapter are for a constant maximum thickness of active layer.

The maximum thickness of the active layer in the plasmonic devices was chosen to be 100 nm (i.e., in the region between adjacent nanoparticles) and the minimum thickness was 40 nm (i.e., the distance between the top of the nanoparticle array and the top of the active layer). To calculate the equivalent volume of active layer material for planar devices, the total volume of the active layer (including nanoparticles, i.e., the paraboloids) was calculated, then the volume of the paraboloids was subtracted from the total volume. The volume of a paraboloid \( V_p \) is given by:

\[
V_p = \frac{1}{2} \pi r^2 h
\]

where \( r \) is the basal radius of the paraboloid. For an aspect ratio of 1, this value was calculated to be 84,823 nm\(^3\) \((2r = h = 60 \text{ nm})\). Since there was only one paraboloid per unit cell (due to symmetry), this value was subtracted from the total volume of the active layer including the paraboloids in the unit cell \( V_i \), which is the volume of a rectangular cuboid, with length and width \( x \) and \( y \), and thickness \( t_{pl} \). For \( \text{AR} = 1 \), having \( x = 90 \text{ nm}, y = 90 \text{ nm}, \) and \( t_{pl} = 100 \text{ nm}, V_i = 810,000 \text{ nm}^3 \) [note \( x \) and \( y \) were determined by taking \( 2r \) and adding the inter-paraboloid distance of 30 nm, i.e., \( 2 \times (30 \text{ nm}) + 30 \text{ nm} = 90 \text{ nm} \)]. The difference between \( V_i \) and \( V_p \) gives \( V_{\text{equiv}} = \)
725,180 nm$^3$, which, when dividing by the cross-sectional area ($x \times y$), a thickness value of $t_{equiv} = 89.258$ nm is obtained. This was the value used for the planar devices assuming an equivalent volume of the active layer.

3.3.4. Depolarization of simulation results

As mentioned in Section 2.3.2.1, the excitation source was $E_x$ polarized light. For planar devices, the absorption in each layer at normal incidence is polarization-independent. However, for the devices with plasmonic metasurfaces, the response of the nanostructures will vary depending on the polarization of the excitation source. Due to the symmetry associated with the square-packed array of paraboloids on the plasmonic metasurface, only a simulation using $E_x$ polarization is required; the excitation source can be effectively depolarized during post-simulation data processing. To obtain the depolarized results, the final electric field intensity values were rotated 90º about the $z$-axis to effectively give the $E_y$ polarization, which was then used in the following equation:

$$|E|^2 = \frac{1}{2}\left(|E_x|^2 + |E_y|^2\right)$$

where $|E|^2$ represents the effective electric field intensity for depolarized optical excitation. Not only does this account for the polarization-dependence of the nanostructures, but this is also more accurately simulates excitation by sunlight (i.e., depolarized light).

3.3.5. Angle-dependent simulations

To promote the in-coupling of incident light into a propagating plasmonic mode, a non-negligible component of the in-plane wavevector ($k_x$) of the incident light is required (see Section 1.3.1.1). This requires off-normal angles of incidence ($\theta$) for the excitation (see Figure 3.8f). The boundary conditions of the FDTD simulations were changed for all off-normal incidence simulations to Bloch boundary conditions in the plane of the device (i.e., in both the $x$- and $y$-
directions). PML boundary conditions (see Section 2.3.2.1) were still used at the simulation boundaries normal to the plane of the device (i.e., in the z-direction).

For conservation of momentum at the Bloch boundaries in the FDTD simulations, the in-plane wavevector is constant for all wavelengths. Since the magnitude of the wavevector is proportional to its wavelength ($k = (2\pi/\lambda)\sin\theta$), for off-normal angles of incidence, the actual excitation angle changes for broadband excitation. Longer wavelengths are incident at larger angles compared to shorter wavelengths. However, due to the use of the Bloch boundary conditions (as opposed to symmetric boundary conditions), the 3D simulations with an off-normal-incidence plane wave excitation are more computationally intensive compared to those with a normal-incidence plane wave excitation. Therefore, all off-normal-incidence excitation simulations reported in this chapter were performed at a single wavelength (650 nm). The initial angle chosen was 15° for all simulations with varying aspect ratios of the AgNPs.

3.4. Results and Discussion

3.4.1. Active layer thickness consideration

First, FDTD electromagnetic simulations of OPV device structures incorporating plasmonic metasurfaces, having nanoparticles with aspect ratios of 1, were carried out, and, for comparison, planar OPV device simulations were performed for both equivalent-volume and equivalent-thickness of the active layer. In most cases, the equivalent-active-layer-volume planar devices (active layer thickness of 89.53 nm) exhibited larger $J_{sc}$ values (between 0.3 % and 5.4 % higher) compared to the equivalent-active-layer-thickness planar devices (active layer thickness of 100 nm), despite having less active material (Table 3.1). This is due to the interference that occurs within thin-film stacks, shifting the peak electric field intensity closer to the center of the active layer when the thickness is 89.53 nm (see Figure 1.9b). Thus, care must be taken when choosing whether to compare results for OPV devices containing plasmonic metasurfaces to those
Table 3.1. Comparison of short-circuit current density values for planar devices having different active layer thicknesses. Comparison of $J_{sc}$ values calculated for planar devices containing various metal electrodes for inverted and conventional configurations using the FDTD method for active layer thicknesses at constant volume ($t = 89.53$ nm) or constant thickness ($t = 100$ nm) compared to plasmonic devices. Negative percentage differences indicate larger $J_{sc}$ values for equivalent volume, whereas positive percentage differences indicate equivalent thickness values were larger. Note $t_{AL}$ refers to the active layer thickness.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\phi$ (eV)</th>
<th>$J_{sc}$ (mA/cm$^2$), Planar ($t_{AL} = 89.53$ nm)</th>
<th>$J_{sc}$ (mA/cm$^2$), Planar ($t_{AL} = 100$ nm)</th>
<th>Percentage Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv.</td>
<td>Inv.</td>
<td>Conv.</td>
<td>Inv.</td>
</tr>
<tr>
<td>Ca</td>
<td>2.9</td>
<td>9.42</td>
<td>9.58</td>
<td>9.38</td>
</tr>
<tr>
<td>ZnO/Al</td>
<td>3.6</td>
<td>12.93</td>
<td>12.51</td>
<td>12.41</td>
</tr>
<tr>
<td>Al</td>
<td>4.3</td>
<td>12.93</td>
<td>12.48</td>
<td>12.52</td>
</tr>
<tr>
<td>Ag</td>
<td>4.3</td>
<td>12.70</td>
<td>12.57</td>
<td>12.06</td>
</tr>
<tr>
<td>Cu</td>
<td>4.7</td>
<td>10.94</td>
<td>10.91</td>
<td>10.61</td>
</tr>
<tr>
<td>Ag$_2$O/Ag</td>
<td>5.0</td>
<td>12.48</td>
<td>12.45</td>
<td>11.81</td>
</tr>
<tr>
<td>NiO/Al</td>
<td>5.0</td>
<td>12.85</td>
<td>12.44</td>
<td>12.37</td>
</tr>
<tr>
<td>Au</td>
<td>5.1</td>
<td>10.97</td>
<td>10.96</td>
<td>10.63</td>
</tr>
<tr>
<td>CuO/Cu</td>
<td>5.3</td>
<td>10.65</td>
<td>10.68</td>
<td>10.36</td>
</tr>
</tbody>
</table>

for planar OPV devices with equivalent-thickness or equivalent-volume of the active layer. For this chapter, we chose to compared results from simulations incorporating plasmonic metasurfaces to those from simulations of planar devices with equivalent maximum thickness (rather than volume), which is experimentally easier to control when fabricating devices because both planar and plasmonic devices can be fabricated on a single substrate.

3.4.2. Variation of plasmonic metasurface nanoparticle aspect ratio
Figure 3.3. Tuning of $J_{sc}$ by varying the aspect ratio of AgNPs on Ag. \( \text{a, Calculated } J_{sc} \text{ in the } x-z \text{ plane as a function of } y\text{-position in inverted, Ag anode devices for both planar (100 nm active layer thickness) and plasmonic (100 nm active layer maximum thickness) configurations, varying AgNP aspect ratio (AR). Inset: electric field intensity contour plot in an } x-y \text{ plane located at the base of the AgNPs for an AR of 1 at an excitation wavelength of 600 nm; the AgNPs are shown above the contour, with the black box denoting one simulated unit cell. Note that for this plot, the excitation source was depolarized for the } J_{sc} \text{ versus } y \text{ plot and the } x-y \text{ electric field intensity contours. For } b-j, \text{ the results are plotted under } x\text{-polarized excitation. b, Calculated average fractional absorption spectra in the active layer (top) and metal layer (bottom) for inverted, Ag anode devices for varying AgNP aspect ratio. For these plots, fractional absorption versus wavelength was calculated by averaging over ten } x-z \text{ planes defined by } y \text{ ranging from } y = 0 \text{ to the maximum } y \text{ value (refer to a and inset). c, Calculated fractional absorption spectra in the active layer in a single } x-z \text{ plane for inverted, Ag anode devices. The } x-z \text{ plane bisects the center of the AgNPs (yellow plane in inset) at the edge of the unit cell. d, Integrated fraction of light} \)
absorbed in the Ag anode for inverted devices, varying AgNP AR (left axis). Overlaid are calculated $J_{sc}$ values (right axis). Note that an aspect ratio of 0 corresponds to the planar device. Total simulated electric field intensity profiles in an x-z plane bisecting the center of the AgNPs (see yellow plane in e, inset) for inverted, Ag anode devices in planar (e, h) and plasmonic configurations (aspect ratios of 5.0 (f, i) and 0.5 (g, j)), at 2 particular wavelengths: 640 nm (e - g) and 380 nm (h - j). The vertical scale bar in e is constant for all plots; the horizontal scale bars in e - g are constant for the corresponding shorter wavelength plots. The colour bar to the right of all the contours is the electric field intensity in normalized units and is used for all contours.

From the data shown in Figure 2.8 of Chapter 2, it was observed that planar devices (conventional or inverted) with Ag-based electrodes exhibited the lowest total absorption in the device stack compared to devices that employed other metal electrodes. For this reason, Ag-based electrodes were considered to have the most potential to be improved using light-trapping techniques such as addition of plasmonic nanostructures, and were the initial focus of study in this chapter. When adding nanostructures to a photovoltaic device, the optical electric field distribution across the device area no longer follows that of the incident, normal plane wave (which occurs in a planar device). Therefore, there will be a non-uniform electric field intensity distribution in the plane of the device (x-y plane, see Figure 3.3a, inset) resulting in local variations in $J_{sc}$. Figure 3.3a shows a plot of the calculated local $J_{sc}$ as a function of y-position in the device given depolarized, normal-incidence excitation conditions. Note that there is no change in $J_{sc}$ with change of y-position for the planar device. At the center of the unit cell ($y = 0$ nm; see inset), the $J_{sc}$ for AR = 0.33 is greater than that of the planar case (13.41 mA/cm$^2$ relative to 12.33 mA/cm$^2$), but for all larger AR AgNPs, the $J_{sc}$ is less than that of the planar case. For all ARs, $J_{sc}$ increases to a value greater than that of the planar device at an x-z plane near the edge of the nanostructures (i.e., for y values at approximately ±15 nm, since the AgNPs have a basal spacing of 30 nm; see inset), with maximum values ranging from 13.42 mA/cm$^2$ to 14.96 mA/cm$^2$. This is attributed to significantly enhanced electric field intensity near the surface of the AgNPs. $J_{sc}$ decreased as the y-position approached an x-z plane bisecting the center of adjacent nanostructures (i.e., the edge of the unit cell) due to the reduction in active material cross-
Figure 3.3b shows the fractional absorption spectra in the active layer (top half), and in the metal (bottom half), averaged (depolarized excitation) over the 10 $x$-$z$ planes where the electric field was monitored (from $y = 0$ nm through to the maximum $y$ value; see Figure 3.3a and 3.4b), for the planar and plasmonic Ag anode devices. There was a significant drop in the absorption in the active layer along the blue-edge of the spectrum (particularly between 370 - 420 nm), for each of the different ARs studied, relative to the planar device. This was attributed to an increase in metal absorption and little or no scattering at 380 nm from the nanoparticles (i.e., the albedo generally decreased with increasing aspect ratio). Longer wavelength (~550 nm to 700 nm) absorption in both the active layer and the metal anode increased with decreasing AR demonstrating that both AgNPA scattering and absorption increased with increasing diameter. For AgNPs with AR $\leq 0.75$, active layer absorption was enhanced relative to the planar case at longer wavelengths, whereas for nanoparticles with AR $\geq 1$, active layer absorption was reduced at longer wavelengths. Since the AM1.5 solar spectrum drops significantly in intensity for wavelengths shorter than 480 nm, enhanced red-edge absorption arising from addition of plasmonic metasurfaces has a greater impact on $J_{sc}$ than absorption enhancements at shorter wavelengths, in general (see Section 3.4.3). Figure 3.3c shows fractional absorption spectra in the active layer for the extreme case where local electric field intensity was most intense (i.e., the $x$-$z$ plane bisecting the center of adjacent nanoparticles; see inset in Figure 3.3c, yellow plane) and for excitation polarized in the $x$-direction. Under these conditions, the absorption trends with AR are similar to those for depolarized excitation (e.g., solar illumination; Figure 3.3b), but the changes are more pronounced overall; see Figure 3.4a.

A plot of $J_{sc}$ and integrated fraction of light absorbed by the plasmonic Ag anode as functions of AR is shown in Figure 3.3d. The $J_{sc}$ was enhanced relative to the planar device (AR = 0) for ARs of 0.5 and 0.33 (attributed to red-edge active layer absorption enhancement outweighing blue-edge absorption reduction). All larger AR AgNPs resulted in a reduced $J_{sc}$
relative to the planar device (total metal absorption outweighed scattering). Notably, all AgNPA-containing devices had an integrated fraction of light absorbed by the Ag greater than that of the planar device. However, due to the large albedo of the AgNPs with ARs of 0.5 and 0.33, the scattering from the AgNPs outweighed the absorption, leading to the enhancements in the $J_{sc}$ for those ARs. Further simulations of other aspect ratios and geometries are the subject of future studies, although the albedo is not expected to increase significantly with progressively smaller aspect ratios (larger diameters) because the albedo saturates for spherical NPs having diameters of 500 nm.223

Figures 3.3e-j show electric field intensity contour plots for three different Ag anode inverted OPV devices (planar; AR = 5.0; AR = 0.5) at two particular wavelengths (640 nm and 380 nm) taken at the x-z plane indicated in the inset of Figure 3.3c. At 640 nm, the electric field intensity in the active layer was enhanced for both AR = 5.0 and 0.5 relative to the planar devices and to a larger degree for AR = 0.5, in keeping with the active layer absorption enhancement spectra (Figure 3.3b,c). However, for AR = 0.5 the electric field intensity penetrated the metal significantly near the AgNP surface, which correlated with the increased metal absorption loss with decreasing AR observed in Figure 3.3b. At 380 nm, active layer electric field intensity enhancement was low in all cases (Fig. 3.3h-j). However, electric field intensity in the metal at 380 nm for AR = 5.0 was very large ($\geq 10$ enhancement) while for AR = 0.5, electric field intensity in the metal was only enhanced by a factor of 2 to 4 near the surface of the nanoparticle. The electric field intensity contours further suggest that lower AR AgNPs have higher albedo at longer wavelengths, and that the albedo in all cases is reduced at shorter wavelengths. Further tuning of the albedo and surface plasmon wavelength of the plasmonic metasurfaces may be achieved by fixing the diameter of the AgNPs while varying height. However, the range of possible AgNP heights is limited by the chosen thickness of the P3HT:PCBM blend; increasing thickness of the blend would result in added series resistance which could degrade the electrical performance of the OPV device. The nanostructure shape, packing density, pitch and material
Figure 3.4. Polarization effects in plasmonic devices. a, (top) Calculated fractional absorption spectra in the active layer in a single x-z plane for inverted, Ag anode devices for both planar and plasmonic configurations, varying AgNP AR. The x-z plane bisects the center of the AgNPs at the edge of the unit cell (see Figure 3.3c and b). a, (bottom) Calculated fractional absorption spectra in the active layer for all x-z planes simulated for inverted, Ag anode plasmonic device having AR = 0.33. The planes in b correspond to the various spectra; beneath the nanoparticles in b is an electric field intensity contour in the x-y plane at a wavelength of 640 nm. Note that for these absorption spectra and the electric field intensity contour, the excitation source was depolarized. Electric field intensity contours in the x-y (c, d) and x-z (e, f) planes taken at maximum z or y values, respectively. In c, e, the excitation source is polarized along the x-direction (see Figure 3.2), whereas in d, f, the excitation source is depolarized.

composition could also be further optimized, which is a subject of future studies.
Figure 3.4 compares the $E_x$ polarized results and the depolarized results calculated using Equation 3.3. Figure 3.4a (top) shows the calculated fractional absorption spectra in the active layer for the $x$-$z$ plane bisecting two nanoparticles (see Figure 3.3c and inset). In this case, the excitation source has been depolarized using Equation 3.3, so the results are starkly different from those in Figure 3.3c. Figure 3.4a (bottom) shows the fractional absorption spectra in the active layer for each $x$-$z$ plane simulated with a AgNP AR of 0.33, for depolarized excitation. Figure 3.4b shows where the 10 $x$-$z$ planes were taken for the simulations for AR = 0.33, and underlying the nanoparticles is an $x$-$y$ contour of the electric field intensity taken from the base of the nanoparticles (for depolarized excitation). To demonstrate the polarization dependence of the excitation source, Figure 3.4c-f shows electric field intensity contours for an $x$-$y$ plane (c, d) and an $x$-$z$ plane (e, f) for $E_x$ polarized (c, e) and depolarized light (d, f). The electric field intensities were more localized and more intense under $E_x$ excitation, whereas for depolarized excitation, the fields were more uniform across the surface of the paraboloid, but less intense overall. When taken as an average, the total fields should converge to the same value. It is noteworthy to mention that since only ten $x$-$z$ planes were used in the simulations (due to computational limitations), but the $dx$ spacing was 0.9 nm, there were many more $x$-points than $y$-points, so when calculating the depolarized excitation data (using Equation 3.3), only 10 linearly-spaced $x$ points could be taken for the average. This resulted in loss of data and, therefore, accuracy, when calculating the fields for depolarized excitation. Hence, the final averaged absorption spectra and $J_{sc}$ values presented in Figure 3.3b,d were thus calculated using only the $E_x$ polarized data, but since the fields were integrated over $x$ and $y$ the final spectra and $J_{sc}$ values are the same regardless of the polarization of the incident electromagnetic radiation.

3.4.3. Importance of long wavelength active layer absorption enhancement to short-circuit current density
Figure 3.5. Solar spectral overlap with theoretical active layer absorption. a, AM1.5 spectrum (obtained from the ASTM G173-03 standard, provided by the National Renewable Energy Laboratory) overlain on the imaginary part of the refractive index, $k$, of P3HT:PCBM (see Appendix A.1.2). b, AM1.5 spectrum overlain on the calculated fractional absorption spectra in the P3HT:PCBM active layer (100 nm thick) for the inverted, planar configuration for various anode materials. c, AM1.5 spectrum overlain on the calculated fractional absorption spectra in the P3HT:PCBM active layer for the inverted, plasmonic Ag anode devices with varying ARs, taken at an $x$-$z$ plane of high electric field intensity (cf. Figure 3.3c).
To emphasize the importance of the long wavelength (i.e., red-edge) absorption enhancement in P3HT:PCBM, the AM1.5 spectrum has been overlaid on the extinction coefficient spectrum of P3HT:PCBM (Figure 3.5a), the calculated absorption spectra in the active layer for various inverted, planar devices (Figure 3.5b), and the calculated absorption spectra in the active layer for inverted, plasmonic Ag anode devices at the $x$-$z$ plane bisecting 2 nanoparticles (Figure 3.5c). When selecting metals as electrodes for photovoltaics, it is important to select metals that have low loss in the region of maximum overlap between the active layer and the solar spectrum (mostly between 380 nm and 600 nm in the case of P3HT:PCBM based BHJ-OPVs). This is largely the reason why Al electrode devices outperform Au and Cu, which are known to be less lossy than Al in general: Al is very lossy at wavelengths longer than 600 nm, but Au and Cu have greater loss between 350 nm and 600 nm (see Appendix Figure A1). Furthermore, when designing plasmonic metasurfaces, to achieve optimum active layer absorption enhancement from the addition of plasmonic nanostructures, the surface plasmon resonance of the nanostructures should occur at a wavelength where the active layer absorbs weakly, but where the AM1.5 spectrum still has a high intensity. In this case, absorption enhancements between 600 nm and 650 nm are optimal to obtain the largest $J_{sc}$ enhancements, and large enough enhancements in this range can even compensate for reductions in the active layer absorption at shorter wavelengths (such as for AR = 0.33, see Figure 3.5c). Note that the fraction of light absorbed in the active layer is more than 1 over certain wavelength ranges and aspect ratios in Figures 3.3c and 3.5c likely because the incident excitation was $x$-polarized, and only absorption from the region with the most intense electric fields is shown. When depolarized, the fraction of light absorbed in the active layer was less than unity for all wavelengths (Figure 3.4a). We will show in Chapters 4 and 5 that red-edge absorption enhancements are nearly ubiquitous for plasmonic-enhanced absorbers with spatially and spectrally overlapping resonances due to exciton-plasmon coupling.
Figure 3.6. Absorption enhancement in P3HT:PCBM active layers for all metals and aspect ratios studied. Absorption enhancement is plotted relative to planar devices of the same metal for a-c low-loss metals (a, Ag; b, Au; c, Cu) and d-f lossy metals (d, Al; e, Ni; f, Ca). The white dashed line in each plot indicates where the absorption band edge wavelength for P3HT occurs.

3.4.4. Variation of metal NPA/metal material

The plasmonic device simulations were repeated for 5 additional metals (Au, Cu, Al, Ni, Ca) for ARs of 0.5, 0.75, 1.0, 1.5, 2.0, and 5.0 (0.33 was neglected due to computational limitations) for normal incidence excitation conditions. The absorption enhancement in the active layer relative to planar devices is shown in Figure 3.6. The largest absorption enhancement arose from small AR NPs for the low-loss metals (Ag, Au, Cu for ARs less than 1.0) for wavelengths beyond the absorption band edge wavelength of P3HT (650 nm). From 650 nm to 750 nm, for Ag, Au, and Cu the absorption enhancement ranged from around 30 % to 60 % for ARs between 0.5 and 1, decreased to around 10 % for ARs approaching 3 (not simulated), and decreased even further towards 0 % for ARs of 5. The absorption enhancement was very low at wavelengths
shorter than the absorption band edge of P3HT (~650 nm) for all metals, and in fact there were significant absorption reductions (up to 30 % less absorption in the active layer in the presence of plasmonic metasurfaces compared to planar electrodes) at shorter wavelengths (350 nm to 400 nm) for all metals, particularly for ARs less than 1. This was attributed to an increase in absorption in the metal NPs, which reduced the amount of light absorbed by P3HT in regions where P3HT absorbs strongly. For the lossy metals (Al, Ni, and Ca), there was only negligible absorption enhancement and mostly absorption reductions in the active layer for all ARs and wavelengths studied. From this, we concluded that surface plasmons from low-loss metal electrodes can improve the performance of BHJ-OPVs at certain wavelengths for large-diameter metal NPs; further optimization may increase the overall enhancement of active layer absorption.

3.4.5. Absorption by different electric field components for various metals and aspect ratios

To gain a better understanding of the absorption enhancement/reduction trends observed in Figure 3.6, the contributions to active layer absorption from each component of the electric field were separated for each AR. Figure 3.7b-g shows the total fraction of light absorbed in the active layer under normal incidence excitation, integrated over all wavelengths, with the contributions to the integrated absorption from the three electric field amplitude components separated: the electric field amplitude in the in-plane direction parallel to the excitation polarization direction ($A_x$); the electric field amplitude in the in-plane direction normal to the excitation polarization direction ($A_y$), and the electric field amplitude in the out-of-plane direction normal to the plane of the device ($A_z$). For all ARs (including planar, AR = 0), Ag and Al had the most absorption in the active layer due to their high reflectivity (Figure 2.7) in the region of maximum spectral overlap between P3HT and the solar spectrum, as described in Section 2.4.3. In general, for the low-loss metals (Ag, Au, Cu; b-d, respectively), $A_x$ tended to decrease relative to the planar controls up to AR = 0.75, then began to increase up to an AR of 5. Simultaneously, $A_y$ tended to increase from AR = 0 through AR = 1, then remained relatively constant through AR
Figure 3.7. Spectrally and spatially integrated fraction of light absorbed in active layer for each metal, AR, and contribution from each electric field component ($E_x$, $E_y$, and $E_z$). a, Schematic of ARs simulated. Note that fractional ARs are for oblate semi-spheroids whereas ARs greater than 1 are for prolate semi-spheroids. b-g Integrated (spectrally and spatially) fractional absorption in active layer, separated into contributions from the three components of the electric field ($A_x$, $A_y$, and $A_z$), for b-d low-loss (b, Ag; c, Au; d, Cu) and e-g lossy metals (e, Al; f, Ni; g, Ca). h-j Electric field intensity enhancements for the three electric field components for a AgNPA/Ag anode having nanoparticle AR = 0.5 at 640 nm (h, $|E_x|^2$; i, $|E_y|^2$; j, $|E_z|^2$). The electric field intensity plots in h-j are on the same length and intensity scales (length scale bars shown in i, and intensity scale shown in color bar).

= 2 and finally decreased again at AR = 5. For the low-loss metals, the contribution to active
layer absorption by the \( A_z \) component was significant for the lowest aspect ratio (AR = 0.5), then decreased with increasing AR.

For the highest-loss metals (Ni and Ca; \( f \) and \( g \), respectively), the \( A_z \) component for the lowest aspect ratio was significantly smaller compared to planar electrodes, then continuously increased with increasing AR. \( A_y \) remained a small fraction and relatively constant from AR = 0.5 through AR = 2, and dropped slightly for AR = 5. Finally, \( A_z \) was much lower than that of the low-loss metals overall, and was slightly larger than the \( A_y \) component for AR = 0.5, then decreased as the AR increased to 5. The absorption in the active layer due to Al electrodes (Figure 3.7e) showed similarities to both the low-loss and lossy metals, due to Al being a metal capable of supporting surface plasmon resonances (large negative real relative permittivity), but is lossier overall compared to Ag, Au, and Cu (large positive imaginary relative permittivity; see Appendix Figure A1). Al shows the same trends for \( A_x \) and \( A_y \) as the lossy metals, but its \( A_z \) component is larger relative to its \( A_y \) and \( A_z \) components, which is more similar to the low-loss metals.

An important feature of these bar plots is that out of all metals and ARs studied, only a Ag electrode with AR = 0.5 showed any improvement in the total amount of light absorbed in the active layer relative to the planar device. While the \( A_z \) component was potentially enhanced relative to the lossy metals (owing to the fact that the \( A_z \) did not follow the same trend for low-loss metals as it did for lossy metals), the main components of the absorption that contributed to the overall enhancement were \( A_y \) and \( A_z \). One way to potentially improve the absorption enhancement could be to use even smaller ARs, such as AR = 0.33 (see Figure 3.3d) or smaller, but due to computational limitations we did not simulate those ARs for the other metals in this chapter. On-going and future work should address these limitations. Another possibility is to improve the total amount of light coupling into propagating modes (which is determined by \( E_z \)) by using an off-normal incident excitation.
Figure 3.8. Off-normal incidence excitation data. **a**, Fractional absorption in the active layer for Ag anode BHJ-OPVs excited at a wavelength of 650 nm for normal incidence (left) and at an angle of incidence of 15° (right). **b-d**, Percentage of total absorption for the contribution to the absorption from each electric field component at an AR = 1.0 for **b**, normal incidence, integrated broadband excitation; **c**, normal incidence, 650 nm excitation; **d**, 15° angled incidence, 650 nm excitation. **e**, Definition of normal incidence. **f**, Definition of angle of incidence.

3.4.6. Off-normal incidence simulations

Figure 3.8 shows active layer absorption components from off-normal incidence excitation for BHJ-OPV devices employing Ag planar electrodes and plasmonic metasurfaces. As discussed in Section 3.3.5, the use of off-normal incidence excitation was computationally intensive for broadband excitation, so only single wavelength excitation was used (650 nm). The wavelength was chosen to coincide with a region of positive absorption enhancement in the active layer for the low-loss metals. Figure 3.8a shows the fraction of light absorbed in the active layer at 650 nm for normal incidence excitation (left) and for excitation at an angle of 15° off-normal...
incidence (right). The total fraction of light absorbed in the active layer using off-normal incidence excitation decreased relative to normal incidence simulations, except for $AR = 1$, which was improved relative to normal incident excitation. The total fraction of light absorbed due to each component for $AR = 1$ is shown in Figure 3.8b-d for: the broadband integrated absorption fraction at normal incidence (Figure 3.8b); single wavelength absorption fraction at normal incidence (Figure 3.8c); and single wavelength absorption fraction at an angle of $15^\circ$ (Figure 3.8d). The off-normal incidence excitation improved the fraction of light absorbed in the active layer arising from the out-of-plane component of the electric field, $E_z$, suggesting a greater fraction of incident light coupled into a propagating in-plane mode. Additional angle-dependent simulations are a subject of on-going and future work.

3.5. Conclusions

In summary, we have found that metal electrodes with low absorption loss in the region of maximum spectral overlap between the active layer and the solar spectrum are essential for photovoltaic devices in general. In particular, Ag, Au, and Cu exhibited the lowest absorption loss throughout the visible spectrum and hence have the greatest potential for light management through use of plasmonic metasurfaces. BHJ-OPV devices incorporating Ag plasmonic metasurfaces were found to result in an enhancement in the short-circuit current density for square-packed nanoparticle arrays having an inter-particle spacing of 30 nm, heights of 60 nm, and diameters of either 120 nm or 180 nm ($i.e.$, ARs of 0.5 or 0.33). All other aspect ratios and metals investigated resulted in reduced short-circuit current densities relative to their planar device controls. Thus, care must be taken to optimize the geometry of the nanoparticles to minimize parasitic absorption while maximizing absorption enhancement in the active layer, otherwise plasmonic metasurfaces as electrodes in BHJ-OPVs can be detrimental to device performance.

To gain a deeper understanding of how plasmonic metasurfaces can lead to improved
BHJ-OPV device efficiency, in the following chapters, we focus more deeply on the interaction between an organic absorber layer and plasmonic metasurfaces without the full device architecture. In Chapters 4 and 5, we investigate the influence of broadband conjugated polymer absorbers on the optical properties of plasmonic metasurfaces and nanoparticles. In Chapters 6 and 7, we show that by functionalizing the plasmonic metasurfaces with ultrathin interfacial layers (MoS$_2$ and Ag$_2$O, respectively), we can simultaneously tune the optical and electronic properties of the metasurface.
Chapter 4. Absorption-Induced Scattering and Surface Plasmon Out-Coupling from Absorber-Coated Plasmonic Metasurfaces

4.1. Abstract

In Chapter 3, we showed that Ag plasmonic metasurfaces can lead to improved absorption in the active layer of BHJ-OPVs for certain nanoparticle geometries. In this chapter, we switch from square-packed Ag nanoparticle arrays to hexagonally close-packed arrays, which can lead to stronger field enhancements by packing the individual nanoparticles more tightly, and can also be fabricated using a large-area nanotemplating technique. We turn our attention from full device configurations to a more fundamental structure: absorber-coated plasmonic metasurfaces.

Interactions between absorbers and plasmonic metasurfaces can give rise to unique optical properties not present for either of the individual materials and can influence the performance of a host of optical sensing and thin-film optoelectronic applications. Here, we identify three distinct mode types of absorber-coated plasmonic metasurfaces: localized and propagating surface plasmons and a previously unidentified optical mode type called absorption-induced scattering. The extinction of the latter mode type can be tuned by controlling the morphology of the absorber coating and the spectral overlap of the absorber with the plasmonic modes. Furthermore, we show that surface plasmons are back-scattered when the crystallinity of the absorber is low but are absorbed for more crystalline absorber coatings. This work furthers our understanding of light-matter interactions between absorbers and surface plasmons to enable practical optoelectronic applications of metasurfaces.

4.2. Background

Plasmonic metasurfaces are emerging as two-dimensional materials capable of manipulating light on the nanoscale with the possibility of being incorporated into optoelectronic
devices. Metasurfaces are typically composed of arrays of sub-wavelength metallic nanostructures where the macroscopic electromagnetic properties of the surface arise from the collective response of the individual nanostructures. This collective response has led to a host of intriguing optical phenomena, such as negative refractive index and permeability, phase control, optical cloaking, and electromagnetic field enhancements. When plasmonic (meta)materials are coated with absorbers, many additional effects have been observed, such as absorption-induced transparency, strong coupling between plasmons and excitons, plasmonic splitting, and enhanced absorption within the absorber. For practical applications, it is important to understand how the properties of plasmonic metasurfaces are influenced by the presence of semiconductor absorber thin-films. Furthermore, besides the unique optical phenomena exhibited by absorber-coated metasurfaces, the effects of morphology and crystallinity of absorber coatings on metasurface optical properties have not been widely considered. Because of their propensity for solution-based deposition and applications for bulk-heterojunction organic photovoltaics (BHJ-OPVs) and polymer light-emitting diodes (PLEDs), organic semiconductors are practical materials to employ in order to investigate the interactions between absorbers and plasmonic metasurfaces.

Here, we elucidate the optical modes supported by silver plasmonic metasurfaces coated with organic semiconductor absorbers using dark-field (DF) scattered-light spectroscopy. In particular, we identify two interesting optical phenomena that arise from the absorber-coated metasurfaces: a previously unidentified optical mode type called absorption-induced scattering (AIS), and out-coupling of surface plasmon polaritons (SPPs). AIS is shown to originate from electromagnetic coupling between optical transitions of absorber materials and scattering modes, regardless of whether the scattering modes are plasmonic, localized, or collective in origin. We then show that the crystallinity of the organic absorber affects out-coupling of SPP modes, with lower crystallinity absorber coatings facilitating greater out-coupling of SPPs. We conclude by showing that these optical modes affect absorption within both the absorber coating and
metasurface materials to different extents: localized surface plasmon resonances (LSPRs) contribute more to absorption in the coating than in the metal, while AIS and SPPs are absorbed more by the metasurface. However, total absorption arising from AIS and SPPs is smaller than that for LSPRs. This work serves to highlight a previously unexplored optical scattering phenomenon that occurs from thin film semiconductor absorber layers and to further our understanding of how to control light-matter interactions at metasurfaces for practical optoelectronic applications.

4.3. Methods

4.3.1. Template-based fabrication of plasmonic metasurfaces

![Diagram of template-based fabrication](image)

**Figure 4.1.** Template-based fabrication of plasmonic metasurface using anodic aluminum oxide (AAO) nanotemplates. *i*) A handle consisting of AAO/Al/AAO is prepared using epoxy to prevent ~2 mm rim from being etched. The top layer of AAO and Al are then etched away using NaOH and FeCl₃, exposing the AAO barrier layer (a). *ii*) Barrier layer removal and pore-widening are performed to open and widen the AAO pores to a diameter of ~100 nm (b). *iii*) The epoxy is removed from the AAO nanotemplate, which is subsequently transferred to a metal film for additional metal to be thermally evaporated through the AAO pores. *iv*) The nanotemplate is removed, resulting in a metallic nanoparticle array on a metal surface (*i.e.*, a plasmonic metasurface; c).
Glass microscope slides (Fisherbrand, Thermo Fisher Scientific, Inc., 1 mm thick) were cut into ~16 mm × 16 mm segments, which were then sonicated in detergent for 15 min., soaked in a solution of ethanol and concentrated hydrochloric acid (1:1) for 15 min., then soaked in isopropanol for 10 min. before being dried individually using compressed air.

The base metal film underlying each of the metallic nanoparticles consisted of 50 nm Ag on 5 nm of Cr (used as an adhesion layer). To prepare the metal films, cleaned substrates were mounted in the thermal evaporation chamber (Edwards, Ltd. E306A) with a shadow mask used to define metal stripes 1 mm in width and 10 mm in length. The pressure of the chamber was less than $8 \times 10^{-6}$ mbar for both Cr and Ag depositions, and the deposition rate was less than 0.1 nm/s. After each evaporation, the chamber was left to cool for at least 30 min. prior to venting.

To prepare through-hole anodic aluminum oxide (AAO) masks, first AAO nanotemplates (Synkera Technologies, Inc.) with an average pore diameter of 55 nm and aluminum oxide thickness of ~500 nm (coated on both sides of aluminum) were cut into 15 mm × 10 mm pieces (Figure 4.1). The back of the nanotemplate was fully protected with epoxy as well as a ~2 mm rim on the front. The exposed AAO layer was etched using NaOH (3 M) for 20 min., then the nanotemplates were subsequently floated on a bath of aqueous FeCl$_3$ (250 g L$^{-1}$) for ~2 h. to etch the aluminum layer. After, the nanotemplates were immersed into an aqueous H$_3$PO$_4$ (5 % w/w) bath, which was held at 30 °C while stirred at 1200 rpm. The H$_3$PO$_4$ was used to remove the barrier layer and widen the pores of the AAO nanotemplate. The AAO nanotemplates were left in the H$_3$PO$_4$ for between 30 - 55 min., until the pores widened to ~100 nm in diameter as confirmed using scanning electron microscopy (SEM). After, the epoxy layer was removed by immersing the nanotemplates in 5 sequential acetone baths, followed by ethanol and, finally, isopropanol baths.

Once prepared, the through-hole AAO nanotemplates were transferred to the metal films. The nanotemplate-covered metal films were mounted in the evaporation chamber and the same shadow masks were used again while evaporating through the nanotemplates, except 1 of the
Figure 4.2. Particle diameter distribution analysis for AgNPs used in this study. The SEM images were taken from similar regions on the AgNPA/Ag where the DF spectra and AFM morphology were acquired, before the corresponding polymers or polymer:fullerene blends indicated in the top left corner of each SEM image were spin-coated onto the substrates. Inset in the top right corner of each of SEM image is a true-color DF image (using Xe lamp illumination) of the AgNPA/Ag metasurface before a polymer or polymer:fullerene blend was spin-coated on top. Inset in the bottom left corner of each SEM image is a fast Fourier Transform of the representative SEM image. The diameter distributions were taken from a minimum of 4 different regions across the 3 AgNPA/Ag stripes for each sample, averaging over >1300 AgNPs for each sample. The mean and standard deviation values of the AgNP diameters are shown as insets in the diameter distribution plots. All of the DF images, SEM images, and FFT images are on the same respective scales (scale bars shown for the bare AgNPA/Ag).

stripes of the shadow mask was blocked off using Kapton tape for the planar Ag electrode. 60 nm of Ag was deposited through the nanotemplate using the same conditions as for the base metal film deposition. After the deposition, the samples were immersed in a stream of isopropanol to remove the AAO nanotemplate. The samples were then dried using compressed air, and stored in
a vacuum desiccator until further characterization or subsequent sample preparation steps. To characterize NP size and coverage, the planar Ag and AgNPA/Ag plasmonic metasurface were imaged using DF microscopy and SEM, with an accelerating voltage of 5.0 kV and a working distance less than 5 mm. See Figures 4.2 and 4.3a for additional SEM and DF images of the electrodes.

The AgNPAs prepared using the template-based nanofabrication method resulted in a distribution of particle diameters and array periods (Figure 4.2). The large-area coverage of AgNPs was confirmed using DF and SEM imaging, in which the scattering of each of the arrays of AgNPs was uniform over each of the stripes (Figures 4.2 and 4.3). The average period of each AgNPA was determined by taking a radial average over the fast Fourier Transform (FFT) images (insets in Figure 4.2) and taking the inverse of the first peak (corresponding to the isotropic ring in the FFT images), resulting in a period of $145.7 \pm 25.8$ nm, averaging $>13,000$ AgNPs.

The large-area coverage of the AgNPAs was further confirmed by taking low-magnification SEM images over the full stripe on the substrates (Figure 4.3a). The contrast revealed regions of high density of AgNPs (bright white regions) compared to regions with either lower density of AgNPs or planar Ag regions (light grey regions). Additionally, the coverage of AgNPs and the collective scattering properties of the coated metasurfaces were visible with the bare eye (Figure 4.3e).
Figure 4.3. Sample images and schematics. (a) Low-magnification SEM images of planar Ag and AgNPA/Ag stripes. The image is composed of 28 SEM images stitched together. Note that the dark circles in the SEM images were a result of the detector used (In-Lens) and the low magnification and always appeared in the center of each individual SEM image. The large-area coverage of AgNPAs was observed by the difference in contrast between the planar Ag and AgNPA/Ag regions, where the brighter regions indicated the presence of the AgNPAs (see Figure 4.2 for high magnification SEM images). (b-c) Cross-sectional schematics of planar Ag (b) and AgNPA/Ag metasurface (c) used in this study. (d) Top-down schematic of planar Ag and plasmonic metasurface sample layout used in this study. (e) Photograph of absorber-coated planar Ag and plasmonic metasurfaces used for all GIWAXS, DF scattered light spectroscopy, and AFM surface morphology measurements reported in the main text.

4.3.2. Polymer solution and thin-film preparation

Neat polymer solutions were prepared with 10 g L⁻¹ concentration. P3HT [Alfa Aesar (Thermo Fisher Scientific, Inc.), product number: 44745; $M_w$: 30,000 - 50,000 g mol⁻¹; >95 %]
regioregularity; polydispersity index (PDI) = 4.5] and PTB7 (Sigma-Aldrich Co. LLC., product number: 772410; \( M_w \): 80,000 - 200,000 g mol\(^{-1}\); PDI \( \leq 3.0 \)) were both separately dissolved in chlorobenzene; PCDTBT (Sigma-Aldrich Co. LLC., product number: 753998; \( M_w \): 20,000 - 100,000 g mol\(^{-1}\); PDI = 4.1) was dissolved in \( o \)-dichlorobenzene. For the blends, P3HT and PC\(_{60}\)BM (Sigma-Aldrich Co. LLC., product number: 684449) in a 1:1 ratio were dissolved in chlorobenzene (20 g L\(^{-1}\) total blend concentration); PCDTBT and PC\(_{70}\)BM (1-Material, Inc., product number OS0633) in a 1:4 ratio were dissolved in \( o \)-dichlorobenzene (50 g L\(^{-1}\) total blend concentration); and PTB7 and PC\(_{70}\)BM in a 1:1.5 ratio were dissolved in a mixture of chlorobenzene and 1,8-diiodooctane (97:3 % v/v) (25 g L\(^{-1}\) total blend concentration). The P3HT, P3HT:PC\(_{60}\)BM, PTB7, and PTB7:PC\(_{70}\)BM solutions were heated to 50 °C and stirred at 1200 rpm for \( \sim 10 \) min; then were stirred for \( \sim 16 \) h at 1200 rpm and room temperature. The PCDTBT and PCDTBT:PC\(_{70}\)BM solutions were heated to 90 °C and stirred at \( \sim 1200 \) rpm for \( \sim 8 \) h. All solutions were spin-coated at varying speeds to achieve \( \sim 80 \) nm thick films, as confirmed using atomic force microscopy (AFM). See Figure 4.4 for details on spin-coating conditions and polymer film thickness measurements.
Figure 4.4. Polymer film thickness measurements and spin-coating conditions. (a) Representative AFM thickness measurement for a PCDTBT film. The left side of the measurement (0 to ~9 µm) was from a region where the polymer was removed with the edge of a tweezers prong. All thickness measurements were performed this way from a minimum of 2 separate regions, and ≥ 2 line scans were extracted from each image to determine the thicknesses. (b) Average thickness measurements determined from a minimum of 4 AFM line scans. Error bars represent standard deviation of 4 - 8 measurements. (c) Solution concentrations and spin-coating speeds used for each polymer, fullerene, or polymer:fullerene blend.

The thickness of each organic semiconductor layer was obtained by first spin-coating all polymers, fullerenes, and polymer:fullerene blends onto cleaned glass substrates, then subsequently removing part of the film using the edge of a flat tweezer. Several regions were removed from one sample. The same conditions for the AFM surface morphology measurements described in Section 4.3.3 were used for the film thicknesses, with the following changes. The samples were probed from the substrate to the film region in an area of 20 µm × 5 µm or 20 µm × 10 µm (i.e., 512 ×128 or 512 × 256 pixels^2) to ensure enough of the organic film was analyzed for
a reasonable thickness measurement. Two separate regions were scanned per sample, and 2-3 line
scans were taken from each region (averaging over 30 pixels). All AFM height images were
leveled iteratively using 3-point leveling, leveling through making facets point upwards, and
removing horizontal scan artifacts (using Gwyddion 2.35 SPM data analysis software). The
height was determined by averaging the heights of the polymer film (far enough away from the
removed polymer layer such that the data was flat) and subtracting the average of the heights of
the substrate. All 4-6 obtained thickness values were averaged to determine the mean thickness
and standard deviation (Figure 4.4b).

4.3.3. Atomic force microscopy

A Veeco Digital Instruments, Inc. Multimode Atomic Force Microscope (AFM) was used
for film thickness and surface morphology characterization. The AFM was used in tapping mode,
and silicon probes (Bruker, Corp., MPP-11100-10) with a nominal tip radius of 8 nm were used
for all measurements. All surface morphology scans were acquired over a 2.0 µm × 2.0 µm area
with a scan rate of 0.250 Hz and 512 samples/line. The images were flattened using Gwyddion
2.35 software, and root-mean-square (r.m.s) roughness values were determined in the software.

4.3.4. Dark-field scattered-light imaging spectroscopy

A Nikon, Corp. Optiphot 66 optical microscope operating in reflection mode was used to
locate AgNPA regions. DF images were taken of these regions using a 20× DF microscope
objective and a color CCD camera. Unless otherwise specified, a halogen lamp (50 W) was used
as the illumination source for all DF images and spectra. DF spectra were collected using an
Andor Technology, Ltd. Shamrock SR 303i imaging spectrometer. Scattered light from each
AgNPA region was excited and collected with a 20× DF microscope objective (N.A. = 0.40) and
the image was directed into the imaging spectrometer. A particular nanoparticle region was
selected by imaging through the entrance slit of the spectrometer (an entrance slit width of 250
µm was used, which corresponded to ~10 µm of the sample), and the height of each region was binned to 40 pixels, which corresponded to ~20 µm such that the total area from which spectra were collected was 10 µm × 20 µm (see boxes in Figure 4.13g). DF reflected-light spectra of the selected region (DFsample) were acquired by inserting an opaque stop in the excitation lamp light path, opening the field and aperture diaphragms fully, and by using an exposure time of 20 s for 6 accumulations using halogen lamp illumination. Background spectra were collected by blocking the light path to the spectrometer and using the same exposure time and accumulations as for the sample (DFsample,bkgd). Spectra were normalized to the lamp spectral intensity using DF spectra of a diffuse reflector (Spectraflect®, i.e., barium sulfate) at the same magnification using an exposure time of 1 s for 6 accumulations (DFdiffuse). A separate background spectrum was taken using the same conditions used for the diffuse reflector (DFdiffuse,bkgd). Scattered light intensity values reported here were calculated using the following equation:

\[
\text{Scattered light intensity} = \frac{DF_{\text{sample}} - DF_{\text{sample,bkgd}}}{DF_{\text{diffuse}} - DF_{\text{diffuse,bkgd}}}
\]

The spectrometer was calibrated based on 3 separate emission lines in a spectrum collected from a Hg vapor lamp. Due to low signal-to-noise ratios, we did not obtain DF scattered-light spectra below 400 nm and above ~800 nm.

4.3.5. Integrating sphere absorption measurements

The integrating sphere absorption measurements were acquired on an SI Photonics, Inc. UV-VIS spectrometer (model 440) using halogen lamp illumination (10 W). Samples were prepared as described above, except the underlying Ag film was 150 nm thick to ensure it was optically opaque. AAO nanotemplates were prepared with an area of >10 mm × 10 mm and placed directly on a large-area Ag film to give AgNPA/Ag regions >10 mm × 10 mm in area.
Samples were mounted to a 9 mm metallic aperture attached to the port of the integrating sphere, which was coated internally with Spectraflect® (i.e., barium sulfate). The SI Photonics, Inc. software automatically determined the exposure time for each spectrum, and 100 spectra were accumulated for each measurement. The reflected light intensity of each sample ($I_s$) was normalized to the reflected light intensity of a diffuse reflector ($I_0$), and the absorptance ($A$) was computed using the equation: $A = 1 - I_s / I_0$.

4.3.6. Grazing-incidence wide-angle x-ray scattering measurements

GIWAXS measurements were performed at the X9 undulator-based beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The incident X-ray beam energy of 14.1 keV ($\lambda = 0.0879$ nm) was collimated using slits and focused onto the sample position using Kirkpatrick-Biaz mirrors. This provided a 100 μm wide × 50 μm high spot at the sample position whose footprint spread along the sample in the direction of propagation of the beam. The sample stage was located inside a vacuum chamber (pressure $\sim 40$ Pa) where the incident angle was computer-controlled. A two-dimensional (2-D) charged-coupled device (CCD) detector was positioned 270 mm from the center of the sample stage to collect 2-D GIWAXS images inside the same vacuum chamber. A rectangular beam stop was positioned just before the CCD to block the primary and the specular reflective beams. Data conversion to $q$-space was accomplished by calibration using Silver Behenate powder. All of the measurements reported here were acquired at an incident angle of 0.12° with respect to the sample plane (i.e., grazing incidence) and were collected with an acquisition time of 10 s.

4.3.7. Back-scattered light simulations

Full-field electromagnetic simulations were performed using commercially available FDTD software (Lumerical FDTD Solutions, Inc.), as introduced in Section 2.3.2.1. The structures were defined in the software to match the fabricated plasmonic metasurfaces as closely
as possible (80 nm polymer or fullerene coating/AgNPA/50 nm Ag/5 nm Cr/glass). The simulated AgNPA was a hexagonally-packed array of paraboloids that were created using the equation:

\[ z = \left( x^2 + y^2 \right) \frac{4h}{d^2} \]

which was rotated about the z-axis, where \( x, y, \) and \( z \) are the Cartesian coordinates corresponding to the spatial grid used in the simulations, \( h \) was the height of the paraboloids (60 nm), and \( d \) was the base diameter of the paraboloids (100 nm). The center-to-center distance between AgNPs (i.e., the period) was 150 nm. To simulate back-scattered light, the excitation source used was a total-field scattered-field (TFSF) plane wave incident at 15° from the surface normal. Due to the fixed \( k \)-vector in the simulations, and since the simulations were broadband, the incident angle of the plane wave varied from 10° ~ 30° from 300 nm - 900 nm. The TFSF source allowed the separation of the scattered electromagnetic fields from the total electromagnetic fields for the structures under study. The source was injected 55 nm above the top of the AgNPA with transverse magnetic (TM) polarization. The TFSF source was extended beyond the \( x \) and \( y \) boundaries of the FDTD simulation region such that the edges of the source extended through the planar Ag region, which was taken as a reference for the subtraction of the total field. The wavelength range of the source was 300 - 900 nm with 4 nm increments and a source pulse length of 1.995 fs. The FDTD simulation region \( x,y \) cross-sectional area was set to 150 nm \( \times \) 260 nm with a depth of 2000 nm in the \( z \)-direction. The boundary conditions used were perfectly matched layers (PML) in the planes parallel to the substrate (\( x,y \) planes) and Bloch boundary conditions in the 2 orthogonal planes (\( x,z \) and \( y,z \) planes). The number of PML layers was adjusted to achieve total PML reflection of \( 10^{-10} \) or less. A frequency-domain power monitor was placed 840 nm above the top of the AgNPA and the transmission through this monitor was used as the simulated back-scattered spectra. The simulation was stopped either after 100 fs of simulation time or when the fields decayed to less than \( 5 \times 10^{-4} \) of their initial value. Note that the stopping point for the simulations was earlier than for the planar simulations described in Section 2.3.2.1 because the
fields stopped decaying by $5 \times 10^{-4}$ of their initial value due to the highly dispersive environment and the off-normal excitation. The fields did not decay less than $5 \times 10^{-4}$ up to 1000 fs, and generally decayed to their equilibrium value in less than 100 fs. A mesh override region was added to cover the TFSF source completely to ensure a constant mesh step size of 0.8 nm throughout the region including the AgNPs in all three spatial directions. The mesh refinement option chosen was “conformal variant 1”, and the mesh accuracy was set to 4 outside of the refinement area (only in free space above the structures and in the glass substrate). See Figure 4.5 for a graphical depiction of the simulation setup. The optical constants used for the simulations were taken from literature values and are shown in Appendix Section A.1.
Figure 4.6. Screenshots of graphical user interface of Lumerical FDTD Solutions for the transmittance through the vertical monitors simulation setup. (a) Overview of full simulation from x-z plane. (b) Schematic of hexagonal cluster of AgNPs from the x-y plane. (c) Magnified schematic of coated plasmonic metasurface from x-z plane, showing the TFSF source and its boundaries. (d) Perspective view of simulation.

4.3.8. Surface plasmon polariton simulations

For the simulated spectra of the forward- and backward-traveling SPPs, the same general setup was employed as described for the back-scattered light simulations, with the following changes. Figure 4.6 shows a graphical depiction of the simulation setup. The FDTD simulation region x,y cross-section was extended to 2000 nm × 2000 nm; the boundary conditions in all directions were set to PML; the TFSF source did not extend beyond the FDTD boundaries, but still was large enough to envelope the 7 AgNPs in the one hexagonal unit cell. The mesh override region was also set to 2 nm due to the larger region simulated and the finite computational memory available. Two frequency-domain power monitors were placed at a distance 100 nm in front of and behind the AgNP unit cell in the y-z plane, normal to the thin film stack. Each of the monitors extended fully through the polymer layer, 25 nm into the Ag film, and 40 nm above the
polymer film in order to collect most of the evanescent fields propagating away from the AgNPs. The transmission through these monitors was summed and reported as the forward+backward vertical monitors in Figure 4.22b-d, and the electric field distributions through the forward-traveling vertical monitors were used in Figure 4.22a and Appendix Figure A13i-n. Another frequency-domain power monitor was placed 115 nm above the top of the polymer coating in the $x$-$y$ plane, parallel to the sample surface. The electric field distributions in these monitors were reported in Appendix Figure A13c-h.

4.3.9. Absorption enhancement simulations

For the absorption enhancement simulations, the same general setup was employed as described for the back-scattered light simulations, with the following changes. Figure 4.7 shows a

**Figure 4.7.** Screenshots of graphical user interface of Lumerical FDTD Solutions for the absorption simulation setup. (a) Overview of full simulation from $x$-$z$ plane. (b) Schematic of hexagonal array of AgNPs, showing one unit cell from the $x$-$y$ plane. (c) Magnified schematic of coated plasmonic metasurface from $x$-$z$ plane. (d) Perspective view of simulation.
graphical depiction of the simulation setup. A normal plane wave source was used instead of a TFSF source, which was injected 400 nm above the top of the AgNPs and extended beyond the $x$ and $y$ boundaries of the FDTD simulation region. A fully three-dimensional frequency-domain power monitor was placed surrounding the thin film stack in the $z$-direction and extended beyond the $x$ and $y$ boundaries of the FDTD simulation region. A three-dimensional refractive index monitor was overlaid on the frequency-domain power monitor. The mesh override region remained 0.8 nm, but the fields were sampled every 1.6 nm, and the wavelength increment was increased to 5 nm due to the finite computational memory associated with three-dimensional field and index monitors.

Absorption in each layer was calculated using the following equation:

$$A(x, y, z, \lambda) = n(x, y, z, \lambda) \alpha(x, y, z, \lambda) \left| \frac{E(x, y, z, \lambda)}{E_0} \right|^2$$

where $n$ is the real part of the complex index of refraction, $\alpha$ is the attenuation coefficient ($4\pi k/\lambda$), and $|E/E_0|^2$ is the normalized electric field intensity squared. The absorption was integrated spatially and normalized to the area illuminated ($S_{\text{illum}}$) to obtain the spectral fraction of light absorbed in each layer:

$$A(\lambda) = \frac{\iiint A(x, y, z, \lambda) \partial x \partial y \partial z}{S_{\text{illum}}}$$

The absorption in the active layer was separated from the absorption in the AgNPA by using the refractive index monitor as a reference. Finally, the integrated absorptance in each layer was weighted by the AM1.5 solar spectrum ($P_{\text{AM1.5}}$) and integrated over all wavelengths:

$$A = \frac{\int P_{\text{AM1.5}}(\lambda) A(\lambda) \partial \lambda}{\int P_{\text{AM1.5}}(\lambda) \partial \lambda}$$

FDTD simulations were also conducted for planar Ag electrodes. These simulations were
identical to the absorption enhancement simulations containing the AgNPA, except that the AgNPA were removed. Absorption enhancement factors were calculated by dividing absorption in the active layer coating the AgNPA/Ag electrodes by the absorption in the active layer coating the planar Ag electrodes.

4.4. Results and Discussion

Figure 4.8. Absorber-coated plasmonic metasurfaces. a, Schematic of a plasmonic metasurface with an organic semiconductor thin-film coating (AgNPA - silver nanoparticle array; h - nanoparticle height; d - nanoparticle diameter; \( \Lambda \) - nanoparticle period). b, Schematic of the dark-field (DF) scattered-light spectroscopy setup. c,d, Scanning electron microscope (SEM) images of a Ag film coated with a AgNPA (i.e., a plasmonic metasurface, c) and a planar Ag film (d). The scale bars are 500 nm. Insets are true-color DF images of the respective electrodes acquired under Xenon lamp illumination; the scale bars are 100 \( \mu \)m. e, Atomic force microscope (AFM) surface topography of a P3HT-coated AgNPA/Ag metasurface. The scale bar is 500 nm. f, DF scattered-light spectra for AgNPA/Ag metasurfaces and planar Ag films, with and without P3HT coatings. g,h, True-color DF images of a P3HT-coated AgNPA/Ag metasurface (g) and a P3HT-coated planar Ag film (h) acquired under Xenon lamp illumination. The scale bars are 100 \( \mu \)m.
4.4.1. Absorber-coated plasmonic metasurfaces

We fabricated large-area disordered plasmonic metasurfaces composed of Ag nanoparticle arrays (AgNPAs) on Ag thin films (i.e., AgNPAs/Ag) by nanotemplating (Figure 4.8a,c; Methods). We prepared disordered metasurfaces due to facile large-area fabrication and because random arrays of nanostructures can couple into a larger number of optical modes than periodic arrays. The collective scattering response of AgNPA/Ag metasurfaces observed by DF imaging was in stark contrast to that of planar Ag films, which exhibited minimal scattering (Figure 4.8b and Figure 4.8c,d insets). We prepared Ag nanoparticles (AgNPs) with heights of 48.9 ± 9.7 nm, base diameters of 88.3 ± 22.5 nm, and an average array period of 145.7 ± 25.8 nm (Figure 4.2). Organic semiconductor absorber coatings were deposited by spin coating on top of the AgNPA/Ag to a thickness of 72.8 ± 10.4 nm (a thickness which has been used frequently throughout the BHJ-OPV literature; Figures 4.3 and 4.4) and partially conformed to the AgNPA/Ag metasurfaces (Figure 4.8e and Figure 4.9). As absorber coatings, we selected three well-known organic conjugated polymers (poly(3-hexylthiophene-2,5-diyl) (P3HT); poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)] (PCDTBT); poly([4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediy]] (PTB7)) and polymer:fullerene active layer systems used for BHJ-OPV devices (P3HT blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM); PCDTBT blended with [6,6]-phenyl-C_{71}-butyric acid methyl ester (PC_{70}BM); and PTB7 blended with PC_{70}BM).
Figure 4.9. Atomic force microscope surface topography. AFM measurements of AgNPA/Ag metasurfaces coated with: (a) P3HT; (b) PCDTBT; (c) PTB7 (d) P3HT:PCBM; (e) PCDTBT:PC70BM; (f) PTB7:PC70BM; (g) PMMA; (h) PCBM; and (i) PC70BM; all images are on the same lateral scale [scale bar shown in (g)]. Height scale bars are shown at the right of each scan. (j) Average root-mean square (R.M.S.) surface roughness values determined from a minimum of 2 AFM topography measurements. Error bars represent standard deviation of 2 - 3 measurements. Inset in (j) shows the AFM surface topography of a bare (uncoated) AgNPA/Ag metasurface.

To determine the optical behavior of the metasurfaces with organic semiconductor absorber coatings, we conducted DF scattered-light spectroscopy in reflection mode using a microscope-coupled spectrometer (Methods and Figure 4.8b). The DF scattered-light spectrum of the uncoated (i.e., “bare”) AgNPA/Ag metasurface displayed a single peak occurring at 400 nm with a shoulder at ~430 nm (Figure 4.8f), which, since this peak was not present in the scattered-light spectrum of the bare planar Ag film, arose from a plasmonic resonance of the AgNPA. When a P3HT absorber coating was applied to the AgNPA/Ag metasurface, a new peak emerged
at 670 nm with a shoulder ~585 nm (Figure 4.8f,g). This scattering peak was an unexpected result and occurred just red-shifted from the absorption edge of the P3HT coating (Appendix Figure A3). Interestingly, the P3HT-coated planar Ag film also displayed this scattering peak (Figure 4.8f,h), although the peak wavelength occurred at 655 nm and the intensity was lower compared to the coated metasurface.

4.4.2. Scattered-light spectra of absorber-coated planar Ag films

To investigate if this new scattering peak occurred ubiquitously for absorber coatings, we conducted DF scattered-light spectroscopy on planar Ag films with various organic semiconductor coatings (Figure 4.10a). The scattering spectra showed peaks occurring at wavelengths red-shifted from the absorption edge for only certain coatings, particularly those coatings with large lateral feature sizes (~100 - 350 nm) or high surface roughness (greater than...
Figure 4.11. Single polymer nanoparticle on coating layer. Simulated scattered-light spectra of single polymer nanoparticles on the surface of the polymer coating, revealing the Mie-AIS peak for the P3HT nanostructured film. Note that the same simulation parameters and nanoparticle dimensions were used for these simulations as in the single metal NP simulations (see Figure 4.21).

~1 nm r. m. s) (Figure 4.10). We attributed the scattering peak observed for coatings with more irregular surfaces to Mie scattering by nanoscale surface features in the organic material modified by its absorption (i.e., Mie-“absorption-induced scattering,” or Mie-AIS), which we have reproduced through simulations (Figure 4.11). Additional coated planar Ag films which did not exhibit this Mie-AIS peak (because the coatings had very planar surfaces) are shown in Figure 4.12.

To check if the Mie-AIS observed in Figure 4.10 could be simulated, we simulated a single P3HT nanoparticle atop a P3HT-coated Ag film (with a transparent PMMA NP atop a PMMA-coated Ag film as a control, Figure 4.11). While both the PMMA-NP/PMMA/Ag and P3HT-NP/P3HT/Ag displayed scattering peaks in the visible spectrum, the scattered-light spectrum of the P3HT NP structure was split, with short and long wavelength peaks. Although the long wavelength peak did not occur at the same position as the Mie-AIS observed experimentally, there was qualitative agreement between the AIS peak positions, with the differences between the simulated and experimental spectra arising from the complex morphology of the nanostructured absorber films (Figure 4.10b).
Figure 4.12. Scattering from smooth absorber films. (a,b) DF scattered-light spectra of bare and organic-coated planar Ag substrates. Inset are true-color DF images of the coatings on planar Ag substrates and were captured from regions where the DF spectra were acquired. All images are on the same scale (scale bar shown for PMMA/Ag). (c-f) AFM surface topography of planar Ag substrates coated with: (c) PMMA; (d) nothing (bare Ag); (e) PCBM; (f) PC\textsubscript{70}BM. Root-mean square (r.m.s.) surface roughness values are shown on each image; all images are on the same lateral scale [scale bar shown in (c)], with the various corresponding height scales shown on the right of each topography image.

For PMMA, PCBM, and PC\textsubscript{70}BM on planar Ag, the coatings displayed small feature sizes and low surface roughness (<0.5 nm; Figure 4.12c,e,f). This led to negligible scattering across the visible spectrum (Figure 4.12a,b), as confirmed by the black background of the DF images. It is notable that, although the bare Ag film had a significantly larger surface roughness (8.8 nm) compared to the polymer and polymer:fullerene films in the main text (0.6 - 4 nm), Ag still displayed negligible scattering, which shows that metal films can tolerate much larger degrees of surface roughness compared to organic semiconductor absorber films before (absorption-induced) scattering becomes significant.
Figure 4.13. Back-scattered-light spectra for various absorber coatings. a, Experimental and simulated scattered-light spectra for: AgNPA/Ag metasurfaces with and without various absorber coatings (a) and dielectric-coated AgNPA/Ag metasurfaces (b). Solid lines represent empirical DF spectra, and dashed lines represent finite-difference time-domain (FDTD) simulations of the back-scattered spectra. Note that the experimental setup was limited to a wavelength range of approximately 380 nm - 860 nm. c-f, Schematic depictions of electric field lines and charge distributions (+ and - represent regions of positive and negative charge accumulation, respectively) for the various modes supported by a dielectric \((n = 2.0)\)-coated AgNPA/Ag metasurface. Note that the schematics were created based on vector plots of the total electric field and the electric field amplitude profiles (shown to the right of the schematics). The Roman numerals in a and b refer to the mode types as referenced in c-f, and were assigned by analyzing the electric field vector plots and amplitude profiles for each peak. The modes occurred at the same or very similar wavelengths between neat conjugated polymers and polymer:fullerene blends and so were only labeled for the neat conjugated polymers. g, True-color DF images indicating the regions from which corresponding spectra were obtained (rectangular regions highlighted); all images are on the same length scale (scale bar is 50 \(\mu m\), and is shown for the PC\(_{70}\)BM coating).
4.4.3. Scattered-light spectra of absorber-coated metasurfaces

Next we investigated how changing the absorber coating affected the scattering from AgNPA/Ag metasurfaces. Figure 4.13a shows both empirical and simulated DF scattered-light spectra for AgNPA/Ag metasurfaces with various coatings (Methods). For bare AgNPA/Ag, a scattering peak was observed in the simulated spectrum at 360 nm, and was attributed to coupled transverse LSPRs of the AgNPs through analysis of the electric field profiles (Mode I; Figure 4.13c). A shoulder was observed at ~390 nm, and was attributed to a hybrid SPP mode between the AgNPA and the Ag film (Mode II; Figure 4.13d), as evidenced from simulated polarization- and angle-dependent scattering spectra (Figure 4.14a). When coated by absorbers, the scattering spectra of all AgNPA/Ag metasurfaces were split with distinct short (~300 - 500 nm) and long (~650 - 900 nm) wavelength scattering regimes (Figure 4.13a). By interpreting electric field profiles and the scattered-light spectrum of a transparent polymer [i.e., poly(methyl methacrylate) (PMMA)] coated-AgNPA/Ag metasurface (Figure 4.13b), the short wavelength scattering was attributed to LSPRs with contributions from coupled transverse LSPRs (i.e., Mode I) in addition to multipolar (i.e., Mode III) and transverse dipolar (i.e., Mode IV) LSPR modes (Figure 4.13a,c,e,f and Figure 4.15). PCDTBT and PTB7 had a dip in the short wavelength scattering due to absorption transitions from S_0 → S_2 for PCTBT and from the third and fourth valence bands to the LUMO for PTB7 (Appendix Figure A3). The scattering from LSPRs was lower in intensity for the polymer:fullerene blends than for the neat conjugated polymers due to absorption from the fullerene derivatives at wavelengths between 300 - 500 nm (Appendix Figure A5). The neat fullerene derivatives had similar scattering behavior to a dielectric coating with n = 2.0 (Figure 4.13b), due to the higher indices of PCBM and PC_{70}BM throughout most of the visible spectrum (Appendix Figure A5). However, since PC_{70}BM absorbed strongly in the 400 - 600 nm wavelength range, LSPR scattering was partially absorbed by PC_{70}BM. There was relatively good agreement between the simulated and empirical scattering data for the LSPR modes.
In the long wavelength regime, the empirically obtained scattering exhibited different behavior depending on the coating. With P3HT, PTB7 and P3HT:PCBM coatings, a single peak occurred at the absorption edge of the coating (670 nm for P3HT and P3HT:PCBM, 756 nm for PTB7). This peak occurred at very similar wavelengths to the Mie-AIS peak observed for absorber-coated planar Ag films; however, nanoscale surface roughness on the absorber coating was not the dominant mechanism responsible for this scattering peak since the peaks were observed in simulated data for coated metasurfaces, even with a planar organic-air interface (Methods). The electric field profiles, in addition to the simulated scattered-light spectrum of a high-index ($n = 2.0$) dielectric coated-AgNPA/Ag metasurface (Figure 4.13b), revealed that this scattering arose predominantly from the hybrid AgNP-Ag film SPP (i.e., Mode II; Figure 4.13d). The peaks were pinned just beyond the absorption edge wavelength of the organic semiconductors due to the large increase in refractive index and significant drop in absorption of the coating (Appendix Figures A3 and A4). Since these scattering peaks arose from the collective response of plasmonic modes modified by absorption transitions of the coatings, this scattering is called “plasmon-AIS.” Plasmon-AIS peaks were observed for all absorber-coated metasurfaces and followed the absorption edge of the coatings. We will discuss the physical origin of AIS extensively in the proceeding section. For P3HT- and P3HT:PCBM-coated metasurfaces, there was an additional plasmon-AIS shoulder at ~580 nm, which arose predominantly from the combined response of the Mode I LSPR and the increased refractive index due to the $S_0 \rightarrow S_1$ 0-1 vibronic absorption in P3HT (Appendix Figure A3).

For the PCDTBT-, PCDTBT:PC$_{70}$BM-, and PTB7:PC$_{70}$BM-coated metasurfaces, there were two distinct components observed empirically for the long wavelength scattering regime: one component occurred just beyond the absorption edge wavelength of the coatings (665 nm for PCDTBT and PCDTBT:PC$_{70}$BM; 772 nm for PTB7:PC$_{70}$BM) due to plasmon-AIS, and another broader and more intense component occurred at even longer wavelengths (740 nm for PCDTBT; 780 nm for PCDTBT:PC$_{70}$BM; $\geq 845$ nm for PTB7:PC$_{70}$BM). Since the broader, more intense
component of the long wavelength peak occurred for absorber-coated AgNPA/Ag metasurfaces, but not for absorber-coated AgNPA/glass (Figure 4.16), and this component appeared to be broadband based on scattering from PMMA-coated AgNPA/Ag metasurfaces (Figure 4.13b; note the elevated baseline relative to the simulated spectrum), we hypothesized that out-coupled SPPs contributed to this scattering. This long wavelength scattering component was not present in the back-scattered simulations and it occurred empirically only for certain coatings. Furthermore, there were no apparent correlations between the occurrence of the long wavelength scattering and the surface morphology of the coated AgNPA/Ag metasurfaces (Figure 4.9). The origins of the long wavelength contribution will be discussed in greater detail in the following sections.

4.4.4. Excitation polarization, incident angle, and refractive index dependent scattered-light simulations for bare or dielectric-coated metasurfaces
Figure 4.14. Excitation polarization (TE, TM), incident angle (0 - 35°), and refractive index (n)-dependent scattered light simulations. (a) Simulated scattered light spectra for bare AgNPA/Ag for TE (top panel) and TM (bottom panel) excitation polarizations. (b) Simulated scattered light spectra for PMMA/AgNPA/Ag for TE (top panel) and TM (bottom panel) excitation polarizations. (c) Simulated scattered light spectra for dielectric(n=2.0)/AgNPA/Ag for TE (top panel) and TM (bottom panel) excitation polarizations. Note that a course mesh (2.0 nm) was used for these particular simulations; all other parameters were the same as described in the Methods.

From the polarization-dependent simulations (Figure 4.14), the shoulder in the scattered-
light spectra at ~400 nm (Figure 4.14a, bare), ~500 nm (Figure 4.14b, PMMA), and ~550 nm (Figure 4.14c, dielectric with $n = 2.0$) was attributed to a hybrid surface plasmon polariton (SPP) mode between the AgNPs and the underlying Ag film. This was due to the fact that this shoulder was present for TM excitation, but not for TE, and increased in intensity with increasing incident angle (i.e., stronger out-of-plane field component). Further, for TM polarization, at incident angles of 35°, several additional peaks were present in all cases, which were again attributed to additional hybridized AgNP-Ag film SPP modes. This suggests that the SPPs excited were indeed broadband and the distinct peaks would likely have been smoothed out experimentally due to variations in the AgNP size and period (Figure 4.2) and the unpolarized, omni-azimuthal excitation.

Figure 4.15 shows the scattered-light intensity for dielectric-coated AgNPA/Ag metasurfaces with varying refractive index of the dielectric coating. The dependence of each mode on refractive index was revealed, with Mode II (hybrid AgNP-Ag film SPP) being the most sensitive to refractive index. Note that certain modes only appeared when the refractive index was

![Figure 4.15](image-url)  

**Figure 4.15.** Simulated scattered-light spectra for dielectric-coated AgNPA/Ag with varying real part of the refractive index, $n$, for the dielectric coating. The imaginary part of the refractive index, $k$, was 0 for these simulations (i.e., no absorption in coating). The four mode types illustrated in Figure 3 are indicated on the plot in addition to a new mode (Mode VI) which appeared for only high-index dielectric coatings.
Figure 4.16. Scattered-light spectra for AgNPA/glass. (a) DF scattered-light spectra and FDTD simulations of AgNPA/glass substrates with various coatings. Solid lines represent empirical DF spectra, and dashed lines represent FDTD simulations of the back-scattered spectra. Note that the experimental spectroscopy setup was limited to a wavelength range of approximately 380 nm - 860 nm. (b) DF images of the corresponding spectra; all images are on the same scale (scale bar shown for the PC$_{70}$BM coating). Note that the scattering from the absorber-coated AgNPA/glass samples was inhomogeneous in some cases due to non-uniform pore widening of the anodic alumina nanotemplates (see Methods). The regions from where spectra were acquired are highlighted as red or blue rectangles on the images and were selected based on the most intense scattering (corresponding to regions where the AgNPA had diameters and periods similar to those shown in Figure 4.2).

large enough (e.g., Mode VI, which was not discussed in the main text, appears at $n \sim 2.0$). The index of 1.0 was for the bare (uncoated) AgNPA/Ag.
4.4.5. Scattered-light spectra of absorber-coated AgNPA/glass

To study the effect of the AgNPA alone, we also acquired DF spectra of AgNPA/glass, which showed a significantly red-shifted LSPR to a center wavelength of ~515 nm (Figure 4.16a). This shift was expected to occur since the AgNPA was partially exposed to a higher refractive index \((n)\) environment \((n_{\text{glass}} \sim 1.5, \ n_{\text{Ag}} \sim 0.15)\). The LSPR of the AgNPA/glass was also quite broad (FWHM ~ 150 nm) likely due to the longer lifetime of the LSPR on glass, and the baseline scattering intensity was notably higher compared to the AgNPA/Ag spectrum (compare Figure 4.16a to Figure 4.13a). The LSPR of the PMMA/AgNP/glass was further red-shifted to ~540 nm, and the simulations revealed an additional peak at ~390 nm.

For P3HT/AgNPA/glass, the long wavelength scattering peak associated with AIS was still observed at ~645 nm and had a shoulder at ~590 nm. The short wavelength peak previously attributed to the LSPR was not observed for P3HT/AgNPA/glass. Since the LSPR of the AgNPA/glass was not observed when coated with P3HT, but was already red-shifted to ~515 nm for bare AgNPA/glass (from a wavelength less than 400 nm for bare AgNPA/Ag; see Figure 4.13a), we expect that the LSPR occurred at wavelengths greater than or equal to 515 nm for P3HT/AgNPA/glass. Thus, the shifted LSPR alone was primarily responsible for the plasmon-AIS peak observed for the P3HT/AgNPA/glass (as opposed to both the hybrid AgNP-Ag film SPP and LSPR as the primary contributors to the plasmon-AIS peak for absorber-coated AgNPA/Ag metasurfaces). Scattered light from the P3HT:PCBM/AgNPA/glass sample (Figure 4.16a) had similar behavior to the P3HT-coated AgNPA/glass but the main scattering peak was blue shifted slightly to 635 nm and reduced in intensity (empirically). For PCBM/AgNPA/glass (Figure 4.16a, bottom panel), the scattering peak was more broadband and was blue-shifted further from P3HT:PCBM/AgNPA/glass to ~610 nm due to the higher index of the PCBM coating (Appendix Figure A5). The other polymer coatings showed similar trends as the P3HT and P3HT:PCBM coatings, with the plasmon-AIS peak following the absorption edge of the
Figure 4.17. Simulations for varying metal NPA material. Back-scattered simulations for various metal NPA/metal substrates coated with: (a) P3HT; (b) PMMA; (c) nothing (bare metal NPA/metal). Note that a course mesh (2.0 nm) was used for these simulations; all other parameters were the same as described in the Methods.

coatings. Thus, the plasmon-AIS peaks observed for the conjugated polymer and polymer:fullerene-coated AgNPA/glass metasurfaces arose from only localized modes, not hybrid
SPP modes, further demonstrating that localized and propagating scattering modes can give rise to AIS. Further, the longer wavelength scattering observed for PCDTBT, PCDTBT:PC$_{70}$BM, and PTB7:PC$_{70}$BM coated on AgNPA/Ag (Figure 4.13a), which was attributed to out-coupled SPPs, was not observed for the AgNPA/glass substrates (Figure 4.16a), giving further support that the mode did indeed arise from SPPs.

4.4.6. Variation of metal NPA/metal metasurface material for simulated scattered-light spectra

To further study the effect of plasmonic resonant scattering on AIS, we varied the metal NPA/metal metasurface material to include a range of plasmonic (i.e., Ag, Au, Cu, and Al) and non-plasmonic (i.e., Ni, Ca, Cr) metals, in addition to studying a dielectric NPA (i.e., PMMA NPA/Ag). Figure 4.17b,c shows the scattering modes for these metasurfaces with and without a PMMA coating, respectively. It was observed that with a PMMA coating, the AgNPA/Ag had the largest scattering intensity, but the LSPR of the materials could be varied from ~440 nm for AgNPA/Ag to ~560 nm for AuNPA/Au to ~640 nm for CuNPA/Cu. The remaining metasurfaces all displayed Mie scattering backgrounds, with scattering roughly increasing as $1/\lambda^4$. When coated with a P3HT absorber layer (Figure 4.17a), all of the metasurfaces (including those composed of non-plasmonic materials) displayed an AIS peak at ~660 nm; however, the plasmonic metasurfaces (i.e., Ag, Au, and Cu) displayed the most intense AIS, with the Cu having the highest AIS peak intensity due to the strong overlap between its LSPR and the absorption edge of the P3HT coating. These spectra demonstrate: 1) either plasmonic or non-plasmonic scattering can give rise to AIS; 2) plasmonic resonant scattering increases the intensity of the AIS peak; and 3) better spectral overlap between the scattering mode and the absorption edge of the absorber coating gives rise to more intense AIS.
Table 4.1. Intensity of the plasmon-AIS peak for absorber-coated AgNPA/Ag metasurfaces from FDTD simulations.

<table>
<thead>
<tr>
<th>Coating</th>
<th>AIS peak intensity</th>
<th>AIS peak λ (nm)</th>
<th>(n^\dagger)</th>
<th>(k^\dagger)</th>
<th>Expected Mode II peak λ (nm)*</th>
<th>Δλ (nm)</th>
<th>Absorption coefficient ((×10^4 \text{ cm}^{-1}))</th>
</tr>
</thead>
<tbody>
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<td>P3HT</td>
<td>0.17</td>
<td>655</td>
<td>1.95</td>
<td>0.13</td>
<td>615.7</td>
<td>39.3</td>
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<td>733</td>
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<td>674.5</td>
<td>58.5</td>
<td>0.91</td>
</tr>
<tr>
<td>PTB7</td>
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<td>750</td>
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</tr>
<tr>
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<td>671.5</td>
<td>9.5</td>
<td>1.03</td>
</tr>
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<tr>
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<td>0.01</td>
<td>633.0</td>
<td>22.0</td>
<td>0.21</td>
</tr>
</tbody>
</table>

\*Note that the expected Mode II peak wavelength was determined from simulated scattered-light spectra of dielectric-coated AgNPA/Ag metasurfaces (Figure 4.15) based on \(n\) for each coating.

\†Optical constants were obtained from the literature for the AIS peak wavelengths (see Appendix Figures A3 and A4).

4.4.7. Physical origin of AIS

In addition to the scattering object composition (e.g., plasmonic or non-plasmonic) and scattering wavelength, the intensity of the plasmon-AIS peaks was also dictated by the real \((n)\) and imaginary \((k)\) parts of the refractive index of the absorbers at the wavelength of the plasmon-AIS peak. The shift of the plasmonic modes (i.e., Modes I and II, Fig. 3c,d) was determined predominantly from \(n\), where larger \(n\) led to greater red-shifts in the modes (Figure 4.15). Using Figure 4.15 as a guide, the expected wavelengths of Mode II could be estimated for each coating based on \(n\) for the absorber at the wavelength of the plasmon-AIS peak (Table 4.1). Since Mode II was expected to red-shift to a larger degree than Mode I (Figure 4.15), it was expected that greater red-shifts in Mode II would result in more intense plasmon-AIS. Table 4.1 shows the difference between the plasmon-AIS peak and the expected Mode II peak wavelengths \((\Delta \lambda)\), where a larger \(\Delta \lambda\) should result in a less intense plasmon-AIS peak due to poorer spectral overlap. In addition, since the absorbers had non-negligible \(k\) values at the wavelengths of plasmon-AIS, the absorption coefficient \((4\pi k / \lambda)\) also contributed to the intensity of the plasmon-AIS, where
greater absorption coefficients resulted in less intense plasmon-AIS. The intensity of the plasmon-AIS was thus dictated by the balance between $\Delta \lambda$ (determined primarily from $n$) and the absorption coefficient (determined primarily from $k$).

AIS was observed for scattering modes, whether plasmonic (i.e., plasmon-AIS, Figure 4.13a) or non-plasmonic (e.g., Mie-AIS, Figure 4.10a; see also Figure 4.17), in the presence of an absorber and followed the absorption edge wavelength of the coating. Additionally, for AIS, the scattering object required close proximity with the absorber, as AIS was not present when a non-absorptive spacer layer was inserted between the scattering object and absorber coating (Figure 4.18). We also observed that, although absorber-coated non-plasmonic scatterers gave rise to AIS peaks (e.g., Ni or PMMA NPs - Figure 4.17a), plasmonic scatterers resulted in more intense AIS, with AIS peak intensity increasing with better spectral overlap between the LSPR of the

**Figure 4.18.** Simulations for varying spacer layer between absorber and scatterer. (a) Simulated scattered-light spectra for AgNPA/Ag metasurfaces coated with: thin (80 nm) and thick (150 nm) PMMA, and a 150-nm-thick PMMA spacer layer separating the top coatings from the AgNPA. (b) Simulated scattered-light spectra for P3HT:PCBM/PMMA-coated metasurfaces, for varying the PMMA spacer thickness. The dashed lines represent when the spacer thickness was $\geq$ the height of the AgNPs (i.e., $\geq$ 60 nm), whereas the solid lines represent when the AgNPs protruded through the PMMA spacer layer and made physical contact with the absorber. Note that a coarse mesh (2.0 nm) was used for these simulations; all other simulation parameters were the same as described in the Methods.
metal NPA and the absorption edge of the coating (Figure 4.17 and Table 4.1).

To determine if the absorber coatings needed to be in close proximity with the scattering objects, we conducted scattered-light simulations with a spacer layer physically separating the absorber coating from the AgNPA/Ag metasurface (Figure 4.18). In Figure 4.18a, we first compared an 80-nm-thick PMMA coated AgNPA/Ag metasurface to a 150-nm-thick PMMA coated metasurface, and observed three peaks present in both cases: Modes I and IV LSPRs (423 nm and 397 nm for the 80-nm-thick coating), and the Mode II NP-film hybrid SPP (495 nm for the 80-nm-thick coating). Since all peaks were present in both cases, just shifted slightly in wavelength and intensity, we then coated the 150-nm-thick PMMA/AgNPA/Ag metasurface with an 80-nm-thick dielectric ($n = 1.8$) layer as a control for a bilayer-coated metasurface; the same three peaks were still present. When we replaced the top dielectric layer of the bilayer coating with an absorber layer (either P3HT:PCBM or PTB7:PC$_{70}$BM), we observed the same three peaks, only slightly shifted in wavelength and reduced in intensity. We did not observe the AIS peak for either coating. We further investigated the dependence of the separation between the absorber and AgNPA/Ag metasurface by varying the spacer thickness for a P3HT:PCBM/PMMA bilayer coating (Figure 4.18b). The AIS peak was not observed until the absorber layer made physical contact with the AgNPs (i.e., PMMA spacer thicknesses < 60 nm) and increased in intensity as the spacer layer thickness was reduced. Thus, from these data, we determined that AIS requires close proximity between the absorber and the scattering object for this mode to occur.
To further elucidate the physical origin of AIS, we varied the NPA period for absorber-coated AgNPA/Ag metasurfaces (Figure 4.19). For periods of \( \sim 150 \) nm, P3HT-coated AgNPA/Ag metasurfaces displayed two dominant peaks: a broad peak (\( \sim 390 \) nm) composed of Mode I, III, and IV LSPRs, and the plasmon-AIS peak (\( \sim 660 \) nm; Figure 4.19a). For periods \( \geq 250 \) nm, two branches of the long wavelength peak were observed: one dispersive, which was attributed to the Mode II hybrid NP-film SPP (based on its presence for the uncoated and dielectric-coated AgNPA/Ag metasurfaces; Figure 4.19b,c and Appendix Figure A12), and one
non-dispersive, corresponding to plasmon-AIS arising from the Mode I LSPR. Thus, plasmon-AIS peaks had contributions from both localized and propagating plasmon modes (i.e., Modes I and II, respectively), which was also supported by transverse electric (TE) simulations (Figure 4.20). Furthermore, isolated metal nanoparticles in the presence of a P3HT coating still displayed an AIS peak (Figure 4.21) arising from a transverse LSPR (Mode IV). Note that for a P3HT-coated glass NPA on a glass substrate, Mie-AIS was observed, which was non-dispersive with array period (Figure 4.19d).

Based on a comparison of TE to TM excitation scattered-light simulations for P3HT/AgNPA/Ag (Figure 4.20a), there was only a slight change in the plasmon-AIS peak between TE and TM excitations. The LSPR peak was unchanged. This suggests that, while the plasmon-AIS peak appeared to be dominated by the hybrid AgNP-Ag SPP (i.e., Mode II, Fig. 3d) under TM excitation, there was a localized resonance component to the plasmon-AIS peak accounting for the longer wavelength peak under TE-polarized excitation. Analysis of the field profiles at a wavelength of 643 nm for the TE-polarized simulations showed that the plasmon-AIS peak arose from an LSPR (i.e., Mode IV, Fig. 3f) under TE excitation. This further confirms that both localized and propagating plasmonic modes can contribute to the plasmon-AIS.
Figure 4.20. Excitation polarization-dependent simulations for P3HT-coated metasurface. (a) Polarization-dependent simulated scattered-light spectra for P3HT/AgNPA/Ag, where the plasmon-AIS peak is still present under TE polarized excitation. (b-c) Electric field amplitudes under TE polarized excitation taken at 643 nm: (b) $E_z$; (c) $E_y$.

To study the single NP in greater detail, we computationally investigated scattering from single metal NPs on metal surfaces (Figure 4.21a-c) and single metal NPs on glass surfaces (Figure 4.21d-f), either bare, or with a PMMA or P3HT coating. Single NP simulations were conducted using the same general layout as the Surface Plasmon Polariton simulations described in Section 4.3.8, except only 1 NP was used instead of a cluster of 7. We varied the metal NP material from Ag, Cu, and Ni. In all cases, P3HT-coated metal NPs on either metal films or glass
substrates displayed the AIS peak, which indicates that AIS can occur from localized resonances from single particles, whether the resonances are plasmonic in origin or not. It should be noted, again, that just as for the array, the scattering was more intense for the plasmonic resonances (i.e., Ag and Cu) than the non-plasmonic scattering (i.e., Ni), and having better spectral overlap between the LSPR and the absorption edge of the coating gave more intense AIS. Notably, collective NP scattering increase the intensity of the AIS compared to isolated NP scattering: for P3HT-coated AgNPA/Ag compared to P3HT-coated single AgNP/Ag, the ratio of plasmon-AIS to LSPR was 0.25 compared to 0.10, showing that the plasmon-AIS was around 2.5× as intense for the array compared to the single AgNP.
Figure 4.21. Single nanoparticle scattered-light simulations. (a-c) Single metal NP/metal films; (d-f) single metal NP/glass substrates.

With this, we have demonstrated that the physical origin of AIS is electromagnetic coupling between the optical transitions of an absorber material and scattering modes, regardless of whether the scattering modes are plasmonic, localized, or collective in origin. The general requirements for AIS to be observed are: 1) the presence of a scattering object and an absorber material; 2) spectral overlap between the scattering mode(s) and absorption transitions; and 3) close proximity between the scattering object and absorber material.
Figure 4.22. Out-coupling of surface plasmon polaritons. a, Spectral in-plane ($E_x$) and out-of-plane ($E_z$) electric field distributions through the forward vertical monitor for P3HT:PCBM-coated AgNPA/Ag metasurface. b-d, Empirical and simulated scattered-light spectra (solid lines) and simulated transmission through the vertical monitors (dashed lines) for P3HT:PCBM (b), PTB7:PC$_{70}$BM (c), and PMMA (d) coatings. Note that the empirical spectra in (b,c) were obtained at an excitation/collection angle of 24°. Inset in (b) shows a schematic of a coated AgNPA/Ag metasurface in which the locations of the back-scattered power monitor (red dotted line) and vertical power monitor (purple dotted line) are indicated. e, Schematic depiction of electric field lines and charge distributions within the near-field of AgNPs that in-couple light to an SPP. Shown to the right of the schematic are real components of the electric field amplitude for the mode.
4.4.8. **Extent of SPP out-coupling**

To determine the origin of the long wavelength (*i.e.*, 740 - 900 nm) scattering component, we conducted additional FDTD simulations in which we studied the transmission through two 2D monitors oriented normal to the substrate plane (*i.e.*, “vertical monitors”) placed at a distance 100 nm in front of and behind a cluster of AgNPs (Methods and Figure 4.22b, inset). For P3HT:PCBM-coated AgNPA/Ag, transmission through the vertical monitors did not match the empirical long wavelength scattering well for wavelengths greater than ~675 nm (Figure 4.22b). The plasmon-AIS peak was observed through the vertical simulation monitors at 650 nm along with an additional mode with a peak at 770 nm. The transmission through the vertical monitor did, however, match the empirical scattered-light spectrum well for the PTB7:PC$_{70}$BM coating (Figure 4.22c). The spectrally-resolved electric field profiles (Figure 4.22a) revealed that the plasmon-AIS peak was dominated by in-plane electric field components ($E_x$), whereas the long wavelength component (at 770 nm) was dominated by out-of-plane electric field components ($E_z$) with the fields bound tightly to the P3HT:PCBM-Ag interface (see Appendix Figures A7 and A8 for additional field profiles), suggesting that the long wavelength scattering component observed empirically for certain coatings (*e.g.*, PTB7:PC$_{70}$BM) arose from an out-coupled SPP. Additionally, angle-dependent empirical scattering spectra support this assignment (Figure 4.23 and Appendix Figure A15). However, since SPPs were not out-coupled by the AgNPs in the simulations (*i.e.*, no long wavelength scattering peak observed with the back-scattered monitor), we attribute the SPP out-coupling that occurred for certain coatings empirically to physical properties of the coating itself that were not accounted for in simulations. The AgNPs, while not causing out-coupling of SPPs, caused near-field excitation (*i.e.*, in-coupling) to the SPPs (Figure 4.22e and Appendix Figure A14).

For PMMA/AgNPA/Ag, broadband SPP modes were also observed through the vertical monitors in addition to LSPR modes at ~430 nm (Figure 4.22d). Excitation at a large incident
Figure 4.23. Angle-dependent DF scattered-light intensity at the longest wavelength scattering peak for various substrates coated with: P3HT (\(\lambda = 663 \pm 18\) nm); PCDTBT (\(\lambda = 715 \pm 11\) nm); and PTB7 (\(\lambda = 757 \pm 3\) nm). The symbols with solid lines represent the empirical data, and the symbols with dashed lines correspond to single wavelength simulations. The Brewster angle (\(\theta_B\)) for the air-polymer interface is indicated on the simulated plots.

Angle (53°) in the experiment for the PMMA/AgNPA/Ag revealed some of the simulated peaks observed from the vertical monitors, supporting the hypothesis that the broadband scattering arose from out-coupled SPPs. Therefore, it was expected that broadband SPPs were also supported by absorber-coated AgNPA/Ag, but, for wavelengths within the absorption bands of the coatings, SPPs were absorbed. Hence, we hypothesize that there should be broadband absorption enhancement in the coated metasurface due to a combination of LSPR, broadband SPP, and plasmon-AIS modes. Polarization-dependent reflectance measurements (70° incident angle) for absorber-coated Ag and AgNPA/Ag substrates showed that under transverse magnetic (TM)-polarized excitation, there was indeed broadband enhancement in the extinction spectra (Figure 4.24), supporting our hypothesis.
The angle-dependent DF measurements were acquired by collecting DF spectra using microscope objectives with varying numerical apertures. Four objectives were used to vary the numerical aperture, which, due to the hollow cone of illumination using the DF setup (Figure 4.8b), allowed for only the largest angles to be included in the excitation path. The DF spectra were normalized to the lamp spectrum as described in the Methods of the main text, ensuring that the same objective used for the sample spectrum was used for the diffuse reflection spectrum.

Larger incident angles were expected to couple into propagating SPP modes more easily, whether the hybrid AgNPA-Ag film SPP (i.e., Mode II) or the longer wavelength Mode V in-coupled SPP. Thus, by varying the incident angle, we expected that the AIS and longer wavelength scattering peaks should increase with increasing incident angle for the absorber-coated AgNPA/Ag metasurfaces, but not for the coated planar Ag or coated AgNPA/glass cases. Figure 4.23 shows the dependence of the measured scattered-light intensity of the long wavelength peak on the incident angle for glass, Ag, AgNPA/Ag, and AgNPA/glass substrates for the three neat conjugated polymer coatings. The peaks presented in Figure 4.23 corresponded to the maximum intensity in the long wavelength regime (600 - 800 nm) for each substrate and incident angle, acquired from the spectra presented in Appendix Figure A15. For all coatings, the glass peak did not change significantly with incident angle and remained at nearly zero intensity. Although there were some changes in the intensity of the long wavelength peak for the planar Ag and AgNPA/glass substrates with the three different coatings, there were no consistent trends observed in the data. The intensity of the peaks for the Ag and AgNPA/glass substrates were consistently higher than those of the glass substrates. For the AgNPA/Ag substrate, particularly with a P3HT coating, the intensity of the long wavelength peak consistently increased with increasing incident angle, and tended to be more intense than the long wavelength peaks of the other substrates. In addition, although the long wavelength peak increased in intensity with incident angle for the P3HT-, PCDTBT-, and PTB7-coated AgNPA/Ag, the LSPR remained mostly constant in intensity with increasing incident angle (Appendix Figure A15). This indicated
that the long wavelength scattering peak had a strong in-plane propagation component, supporting the claim that it arose from an SPP mode. For P3HT and PTB7 coatings, the long wavelength scattering peak was attributed primarily to plasmon-AIS, increasing in intensity due to a combination of: better excitation of the hybrid AgNPA-Ag film SPP (Mode II) due to the increased incident angle (compare to Figure 4.14); and also the expected red-shifting of Mode II to spectrally overlap better with the absorption edge of the coatings due to the dispersive nature of Mode II (Figure 4.19). Additionally, it was likely that the Mode V in-coupled SPP also contributed to the long wavelength scattering peak for P3HT- and PTB7- coated metasurfaces at these incident angles, although further experiments are necessary to confirm this (see Discussion of main text). For the PCDTBT coating, the long wavelength scattering peak was attributed to a combination of the Mode V in-coupled SPP and, to a lesser degree, the plasmon-AIS peak.

Figure 4.24. Wide-angle excitation polarization-dependent extinction measurements. (a) Polarization-dependent extinction spectra for an angle of incidence of 70° for planar Ag and AgNPA/Ag with neat conjugated polymer coatings. (b) Extinction enhancement factor for spectra shown in (a).
Furthermore, single-wavelength, angle-dependent FDTD simulations using TM-polarized light also showed an increase in the intensity of the long wavelength peak with increasing incident angle for the P3HT, PCDTBT, and PTB7 coatings, up to a certain angle. For P3HT and PCDTBT, the intensity dropped for an incident angle of 70°. The reason for the drop, however, was because 70° is greater than the Brewster angle for P3HT and PCDTBT, in which the reflection coefficient for TM polarized light should rise rapidly. Thus, although the scattering intensity was reduced for an incident angle of 70°, it was expected that less incident light reached the AgNPA when very large incident angles were employed in the simulations. Therefore, although this long wavelength peak can be excited more strongly by larger incident angles, for very oblique incident angles, a significant fraction of the incident light intensity is lost to air-polymer reflections. Finally, although the simulations showed similar trends to the experimental data, the intensities for the P3HT and PCDTBT coatings were lower in the simulation than the experiment. This can be explained by a greater out-coupling of the Mode V in-coupled SPPs in the experiment compared with the theory due to effects such as surface roughness, crystallinity, grain boundaries, and the conformal nature of the coatings not accounted for in the simulations. The fact that the simulated and experimental scattered-light intensity for the PTB7-coated AgNPA/Ag metasurfaces agreed so well suggest that for this coating, the Mode V in-coupled SPPs were not out-coupled very well, and the scattering peak arose predominantly from plasmon-AIS.

A Jobin-Yvon Horiba Uvisel Ellipsometer was used in reflection mode for the wide-angle reflectance measurements in Figure 4.24. The angle of incidence was 70°; a 2 nm wavelength step size was used from 350 - 900 nm; one accumulation and 200 ms exposure time was used; the high voltage of the photomultiplier tube was fixed at 315 V; and Xe lamp illumination (75 W) was used. The dark current was automatically subtracted in the software. The photoelastic modulator angle was fixed at 0°, and the incident polarizer (analyzer) angle was set to either 0° for TM polarization or 90° for TE polarization. All reflectance measurements were normalized to
the reflectance from a planar Ag film, and extinction was calculated as 1 minus the reflectance.

For the TM reflectance measurements, a broadband extinction enhancement occurred for all three neat conjugated polymer coated AgNPA/Ag metasurfaces (Figure 4.24). This was likely due to a combination of LSPRs, plasmon-AIS, and, most importantly at this incidence angle, excitation of broadband SPPs. From the extinction measurements alone, it is not clear how much of this enhancement was absorbed vs. scattered, but based on the scattered-light spectra and absorption measurements and simulations, it is likely that all three modes contributed to both scattering and absorption to some degree. The TE polarized reflectance measurements showed almost no change between the coated AgNPA/Ag metasurfaces and the coated planar Ag films, suggesting that broadband SPPs played a larger role in the extinction enhancement at this incident angle.
4.4.9. Influence of AgNPA/Ag metasurfaces on polymer crystallinity

Although all organic semiconductor coated-AgNPA/Ag metasurfaces supported SPPs, only certain coatings out-coupled SPPs well to the far-field in experiments, whereas the other coatings trapped SPPs more efficiently. Since we did not observe a correlation between absorber
coating surface morphology and SPP out-coupling (Figure 4.9), we chose to investigate the crystallinity and molecular orientation of the organic absorber coatings using grazing-incidence wide-angle X-ray scattering (GIWAXS; Appendix Figure A16-13). Figure 4.25a-c shows the expected crystal lattice spacings in the [100] and [010] directions (assigned to the distance between two adjacent backbone chains, and to the π-π stacking distance, respectively) for each neat conjugated polymer. Line profiles were taken either in the out-of-plane (q_z) or the in-plane (q_r) direction depending on which direction the dominant scattering peak was oriented for each polymer (Appendix Figure A16). Overall, P3HT, P3HT:PCBM and PTB7 coatings had a higher degree of crystallinity compared to the other coatings, based on (100) reflection intensities, regardless of the substrate type. Figure 4.25d-f shows 1D GIWAXS line profiles of the three neat polymers on glass, planar Ag and AgNPA/Ag substrates. The intensities of the (100) peak of each of the neat polymers were reduced for AgNPA/Ag substrates relative to planar Ag or glass substrates. This trend held for the other polymer reflections for both in-plane and out-of-plane directions (Appendix Figure A18a-c), suggesting that there was a reduction in the crystallinity of neat polymers when coated onto AgNPA/Ag substrates. This trend did not hold for polymer:fullerene blends (Figure 4.25g-i). For P3HT:PCBM (Figure 4.25g), the (100) P3HT peak was more intense for the AgNPA/Ag substrate relative to both Ag and glass substrates. However, the in-plane (100) peak was reduced for the AgNPA/Ag substrate (see Appendix Figure A18d), indicating that for P3HT:PCBM, the AgNPA oriented the P3HT molecules in a more edge-on configuration relative to planar Ag or glass substrates. Since the PCDTBT:PC_{70}BM blend was amorphous, there wasn’t a notable trend for the PCDTBT reflections for the three substrates (Figure 4.25h). For PTB7:PC_{70}BM, the (100) in-plane peak was more intense for the AgNPA/Ag substrate relative to the blend on both planar Ag and glass (Figure 4.25i), as was the (010) out-of-plane reflection (Appendix Figure A18f), indicating that the AgNPA increased the overall crystallinity of the PTB7 in the blend.

The differences in the observed trends between polymer:fullerene blends could have
arisen from differences in: molecular orientation of the polymer crystallites (edge-on for P3HT, face-on for PTB7); molecular weights of the polymers; polymer:fullerene blend ratios; solvents used for the deposition; or the identity of the fullerene derivatives. Further studies are necessary to determine if AgNPA/Ag metasurfaces impact polymer:fullerene morphology in a predictable manner. In the Discussions section, we correlate the observed differences in crystallinity between the coatings to the extent of SPP out-coupling observed empirically in scattering light spectra. Note: while outside the scope of this study, improvement of the order and alignment of the polymers in the polymer:fullerene blends could be useful for improving the charge extraction efficiency for BHJ-OPV devices incorporating metasurfaces as electrodes. However, since charge extraction is improved for the face-on orientation,\textsuperscript{244,270} metasurfaces which re-orient the molecules in the face-on direction would be preferred. Since PTB7 crystallizes in the face-on direction, the AgNPA may be more useful for improving the charge extraction efficiency from PTB7-based BHJ-OPVs compared to P3HT- and PCDTBT-based BHJ-OPVs.

4.4.10. Absorption spectra of absorber-coated AgNPA/Ag metasurfaces

To determine how effectively the various optical modes (\textit{i.e.}, LSPRs, plasmon-AIS, and SPPs) improved absorption in the coated AgNPA/Ag metasurfaces, integrating sphere reflectance measurements were employed (Methods); Figure 4.26a. Compared to bare planar Ag (which exhibited minimal absorption) and bare AgNPA/Ag (where part of the LSPR was observed at \~370 nm), absorption increased upon coating with a transparent PMMA film, which we attribute to red-shifts and trapping of LSPRs and SPPs due to the higher refractive index environment. For conjugated polymer:fullerene coatings, absorption was improved between 360 - 450 nm, where LSPRs had the greatest contribution; PCDTBT:PC\textsubscript{70}BM and PTB7:PC\textsubscript{70}BM both displayed broadband absorptance enhancement, especially the latter coating. The greatest enhancement occurred at wavelengths >630 nm for P3HT:PCBM and >700 nm for PCDTBT:PC\textsubscript{70}BM and PTB7:PC\textsubscript{70}BM, attributed to SPPs, with enhancement factors reaching nearly 6 at 800 nm for
PTB7:PC$_{70}$BM. Although these enhancement factors were reasonably large, parasitic absorption by the Ag or AgNPA could not be ruled out from the integrating sphere absorption measurements.

Electromagnetic simulations were employed to determine how much of the enhanced absorption in the presence of the AgNPA was beneficial (i.e., absorbed by the absorber coating alone) as opposed to parasitic (i.e., absorbed by the AgNPA, Ag, or Cr layers); see Figure 4.26b,c. In general, the maximum absorptance enhancement for all three coatings occurred at wavelengths

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**Figure 4.26.** Absorption measurements and simulations. a, Integrating sphere absorption measurements for polymer:fullerene films coated on optically-thick Ag and AgNPA/Ag films. Bottom panel of a shows the enhancement factor of the polymer:fullerene-coated AgNPA/Ag metasurface relative to the polymer:fullerene-coated Ag substrate on a reciprocal scale for the vertical axis. b, Simulated absorption enhancement in the coating for the polymer:fullerene-coated AgNPA/Ag or CuNPA/Cu metasurface relative to the polymer:fullerene-coated planar Ag or Cu substrates, respectively (solid lines). The simulated scattered-light spectra are shown as dashed lines for comparison. c, Integrated absorptance weighted by the AM1.5 solar spectrum for each layer. The solid bars represent the AgNPA/Ag substrates, and the cross-hatched bars represent the planar Ag substrates. The numbers over the planar polymer:fullerene bars indicate the total percent absorptance difference in the active layer for AgNPA/Ag substrates relative to planar Ag substrates, integrated over all wavelengths.
corresponding to the LSPR peaks from the AgNPA (~340 - 480 nm), with a maximum enhancement factor of 1.36 observed in this wavelength range for PTB7:PC_{70}BM/AgNPA/Ag relative to PTB7:PC_{70}BM/Ag (Figure 4.26b). The absorptance enhancement remained large for wavelengths beyond the absorption edge of each of coating, with enhancement factors reaching values up to 1.34 for P3HT:PCBM/AgNPA/Ag at 710 nm (attributed to coupling into SPPs) relative to P3HT:PCBM/Ag. Near the plasmon-AIS peak wavelength, particularly for P3HT:PCBM and PCDTBT:PC_{70}BM coatings, dips in the coating absorptance enhancements occurred, indicating increases in scattering losses and/or parasitic absorption loss in the metal. However, on either side of the plasmon-AIS peak, there were peaks in the absorptance enhancement, confirming that there was electromagnetic coupling between the absorber optical transition and scattering mode.\textsuperscript{342} The absorptance enhancement dip was not observed for the PTB7:PC_{70}BM coating because of the poor spectral overlap between the absorption edge and the scattering modes (note the lower intensity of the plasmon-AIS peak for PTB7:PC_{70}BM compared to the other two coatings). When the LSPR of the metasurface was tuned to spectrally overlap with the absorption edge of the coating (\textit{i.e.}, by switching from a AgNPA/Ag metasurface to a CuNPA/Cu metasurface with a P3HT:PCBM coating), the absorptance enhancement at the absorption edge of the coating was greatly enhanced (by a factor of ~1.5) relative to P3HT:PCBM/Cu, and the absorptance enhancement had very well-defined peaks on either side of the plasmon-AIS peak, suggesting stronger coupling between the P3HT:PCBM optical transitions with the LSPR of the CuNPA/Cu metasurface. However, for other spectral regimes, the absorptance in the P3HT:PCBM coating was reduced relative to P3HT:PCBM/Cu. Thus, although there was a dip in the absorptance enhancement at the peak wavelength of plasmon-AIS, the enhanced absorptance on either side of the plasmon-AIS peak can be of benefit to photovoltaics, particularly when the scattering mode spectrally overlaps the absorption edge of the coating. Note that absorptance in the metal NPA/metal film was also enhanced at these wavelengths (Figure 4.27e and Appendix Figure A20b), which could be of interest for plasmon-
enhanced hot carrier generation.\textsuperscript{258}

Figure 4.26c shows the computed integrated absorptance weighted by the AM1.5 spectrum in each layer for the AgNPA/Ag substrates and planar Ag substrates. The total parasitic absorptance in the Ag and Cr materials for the planar substrates was less than 8 % for all active layer coatings and up to 14 % for AgNPA/Ag with a P3HT:PCBM coating. However, even though parasitic absorption increased in the presence of AgNPA/Ag, total coating absorption was improved for all coating materials from absorptance values between 59 and 66 % for the coated-planar Ag substrates to absorptance values between 66 and 76 % for the coated-AgNPA/Ag metasurfaces. LSPRs improved absorptance in the coating (by up to 6 %) to a larger degree than in the metal (3 %), whereas plasmon-AIS and SPPs increased absorptance in the metal (by up to 1.6 %) to a larger degree than in the coating (Table 4.2). This was attributed to very small or negligible absorption coefficients of the organic semiconductors in the wavelength regimes of plasmon-AIS and SPPs compared to those in the wavelength regimes of the LSPRs, coupled with the fact that absorptance enhancement had both dips and peaks in the wavelength regime of plasmon-AIS.

Table 4.2 breaks down the absorptance increases for each spectral regime corresponding to where scattering was maximal for LSPRs, plasmon-AIS, and SPPs. This demonstrates that the LSPRs had the greatest impact on increasing absorptance in both the coating and the metasurface materials, with a greater impact on coating absorptance, and the plasmon-AIS and SPPs had a greater impact on increasing absorptance in the metasurface material compared to the coating.
Table 4.2. Integrated absorptance increases in the various absorber coating layers and AgNPA/Ag for the metasurface substrate relative to the planar substrates separated into wavelength regimes of the various mode types.

<table>
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<th>Case</th>
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<th>SPP</th>
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<td>684-900</td>
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<tr>
<td>( A_{ms} - A_{pl}^{\text{P3HT:PCBM}} )</td>
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<td>0.07</td>
<td>0.73</td>
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</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{P3HT:PCBM}} )</td>
<td>1.48</td>
<td>-0.27</td>
<td>0.14</td>
<td>-0.02</td>
<td>1.33</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{AgNPA/Ag}} )</td>
<td>2.08</td>
<td>1.66</td>
<td>1.23</td>
<td>2.40</td>
<td>7.36</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{AgNPA/Ag}} )</td>
<td>1.91</td>
<td>1.43</td>
<td>1.27</td>
<td>2.13</td>
<td>6.74</td>
</tr>
</tbody>
</table>

Integrated absorptance increase for PCDTBT:PC70BM coating (%)

<table>
<thead>
<tr>
<th>Case</th>
<th>LSPR</th>
<th>plasmon-AIS</th>
<th>SPP</th>
<th>other</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range (nm)</td>
<td>331-464</td>
<td>593-757</td>
<td>757-900</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{PCDTBT:PC70BM}} )</td>
<td>5.27</td>
<td>0.80</td>
<td>0.22</td>
<td>0.8114</td>
<td>7.10</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{PCDTBT:PC70BM}} )</td>
<td>3.85</td>
<td>-0.08</td>
<td>0.41</td>
<td>0.1371</td>
<td>4.31</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{AgNPA/Ag}} )</td>
<td>1.96</td>
<td>1.59</td>
<td>0.79</td>
<td>1.91</td>
<td>6.25</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{AgNPA/Ag}} )</td>
<td>1.78</td>
<td>1.35</td>
<td>0.81</td>
<td>1.64</td>
<td>5.58</td>
</tr>
</tbody>
</table>

Integrated absorptance increase in PTB7:PC70BM (%)

<table>
<thead>
<tr>
<th>Case</th>
<th>LSPR</th>
<th>plasmon-AIS</th>
<th>SPP</th>
<th>other</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range (nm)</td>
<td>328-458</td>
<td>685-786</td>
<td>786-900</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{PTB7:PC70BM}} )</td>
<td>6.17</td>
<td>0.16</td>
<td>0.04</td>
<td>-0.64</td>
<td>5.74</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{PTB7:PC70BM}} )</td>
<td>4.80</td>
<td>-0.04</td>
<td>0.10</td>
<td>-1.53</td>
<td>3.32</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{AgNPA/Ag}} )</td>
<td>3.28</td>
<td>0.70</td>
<td>0.59</td>
<td>2.47</td>
<td>7.04</td>
</tr>
<tr>
<td>( A_{ms} - A_{pl}^{\text{AgNPA/Ag}} )</td>
<td>3.08</td>
<td>0.59</td>
<td>0.64</td>
<td>2.06</td>
<td>6.37</td>
</tr>
</tbody>
</table>

\( A_{ms} \), absorptance in the metasurface sample; \( A_{pl}^{\text{P3HT:PCBM}} \), absorptance in the planar sample for equivalent thickness of coating; \( A_{pl}^{\text{PCDTBT:PC70BM}} \), absorptance in the planar sample for equivalent volume of coating; the subscripts outside of the brackets in the first column indicate whether the absorptance was in the coating (i.e., P3HT:PCBM, PCDTBT:PC70BM, or PTB7:PC70BM) or in the AgNPA/Ag. Note that the “other” regime includes the wavelength regimes less than the LSPR and between the LSPR and plasmon-AIS wavelength regimes.

4.4.11. Scattered-light and absorption spectra for coated CuNPA/Cu metasurfaces

The scattered-light spectra showed similar trends as expected for coated CuNPA/Cu metasurfaces and planar Cu films (Figure 4.27a): planar Cu and PMMA/Cu exhibited minimal scattering across the visible spectrum, and P3HT:PCBM/CuNPA/Cu displayed a single peak at the absorption edge of the P3HT:PCBM coating, attributed to Mie-AIS from the likely roughened
organic surface. The bare CuNPA/Cu displayed a peak at ~580 nm, with scattering increasing with decreasing wavelength due to the Mie scattering background. When coated by PMMA, the LSPR was increased in intensity and shifted to ~590 nm. For the P3HT:PCBM/AgNPA/Ag metasurface, two peaks were observed in the scattered-light spectrum: one at ~600 nm, and one at

Figure 4.27. Scattering and absorption measurements and simulations for absorber-coated CuNPA/Cu metasurfaces. (a) DF scattered-light spectroscopy for bare, PMMA-, and P3HT:PCBM-coated planar Cu films and CuNPA/Cu metasurfaces. (b) True-color DF images of the coated Cu films and CuNPA/Cu metasurfaces from regions where the DF spectra were acquired. (c) Integrating-sphere UV-VIS absorptance measurements for the coated Cu films and CuNPA/Cu metasurfaces. (d,e) Simulated absorptance in (d) the P3HT:PCBM layer and (e) the CuNPA/Cu metasurface and Cu film. The absorptance enhancement factors are shown in the bottom panels of (d,e).
\(~640\) nm. This was attributed to plasmon-AIS from coupling between the LSPR of the CuNPA/Cu and the 0-1 and 0-0 vibronic transitions of the P3HT:PCBM coating, respectively.

The absorptance from the CuNPA/Cu metasurfaces was, in general, higher than the planar Cu films for all wavelength regimes due to the strong absorption from Cu across the visible spectrum (Figure 4.27c). Both coating and metasurface absorptance enhancement displayed two peaks, occurring on either side of the plasmon-AIS peak for P3HT:PCBM/CuNPA/Cu (Figure 4.27 d,e; compare with Figure 4.26b). This demonstrates that by tuning the scattering mode to overlap spectrally with the absorption edge of the coating, stronger electromagnetic coupling can be achieved; however, the shorter wavelength absorption in the coating was decreased for the P3HT:PCBM/CuNPA/Cu. Thus, spectrally overlapping the LSPR mode with the absorption edge of the coating is most useful for enhancing absorption at particular wavelengths, which could be useful for sensors or photodetectors. Incorporating multiple plasmonic resonances comprised of strong short and long wavelength components could be beneficial for increasing absorption across the visible spectrum.

4.4.12. Discussion

Several conclusions can be drawn from the results of the scattered-light spectroscopy, electromagnetic simulations, surface morphology, and crystallinity studies for the various organic semiconductor absorber coatings and are schematically represented in Figure 4.28. For absorber coatings on planar Ag, nanoscale surface features in the coating resulted in Mie-AIS occurring at wavelengths just red-shifted from the absorption edge of the coating. This may be of interest for improved light trapping in photovoltaic applications - in cases where nanoscale surface roughness does not degrade other performance parameters of a device, it may be beneficial to incorporate some degree of roughness in thin-film absorber layers to help scatter sub-bandgap light where absorption is weakest.

There were three dominant mode types observed for the absorber-coated AgNPA/Ag
metasurfaces: LSPRs of individual AgNPs (Modes I, III, and IV in Figure 4.13) at short wavelengths (~350 - 550 nm); plasmon-AIS just red-shifted from the absorption edge of the coatings [arising from both localized (Mode I) and propagating (Mode II) modes], and out-coupled SPPs (from Mode V) at wavelengths longer than plasmon-AIS. The plasmonic scattering modes which spectrally overlapped the optical transitions of the absorber (Modes I and II) became pinned to wavelengths just red-shifted from the absorption edge of the absorber, arising from the increased refractive index and minimal absorption from the coating at these wavelengths. This pinning of the plasmonic modes gave rise to plasmon-AIS, which we speculate has been observed indirectly in prior studies of plasmon-enhanced inorganic photovoltaics,\textsuperscript{185,186,188,189} plasmonic nanoparticles embedded in organic photovoltaic active layers,\textsuperscript{359-361} and organic photovoltaics employing nanostructured back electrodes (similar to the metasurfaces described here).\textsuperscript{66,67,70,201,254} In all of these studies, a strong absorption and/or photocurrent enhancement was observed just red-shifted from the absorption edge of the photovoltaic absorber and was primarily attributed to either efficient scattering from dipolar or multipolar LSPRs,\textsuperscript{70,185,186,188,189} which, in some cases, were shifted by the refractive index of the active layer,\textsuperscript{201,359,360} or excitation of SPPs at these wavelengths.\textsuperscript{66,254} Since, in this work, we have shown that the physical origin of AIS is electromagnetic coupling between optical transitions of absorber materials and scattering modes, we expect that AIS was present in these and other prior studies and contributed to some extent to the enhanced absorption or photocurrent near the absorption edge of the semiconductor.
By comparing empirical scattered-light spectra with GIWAXS results, scattering from out-coupled SPPs was found to be lower in intensity for polymer or polymer:fullerene coatings with higher degrees of crystallinity (P3HT, P3HT:PCBM, PTB7) than for the more amorphous coatings (PCDTBT, PCDTBT:PC$_{70}$BM, PTB7:PC$_{70}$BM). We suggest that amorphous coatings out-coupled SPPs to a greater extent than semi-crystalline coatings due to a combination of: 1)
total internal reflection at the absorber-air interface, since semi-crystalline materials tend to have higher refractive indices than amorphous materials; 2) more tightly bound, shorter propagation length SPPs, again due to the higher refractive indices of semi-crystalline coatings; 3) absorption of long wavelength SPPs by photo-induced absorption from delocalized polarons in crystalline domains, which is known to occur at ~730 nm for regioregular P3HT\textsuperscript{165,362} (photo-induced absorption from localized polarons in disordered P3HT domains occurs at ~950 nm\textsuperscript{165}). The SPPs were out-coupled to a larger degree empirically because the simulations did not account for effects such as surface roughness, crystallinity and the conformal nature of the organic coatings, or regions of the metasurface where there were no AgNPs. In these studies, although amorphous coatings facilitated out-coupling of SPP modes and, hence, their detection by DF spectroscopy, since semi-crystalline coatings trapped SPPs better, SPP modes should be more efficiently absorbed by semi-crystalline polymers and polymer:fullerene blends. We suggest that if these AgNPA/Ag metasurfaces are employed as electrodes in polymer light-emitting diodes (PLEDs), amorphous polymer coatings could increase the out-coupling efficiency of emitted light coupled to tightly-bound SPP modes, which is a major loss channel in PLED devices\textsuperscript{363}. From our results, it is apparent that assessment of the impact of metasurfaces on organic semiconductor morphology and crystallinity should be conducted along with optical studies to fully account for the empirically observed optical properties.

Although total integrated absorption enhancements in the organic semiconductor layers were modest using metasurfaces (values as large as 12 %), it is expected that when incorporated into a full device (\textit{i.e.}, addition of charge transport layers, transparent electrode, and anti-reflection layers), total absorption could be improved by minimizing reflection losses at the air-polymer:fullerene interface. Additionally, although absorption enhancements were large for wavelengths greater than the absorption edge of the polymer:fullerene blends (Figure 4.26b), the total computed absorptance was still very low for these wavelengths (~1 % or less). However, empirical studies have demonstrated that there can be significant external quantum efficiency
(EQE) enhancements for sub-bandgap wavelengths \((e.g.,\) contributing to photo-induced absorption by charge transfer states or polarons\(^{165,362}\)), suggesting that the optical modes observed through our scattering experiments and simulations could be more beneficial to optoelectronic device performance than predicted by optical absorption simulations alone. This drives the need for electrical and device measurements to fully explore the usefulness of these sub-bandgap optical modes.

4.5. Conclusions

In summary, large-area metasurfaces composed of Ag nanoparticle arrays on Ag thin films coated with various organic conjugated polymer and polymer:fullerene absorber layers were characterized. Dark-field scattering studies in conjunction with atomic force microscope topography measurements and electromagnetic simulations revealed several optical modes supported by the organic semiconductor-coated metasurfaces: LSPRs; hybrid SPPs between nanoparticles and the underlying metal film; AIS, both from nanoscale organic semiconductor surface features and from coupling of surface plasmon modes to absorbers; and broadband propagating SPP modes. We identified the physical origin of the previously unidentified optical mode, AIS, as electromagnetic coupling of absorber transitions and scattering modes, whether the scattering modes are plasmonic, localized, or collective in origin. Grazing-incidence X-ray scattering results demonstrated that the crystallinity of neat polymers was reduced in the presence of the metasurface, whereas the alignment of P3HT molecules and the crystallinity of PTB7 molecules in the polymer:fullerene blends were improved in the presence of the metasurface. By correlating polymer crystallinity with scattered-light spectra of the absorber-coated metasurfaces, semi-crystalline polymer coatings were found to trap SPP modes better than amorphous polymer coatings. The total absorption from these structures was measured using integrating sphere reflectance spectroscopy and parasitic absorption was separated from active layer absorption using optical simulations. It was found that LSPRs led to the maximal absorption enhancement in
the organic coating, although broadband SPPs and plasmon-AIS still resulted in improved absorption in the organic coatings, albeit to a lesser degree. We expect that the usefulness of the near- and sub-bandgap optical modes (i.e., plasmon-AIS and SPPs) was underestimated by performing optical simulations alone, and could be exploited to a greater extent in completed photovoltaic devices. Further tuning of the coupling between absorber optical transitions and scattering modes will likely result in greater absorption enhancements.

In this chapter, we demonstrated that absorber optical transitions, which are intrinsically singlet excitonic absorption, can couple to scattering from plasmonic metasurfaces. This is one of the few studies that has investigated the electromagnetic coupling between broadband organic absorbers and plasmonic resonances, since strongly coupled systems generally employ spectrally narrow resonances. We focused most of our attention on the absorption-induced scattering peak that occurred red-shifted from the excitonic resonance. However, several questions remained unresolved at the end of this study: 1) were the short wavelength modes from the absorber-coated plasmonic metasurfaces uncoupled plasmonic resonances, or were they the high-energy mode of the coupled exciton-plasmon system? 2) can strong coupling occur between broadband organic absorbers and surface plasmons, giving rise to the large splitting (>1 eV) between the scattering modes from the absorber-coated metasurfaces observed in this chapter? To answer these questions, we focus our attention in the Chapter 5 on a more fundamental system to investigate the coupling between excitons in conjugated polymers and surface plasmons.
Chapter 5. Strong Exciton-Plasmon Coupling with Broad Spectral Linewidth Excitonic Materials

5.1. Abstract

Expanding on the results presented in Chapter 4, in this chapter, we seek to gain a deeper understanding of the nature of the electromagnetic coupling between broadband absorbers and surface plasmons that give rise to effects such as absorption-induced scattering. Because the plasmonic metasurfaces investigated in Chapter 4 support both localized and propagating surface plasmons, in addition to both single and collective resonances from the Ag nanoparticle arrays, in this chapter, we employed a single Ag nanoparticle as the source of localized dipolar surface plasmons. This allowed us to focus on changes to the organic absorber material, allowing us to determine if broadband excitonic transitions can strongly couple to surface plasmons, giving rise to splitting in the hybrid exciton-plasmon modes of greater than 1 eV.

Electromagnetic coupling between strongly-bound excitons and surface plasmons has been studied extensively for organic dye-metal hybrid nanostructures due to their strong, well-defined and narrow-linewidth resonances and their relative ease of fabrication. However, conventionally, it has been assumed that to achieve strong coupling, narrow exciton and plasmon spectral linewidths are necessary properties of the excitonic and plasmonic materials, respectively. Here, we computationally demonstrate that strong exciton-plasmon coupling can be achieved for Ag-conjugated polymer core-shell nanostructures, despite the broad spectral linewidth of conjugated polymers. In contrast to organic dyes and organic \(J\)-aggregates, organic conjugated polymers tend to have larger excitonic absorption spectral linewidths, higher dielectric constants and exhibit several absorption peaks resulting from their vibrational energy levels. We show that the strong exciton-plasmon coupling arises from the use of thick shells, large oscillator strengths, and multiple vibronic resonances characteristic of typical conjugated polymers, and that Rabi splitting energies of over 1000 meV can be obtained using realistic material dispersive dielectric
constant parameters. The results presented herein give insight into the mechanisms of exciton-plasmon coupling when broadband excitonic materials are employed, and are relevant to organic optoelectronic devices and hybrid metal-organic photonic nanostructures.

5.2. Introduction

Strong light-matter interactions involving organic semiconductors are important for a number of technical applications, including low-threshold lasing, room-temperature exciton-polariton Bose-Einstein condensates, and strongly-coupled organic microcavities. Hybridization between excitons in organic semiconductors and photons in cavities results in the formation of polaritons, which have been observed experimentally and theoretically as energetic splitting in the normal modes of the coupled system, \( i.e., \text{Rabi splitting} \). Room-temperature, Rabi splitting values as large as 100 meV to 200 meV have been reported for organic microcavities, substantially larger than those observed for inorganic semiconductors within microcavities (~10 meV) due to the larger binding energy of Frenkel-type excitons in organic semiconductors.

Excitons in organic materials have also been shown to hybridize with surface plasmons, forming exciton-plasmon polaritons, or “plexcitons.” Strong coupling between excitons and plasmons has had applications in optoelectronics, optical sensing, and reversible switching. For both exciton-photon and exciton-plasmon coupling, the coupling strength is given by the rate of energy exchange between the excitons and the photons/plasmons, 

\[ g = \frac{\hbar \Omega}{2} = \int \vec{\mu}_\text{ex} \cdot \vec{E}_\text{v} \, dV, \]

where \( \hbar \Omega \) is the Rabi splitting energy determined from the energetic splitting between the hybridized peaks in the absorption or scattering spectra of the coupled system, \( \vec{\mu}_\text{ex} \) is the transition dipole moment of the exciton and \( \vec{E}_\text{v} \) is the vacuum electric field. Exciton-plasmon coupling can thus be much stronger than exciton-photon coupling due to the extreme confinement of light to the nanoscale by coupling to surface plasmons.
resulting in stronger field enhancements than what can be achieved using microcavities. To achieve strong exciton-plasmon coupling, the splitting energy, $h\Omega$, of the exciton-plasmon hybrid modes should be greater than the linewidths of the uncoupled exciton and plasmon resonances (i.e., $\gamma_{\text{ex}}$ and $\gamma_{\text{sp}}$, respectively). This suggests that extremely narrow exciton and plasmon resonances are necessary to achieve strong coupling. Most prior studies have investigated the coupling between $J$-aggregates of organic dyes and localized surface plasmon resonances (LSPRs) using a core-shell geometry due to the narrow linewidths of $J$-aggregates (~50 meV). However, for many applications, including plasmon-enhanced photovoltaics, light-emitting diodes, and spasers (the surface plasmon analogue to a laser), coupling between surface plasmons and excitons within conjugated polymers is of great interest.

Although conjugated polymers have broader spectral linewidths (50 meV to greater than 1 eV) than typical excitonic materials employed in strong coupling studies, their large chromophore density manifests in very large $\mu_{\text{ex}}$, which, when coupled to the strong electromagnetic fields from LSPRs, can potentially result in $h\Omega$ exceeding both $\gamma_{\text{ex}}$ and $\gamma_{\text{sp}}$. We have previously demonstrated coupling between excitons in conjugated polymers and surface plasmons arising from metasurfaces, nanoparticle-on-mirror, and semiconductor-metal-insulator waveguide geometries. Additionally, it has been demonstrated that when plasmonic nanostructures are embedded into broadband polymer:fullerene photovoltaic absorber layers that the largest absorption enhancements occur at wavelengths slightly red-shifted from the absorption edge of the absorber (i.e., at the “red-edge”). This red-edge absorption enhancement occurs frequently for a wide range of different plasmonic-enhanced conjugated polymer photovoltaics, which suggests the pervasive presence of exciton-plasmon coupling, where the long wavelength exciton-plasmon hybrid mode leads to the strongest absorption enhancement.

In this chapter, we demonstrate, using electromagnetic simulations, that, despite the large
absorption bandwidth of conjugated polymers, exciton-plasmon coupling using realistically modeled conjugated polymers can result in ultrastrong coupling, with Rabi splitting energies reaching values greater than 1000 meV. We investigate exciton-plasmon coupling using a conventional core-shell hybrid nanostructure (Figure 5.1a), with spherical Ag nanoparticles (AgNPs) as the core of the hybrid structures and model conjugated polymers as the shell. The complex relative permittivity, \( \varepsilon(\omega) \), of excitonic materials, such as J-aggregates of organic dyes, is modelled by a single Lorentzian oscillator (since excitons are equivalent to electric dipole oscillators) given by:

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{f \omega_0^2}{\omega_0^2 - \omega^2 - i\gamma\omega}
\]

(5.1)

where \( \varepsilon_\infty \) is the high-frequency relative permittivity, \( f \) is the oscillator strength, \( \omega_0 \) is the resonance frequency of the oscillator, \( \gamma \) is the resonance linewidth, and \( \omega \) is the frequency of electromagnetic radiation. Note that throughout this chapter, the resonance wavelength, \( \lambda_0 \), will be reported instead of the resonance frequency of the oscillator, where: \( \lambda_0 = \frac{2\pi c}{\omega_0} \) (\( c \) is the speed of light), and the resonance linewidth will be represented in energy units (i.e., \( h\gamma \); in eV).

For typical J-aggregates, \( f \) is in the range of 0.01 to 1.0,\(^{381,382,392,395,407-410}\) and \( \varepsilon_\infty \) is taken as either 1 (air)\(^{394,395}\) or 1.77 (water)\(^{342,345,382,408,409}\). Unlike J-aggregates, conjugated polymers typically have optical line shapes with multiple vibronic features, have broader linewidths (0.05 eV to over 1 eV), large oscillator strengths (~0.02 to 5) for each individual oscillator, and larger \( \varepsilon_\infty \) values (~2 to 4).\(^{396-401}\) To model the relative permittivity of conjugated polymers, we employed a summation of Lorentzian oscillators\(^{397-401,411}\) given by:

\[
\varepsilon(\omega) = \varepsilon_\infty + \sum_n \frac{f \left[ \omega_0 + (n-1)\Delta\omega \right]^2}{\left[ \omega_0 + (n-1)\Delta\omega \right]^2 - \omega^2 - i\gamma\omega}
\]

(5.2)

where \( n \) is the number of oscillators (corresponding to discrete vibrational modes) and \( \Delta\omega \) is the frequency spacing between oscillators. This is a valid model for excitonic materials exhibiting
strong vibrational-electronic \((i.e., \textit{vibronic})\) coupling. In this chapter, we varied the thickness and material parameters \((i.e., \text{oscillator strength, resonance linewidth, number of oscillators, and high-frequency relative permittivity})\) to systematically observe changes in exciton-plasmon coupling in core-shell hybrid nanostructures.

5.3. Methods

FDTD simulations of the scattering and absorption from core-shell NPs were conducted using the same methods as described in Sections 4.3.7 and 4.3.9, with the following changes. The AgNP core had a fixed radius of 25 nm, and its relative permittivity was obtained from the Handbook of Optical Constants.\(^{317}\) The relative permittivity for the conjugated polymer shells were input as analytical equations into the software using Equation 5.2 and the parameters described in Section 5.4. The excitation source used was a linearly polarized total-field scattered-field (TFSF) plane wave normally incident onto the core-shell NP. The TFSF source dimensions were fixed as 100 nm larger than the diameter of the core-shell hybrid NP. The wavelength range of the source was 300 nm to 900 nm with 5 nm increments and a source pulse length of 1.995 fs. Perfectly matched layer (PML) boundary conditions were used in all directions, and the FDTD simulation region was fixed as 1000 nm larger than the diameter of the core-shell hybrid NP. The background permittivity of the simulations was set to that of water (1.77), unless otherwise specified. A mesh override region of 1.0 nm in all directions was used for the region surrounding the core-shell NP (note that for shell thicknesses greater than 40 nm, a 2.0 nm mesh override region was used over the entire core-shell structure, with a 1.0 nm mesh override region over the core and extending 10 nm in each direction into the shell). The simulations continued until either the fields decayed to \(10^{-5}\) of their initial value, or after 100 fs of simulation time (typically the former).

For the simulations of actual conjugated polymer materials, the dispersive relative permittivity for each material was obtained from the literature (Appendix A.1.2); for TDBC, the
relative permittivity was obtained from Bradley et al.\textsuperscript{412} The prolate Ag nanorods were designed such that their longitudinal LSPR, when immersed in a background relative permittivity similar to the high-frequency relative permittivity of respective materials (\textit{i.e.}, 2.44, 2.74, and 3.13 for MEH-PPV, P3HT, and PTB7 respectively), was resonant with the center peak wavelength for the respective shell. To achieve this, we used short axes of 25 nm and long axes of 28.2 nm, 33.2 nm, and 37.2 nm for MEH-PPV, P3HT, and PTB7, respectively.

The scattering spectra were acquired by summing the transmission through a box of six frequency-domain power monitors surrounding the core-shell NP, located outside of the TFSF source. A three-dimensional frequency-domain power monitor was placed surrounding the core-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Core-shell nanoparticle structure used to investigate coupling between excitons in conjugated polymers (CPs) and localized surface plasmon resonances (LSPRs). The silver nanoparticle (AgNP) core radius is given by \( r \), and the CP shell thickness is given by \( h \). (b) Normalized absorption spectra of various conjugated polymers (MEH-PPV, P3HT, and PTB7) and a typical cyanine dye \( J \)-aggregate (TDBC-JA; see abbreviations section for full names of polymers and dye). (c) Real and imaginary parts of the relative permittivity for a single Lorentzian oscillator used as the basis for modeling \( J \)-aggregate optical properties. (d) Real and imaginary parts of the relative permittivity for a Lorentzian shell comprised of five oscillators used as the basis for modeling the CP optical properties. Symbols used: 0-\( \nu \) = absorption transition from the singlet exciton ground state, \( S_0 \), to the first-excited singlet exciton state, \( S_1 \), into the \( \nu \)th vibrational level; \( \lambda_0 \) = resonance wavelength; \( \lambda_{0,2} \) = resonance wavelength for 0-2 transition; \( f \) = oscillator strength; \( h\gamma \) = resonance linewidth; \( \epsilon_{\infty} \) = high-frequency relative permittivity; \( \Delta E \) = spacing between oscillators.}
\end{figure}
shell NP, located inside of the TFSF source to monitor the total electric field within the hybrid NP. A three-dimensional refractive index monitor was overlaid on the total-field frequency-domain power monitor. For the total-field monitor, the fields were sampled at every other mesh point. Absorption in each layer was calculated using Equations 4.3 and 4.4. The absorption in the core and shell were separated from each by using the refractive index monitor as a reference. Shell absorption enhancement values were obtained by simulating an identical core-shell nanostructure to the Ag core - conjugated polymer shell structure of interest, where the core was replaced with a dielectric material having a fixed relative permittivity of 1.77. The absorption in the shell with a dielectric core was then divided by the absorption in the shell with a Ag core to obtain the shell absorption enhancement factors.

5.4. Results and Discussion

Figure 5.1b shows intensity-normalized absorption spectra for three common conjugated polymers (MEH-PPV, P3HT, and PTB7) and for a typical cyanine-based dye J-aggregate (TDBC-JA; see List of Acronyms for full names of the polymers and the dye). The linewidth of the J-aggregate absorption spectrum was significantly narrower than those of the three conjugated polymers. Additionally, the vibronic structure of P3HT and PTB7 was evident by the multiple peaks apparent in the absorption spectra. The real and imaginary parts of the relative permittivity from the Lorentzian oscillator models of the J-aggregate and conjugated polymer materials (given by Equations 5.1 and 5.2) are shown in Figure 5.1c,d for oscillator parameters selected based on those of a typical J-aggregate and conjugated polymer, respectively. The key Lorentzian oscillator parameters that are significantly different for conjugated polymers compared to J-aggregates are the oscillator strength, resonance linewidth, number of oscillators, and high-frequency relative permittivity. As described in Section 1.1, absorption transitions in conjugated polymers are typically designated by both their electronic energy level and vibrational energy level, \( \nu \), where \( \nu \) is a positive integer (0,1,2,…). For steady-state visible light absorption, the
Figure 5.2. (a) Normalized scattering, (b) absorption, and (c) shell absorption enhancement from core-shell nanoparticles with shell relative permittivity described by a single Lorentzian oscillator. The AgNP radius and shell thickness were $r = 25$ nm and $h = 5$ nm, respectively, and the shell parameters used were: $\lambda_0 = 420$ nm; $f = 0.05$; $\hbar \gamma = 0.10$ eV; $\varepsilon_\infty = 1.77$. Note that $\hbar \Omega$ represents the splitting energy between the exciton-plasmon hybrid modes, obtained from the scattering spectra, as shown in (a).

Conjugated polymer absorption spectra represent electronic energy level transitions from the singlet exciton ground state ($S_0$) to the first singlet exciton excited state ($S_1$). Absorption typically takes place from the first vibrational energy level in the $S_0$ state (i.e., $v = 0$) to the $v^{th}$ vibrational energy level in the $S_1$ state. As such, the vibronic absorption peaks are usually classified as $S_0 \rightarrow S_1 0-v$ (Figure 5.1d), with $v$ increasing from the lowest to the highest energy vibrational energy level. Thus, the relative permittivity of a material with 5 vibrational energy levels (i.e., $v$ corresponding to integer values ranging from 0 to 4) can be described by a summation of $n = 5$ Lorentzian oscillators (see Equation 5.2).

We began our study by employing optical-frequency material parameters similar to those of a typical J-aggregate (i.e., $f = 0.05$; $\hbar \gamma = 0.10$ eV; single oscillator (i.e., $n = 1$)); then we systematically varied the parameters to approach those of a typical conjugated polymer.
Initially, we investigated core-shell nanostructures with a Ag core radius, $r$, of 25 nm and a shell thickness, $h$, of 5 nm, which was chosen as an upper limit for the thickness of typical $J$-aggregates adsorbed to Au or Ag nanostructures. The resonance wavelength ($\lambda_0$) was selected to overlap with the dipolar LSPR wavelength for the bare AgNP (i.e., $\lambda_0 = 420$ nm), as identified by the scattering spectrum (Figure 5.2a). When coated by a shell with relative permittivity described by a single Lorentzian oscillator, the hybrid core-shell NP displayed splitting in its scattering spectrum, represented by two peaks which occurred at wavelengths red- and blue-shifted from the dipolar LSPR wavelength (the red-shifted peak exhibited greater intensity than the blue-shifted one). This type of splitting is characteristic of exciton-plasmon coupling.

To classify the strength of coupling between excitons within conjugated polymers and surface plasmons, we identified the coupling regime based on previous studies on exciton-plasmon and exciton-photon coupling. There exist three dominant regimes for coupling strength between excitons and plasmons: the weak-coupling regime (which has also been called enhanced absorption, energy transfer, or the asymmetric-Fano regime), the intermediate-coupling regime (i.e., induced-transparency regime, or anti-resonance Fano regime), and the strong-coupling regime (i.e., plasmonic splitting, which is the plasmonic analogue of Rabi splitting). The coupling regime can be identified by comparing $h\Omega$ (the splitting energy) to the widths of the plasmon and exciton resonances (i.e., $\gamma_{sp}$ and $\gamma_{ex}$, respectively):

\[
\begin{align*}
    h\Omega &< \sqrt{\gamma_{sp}\gamma_{ex}} & \text{Weak coupling} \\
    \sqrt{\gamma_{sp}\gamma_{ex}} &< h\Omega < \left(\gamma_{sp} + \gamma_{ex}\right) & \text{Intermediate coupling} \\
    h\Omega &> \left(\gamma_{sp} + \gamma_{ex}\right) & \text{Strong coupling}
\end{align*}
\]

The splitting energy obtained from the scattering spectrum of the coated AgNP in Figure 5.2a (by taking the difference in energy between the blue-shifted peak and the red-shifted peak)
was 290 meV, which, since it was less than $\gamma_p$ (378 meV) but greater than $(\gamma_p \gamma_{ex})^{1/2}$ (194 meV), confirmed that the core-shell nanostructure was within the intermediate coupling regime. In the intermediate coupling regime, since the total absorption (Figure 5.2b) and scattering both displayed dips at the resonance wavelength, a transparency was induced within the hybrid core-shell nanostructure. The absorption in each layer was separated (Figure 5.2b), and the AgNP core absorption showed the same spectral features as the scattering from the core-shell structure. The absorption in the shell mostly resembled the Lorentzian lineshape of the uncoupled absorption transition, but was broadened and significantly enhanced (up to a factor of 160) relative to the absorption in an identical shell without the AgNP core. The shell absorption enhancement spectrum (i.e., absorption in the shell with the AgNP relative to absorption in the shell without the AgNP core; Figure 5.2c), which is a measure of the usefulness of employing plasmonic nanostructures for improving absorption within a dye or conjugated polymer shell, also showed the same spectral features as the scattering and core absorption. Thus, either the scattering spectrum, the core absorption spectrum, or the shell absorption enhancement spectrum can be used to identify the exciton-plasmon hybrid modes. This indicates that the exciton-plasmon hybrid modes gave rise to the most useful absorption enhancements.
We initially studied very thin absorber shells, which have been the primary focus of core-shell exciton-plasmon coupling studies to-date. This is because for core-shell nanostructures, typically only a monolayer of the J-aggregates adsorbs to the surface of the metallic nanoparticle. In addition, the photoluminescence of thin-films of J-aggregates (with thicknesses greater than that of monolayers) is known to be drastically quenched relative to J-aggregates in the monolayer.\textsuperscript{340} However, in many instances of metal nanoparticle-conjugated polymer...
heterostructures, the conjugated polymer layer is significantly thicker\textsuperscript{362,383,384,417-419} because conjugated polymers undergo minimal photoluminescence quenching in the solid state. Therefore, we investigated the dependence of the shell thickness on the scattering and absorption from the core-shell NPs, initially using a single Lorentzian oscillator model for the relative permittivity of the shell material (Figure 5.3) with $f = 0.05$ and $\hbar \gamma = 0.10 \text{ eV}$. As $h$ increased, the splitting energy between the hybridized modes increased (Figure 5.3a,d). As $h$ increased to 20 nm and beyond, the coupling regime transitioned from induced transparency to strong coupling (Figure 5.3d), and a third peak started to develop at the resonance wavelength (Figure 5.3a). The formation of a three-peaked-spectrum has been reported previously in studies of exciton-plasmon coupling, and the central peak was attributed to a shell mode that screens the metal core from the incident electromagnetic fields (Figure 5.3a, inset).\textsuperscript{342,413} As $h$ was increased further, the shell mode became more dominant, suggesting that the Ag core became screened to a larger extent as the shell thickness increased. The splitting energies began to saturate for $h \geq 30 \text{ nm}$ (Figure 5.3d), because the localized electric field enhancement from the LSPR of the AgNP decayed to a value of unity at a distance of 40 nm from the NP surface (Figure 5.3c). Therefore, for shell thicknesses greater than 30 nm, only the portion of the shell within the first 30 nm was strongly coupled to the LSPR from the Ag core, and the remaining portion of the shell was weakly coupled or uncoupled and acted simply as an optical filter.

The smallest values of $h$ resulted in the largest shell absorption enhancements, with maximal absorption enhancement factor greater than 200 for 2-nm-thick shells (Figure 5.3b). The absorption enhancement values decreased exponentially for increasing shell thickness, with 100-nm-thick shells experiencing enhancement factors near unity ($i.e.$, absorption averaged over the entire shell area was almost the same with or without the Ag core) throughout the visible spectrum. The absorption enhancement values in the thinner shells were very large compared to many values reported in the plasmonic-enhanced photovoltaic literature.\textsuperscript{420} This was due to the thin shells absorbing only a small fraction of the incident light on their own ($i.e.$, they were
Figure 5.4. Variation of resonance linewidth, $h\gamma$, for core-shell structures with a single Lorentzian oscillator shell for $r = 25$ nm and $h = 40$ nm. (a) Scattering; (b) total absorption; (c) peak splitting; and (d) shell absorption enhancement. The coupling regimes in (c) are defined by the linewidths of the surface plasmon ($\gamma_{sp}$ - blue line), the exciton ($\gamma_{ex}$ - red line), and the relationship: $\sqrt{\gamma_{sp}\gamma_{ex}}$ (purple line), as defined by Equation 5.3. The shell optical properties consisted of a single Lorentzian oscillator with $\varepsilon_{\infty} = 1.77$; $\lambda_0 = 420$ nm; and $f = 0.05$.

“optically-thin”), which gave them the potential to become more absorptive when the local electric field intensity was enhanced. The plasmonic AgNPs increased the electric field intensity by factors of nearly 100 at their surfaces (Figure 5.3c, inset). Thus, the thinnest shells, which absorb weakest on their own, exhibited the largest enhancements due to having most of their volume located closest to the most intense electric fields (Figure 5.3c). The shell absorption enhancement spectra resembled the scattering spectra, except that the absorption enhancement plots did not display the third shell mode at the resonance wavelength. Only the low and high energy plasmon-exciton hybrid modes contributed to the absorption enhancement in the shell.

To define a more realistic conjugated polymer shell, we increased the Lorentzian linewidth to values typical for conjugated polymers. We selected $h = 40$ nm for the remaining investigations, which is a modest thickness for conjugated polymer thin-films for optoelectronic applications and is just beyond the LSPR decay length of the 25-nm AgNP cores (Figure 5.3c).
Figure 5.5. Variation of oscillator strength, $f$, for core-shell structures with a single Lorentzian oscillator shell for $h = 40$ nm. (a) Normalized scattering; (b) shell absorption enhancement; and (c) splitting energy for hybrid exciton-plasmon modes. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon ($\gamma_{sp}$ - blue line), the exciton ($\gamma_{ex}$ - red line), and the relationship: $\sqrt{\gamma_{sp}/\gamma_{ex}}$ (purple line), given in Equation 5.3. The shell optical properties consisted of a single Lorentzian oscillator with $\varepsilon_c = 1.77$; $\lambda_0 = 420$ nm; and $h\gamma = 0.30$ eV.

For $f = 0.05$, there were minimal changes in the splitting energy as $h\gamma$ varied from 0.02 eV to 0.2 eV (Figure 5.4). For very narrow $h\gamma$ values, the scattering and total absorption spectra showed an intense peak at the resonance wavelength (Figure 5.4a,b), which was due to the shell mode screening the AgNP core from the electromagnetic fields. This was further evidenced by the dip in the shell absorption enhancement at the resonance wavelength (Figure 5.4d), with the narrowest $h\gamma$ (0.02 eV) having an enhancement factor of 1 (i.e., no enhancement relative to the empty shell) at 420 nm. As $h\gamma$ increased, the splitting increased slightly (Figure 5.4a,c), but the peak from the shell mode in the scattering and total absorption, as well as the dip in the shell
absorption enhancement, all decreased. Beyond 0.2 eV, the splitting energy began to decrease, and transitioned from the strong to the weak coupling regime by $\hbar \gamma = 0.38$ eV, which is beyond the typical linewidth for conjugated polymers. Thus, the broad linewidth of the conjugated polymer shells had little influence on the strength of the coupling.

We next chose $\hbar \gamma = 0.30$ eV as representative of typical conjugated polymers, and varied $f$ for $h = 40$ nm (Figure 5.5). Conjugated polymers typically have $f$ ranging from ~0.02 to 5 for each oscillator. As $f$ increased, the splitting in the scattering and shell absorption enhancement spectra increased (Figure 5.5), showing the expected square-root dependence on $f$. The core-shell structure shifted from the weak coupling regime for $f < 0.05$, to the strong coupling regime for $f \geq 0.05$. For $f > 0.05$, three peaks were observed in the scattering spectra. As $f$ increased, all three of the scattering peaks increased in intensity (see Figure 5.6a for non-normalized spectra), and the splitting between the highest and lowest energy hybrid modes also increased. Splitting was also observed in the shell absorption spectra for $f > 0.05$, which is typically only observed within the strong coupling regime (Figure 5.6b). The shell absorption enhancement spectra (Figure 5.5b) showed only the exciton-plasmon hybrid modes, with the ratio of the intensity of the long wavelength mode to that of the short wavelength mode increasing with increasing $f$ and splitting energy. This was attributed to the already strong absorption in the shell without the AgNP at wavelengths shorter than $\lambda_0$, such that the impact of the short wavelength exciton-plasmon hybrid mode was negligible. Thus, the long wavelength exciton-plasmon hybrid mode was more important for achieving significant absorption enhancement within the conjugated polymer shell. We observed maximal splitting values of 1400 meV for $f = 0.7$, which is among the largest predicted to-date for exciton-plasmon coupling. As such, Ag-conjugated polymer core-shell nanostructures are excellent candidates for achieving strongly coupled exciton-plasmon systems.
Figure 5.6. Variation of oscillator strength, $f$, for core-shell structures with a single Lorentzian oscillator shell for $h = 40$ nm. (a) Non-normalized scattering; and (b) shell absorption. The shell optical properties consisted of a single Lorentzian oscillator with $\varepsilon_\infty = 1.77$; $\lambda_0 = 420$ nm; and $\hbar \gamma = 0.30$ eV.

Figure 5.7. a) Normalized scattering spectra for variation of high-frequency relative permittivity, $\varepsilon_\infty$, for core-shell structures with a single Lorentzian oscillator shell for fixed $\lambda_0 = 420$ nm and $h = 40$ nm. The remaining shell optical properties were: $f = 0.10$; and $\hbar \gamma = 0.30$ eV. b) Dispersion curve showing the peak energies of the hybrid states from the core-shell structures for varying $\lambda_0$ of the shell for $r = 25$ nm, $h = 40$ nm, $f = 0.10$; and $\hbar \gamma = 0.15$ eV, and $\varepsilon_\infty = 3.0$. The uncoupled exciton resonance energies of the shell and the fitted LSPR energy are overlaid as solid lines.
So far, we have assumed a fixed value of 1.77 for $\varepsilon_\infty$ for the conjugated polymer shell. Previous exciton-plasmon studies involving $J$-aggregates as the excitonic materials have typically investigated core-shell nanostructures in solution or single nanostructures in air,\textsuperscript{342,345,382,408,409} such that $\varepsilon_\infty$ has been usually fixed as either 1.77 (water) or 1 (air). However, realistic conjugated polymers have larger $\varepsilon_\infty$ values (typically ranging between 2 and 4).\textsuperscript{396-401} Thus, we varied $\varepsilon_\infty$ for core-shell structures with single Lorentzian oscillator shells, having $f = 0.10$, $\hbar\gamma = 0.30$ eV, and $h = 40$ nm (Figure 5.7). For a core-shell structure with a fixed $\lambda_0$, as $\varepsilon_\infty$ increased, the long wavelength scattering peak increased in intensity and red-shifted; the short wavelength peak also red-shifted slightly to 430 nm for $\varepsilon_\infty = 4.0$ (Figure 5.7a). Since there was a flat increase in the real part of the relative permittivity of the conjugated polymer shell, the uncoupled LSPR of the AgNP could no longer be taken as the wavelength of the bare AgNP in a medium with a background relative permittivity ($\varepsilon_{\text{bkgd}}$) of 1.77. By increasing $\varepsilon_\infty$, the LSPR of the AgNP core red-shifted away from the resonance of the excitonic transition (Figure 5.7). The wavelength of the uncoupled LSPR of the AgNP was determined by fixing $r = 25$ nm and varying $\lambda_0$ of the conjugated polymer shell for a fixed $\varepsilon_\infty = 3.0$ (Figure 5.7b). From this dispersion plot, the red-shifted uncoupled LSPR was determined to occur at 500 nm (\textit{i.e.}, 2.48 eV), which was the same wavelength for the LSPR of a AgNP in a medium with $\varepsilon_{\text{bkgd}} = 3.0$ (Figure 5.8a). Thus, to ensure that the plasmon and exciton were resonant, we first determined the red-shifted LSPR wavelengths for bare AgNPs immersed in $\varepsilon_{\text{bkgd}}$ equal to each $\varepsilon_\infty$. The $\lambda_0$ of the conjugated polymer shells were then adjusted such that the excitons were resonant with the LSPRs for each $\varepsilon_\infty$ (listed in Figure 5.8a). The normalized scattering is shown as a function of detuning, where detuning is the energy difference away from $\lambda_0$. As $\varepsilon_\infty$ increased, the splitting energy decreased due to the increased screening of the electric fields in the shells with higher permittivities. Therefore, compared to $J$-aggregates, the $\varepsilon_\infty$ of conjugated polymers decreased the coupling strength. Despite the decrease in splitting energy for larger $\varepsilon_\infty$, strong coupling was still
achieveable for $\varepsilon_\infty$ up to 2.5, and the intermediate coupling regime was achievable for $\varepsilon_\infty$ of 3 to 3.5. The decrease in splitting energy for increasing $\varepsilon_\infty$ is also a likely factor for the significantly lower splitting energies observed in inorganic exciton-plasmon coupling studies.\cite{368,374}

**Figure 5.8.** (a) Normalized scattering spectra for core-shell structures with a single Lorentzian oscillator shell for varying high-frequency relative permittivity, $\varepsilon_\infty$, with $h = 40$ nm, $f = 0.10$, and $h\gamma = 0.30$ eV. Note that $\lambda_0$ was selected as the LSPR wavelength of bare AgNPs in a background relative permittivity equal to $\varepsilon_\infty$. (b) Splitting energy for hybrid exciton-plasmon modes extracted from the scattering spectra. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon ($\gamma_{sp}$ - blue line), the exciton ($\gamma_{ex}$ - red line), and the relationship: $\sqrt{\gamma_{sp}^{2} + \gamma_{ex}^{2}}$ (purple line), given in Equation 5.3.
Figure 5.9. a) Normalized scattering spectra for variation of the number of oscillators for core-shell structures with $h = 40$ nm; $f = 0.10$; $h \gamma = 0.15$ eV; $\Delta E = 0.15$ eV; and $\varepsilon \infty = 3.0$. The center oscillator (i.e., 0-0, 0-0, 0-1, 0-1, and 0-2 transitions for 1-5 oscillators, respectively) was resonant with the uncoupled LSPR of the AgNP (i.e., 500 nm), with additional vibrational modes either blue- or red-shifted from the uncoupled LSPR. b) Splitting energy for hybrid exciton-plasmon modes for variation of the number of oscillators. The background shading represents the coupling regimes (green - strong coupling; blue - intermediate coupling; red - weak coupling) as defined by the linewidths of the surface plasmon ($\gamma_s$ - blue line), the exciton ($\gamma_e$ - red line), and the relationship: $\sqrt{\gamma_s \gamma_e}$ (purple line), given in Equation 5.3. The peak splitting was obtained from the scattering spectra as the difference in energy between the highest and lowest energy hybrid modes.

To further model conjugated polymers more realistically, we added multiple oscillators to the Lorentzian model to simulate the vibronic structure present in most conjugated polymers (Figure 5.9). The number of vibronic modes represented as individual oscillators for conjugated polymers typically vary from 1 to 5, and it is common for $h \gamma$ to be fixed or similar for all the oscillators. Typically, as the vibronic modes become more well-resolved, $h \gamma$ for each individual oscillator becomes reduced relative to conjugated polymers with only one, broad absorption feature (single oscillator). Therefore, we fixed $h \gamma = 0.15$ eV, $f = 0.10$, and $\varepsilon \infty = 3.0$ for all oscillators and investigated scattering from core-shell nanostructures with $h = 40$ nm.
Figure 5.10. (a-c) Normalized scattering and (d-f) shell absorption (left axis) and absorption enhancement (right axis) for prolate Ag nanorod core-shell structures with dispersive relative permittivities for common conjugated polymer materials used as the shells for \( h = 40 \) nm. The nanorod short axes were 25 nm and the long axes were: 28.2 nm (MEH-PPV); 33.2 nm (P3HT); and 37.2 nm (PTB7).
longitudinal LSPR by varying the length of the nanorod, allowing a plasmonic mode to be resonant with the conjugated polymer absorption.\textsuperscript{225} The nanorods were modeled such that their longitudinal LSPR was the only mode excited (by controlling excitation polarization), and was resonant with the central peak wavelength of the various conjugated polymers (see Methods and Figure 5.10). For these core-shell structures, $h = 40$ nm, and for the nanorod, the long axis length was varied to tune the LSPR wavelength, and the short axis had a fixed radius of 25 nm. For the three conjugated polymers studied here, MEH-PPV, P3HT, and PTB7, all the scattering spectra for the core-shell structures showed an intense long wavelength exciton-plasmon hybrid mode, and weak, short-wavelength hybrid modes that were broadened due to the large linewidth of the absorption resonances of the conjugated polymer materials. As with proper reports on plasmon-enhanced conjugated polymer structures,\textsuperscript{66,67,70,201,254,359-361,404} we observed the largest absorption enhancement in the conjugated polymer shell at wavelengths red-shifted from the absorption of the uncoupled polymer (Figure 5.10d-f). This red-edge absorption enhancement, which has been frequently reported in the literature, can now be attributed to the long wavelength hybrid mode of a coupled exciton-plasmon system. The splitting energies observed for these polymers were 787 meV, 751 meV, and 912 meV for MEH-PPV, P3HT, and PTB7, respectively, placing each of these core-shell structures in the strong coupling regime. In fact, because the splitting energies were between 30 \% and 45 \% of the resonance energies (\textit{i.e.}, 2.53 eV, 2.23 eV, and 2.0 eV for MEH-PPV, P3HT, and PTB7, respectively) in the uncoupled conjugated polymers, the Ag nanorod-conjugated polymer core-shell structures were in the ultrastrong coupling regime.\textsuperscript{386,389,421} We note that the intensities of the long wavelength scattering peaks were large considering the 40-nm-thick conjugated polymer shells (Figure 5.11), ranging from 23 \% to 64 \% of the scattering intensity from the bare Ag nanorods. In Chapter 4, we observed a similar intense long wavelength scattering peak for conjugated polymers coated onto plasmonic metasurfaces, and called the peak, “Absorption-Induced Scattering” (AIS) resulting from coupling between excitons and scattering modes.\textsuperscript{404} In that chapter, the coupling between modes was not as clear
Figure 5.11. Non-normalized scattering spectra for prolate Ag nanorod core-shell structures with dispersive relative permittivities for common conjugated polymer materials used as the shells for $h = 40$ nm. The nanorod short axes were 25 nm and the long axes were: 28.2 nm (a; MEH-PPV); 33.2 nm (b; P3HT); and 37.2 nm (c; PTB7). Same data as shown in Figure 5.10a-c, except not normalized.

due to the multiple broad resonances associated with both the conjugated polymer coatings and the plasmonic metasurfaces. However, the splitting observed was as large as 1.4 eV, much greater than the linewidths of the exciton and plasmon modes. Although the plasmonic resonances were not carefully tuned to be resonant with each conjugated polymer absorber, there was still strong spectral overlap between exciton and plasmon transitions. In this chapter, we confirmed that AIS is in fact the long wavelength exciton-plasmon hybrid mode for conjugated polymer-metal nanostructures, and is a signature of strong coupling. Thus, conjugated polymers serve as excellent candidates for applications requiring strong coupling between plasmons and excitons.

5.5. Conclusions

In conclusion, we have systematically investigated exciton-plasmon coupling in Ag-conjugated polymer core-shell nanostructures using computational finite-difference time-domain methods. Compared to a thin (less than 5 nm) organic dye $J$-aggregate shell, which has been the
focus of most prior theoretical and experimental studies, we have demonstrated that it is possible to achieve strong exciton-plasmon coupling with conjugated polymers, despite their larger linewidths and high-frequency relative permittivities. This is attributed to a combination of their large oscillator strengths, multiple vibronic resonances, and the practicality of employing physically thicker shells. We calculated splitting energies ranging from 400 meV to greater than 1,000 meV for conjugated polymer-coated AgNPs within the strong coupling regime. We found that pronounced scattering occurring at wavelengths longer than the absorption band edge wavelength of the conjugated polymer (previously identified as Absorption-Induced Scattering) is a signature of strong exciton-plasmon coupling. Strong coupling led to the highest absorption enhancement (3.5 to 25) in the conjugated polymer shell at wavelengths red-shifted from the absorption band edge because the lowest energy hybrid mode was dominant for the strongest coupling. These findings will help stimulate interest in designing conjugated polymer optoelectronic devices enhanced by plasmonic nanostructures, including solar cells, light-emitting diodes, and spasers, and the conditions to achieve strongly coupled excitons and plasmons have been identified.
Chapter 6. Ultrafast Charge Transfer and Enhanced Absorption in MoS$_2$ - Organic van der Waals Heterojunctions using Plasmonic Metasurfaces

6.1. Abstract

In Chapters 4 and 5, we demonstrated that strong coupling can be achieved between excitons in organic semiconductors with broad absorption bands and surface plasmons supported by both metasurfaces and discrete nanoparticles, and that this strong coupling is responsible for the enhanced absorption and scattering commonly observed at wavelengths at the red-edge of the semiconductor’s absorption band. This new knowledge can help us understand how to maximize absorption enhancement in organic solar cells employing plasmonic metasurfaces as electrodes. Recall from Chapter 2 that, although Ag electrodes had the lowest parasitic absorption losses, the workfunction of Ag is too low to achieve the maximum $V_{oc}$ in typical organic photovoltaic devices. However, by incorporating an ultrathin interfacial layer between the Ag electrode and the organic active layer, the efficiency can be maximized by matching the workfunction of the interfacial layer to the appropriate energy level of either the $p$- or $n$-type organic material, while minimizing parasitic absorption from the electrode. The thickness of the interfacial layer is particularly important when employing plasmonic metasurfaces as electrodes, since the near-field enhancement decays exponentially away from the metallic nanostructures. In this chapter and in Chapter 7, we explore two different approaches to incorporating ultrathin ($t < 5$ nm) interfacial layers on plasmonic metasurface electrodes for organic photovoltaics: by applying two-dimensional (2D) semiconductors to the metasurface; and by partially oxidizing the Ag plasmonic metasurface. In this chapter, we investigate the use of large-area $n$-type MoS$_2$ as the 2D interfacial layer to modify the workfunction of Ag plasmonic metasurfaces while minimizing changes to the optical properties. We found unexpected results when employing MoS$_2$ as interfacial layers: MoS$_2$ played an active role in the charge photogeneration process, resulting in the formation of a hybrid MoS$_2$-organic active layer.
Hybrid organic-inorganic heterostructures are attracting tremendous attention for optoelectronic applications due to their potential for low-cost processing and high performance in devices. In particular, van der Waals p-n heterojunctions formed between inorganic two-dimensional (2D) materials and organic semiconductors are an emerging class of hybrid optoelectronic materials. 2D and organic semiconductors both lack dangling bonds and native surface oxides, promoting their propensity for interacting via van der Waals forces and efficient charge transfer across their interface. The interest in using 2D semiconductors arises from their quantum confinement effects, giving rise to thickness-dependent optical and electronic properties not observed in the bulk. For example, several transition metal dichalcogenides (TMDCs) become direct bandgap semiconductors only as monolayers, giving rise to significantly larger absorption cross-sections than their bulk counterparts. In fact, just a single monolayer of 2D MoS$_2$ absorbs the same amount of light as 50 nm of Si. Coupling 2D semiconductors with organic semiconductors, whose physical properties can be controlled through synthetic chemistry, can potentially allow for ultrathin p-n heterojunctions with a high degree of tunable optoelectronic properties. However, for photovoltaic applications, hybrid 2D-organic heterojunctions have to-date demonstrated low power conversion efficiencies due to the limited absorption from constraints on the physical thickness of each layer. Here, we investigate the ultrafast charge transfer dynamics between an organic polymer:fullerene blend and 2D n-type MoS$_2$ using transient pump-probe reflectometry. We employ plasmonic metasurfaces to enhance the absorption and charge photogeneration within the physically-thin hybrid MoS$_2$-organic heterojunction. For the hybrid MoS$_2$-organic heterojunction in the presence of the plasmonic metasurface, the charge generation within the polymer is enhanced six-fold, and the total active layer spectral absorption bandwidth is increased by 90 nm relative to the polymer:fullerene blend alone. We demonstrate that MoS$_2$-organic heterojunctions can serve as the active layer of hybrid solar cells, and their efficiencies can be improved using plasmonic metasurfaces.
6.2. Background

A great deal of interest has been generated recently for thin-film photovoltaics because of the reduced material waste, low-cost manufacturing, and flexible, light-weight devices associated with this next-generation solar energy technology.\textsuperscript{424} Emerging thin-film photovoltaics have relied heavily on hybrid active layers composed of organic-inorganic heterojunctions, which tend to be less expensive and well-suited to more versatile applications than conventional Si-based photovoltaics.\textsuperscript{142,146,425-430} For example, hybrid organic-inorganic perovskites have had the fastest growth in their power conversion efficiencies (PCEs) since 2009,\textsuperscript{431} reaching values of more than 20\% by 2015.\textsuperscript{432} Additionally, heterojunctions have been formed between organic dyes or polymers with either quantum dots,\textsuperscript{433-435} metal oxide nanoparticles,\textsuperscript{436,437} or mesoporous TiO\textsubscript{2} (i.e., dye-sensitized solar cells).\textsuperscript{429,430,438-441} These types of hybrid organic-inorganic materials combine the properties of organic semiconductors (e.g., solution-based processing,\textsuperscript{74,133} large absorption cross-sections,\textsuperscript{82,422} synthetic tunability,\textsuperscript{90,442} and mechanical flexibility\textsuperscript{137}) with those of traditional inorganic semiconductors (e.g., large carrier mobilities, stability) to create heterostructures with advanced functionalities. More recently, \textit{p-n} van der Waals heterojunctions have been fabricated using inorganic two-dimensional (2D) materials combined with organic semiconductors.\textsuperscript{443-446} Both 2D and organic semiconductors lack dangling bonds and surface oxides, which allows them to interact \textit{via} van der Waals forces, and limits the trap states at the interface between the two materials.\textsuperscript{444} Because of the extensive developing library of 2D materials,\textsuperscript{447-449} including graphene, hexagonal boron nitride, transition metal dichalcogenides, and layered oxides, coupled with the synthetic tunability of organic semiconductors, van der Waals heterostructures formed between 2D materials and organic semiconductors allow for nearly limitless tailoring of the resulting optoelectronic properties of the hybrid material. MoS\textsubscript{2} is particularly interesting as the \textit{n}-type material in hybrid solar cells due to its direct bandgap in the monolayer,\textsuperscript{14,450,451} high absorption coefficient,\textsuperscript{14,452-454} and tunable bandgap for multilayer thin-films.\textsuperscript{14,455-458} Because of its direct bandgap, monolayer MoS\textsubscript{2} is desirable for photovoltaic
applications due to its larger absorption coefficient than its bulk counterpart, although the total absorption is restricted due to its sub-nanometer thickness. For example, single crystal 2D MoS$_2$ has been employed as the $n$-type material in heterojunctions with few-layer molecular crystals$^{443,445}$ and small-molecule thin-films,$^{444,446}$ and liquid-phase exfoliated MoS$_2$ flakes have been used in heterojunctions with conjugated polymer thin-films.$^{456}$ In these studies, rectification ratios of up to $10^5$ have been observed,$^{443,445}$ and the photovoltaic effect has been demonstrated, suggesting charge transfer from the $p$-type organic material to the $n$-type MoS$_2$. However, there have been limited studies exploring the charge transfer process across the interface between 2D and organic semiconductors.

Organic - 2D $p$-$n$ heterojunctions that have exhibited photovoltaic responses have, to-date, had extremely low solar PCEs (less than 1 %).$^{443,444,446}$ One major cause of the low $\eta_p$ is the limited thickness of the active layer: to exploit the quantum confinement effects of the 2D material, the material should be either single or few-layers in thickness. Similarly, organic semiconductors, which have low carrier mobilities, should be kept physically thin to minimize charge recombination in the active layer.$^{18,22,193}$ However, keeping the active layer materials physically thin prevents them from being optically thick. Plasmonic nanostructures and metasurfaces have been shown to increase absorption in ultrathin organic films$^{66,195,342,346,404,406,459}$ and 2D semiconductors$^{460-469}$ due to their large scattering cross-sections and local electromagnetic field enhancements near the surface of the metallic nanostructure. In addition, plasmonic metasurfaces ($i.e.$, nanostructured metallic films) can couple incident light into surface plasmon polaritons (SPPs), which propagate along the interface between the metasurface and the active layer coating. This allows the unabsorbed incident light to be redirected into in-plane guided modes that can propagate for distance that are several orders of magnitude longer than the physical thickness of the active layer.$^{184,187,190}$ This can allow the ultrathin active layers to become optically-thick while maintaining a physically-thin film to preserve the monolayer properties of the 2D material and minimize charge carrier recombination in the organic layer, thereby
potentially leading to an improved $\eta_p$.

Here, we combine a hybrid MoS$_2$-organic heterojunction active layer with a disordered plasmonic metasurface in order to increase the absorption within the physically-thin hybrid active layer. We investigate a hybrid active layer composed of poly(3-hexylthiophene) (P3HT) blended with phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as the organic component, interfaced with $n$-type monolayer MoS$_2$ as the inorganic 2D material. We perform optical absorption measurements in the visible to understand the influence of the plasmonic metasurface on the efficiency of carrier generation in the P3HT:PCBM/MoS$_2$ heterojunction above the bandgap. Using time-resolved visible pump - NIR probe reflectometry, we study the dynamics of the polaron and exciton states that form after photoexcitation. We observe a six-fold enhancement in the P3HT polaron signal and a 90 nm increase in the absorption bandwidth for the hybrid MoS$_2$-organic active layer in the presence of the plasmonic metasurface. We show that the six-fold enhancement in the P3HT polaron signal arose from a combination of increased absorption in both the P3HT:PCBM and MoS$_2$ layers with ultrafast hole transfer from MoS$_2$ to P3HT. Thus, we demonstrate that through the combined synergistic effect of hybrid 2D-organic heterojunctions and plasmonic metasurfaces, one can potentially enhance efficiencies of thin-film solar cells.

6.3. Methods

6.3.1. Overview

To study the influence of the plasmonic metasurfaces on hybrid MoS$_2$-organic active layers, first, we prepared large-area plasmonic metasurfaces composed of disordered Ag nanoparticle arrays on Ag films (AgNPA/Ag) by employing the nanotemplating method, as described in Section 4.3.1 (Figure 6.1a,c and Figure 4.1).\textsuperscript{72,201,404} The only difference from the planar Ag films and plasmonic metasurfaces employed in Chapter 4 was that the thickness of the underlying Ag film was 150 nm to ensure it was optically-thick. Single-layer 2H-phase MoS$_2$ thin-films (Figure 6.1b) were grown on SiO$_2$/Si wafers by chemical vapor deposition (CVD) over
Figure 6.1. (a) Schematic of the hybrid P3HT:PCBM/MoS$_2$ heterojunction on a plasmonic metasurface. (b) Cross-sectional schematic of monolayer MoS$_2$. (c) True-color dark-field image of Ag nanoparticle array on Ag film plasmonic metasurface; scale bar value shown in (f). (d) SEM image of MoS$_2$ on the plasmonic metasurface prior to application of P3HT:PCBM. Inset is a magnified view of the MoS$_2$-coated metasurface. (e,f) Optical images for P3HT:PCBM/MoS$_2$ on a plasmonic metasurface. The bright-field image (e) is labeled with different regions near the edges of the MoS$_2$ film; the dark-field image (f) was acquired from the same area and helped to identify the different regions. Bright- and dark-field images are on the same scale (value shown in (f)). (g) Raman spectra of CVD-grown MoS$_2$ thin-films after being transferred onto the Ag and metasurface substrates. The two dominant vibrational modes are labeled.

an area larger than 1 mm$^2$ (see Section 6.3.2 and Figures 6.2 and 6.3). The MoS$_2$ films were then transferred to either planar Ag surfaces or plasmonic metasurfaces (Figure 6.1d-f). Raman spectra obtained from the transferred MoS$_2$ (Figure 6.1g) showed the two dominant vibrational modes: the in-plane mode, $E_{12g}$, and the out-of-plane mode, $A_{1g}$. The frequency difference between the two modes ($\Delta$) was $\sim 20$ cm$^{-1}$ (with the difference between the MoS$_2$ on the planar Ag compared to the metasurface arising from the strain exerted by the metasurface on the MoS$_2$), which
confirmed the single-layer nature of the films as measured using Atomic Force Microscopy (Figure 6.2). We note that the MoS$_2$ film was uniform on the planar Ag substrate (Figure 6.4), whereas the MoS$_2$ on the plasmonic metasurface partially conformed to the surface of the Ag nanoparticles (AgNPs) as seen by the dark patches in the SEM image (Figure 6.1d and Figure 6.4d). The P3HT:PCBM active layer coating was then deposited by spin-coating to achieve a thickness of 79.3 ± 7.2 nm. Bright- and dark-field images of P3HT:PCBM/MoS$_2$ on the plasmonic metasurface show the large-area coverage of the MoS$_2$ films and the plasmonic metasurface (Figure 6.1e,f).

6.3.2. MoS$_2$ growth and transfer

Single-layer MoS$_2$ nanosheets were grown by chemical vapor deposition (CVD) using MoO$_3$ (Sigma-Aldrich Co. LLC., 50 mg) and sulfur (Sigma-Aldrich Co. LLC., 250 mg) powders as solid precursors. SiO$_2$/Si wafers (2 cm × 1 cm), facing-down, were placed above the MoO$_3$ powder in the center of a 1-inch quartz tube in the hot region of the furnace. Sulfur was located upstream at the entrance of the furnace (~20 cm from the MoO$_3$ boat). Prior to growth, air was evacuated by flowing Ar (ultrahigh purity, Airgas, Inc.) for 15 min at 200 sccm, after which the tube was heated at 200 °C for 15 min to remove moisture from the precursors. The temperature was then increased to 750 °C under a 90 sccm Ar flow. At this temperature, MoO$_3$ powder was reduced by the sulfur vapor to MoO$_{3-x}$. The suboxides diffused to the SiO$_2$-side of the wafer and further reacted with the sulfur vapor to grow MoS$_2$ films. After 45 min, the furnace was naturally cooled down to room temperature and samples were removed from the tube.

The wafers were further observed by bright-field optical microscopy. Individual MoS$_2$ crystals are typically between 5 µm to 30 µm in size (Figure 6.2a-c) and grow in the center of the wafer. When looking closer to the edge of the wafer located upstream, the size of the crystals increases. The crystals eventually get connected (Figure 6.2d-f) and a continuous single-layer MoS$_2$ film starts to form. Large-area polycrystalline domains without pinholes can be obtained
with dimensions over 1 mm² (Figure 6.2g-i).

To confirm the thickness of the large-area CVD-grown MoS₂ film, we collected photoluminescence (PL) spectral maps from 100 µm × 100 µm regions (Figure 6.3a). Monolayer regions were observed to have a dominant PL peak corresponding to the A-exciton transition at 660 nm, with a contribution from the indirect transition at 800 nm (Figure 6.3c). In addition, Raman spectra taken from identical points showed the difference between the two dominant

**Figure 6.2.** Optical, scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of single-layer MoS₂ (light purple in the optical image) grown by chemical vapor deposition on SiO₂/Si wafer (pink in the optical image). MoS₂ crystals can be observed either isolated (a-c) or interconnected (d-f). At higher density of materials deposited, large-area polycrystalline MoS₂ film can form (g-i). The film was intentionally scratched in (g) to show the color contrast between MoS₂ and the substrate. Data acquired and figure prepared by Damien Voiry.
vibrational modes, $\Delta$, was $\sim$20 cm$^{-1}$ to 21 cm$^{-1}$ (Figure 6.3d), which has been reported for exfoliated MoS$_2$ monolayers. The few-layer regions were characterized by red-shifted and more intense PL from the indirect band transitions at wavelengths longer than 850 nm, in addition to $\Delta > 22$ cm$^{-1}$. $\Delta$ increased with increasing number of MoS$_2$ layers because of a softening (red-shift) of the E$_{12g}$ mode and a stiffening (blue-shift) of the A$_{1g}$ mode. The stiffening of the A$_{1g}$ mode arose from coupled harmonic oscillators between van der Waals bonded layers; however, the E$_{12g}$ softening likely arose from either stacking-induced changes in intralayer bonding and/or the presence of Coulombic interactions in MoS$_2$. Monolayer coverage was observed for $> 90\%$ of the region based on threshold analysis of the PL map.

MoS$_2$ on SiO$_2$/Si wafers was transferred on Ag and metasurface substrates using poly(methyl methacrylate) (PMMA). A6 PMMA (i.e., 6 % PMMA in anisole) was spin-coated on
the SiO$_2$/Si wafer covered with the MoS$_2$ nanosheets (4000 rpm for 45 s) and baked at 120 °C for 5 min to ensure good adhesion between MoS$_2$ and PMMA. The wafer was then etched using 1 M NaOH solution at 50 °C. After delamination, the PMMA layer was transferred on various substrates and dried in air. Once dried in air, the substrates were further dried in vacuum for 5 hours. Finally the PMMA layer was then dissolved using acetone (4 × 50 mL).

6.3.3. Polymer:fullerene solution and thin-film preparation

P3HT (Rieke Metals, Inc., product number: RMI-001EE; $M_w$: 69,000 g mol$^{-1}$; polydispersity index: 2.3; regioregularity: 96 %) and PCBM (1-Material, Inc., product number: OS0266) in a 1:1 ratio were dissolved in chlorobenzene (40 g L$^{-1}$ total blend concentration) by

Figure 6.4. SEM images of substrates employed for organic film deposition: a) Ag film (150 nm); b) polycrystalline MoS$_2$ film on Ag; c) plasmonic metasurface composed of a Ag nanoparticle array on a Ag film (AgNPA/Ag); d) polycrystalline MoS$_2$ film on plasmonic metasurface. Inset in each image are high-resolution SEM images taken from the same regions. All images and insets are on the same respective scales (scale bar values shown in (a)).
heating to 60 °C while stirring at 1200 rpm for more than 5 hours. Once cooled to room temperature, the solution was then filtered by first withdrawing the solution from the septum in the vial using a hypodermic needle and a 1 mL polypropylene luer-lock syringe. The needle was then replaced by a 0.2 µm pore regenerated cellulose filter, through which the solution was passed and deposited into a cleaned vial. The filtered solution was spin-coated onto the various substrates (planar Ag, Ag metasurface, MoS₂/Ag, and MoS₂-metasurface) at 5000 rpm to achieve P3HT:PCBM coatings of ~80 nm, as confirmed through atomic force microscopy measurements (see Section 4.3.3).

6.3.4. **Ultrafast two-color pump-probe reflection measurements**

Ultrafast two-color transient pump-probe reflection measurements were obtained using a 1 kHz, 800 nm, 70 fs Ti:sapphire amplified laser (Newport, Corp. Spectra-Physics Spitfire Ace). We used pump wavelengths of either 400 nm by frequency doubling a portion of the fundamental 800 nm laser output, or 800 nm itself. The pump was chopped at 500 Hz and a fluence of ~25 µJ cm⁻² was used to minimize damage to the P3HT:PCBM film during the measurements (see Appendix Figure A21 for stability tests). The remainder of the laser power was directed to an Optical Parametric Amplifier (Newport, Corp. Spectra-Physics TOPAS prime) to generate probe wavelengths of either 1000 nm or 1150 nm. The reflected probe beam (diameter ~ 75 µm) was directed to a lock-in amplifier to collect the signal, and a fluence of ~5 µJ cm⁻² was used. A delay stage step size of 50 fs was used for the 10 ps dynamics, and a step size of 10 ps was used for the 800 ps dynamics. For all measurements, at least 20 scans were averaged to improve the signal-to-noise ratio. Note that for the 800 nm pump, 1000 nm probe measurements, the pump fluence was increased to ~240 µJ cm⁻² because of the weaker signal from sub-bandgap excitation.

6.3.5. **Steady-state optical spectroscopy**
Extinction measurements were obtained using a microscope-coupled spectrometer (Tokyo Instruments, Inc. Nanofinder 30) using halogen lamp illumination and a 100× microscope objective (N.A. = 0.95). Bright-field (BF) reflected-light spectra of the selected region (BFsample) were acquired using a pinhole diameter of 250 µm, in addition to an exposure time of 50 ms with 10 accumulations. The total area from which the spectra were collected, which was selected digitally, was approximately 5 µm². Spectra were collected from a minimum of 3 regions for the most uniform samples (i.e., for P3HT:PCBM) and a maximum of 7 regions for the most non-uniform samples (i.e., for P3HT:PCBM/MoS2/metasurface; see Appendix Figure A25 for individual spectra). Background spectra were collected by blocking the light path to the spectrometer (BFbkgd). Spectra were normalized to the lamp spectral intensity using the BF reflection spectrum from a planar Ag film (BFAg). Extinction was calculated using Equation 6.1:

\[
\text{Extinction} = 1 - \frac{BF_{\text{sample}} - BF_{\text{bkgd}}}{BF_{\text{Ag}} - BF_{\text{bkgd}}}
\]  

Dark-field (DF) scattered-light images were acquired using an Olympus, Inc. BX51 under Xenon lamp illumination in reflection mode with a 10× DF microscope objective (N.A. = 0.30).

6.3.6. **FDTD simulations**

FDTD simulations were conducted as described in Sections 4.3.7 and 4.3.9 using FDTD Solutions (Lumerical Solutions, Inc.), with the following modifications. For the hybrid MoS2/organic heterostructures, monolayer MoS2 (thickness of 0.67 nm) was used to conformally coat the AgNPs. This idealized, periodic structure does not perfectly match the experimentally prepared MoS2-metasurface heterostructures, and the main differences are described below in Section 6.4.3. The optical constants used for each layer were obtained from the literature (Appendix A.1). The excitation source used was a total-field scattered-field (TFSF) plane wave incident at 5° from the surface normal with a wavelength range of 300 nm to 900 nm with 5 nm
Figure 6.5. ps-scale transient pump-probe reflection measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS\(_2\) active layers with and without the plasmonic metasurfaces using a pump wavelength of 400 nm and probe wavelengths of: a) 1000 nm (i.e., probing the polaron and exciton dynamics in P3HT); and b) 1150 nm (i.e., probing the exciton dynamics in P3HT).

6.4. Results and Discussion

6.4.1. Pump-probe dynamics at short (10 ps) time-scales

To study the charge photogeneration and transfer in the hybrid MoS\(_2\)-organic active layer, with and without the plasmonic metasurface, we employed two-color transient pump-probe reflection measurements (Figure 6.5) using a 1 kHz, 800 nm, 70 fs amplified laser. We used pump wavelengths of either 400 nm, by frequency doubling a portion of the fundamental 800 nm laser output, or 800 nm itself. The remainder of the laser power was directed to an Optical Parametric Amplifier (OPA) to generate probe wavelengths of either 1000 nm (Figure 6.5a) or 1150 nm (Figure 6.5b), thereby allowing the investigation of polaron and exciton dynamics.
within the organic polymer, P3HT, as explained below. The transient pump-probe reflection signal ($\Delta R/R$) at 1000 nm originated from the populations of both P3HT excitons (i.e., bound electron-hole pairs) and polarons (i.e., free charges within the polarizable organic polymer).\textsuperscript{165,362,472,473} For the 1000 nm probe wavelength, the $\Delta R/R$ signal was larger for the hybrid P3HT:PCBM/MoS$_2$ active layer relative to P3HT:PCBM alone, demonstrating that MoS$_2$ contributed to the polaron or exciton population within P3HT:PCBM (note that the $\Delta R/R$ signal was zero for MoS$_2$ alone, see Appendix Figure A22). The $\Delta R/R$ signal at 1150 nm (Figure 6.5b), which originated from the population of P3HT excitons alone,\textsuperscript{362,472,473} was almost unchanged for the hybrid P3HT:PCBM/MoS$_2$ active layer compared to P3HT:PCBM alone, which demonstrated that the increased $\Delta R/R$ signal at 1000 nm arose from an increased P3HT polaron population. This suggested that hole transfer occurred from the MoS$_2$ to the P3HT. Because the $\Delta R/R$ signal was enhanced from the earliest, instrument-limited time scales, this hole transfer process was determined to occur within 100 fs of initial excitation.

To determine whether the charge transfer from MoS$_2$ to P3HT could be used to broaden the spectral range of the absorption in P3HT:PCBM, we investigated the transient pump-probe

**Figure 6.6.** Picosecond-scale transient pump-probe reflection measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurfaces using pump and probe wavelengths of 800 nm and 1000 nm, respectively (i.e., probing the polaron and exciton dynamics in P3HT).
reflection using a pump wavelength of 800 nm, below the bandgap of P3HT:PCBM (Figure 6.6), but where MoS$_2$ still had moderate absorption (see Section 6.4.3). Although we still observed a $\Delta R/R$ signal for P3HT:PCBM, the signal strength was very weak (0.06 % at $\tau = 0$ ps), even at a significantly higher excitation fluence (240 $\mu$J/cm$^2$ for the 800 nm pump cf. 25 $\mu$J/cm$^2$ for the 400 nm pump), which was attributed to tail state absorption in P3HT:PCBM.\textsuperscript{474} However, the $\Delta R/R$ signal for the hybrid P3HT:PCBM/MoS$_2$ in the presence of the plasmonic metasurface was increased to 0.32 %, an enhancement factor of 5.6 relative to P3HT:PCBM alone. This demonstrates that MoS$_2$ transfers holes to P3HT outside of the absorption band of P3HT:PCBM, making hybrid MoS$_2$-organic heterostructures employing plasmonic metasurfaces a viable option for broadening the absorption spectrum of organic-based photovoltaics. We expect that if the MoS$_2$ coated the metasurface conformally, the $\Delta R/R$ signal when pumped at 800 nm would have been higher due to increased absorption from the MoS$_2$ for the conformal coating at this wavelength (compare the measured extinction, Figure 6.11a, to the simulated absorption, Figure 6.11b).

The hybrid P3HT:PCBM/MoS$_2$ active layer employing the plasmonic metasurface exhibited more than a six-fold enhancement in the $\Delta R/R$ signal at 1000 nm relative to P3HT:PCBM alone for both 400 nm (Figure 6.5a) and 800 nm excitation (Figure 6.6). Although the plasmonic metasurface also led to enhancement of the $\Delta R/R$ signal in the pure organic active layer (P3HT:PCBM), the enhancement was significantly larger for the hybrid MoS$_2$-organic active layer. The small increases observed in the $\Delta R/R$ signal at 1150 nm in the presence of the plasmonic metasurface arose from collective electric field enhancements of the metasurface\textsuperscript{404} and increased light scattering from MoS$_2$ (see Figure 6.7); we note that interference effects from the addition of the monolayer MoS$_2$ film between P3HT:PCBM and Ag did not significantly impact the $\Delta R/R$ signals (see Figure 6.8). However, the $\Delta R/R$ signal at 1000 nm exhibited a much larger increase, thus demonstrating that the P3HT polaron population was enhanced to a much
larger degree than the exciton population in the hybrid MoS$_2$-organic heterojunction employing the plasmonic metasurface. In addition to ultrafast hole transfer between MoS$_2$ and P3HT, which occurred both within the absorption band of P3HT (i.e., 400 nm pump, Figure 6.5a) as well as for sub-bandgap wavelengths (i.e., 800 nm pump, Figure 6.6), the enhanced $\Delta R/R$ signal for the hybrid P3HT:PCBM/MoS$_2$ active layer employing the plasmonic metasurface arose from increased absorption in both the MoS$_2$ and P3HT:PCBM layers, as demonstrated below.

Exciton generation within P3HT:PCBM layers can be improved by enhanced electromagnetic fields from plasmonic modes,$^{100}$ in addition to increased optical path length from light scattering. The small improvements in the $\Delta R/R$ signal when pumped at 400 nm and probed at 1150 nm (Figure 6.5b) arose from increased scattering from the MoS$_2$ film, as evidenced by the dark-field (DF) images of P3HT:PCBM on planar Ag and on MoS$_2$/Ag (Figure 6.7a,b, respectively). The metasurface, with or without the MoS$_2$, led to a larger increase in the $\Delta R/R$ signal when probed at 1150 nm (Figure 6.5b) due to the strong electromagnetic field enhancements from the plasmonic modes, as evidenced through the intense scattering in the DF images, Figure 6.7c,d. However, because of the relatively small increases in the $\Delta R/R$ signal...
when probed at 1150 nm (Figure 6.5b) compared to the signal increases when probed at 1000 nm (Figure 6.5a), light scattering and plasmonic field enhancements alone could not account for the enhancement of the polaron signal. Thus, we determined that the combined synergistic effects of plasmonic field enhancements giving rise to increased absorption in both the P3HT:PCBM and the MoS$_2$ films, in addition to photoinduced hole transfer from MoS$_2$ to P3HT must be the mechanisms by which the 1000 nm probe signal was increased to such a large degree, since transferred holes would only contribute to the polaron signal (1000 nm probe).

Besides light-scattering from the MoS$_2$/metasurface, we investigated whether interference effects arising from P3HT:PCBM sitting further from the reflective Ag surface due to the addition of the MoS$_2$ impacted the active layer absorption. We performed TMM calculations$^2$ to investigate the dependence of the spatial position of the electric field intensity within the heterostructure while varying the number of MoS$_2$ layers (see Figure 6.8). We found that interference effects arising from the addition of MoS$_2$ became significant when 25 MoS$_2$ layers were added, where destructive interference of the electric field intensity was first observed within P3HT:PCBM. However, for less than 10 layers of MoS$_2$, the peak position of the electric field intensity varied minimally (i.e., by less than 1 nm for the addition of every MoS$_2$ monolayer).

Figure 6.8. Spatial distribution of the electric field intensity in the heterostructure for selected number of MoS$_2$ layers (from top to bottom: 0, 1, 5, 10, 25, and 70 layers), calculated using the transfer matrix method.$^2$
Figure 6.9. Nanosecond-scale transient pump-probe reflection measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS$_2$ active layers with and without the plasmonic metasurfaces using a pump wavelength of 400 nm and a probe wavelength of 1000 nm: a) magnitude of transient reflectometry; b) normalized data.

Thus, since monolayer MoS$_2$ was employed in the aforementioned experiments, we concluded that interference effects did not significantly impact the P3HT polaron signal or the active layer absorptance

6.4.2. Pump-probe dynamics at long (1 ns) time-scales

For all pump and probe wavelengths, the P3HT polarons and excitons showed the same decay dynamics for both P3HT:PCBM and P3HT:PCBM/MoS$_2$, with and without the metasurface, within the first 10 ps (see Appendix Figure A23 and Table A9). However, the nanosecond-scale decay dynamics of the P3HT polarons were significantly modified for the hybrid MoS$_2$-organic active layer, with and without the metasurface (Figure 6.9). Over the 1 ns time scale, the magnitude of the $\Delta R/R$ signal showed the same trend as the 10 ps time scales.
Table 6.1. Decay parameters obtained from fitting the ns-scale $\Delta R/R$ curves to the following equation: 

$$\Delta R/R = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)} + C,$$

where $t$ is the decay time, $A_1$ and $A_2$ are the amplitudes of the components of the decay, $\tau_1$ and $\tau_2$ are the lifetimes of the components of the decay, and $C$ is a constant for the excited states that did not decay within the time range (800 ps). The amplitude values are reported as actual $\Delta R/R$ percentages.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$, ps ($A_1$)</th>
<th>$\tau_2$, ps ($A_2$)</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>-</td>
<td>-</td>
<td>long (0.249)</td>
</tr>
<tr>
<td>P3HT:PCBM/metasurface</td>
<td>-</td>
<td>6892.5 (0.868)</td>
<td>-</td>
</tr>
<tr>
<td>P3HT:PCBM/MoS$_2$</td>
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<td>-</td>
<td>long (0.594)</td>
</tr>
<tr>
<td>P3HT:PCBM/MoS$_2$/metasurface</td>
<td>68.5 (0.361)</td>
<td>3067.1 (1.439)</td>
<td>-</td>
</tr>
</tbody>
</table>

(Figure 6.9a). However, the P3HT polaron lifetime was reduced for the P3HT:PCBM/MoS$_2$ hybrid active layer relative to P3HT:PCBM alone (Figure 6.9b; Appendix Figure A24 and Table 6.1). The presence of the MoS$_2$ resulted in an extra decay component, with a decay constant of ~160 ps, compared to P3HT:PCBM alone, which was fit to a constant value within this time regime. This extra decay component was attributed to the excess polarons transferred to the P3HT from the MoS$_2$. Similarly, the presence of the metasurface also resulted in a reduced P3HT polaron lifetime compared to the P3HT:PCBM alone, with a decay constant of ~7 ns (Figure 6.9b; Appendix Figure A24 and Table 6.1). The hybrid P3HT:PCBM/MoS$_2$ active layer with the plasmonic metasurface was comprised of two decay components, both with significantly reduced lifetimes relative to P3HT:PCBM alone (Figure 6.9b; Appendix Figure A24 and Table 6.1), where the fast decay component was ~70 ps, and the slow component was ~3 ns. These two components were thus attributed to the excess polarons transferred to the P3HT from the MoS$_2$ (fast component) in addition to the excess polarons generated from the plasmonic metasurface (slow component). The lifetimes of these P3HT polarons were reduced relative to P3HT:PCBM/MoS$_2$ (160 ps) or P3HT:PCBM/metasurface (~7 ns) alone due to the larger population of carriers within the P3HT:PCBM layer, since carrier concentration is inversely
proportional to carrier lifetime.\textsuperscript{179} However, even with the short polaron lifetime for the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the metasurface, the overall polaron population was still more than 4 times higher than that of the P3HT:PCBM alone after 800 ps (Figure 6.9a). This suggests that a greater population of charge carriers would be available for collection at the electrodes if the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the plasmonic metasurface were employed in a completed device. The larger P3HT polaron population within the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the plasmonic metasurface is further confirmed by the enhanced photoluminescence (PL) from P3HT:PCBM (Figure 6.10).

The photoluminescence (PL) spectra from P3HT:PCBM are good indicators of the population of charges within the organic blend. Since the PL was enhanced in the presence of the plasmonic metasurface and for the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the metasurface, this further supports the hypothesis that there were more charges generated in the P3HT:PCBM layer in the presence of the metasurface. The hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the

![Figure 6.10. Photoluminescence (PL) spectra from P3HT:PCBM and the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with and without the plasmonic metasurface. Spectra were acquired using a Nanofinder 30 spectrometer (Tokyo Instruments) under 532 nm laser excitation (0.05 mW initial power) directed through a 100× microscope objective (0.95 numerical aperture). The laser and PL signal from the sample were passed through a high-pass filter, then through a 500 \(\mu\)m pinhole prior to the CCD detector. Each spectrum shown was acquired using 1 s exposure time, 5 accumulations/spot, and between 5 (P3HT:PCBM only) to 17 (P3HT:PCBM and P3HT:PCBM/MoS\textsubscript{2} with metasurface) spots were averaged for each sample.](image-url)
metasurface displayed a more intense PL signal than the P3HT:PCBM with the metasurface, suggesting that charge transfer occurred from MoS$_2$ to P3HT and radiatively recombined, with both P3HT:PCBM and MoS$_2$ having enhanced absorption from the metasurface.

6.4.3. Steady-state active layer absorption

Having demonstrated increased photogeneration in the hybrid P3HT:PCBM/MoS$_2$ active layer in the presence of the plasmonic metasurface, we now turn our attention to the impact of the plasmonic metasurfaces on the active layer absorption. We performed steady-state extinction measurements using a microscope-coupled spectrometer on the hybrid P3HT:PCBM/MoS$_2$ active layer with and without the metasurface (Figure 6.11a). Comparing the hybrid P3HT:PCBM/MoS$_2$ with the metasurface to P3HT:PCBM alone, we observed increased extinction across the visible spectrum, particularly for longer wavelengths, suggesting an increase in the absorption bandwidth. For P3HT:PCBM on the metasurface alone, the extinction was notably improved for shorter wavelengths, but only slightly increased for longer wavelengths, suggesting that the MoS$_2$ plays the dominant role in the improved extinction at longer wavelengths. For the hybrid P3HT:PCBM/MoS$_2$ active layer with the metasurface, we obtained extinction enhancement factors of 1.5 at 410 nm and 2.9 at 670 nm (Figure 6.12a) relative to P3HT:PCBM alone, and a spectrally-integrated extinction enhancement factor of 1.4.
Figure 6.11. a) Microscope-coupled extinction measurements from P3HT:PCBM and the hybrid P3HT:PCBM/MoS\(_2\) active layers with and without the plasmonic metasurface. b) Simulated active layer absorptance, defined as the P3HT:PCBM absorptance plus the MoS\(_2\) absorptance. c,d) Spatially-varying cross-sectional simulated absorption (calculated using Equation 4.3) in the heterostructure at two different wavelengths: c) 400 nm and d) 660 nm. The plots in (c,d) are on the same scale, and the scale bar is shown in (d).

To understand these differences, and to distinguish between useful absorption (i.e., absorptance in the active layers) and scattering within the extinction measurements, we performed finite-difference time-domain (FDTD) simulations (Figure 6.11b-d). As in the extinction measurements, we observed a generally broadband active layer absorption increase for the P3HT:PCBM/MoS\(_2\) active layer with the metasurface compared to P3HT:PCBM alone. The active layer absorption enhancement was largest at wavelengths between 350 nm and 450 nm and at or above 550 nm for the hybrid P3HT:PCBM/MoS\(_2\) active layers in the presence of the
metasurface (Figure 6.11b and Figure 6.12b). The reason for the absorption enhancements at these wavelengths was due to the formation of plasmon-exciton hybrid modes. When plasmonic metasurfaces are coated by absorbers (such as MoS$_2$ or P3HT:PCBM), the plasmonic modes are known to demonstrate splitting from coupling with the excitonic transitions of the absorber.\textsuperscript{342,346,376,378-380,382,404,475-478} The presence of the 80-nm-thick P3HT:PCBM layer red-shifted and split the plasmonic modes to a much larger degree than the monolayer MoS$_2$ alone, as identified by scattered-light simulations (Figure 6.12d). In the presence of the P3HT:PCBM (with or without MoS$_2$), the short wavelength plasmon-exciton mode led to the absorptance enhancements observed between 350 nm and 450 nm. However, the long wavelength plasmon-exciton hybrid mode was red-shifted outside of the absorption band of P3HT:PCBM, but spectrally overlapped with the strong absorption features in MoS$_2$ between 550 nm and 700 nm.\textsuperscript{14,451} This led to a greater than 10-fold absorption enhancement within the MoS$_2$ layer for wavelengths between 550 nm and 900 nm (Figure 6.12c). Without the P3HT:PCBM, the absorption enhancement within the MoS$_2$ was much lower for wavelengths greater than 500 nm (~5; Figure 6.12c). Thus, the synergistic effect of the P3HT:PCBM, MoS$_2$, and metasurface combined gave rise to the maximum absorptance within the active layer. As a result, the active layer absorption bandwidth (\textit{i.e.}, full-width, half-maximum) of the hybrid P3HT:PCBM/MoS$_2$ active layer in the presence of the plasmonic metasurface was increased by 90 nm relative to that of P3HT:PCBM alone. We calculated a spectrally-integrated enhancement factor weighted by the AM1.5 solar spectrum of 1.3 for the hybrid P3HT:PCBM/MoS$_2$ active layer with the metasurface (\textit{cf.} less than 1.1 for P3HT:PCBM with the metasurface and less than 1.0 for P3HT:PCBM/MoS$_2$ without the metasurface).
Figure 6.12. a) Measured extinction enhancement factor (i.e., extinction from P3HT:PCBM/metasurface or P3HT:PCBM/MoS$_2$/metasurface divided by extinction from P3HT:PCBM/Ag). b) Simulated absorptance enhancement factor in the total active layer (P3HT:PCBM + MoS$_2$) for P3HT:PCBM/metasurface with and without the MoS$_2$ layer relative to P3HT:PCBM alone. c) Simulated absorptance enhancement factor in the MoS$_2$ layer for MoS$_2$/metasurface with and without the P3HT:PCBM layer relative to MoS$_2$ alone. d) Normalized simulated scattered-light spectra for the metasurface with various coatings. Note that each of the scattering spectra is offset for clarity.
Figure 6.11c,d shows cross-sections of the simulated spatially-varying absorption distribution for the hybrid P3HT:PCBM/MoS$_2$ active layer with the metasurface within the different layers at two different wavelengths (i.e., 400 nm and 660 nm). At both wavelengths, absorption was stronger in the MoS$_2$ than in the P3HT:PCBM, due to the stronger absorption coefficient of MoS$_2$ and its closer proximity to the metasurface. At 400 nm (Figure 6.11c), absorption was strongest at the tip of the AgNP. This suggests that, even though the MoS$_2$ film did not conform perfectly to the surface of the AgNPA in the experiments (Figure 6.1d), absorption in the MoS$_2$ was still increased quite strongly due to the intense electromagnetic fields near the tips of the AgNPs. At 660 nm (Figure 6.11d and Figure 6.12b,c), active layer absorption predominantly occurred in the MoS$_2$, and most of the absorption in the MoS$_2$ was confined to the base of the AgNPs due to the coupling between the AgNPs with the planar Ag film.\(^{404}\) Because the MoS$_2$ film remained rigid in some regions, sitting on top of several 10s of particles (dark regions in Figure 6.1d), the experimentally-observed extinction enhancement was not maximized (c.f. Figure 6.12a,b). This demonstrates the need to have a fully conformal coating of the MoS$_2$ on the AgNPs in order to achieve the maximum broadening of the active layer absorptance - if the MoS$_2$ is not in close contact with the Ag surface near the base of the AgNPs, the long wavelength absorption will not be maximized. Li et al. have recently demonstrated a method of achieving completely conformal coverage of monolayer MoS$_2$ on a SiO$_2$ nanocone array using capillary-pressure-induced nanoindentation.\(^{26}\)

6.4.4. *Mechanism of enhanced polaron population and steady-state active layer absorption*

Utilizing the demonstrated enhanced absorption and charge photogeneration due to the hybrid P3HT:PCBM/MoS$_2$ heterojunction with the plasmonic metasurface, we outline the combined mechanisms that would lead to enhanced solar cell device efficiencies, which are depicted in Figure 6.13. Upon photoexcitation (Figure 6.13a), both the MoS$_2$ and P3HT absorb
Figure 6.13. Energy level diagrams and photophysical processes for the different components of the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the plasmonic metasurface for two different time scales: a) instantaneously after photoexcitation, \textit{i.e.}, carriers are promoted to the first excited state and the plasmonic modes of the metasurface are excited; b) less than 100 fs after photoexcitation, when charge transfer processes occur. The black circles represent electrons, white circles represent holes; the orange arrow indicates the lowest energy absorption transition in P3HT; the red arrow indicates the lowest energy absorption transition in MoS\textsubscript{2}; the purple arrows indicate the direction of charge transfer. \(E_F\) = Fermi level;\textsuperscript{12} CB = conduction band; VB = valence band;\textsuperscript{13-15} LUMO = lowest unoccupied molecular orbital; HOMO = highest occupied molecular orbital\textsuperscript{23,24}. Note that due to the conformal nature of MoS\textsubscript{2} on the metasurface, the PL emission from MoS\textsubscript{2} shifted by 27 meV relative to planar MoS\textsubscript{2} (Figure 6.14).\textsuperscript{26} This relatively small shift (represented by the width of the grey line for the VB of MoS\textsubscript{2}) does not significantly influence the charge transfer between MoS\textsubscript{2} and P3HT.

light, promoting electrons from their valence band (VB) and highest occupied molecular orbital (HOMO), respectively, to their conduction band (CB) and lowest unoccupied molecular orbital (LUMO), respectively. In the first excited state, the electrons and holes are coulombically bound, forming excitons. At the same time, surface plasmons are excited on the metasurface by a portion of the incident light, increasing the generation of excitons in both MoS\textsubscript{2} and P3HT. Since the CB of MoS\textsubscript{2} lies between the Fermi level \((E_F)\) of Ag and the LUMO of P3HT, MoS\textsubscript{2} is expected to
serve as an efficient electron transport layer. Due to the relatively low work function of Ag, its $E_f$ is pinned close to the CB of MoS$_2$, resulting in a much smaller barrier for electron collection than for hole collection. In addition, based on their staggered energy levels, P3HT and MoS$_2$ form a type-II $p$-$n$ heterojunction, allowing for the efficient transfer of electrons from P3HT to MoS$_2$ and holes from MoS$_2$ to P3HT, forming positive polarons (Figure 6.13b). This was evidenced by the increased $\Delta R/R$ signal at 1000 nm within the time-resolution of our ultrafast measurements ($< 100$ fs). We note that CVD-grown MoS$_2$, which was employed in this study, typically exhibits $n$-type conduction in standard field-effect transistors and in van der Waals heterojunctions, demonstrating its use as an electron transport layer. By contrast, chemically-exfoliated MoS$_2$ exhibits $p$-type conduction, thus demonstrating its use as a hole transport layer.

We observed a shift of 27 meV in the PL from the A-exciton of MoS$_2$ in the presence of the metasurface relative to planar MoS$_2$, likely due to the strain arising from the partial conformation of MoS$_2$ to the metasurface. However, because the difference in the band edges of MoS$_2$ and P3HT is $\sim$1 eV (Figure 6.13), we do not expect the 27 meV shift to significantly influence the charge transfer characteristics.

![Figure 6.14](image.png)

**Figure 6.14.** Microscope-coupled PL spectra from MoS$_2$ with and without the plasmonic metasurface. Spectra were acquired from 10 spots on each sample, and the averaged and normalized spectra are shown.
We note that the results presented in this chapter were based on a 2D-organic van der Waals heterostructure between P3HT:PCBM and monolayer MoS$_2$; however, the charge transfer and enhanced absorption are applicable to other 2D-organic systems, including neat P3HT-MoS$_2$ heterojunctions. In these studies, PCBM served the role of aiding the formation of polarons in the organic blend. Without PCBM, the P3HT polaron population (without MoS$_2$) would have been significantly lower at short time scales, and the exciton population would have been much higher. However, P3HT polarons in P3HT:PCBM blends are known to form at ultrafast time scales (less than 100 fs), giving rise to the larger polaron signals shown in Figure 6.5a. We expect that if the P3HT:PCBM/MoS$_2$ hybrid active layer was employed in a completed device, the device would be a parallel-like solar cell, with a bulk heterojunction interfaced with a bilayer heterojunction.

6.5. Conclusions

In conclusion, we have demonstrated ultrafast hole transfer between an inorganic 2D material, MoS$_2$, and an organic semiconductor blend, P3HT:PCBM. We have observed a six-fold increase in the P3HT polaron transient pump-probe signal in the hybrid P3HT:PCBM/MoS$_2$ heterojunction in the presence of a Ag nanoparticle array plasmonic metasurface, which we have shown was a result of the combined effects of absorption enhancement in both the P3HT:PCBM and MoS$_2$ layers combined with hole transfer from MoS$_2$ to P3HT. The hole transfer from MoS$_2$ was observed at both 400 nm and 800 nm pump wavelengths, demonstrating that hole transfer occurs both within the absorption band of P3HT as well as for sub-bandgap wavelengths. We observed an increase in the active layer absorption bandwidth of 90 nm through reflection measurements and optical simulations for the hybrid P3HT:PCBM/MoS$_2$ active layer in the presence of plasmonic metasurface. Future work includes fabricating full photovoltaic devices employing hybrid 2D-organic heterojunctions, with and without plasmonic metasurfaces to make use of the broadened and enhanced solar spectrum. The enhancements we observed in these hybrid P3HT:PCBM/MoS$_2$ active layers in the presence of the plasmonic metasurface could also
be applied to other thin-film photovoltaic active layers, such as amorphous Si, CdTe, or hybrid organic-inorganic perovskites. In this chapter, we have demonstrated that MoS$_2$ serves as part of the active layer, rather than a passive interfacial layer, when being incorporated into organic photovoltaic multilayers. In Chapter 7, we will investigate the effects that a passive, $p$-type interfacial layer has on the optoelectronic properties of organic active layers with plasmonic metasurfaces.
Chapter 7. Oxidation of Planar and Plasmonic Ag Surfaces by Exposure to O$_2$/Ar Plasma for Organic Optoelectronic Applications

7.1. Abstract

In Chapter 6, we showed that by inserting monolayer-thick MoS$_2$ between a plasmonic metasurface and an organic active layer, the MoS$_2$ contributes to the charge photogeneration process, and the absorption of the combined MoS$_2$-organic active layer was enhanced by the presence of the metasurface. Here, we return to intended goal of designing a plasmonic metasurface with an ultrathin surface layer that modifies the workfunction of the metasurface while impacting the optical properties minimally. As reported in Chapter 2, a native oxide layer (composed of Ag$_2$O) has been shown to increase the workfunction of Ag from 4.3 eV to 5.0 eV,\textsuperscript{32,33,275} giving rise to highly efficient inverted organic photovoltaic devices (Figure 2.9).

Here, we expose planar and plasmonic Ag surfaces to a low-power O$_2$/Ar plasma to form an ultrathin surface oxide layer. We study the chemical state and morphology of the plasma-treated Ag surfaces using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and dark-field microscopy. We find that an ultrathin layer (less than 5 nm thick) composed of both AgO$_x$ and Ag$_2$CO$_3$ forms on the surface of Ag for a plasma exposure time of 1 s by investigating shifts in the Ag3d, O1s, and C1s core level binding energies in the XPS spectra. Additionally, the nanoscale surface structure of the planar and plasmonic Ag surfaces remains unchanged for a plasma exposure time of 1 s. However, the planar Ag surfaces become porous and exhibit increased surface roughness for exposure times of 5 s to 30 s. We demonstrate that the plasma-treated planar and plasmonic Ag surfaces lead to improvements in the excited-state population of a polymer:fullerene coating through ultrafast pump-probe reflectometry.

7.2. Background

Plasmonic surfaces, which are nanostructured metallic films capable of supporting
surface plasmons in the visible regime, have been shown to improve optoelectronic device efficiency by enhancing absorption in or emission from the photoactive layer.\textsuperscript{193,348,420} Silver (Ag) is one of the most suitable metals for electrodes for optoelectronic devices due to its high reflectivity and its ability to support low-loss surface plasmon resonances within the visible regime.\textsuperscript{500,501} However, the electronic workfunction of Ag (\textsim 4.3 eV)\textsuperscript{12} is not ideal for use as the cathode or the anode of optoelectronic devices, which, typically, should either be much lower (less than 3 eV) for cathodes or higher (greater than 5 eV) for anodes.\textsuperscript{501} By forming a thin, native oxide on the surface of Ag, its workfunction can increase to a value close to 5 eV, making oxidized Ag surfaces (AgO\textsubscript{x}/Ag) ideal anodes for inverted optoelectronic devices.\textsuperscript{33,36}

In this chapter, we demonstrate a method to form an ultrathin (less than 5 nm) AgO\textsubscript{x} surface layer on plasmonic Ag surfaces to benefit from the high workfunction of AgO\textsubscript{x} without degrading the optical properties. We show that planar and plasmonic Ag surfaces can form a surface layer of AgO\textsubscript{x} when exposed to an O\textsubscript{2}/Ar plasma for short durations, which we confirm using X-ray photoelectron spectroscopy (XPS). We observe morphological changes of the oxidized films using scanning electron microscopy (SEM) and dark-field microscopy (DFM). Lastly, using pump-probe reflectometry, we demonstrate that both oxidized planar and plasmonic Ag surfaces improve the population of excited-states in a polymer:fullerene coating due to increased scattering from the oxidized surfaces.

7.3. Methods

Planar Ag and plasmonic Ag metasurfaces were prepared as described in Section 4.3.1, with the underlying Ag film thickness being 150 nm in order to be optically-thick. In this study, the Ag nanoparticles had diameters of \textsim 100 nm and heights of either 30 or 60 nm. We used a plasma cleaner (Harrick Plasma, Inc. PDC-32G) to generate the O\textsubscript{2}/Ar plasma to controllably oxidize the Ag surfaces. Ag films were loaded into the plasma chamber individually and were placed in the center of the Pyrex chamber. We used a 20% O\textsubscript{2}, 80% Ar process gas with a gauge
pressure of 5 psig. The flow rate of ~10 mL/min was controlled using a metering valve, and the chamber was evacuated to a pressure less than 1000 mTorr using a dry oxygen pump. The radio frequency (RF) power was set to the lowest setting (i.e., 6.8 W) as higher powers resulted in severe film delamination for even very short process times. We varied the exposure time for the Ag surfaces from 1 s to 30 s to determine the conditions necessary to form an ultrathin (i.e., less than 5 nm thick) oxide layer.

XPS spectra were acquired using a Thermo Fisher Scientific, Inc. K-Alpha System with a monochromated Al K-α X-ray source. The C1s, O1s, and Ag3d5/2 core levels were investigated to determine the oxidation state and composition of the Ag surfaces. DF images were acquired using an Olympus, Inc. BX51 microscope in reflection mode with Xe lamp illumination and a 10× DF microscope objective. For the ultrafast pump-probe measurements, Ag surfaces were coated with a polymer:fullerene blend as described in Section 6.3.3. Pump-probe reflection measurements were obtained as described in Section 6.3.4 using pump and probe wavelengths of 400 nm and 1000 nm, respectively.

7.4. Results and Discussion

7.4.1. X-ray photoelectron spectroscopy

We first varied the O2/Ar plasma exposure time for the planar Ag surfaces to vary the thickness of the oxidized surface layer. We used XPS to determine the composition of the oxidized Ag surfaces (Figure 7.1). The Ag3d5/2 core electrons for the untreated Ag surface (0 s) had a binding energy of 368.3 eV (Figure 7.1a) and displayed the bulk plasmon peak at 371.9 eV (Figure 7.1b), corresponding to Ag in the neutral state (Ag0). Upon exposure to the O2/Ar plasma for 1 s, the Ag3d5/2 peak shifted to a lower binding energy (368.2 eV) and broadened, particularly on the lower binding energy side. Shifts in the Ag3d5/2 peak to lower binding energies have been shown to arise from oxidized Ag (Ag+ or Ag2+) However, for 1 s exposure time, the bulk plasmon peak was still present at 371.9 eV, and the Ag3d5/2 peak shift was small (0.1
This suggests that electrons from both AgOx and Ag were detected, and since XPS is surface sensitive, only detecting electrons from the top ~10 nm of the surface (due to the short inelastic mean free path of electrons\textsuperscript{504}), the AgOx formed was less than 10 nm in thickness. Based on the peak ratio of Ag\textsuperscript{+} to Ag\textsuperscript{0} for the 1 s exposure, the AgOx layer was likely much less than 5 nm in thickness. As the O\textsubscript{2}/Ar plasma exposure time increased, the Ag3d\textsubscript{5/2} peak shifted to lower binding energies, reaching 367.6 eV for an exposure time of 30 s. Additionally, the bulk plasmon peak was no longer observed for exposure times greater than 5 s, suggesting that more than 10 nm of the surface had been oxidized.

To further identify the chemical composition of the formed oxide layer, we also investigated the O1s and C1s core level photoelectron spectra (Figure 7.1c,d). Metal oxides display a relatively sharp peak in the O1s core level spectrum at ~529 eV, distinct from most other oxygen species.\textsuperscript{502,503} We observed the formation of a peak in the O1s core level spectra at 529.2 eV for an exposure time of 1 s, which increased in intensity and shifted to lower binding energies for longer exposure times (shifting to 529.1 eV for an exposure time of 30 s; Figure

\textbf{Figure 7.1}: XPS core level spectra for oxidized planar Ag surfaces: a) Ag3d\textsubscript{5/2} core electrons; b) magnified region of the Ag3d\textsubscript{5/2} plasmon arising from unoxidized Ag; c) O1s core electrons; d) C1s core electrons.
This peak was not present for the untreated Ag film, confirming the formation of an oxidized Ag species. However, we also observed an increase in the intensity of O1s core electrons having higher binding energies (530.5 - 530.8 eV). The larger binding energy peak increased in intensity for an exposure time of 1 s, exhibited a further substantial increase for an exposure time of 5 s, then significantly decreased for an exposure time of 10 s. This peak was not observed for exposure times of 20 or 30 s, or for the untreated film. One possibility for the identity of this peak was silver carbonate (Ag$_2$CO$_3$) which has been reported to have O1s binding energies of 531 eV.\textsuperscript{502,505} This was further supported by the C1s core level spectra, which showed an intense peak at 288.7 eV (Figure 7.1d) for an exposure time of 5 s, which is in agreement with C1s binding energies reported for Ag$_2$CO$_3$ previously.\textsuperscript{502,505} We note that although Ag is known to form silver sulfide (Ag$_2$S) when it tarnishes, we did not observe the presence of S in our XPS spectra for any of the samples.\textsuperscript{506}

Based on the XPS data, we propose that for an O$_2$/Ar plasma exposure time of 1 s, an ultrathin layer (less than 5 nm thick) composed of both Ag$_2$CO$_3$ and AgO$_x$ was formed on the surface of the Ag film. As the exposure time increased to 5 s, the Ag$_2$CO$_3$ species increased relative to the AgO$_x$ species. As the exposure time continued to increase, the AgO$_x$ species continued to form as the Ag$_2$CO$_3$ species diminished. Within 20 - 30 s, the entire surface of the Ag film was fully oxidized.

The bandgap of $p$-type Ag$_2$CO$_3$ has been reported between 2.3 eV and 2.62 eV, with its VB edge between 2.7 eV and 2.8 eV.\textsuperscript{507,508} Because of its low VB edge (and correspondingly low workfunction), Ag$_2$CO$_3$ is expected to reduce the workfunction of the oxidized Ag surface relative to planar Ag. However, since Ag$_2$O has a workfunction of 5 eV, the overall change in workfunction will be determined by the ratio of AgO$_x$ to Ag$_2$CO$_3$. Workfunction measurements of oxidized planar and plasmonic Ag films are a subject of future studies (see Chapter 8). Minimizing the formation of Ag$_2$CO$_3$ while maximizing the formation of AgO$_x$ (in particular Ag$_2$O) are important next steps for improving the electrical properties of oxidized Ag surfaces.
However, since our purpose in these initial studies was to investigate the morphological and optical changes, if any, to planar and plasmonic Ag surfaces with the formation of ultrathin surface oxide layers, we continued our studies using oxidized Ag films with surface layers composed of both AgOₓ and Ag₂CO₃.

7.4.2. Surface morphology

We next investigated the surface morphology of the planar oxidized Ag surfaces (Figure 7.2). When exposed to the O₂/Ar plasma, the color of the Ag films changed (see insets in top left corner of each panel of Figure 7.2). By observing the SEM micrographs, we found that almost no change in the grain structure occurred between an untreated Ag surface and one exposed to the plasma for 1 s (Figure 7.2a,b). However, the DF images revealed an increase in light scattering intensity from the Ag surface exposed to the plasma for 1 s relative to that from the untreated Ag surface (insets in top right corner of Figure 7.2a,b). As the plasma exposure time increased to 5 s, 10 s, and 20 s, the Ag film started to become porous and roughened. These films also showed dramatic increases in light scattering intensity from the surface in the DF images (Figure 7.2c-e, right insets). For an exposure time of 30 s, the porosity of the film increased to a much greater degree, although the scattering intensity was similar to that from the Ag surface exposed for 20 s (Figure 7.2f). We also exposed Ag films to the O₂/Ar plasma without having the Cr adhesion layer, but the films delaminated from the glass severely (data not shown). We suspect that the formation of the pores is a type of plasma-assisted dewetting, similar to the thermally-assisted dewetting method of forming nanoporous Ag films.⁴⁰⁵ Thus, exposing Ag films to an O₂/Ar plasma is a potential method of forming nanoporous AgOₓ/Ag surfaces, potentially for plasmonic applications⁴²⁰ or as platforms for improving the chain alignment in conjugated polymer coatings.⁴⁰⁵
To enable the structure of the AgNPA to be maintained while tuning the electronic workfunction of the surface through controllable oxidation, we sought oxidation conditions that would result in the formation of an ultrathin oxide layer (less than 5 nm) that leaves the surface morphology mostly unchanged. We thus used an exposure time of 1 s for the plasmonic Ag surfaces, which, as shown above, meets both requirements. We exposed plasmonic Ag surfaces composed of nanoparticles having heights of both 30 nm and 60 nm to the O\textsubscript{2}/Ar plasma for 1 s and did not observe a change in the surface morphology of the AgNPA based on SEM micrographs (Figure 7.3). However, there was an increase in the light scattering intensity from the oxidized plasmonic Ag surfaces, which was likely due to the increased refractive index of the dielectric environment of the AgNPA from the AgO\textsubscript{x}/Ag\textsubscript{2}CO\textsubscript{3} layer compared to the untreated plasmonic Ag surfaces (see insets in Figure 7.3). Thus, we have developed a method for fabricating plasmonic Ag surfaces with ultrathin oxide coatings to be employed as high-workfunction, optically-active electrodes for optoelectronic applications. We note that the color difference between the light scattered from the AgNPA with heights of 60 nm (Figure 7.3c,d...
Figure 7.3: SEM micrographs of oxidized plasmonic Ag surfaces exposed to O₂/Ar plasma for either 0 s (untreated; (a) and (c)) or 1 s ((b) and (d)). The height of the nanoparticles on the plasmonic Ag surfaces is indicated in the images. Inset in the top right corner of each panel are DF images of the plasmonic Ag surfaces. All SEM and DF images are on the same respective scales (scale values indicated in (a)). Note that the bright spots observed in the insets are scattering from surface imperfections.

7.4.3. *Two-color pump-probe reflectometry*

To demonstrate the usefulness of the oxidized planar and plasmonic Ag surfaces for organic photovoltaic applications, we conducted two-color pump-probe reflection measurements from a polymer:fullerene blend (P3HT:PCBM) spin-coated onto the oxidized surfaces (Figure 7.4). Pump-probe measurements were conducted by pumping the P3HT:PCBM at 400 nm (generating excited states within the P3HT domains), then probing with a second optical pulse at 1000 nm. This allowed us to investigate the population of excited-state species in the P3HT domains (specifically, both excitons and polarons). A more intense pump-probe signal (ΔR/R) corresponds to a higher population of excited states. For the oxidized planar Ag surfaces, the ΔR/R signal increased with increasing plasma exposure time, reaching a maximum value of 2.3% for an exposure time of 20 s (Figure 7.4a,c). The signal decreased for P3HT:PCBM coated onto the planar Ag surface exposed for 30 s. The ΔR/R signal increases were attributed to increased
Figure 7.4: Transient pump-probe reflection measurements from P3HT:PCBM films coated onto planar (a) and plasmonic (b) Ag surfaces exposed to O₂/Ar plasma for various times. The pump wavelength was 400 nm, and the probe wavelength was 1000 nm (i.e., probing exciton and polaron dynamics in P3HT). (c) Peak ΔR/R signals from P3HT:PCBM coated onto planar and plasmonic Ag surfaces for different O₂/Ar plasma exposure times.

scattering of the pump beam from the oxidized Ag surfaces (see Figure 7.2 insets) relative to the planar Ag surface, resulting in an increase in the generation rate of excited states in P3HT. For P3HT:PCBM coated on the plasmonic Ag surfaces, the ΔR/R signal was more intense for the untreated plasmonic Ag surfaces compared to the untreated planar Ag surface, particularly for the nanoparticles having height of 60 nm (Figure 7.4b,c). This was due to the increased scattering and local electromagnetic field enhancements from the plasmonic Ag surfaces at the pump wavelength; see Figure 7.3 insets and Section 4.4. However, for the oxidized plasmonic Ag surfaces, the ΔR/R signal increased two-fold for the nanoparticles having heights of 30 nm (due to increased scattering, see insets in Figure 7.3a,b) but was relatively unchanged for the nanoparticles having heights of 60 nm. This demonstrates that the presence of the oxide on the plasmonic Ag surfaces does not negatively impact the excited state population enhancements observed in the P3HT:PCBM, and, in fact, can lead to further enhancements.

7.5. Conclusions

We investigated the oxidation of planar and plasmonic Ag surfaces when exposed to an O₂/Ar plasma for various times. Using XPS, we identified the formation of an ultrathin mixed layer of AgOₓ and Ag₂CO₃ within the top 5 nm of planar Ag films when exposed to the plasma.
By varying the exposure time, we controlled the morphology of the oxidized planar Ag surfaces to improve their light scattering properties. We demonstrated that the oxidized planar and plasmonic Ag surfaces led to enhancements in the population of excited states in a polymer:fullerene coating using transient pump-probe reflectometry measurements. Future work will test the effect of the partially-oxidized Ag surfaces on charge collection/injection into organic semiconductors.

Although this was a short study, the results presented in this chapter show great potential for employing oxidized Ag plasmonic metasurfaces in organic photovoltaic devices. In Section 8.2.1 of the future directions, we discuss the preliminary measurements conducted on determining the workfunction of planar and plasmonic Ag electrodes, with and without an ultrathin surface oxide layer, and we then outline the next steps to be taken to incorporate these structures into actual devices in Section 8.3.
Chapter 8. Conclusions, Future Work, and Further Directions

8.1. Conclusions

In Chapter 2, we conducted systematic performance parameter comparisons between conventional and inverted bulk-heterojunction organic photovoltaics, considering a range of different metal electrode types and surface workfunctions. We showed that highly-efficient and stable inverted organic photovoltaics can be achieved through selection of metal electrodes with low parasitic absorption and high workfunction, which was achieved for Ag electrodes with ultrathin AgO_x surface layer. We then designed plasmonic metasurfaces comprised of Ag nanoparticle arrays on Ag films in Chapters 3 and 4, which led to absorption enhancements in absorber coatings of up to 12 % for nanoparticles with large aspect ratios. We demonstrated that the absorber-coated plasmonic metasurfaces supported localized surface plasmon resonances, hybrid surface plasmon polaritons, and a previously unidentified optical mode type called absorption-induced scattering. We identified the physical origin of absorption-induced scattering as electromagnetic coupling of absorber transitions and scattering modes, whether the scattering modes are plasmonic, localized, or collective in origin. We also showed that the crystallinity of the absorber coating determines whether surface plasmon polaritons are trapped (semi-crystalline coatings) or out-coupled (amorphous coatings). In Chapter 5, we further explored the electromagnetic coupling between plasmons and excitons in conjugated polymers, demonstrating that strong coupling is achievable and that absorption-induced scattering is the low energy hybrid mode of plasmon-exciton coupled states. However, excitons are beneficial, but not necessary, for absorption-induced scattering, which was observed generally for any material with absorption bands overlapping scattering modes.

In Chapters 6 and 7, we experimentally investigated the physical, optical, and ultrafast electronic properties of multifunctional plasmonic metasurfaces comprised of Ag metasurfaces with ultrathin interfacial layers. We showed that monolayer MoS_2 can serve as an active
interfacial layer, and we observed ultrafast charge transfer between MoS$_2$ and the conjugated polymer, P3HT. We observed a six-fold increase in the P3HT positive polaron signal and an increase in the bandwidth of the absorption spectrum of the active layer of 90 nm in a P3HT:PCBM/MoS$_2$ heterojunction using a plasmonic metasurface. In Chapter 7, we controllably oxidized Ag planar and plasmonic surfaces to form an ultrathin (less than 5 nm) AgO$_x$ surface layer, which did not impact the optical properties of the Ag plasmonic metasurface. We expect these multifunctional plasmonic metasurfaces can enable improvements in the photocurrent and open-circuit voltage in functional photovoltaic devices through control of both the optical and electronic properties of the metasurfaces.

8.2. Future Work

8.2.1. Workfunction measurements on multifunctional plasmonic metasurfaces

As demonstrated in Chapter 2, the workfunction of metallic electrodes in BHJ-OPVs is a critical parameter for optimizing the $V_{oc}$ of the device. In Chapters 3 - 5, we showed that plasmonic metasurfaces can lead to enhanced absorption in the active layers of BHJ-OPVs through a combination of plasmonic resonances and plasmon-exciton hybridization, which is expected to give rise to an increased $J_{sc}$ in functioning devices. In Chapters 6 and 7, we proposed that application of an ultrathin interfacial layer to plasmonic metasurfaces can lead to enhancements in both the $J_{sc}$ and $V_{oc}$ of BHJ-OPVs through control of both the optical and electrical properties of the metasurface. Specifically, we showed that ultrathin MoS$_2$ and AgO$_x$ have minimal impact on the plasmonic modes supported by Ag plasmonic metasurfaces, but were expected to modify the workfunction of the metasurface. Although measurements of the workfunction of these multifunctional plasmonic metasurfaces were beyond the scope of this thesis, preliminary experiments have been conducted which have laid the foundation for these measurements to be completed.

In investigating the workfunction of multifunctional plasmonic metasurfaces, we wanted
to answer three key questions: 1) Does the workfunction change for a nanostructured metal electrode (relative to a planar metal electrode)?; 2) How does the workfunction change upon addition of a native metal oxide layer?; and 3) How does the workfunction change upon excitation of different plasmonic modes? There are several techniques available to determine the workfunction of materials, including: Ultraviolet photoelectron spectroscopy (UPS); Kelvin probe measurements; and current-voltage ($I-V$) or capacitance-voltage ($C-V$) measurements from Schottky barrier photodiodes, where the material of interest forms a rectifying barrier with a semiconductor having known energy levels. Because we are interested specifically in employing multifunctional plasmonic metasurfaces in conjugated polymer-based optoelectronic devices, we want to specifically investigate the barrier height between the metasurface and a conjugated polymer. The barrier height can be calculated from electrical measurements and, for a metal-$p$-type Schottky barrier interface, is equal to the difference between the workfunction of the metal and the HOMO of the conjugated polymer. As such, our initial investigations involved fabrication of metal-semiconductor-metal photodiodes, where one of the metals formed an ohmic contact with the semiconductor, and the other formed a Schottky barrier. We then began to investigate $I-V$ and $C-V$ measurements of these photodiodes to determine the Schottky barrier height.

The structure of the photodiodes investigated was Au (15 nm) / MoO$_3$ (5 nm) / PCDTBT (80 nm) / Ag (150 nm), where the Au/MoO$_3$ served as the transparent electrode making ohmic contact to the PCDTBT, and the $p$-type Schottky barrier was formed between PCDTBT and Ag. PCDTBT was selected because it has a low-lying HOMO (5.5 eV), enabling its resistance to oxidation and allowing it to easily form Schottky barriers with most metals. The challenges in working with PCDTBT are that it has low solubility in most organic solvents, making it difficult to form uniform thin-films through spin-coating. Use of a low molecular weight ($M_w \sim 10$ kDa to 20 kDa) variant of PCDTBT allowed for greater solubility (solutions of up to 35 g/L were able to be prepared in $o$-dichlorobenzene), allowing uniform films to be prepared up to 200 nm in thickness. We note, however, that while low molecular weight PCDTBT formed the most
uniform neat thin-films, in completed BHJ-OPV devices, in which PC$_{70}$BM is blended with the polymer, higher molecular weight PCDTBT ($M_w$ $\sim$ 35 kDa to $\sim$ 65 kDa) has been shown to be more efficient.$^{509,510}$ Photodiodes were prepared (25 devices/substrate; 0.01 cm$^2$ area/device) using thermal evaporation of Au, MoO$_3$, and Ag and spin-coating of PCDTBT and were measured using a Newport, Corp. solar simulator and HP, Inc. 4140B pA meter in Prof. Manish Chhowalla’s lab. However, short-circuiting of devices was a frequent problem, which was largely overcome by: use of SiO$_2$/Si substrates, cleaned using the RCA cleaning protocol;$^{511}$ filtering low molecular weight PCDTBT solutions once fully solubilized; and spin-coating either thick PCDTBT films ($\sim$ 200 nm) or multiple PCDTBT thin-films (to a thickness of $\sim$ 80 nm) to minimize pinhole formation. Initial barrier heights for the Ag-PCDTBT interface were estimated to be between 0.84 eV and 0.89 eV based on fitting the dark $I$-$V$ to the non-ideal diode equation (Equation 1.1, where the $R_s$ and $R_{shunt}$ have been ignored and a diode ideality factor included in the denominator of the exponent), which is close to the expected value of 1.2 eV. Assuming the HOMO level of PCDTBT is 5.5 eV, we estimate the workfunction of the planar, unoxidized Ag films to be between 4.61 eV and 4.66 eV (expected value: 4.3 eV). However, additional measurements are required to verify the accuracy of these results.

The next steps for this project are to repeat the measurements of the barrier height of Ag-PCDTBT photodiodes with and without the ultrathin AgO$_x$ layer. Determining the barrier height will directly reflect changes in the workfunction of the Ag electrode, since the barrier height is determined by the difference between the workfunction of the metal and the HOMO level of PCDTBT. After determining the change in workfunction upon formation of an ultrathin AgO$_x$ layer, the barrier height measurements will be conducted for Ag plasmonic metasurface - PCDTBT photodiodes, with and without the AgO$_x$ layer. In addition to $I$-$V$ measurements,$^{179,512,513}$ $C$-$V$ measurements will also be conducted to verify the accuracy of the results.$^{15,179,453,512,513}$ Since the $I$-$V$ and $C$-$V$ measurements determine the surface-averaged barrier heights of the metasurface, Kelvin probe microscopy measurements could also be conducted.$^{453,514-517}$ These measurements
could provide insight into the nanoscale changes in the barrier height within the metasurface. Finally, the barrier heights will be measured while specific plasmonic modes of the metasurface-PCDTBT photodiodes are excited. These measurements will give insight into how both the optical and electronic properties of electrodes can be tailored by employing multifunctional plasmonic metasurfaces.

8.2.2. **BHJ-OPV devices incorporating multifunctional plasmonic metasurfaces**

In addition to determining the workfunction of multifunctional plasmonic metasurfaces, the next major direction for this work is to fabricate fully functional BHJ-OPV devices employing these metasurfaces. Initial devices have been fabricated in parallel to the PCDTBT photodiodes, replacing the neat polymer with PCDTBT:PC$_{70}$BM - however, short-circuiting was a major challenge for these devices as well. More device fabrication trials are necessary to determine the cause of the short-circuiting and to prepare working BHJ-OPV devices. The initial set of BHJ-OPV devices to be studied will have the general structure: ZnO / Ag / ZnO / PCDTBT:PC$_{70}$BM / metal electrode, where the ZnO/Ag/ZnO serves as the transparent conductive cathode and the metal electrode serves as the anode. The metal anode will be varied from: Ag; Ag plasmonic metasurface; AgO$_x$; AgO$_x$/Ag plasmonic metasurface. $I$-$V$ measurements, external quantum efficiency, and reflectance measurements will be conducted for each of these device structures to quantify the performance parameters and the influence of the metasurface on the extinction and spectral incident-photon-to-converted-electron efficiencies.

In conjunction, MoS$_2$-organic heterojunction devices will also be fabricated. These device sets will be two-fold: 1) MoO$_3$ / Au / MoO$_3$ / P3HT:PCBM / MoS$_2$ / metal; and 2) MoO$_3$ / Au / MoO$_3$ / P3HT / MoS$_2$ / metal. For these devices, the metal electrode will be either planar Ag or Ag plasmonic metasurfaces. Through these device measurements, we will determine if these MoS$_2$-organic heterojunction devices work more efficiently in series with the BHJ, or if bilayer MoS$_2$-P3HT heterojunctions can also operate efficiently. Here, P3HT will be used as the
conjugated polymer because its HOMO allows for efficient charge transfer with MoS$_2$, and its absorption spectrum sets the AIS peak (655 nm) to overlap with the $A$-exciton in MoS$_2$ (660 nm), giving rise to a strong absorption enhancement. Other higher-efficiency conjugated polymers, such as PCDTBT or PTB7, could also be employed based on their HOMO alignment with the conduction band of MoS$_2$, but they would likely lead to lower absorption enhancement due to their red-shifted AIS peaks (680 nm and 750 nm, respectively; see Table 4.1). However, other 2D transition metal dichalcogenides, such as MoSe$_2$ or WSe$_2$, which have excitonic transitions between 700 nm and 800 nm, could be interfaced with PCDTBT or PTB7 to potentially lead to higher efficiency devices while maximizing the absorption enhancement at the AIS wavelength. These devices will be fabricated using the clean room facilities in Okinawa Institute of Science and Technology, in collaboration with Prof. Keshav Dani’s unit. In addition to $I-V$, external quantum efficiency, and reflectance measurements, in-operando transient pump-probe reflection measurements will be conducted using 400 nm pump excitation and a white light probe, allowing for elucidation of the charge generation and transfer dynamics after energy level alignment occurs, and under dynamic control of the band bending within operational devices. The results from this study will greatly impact the developing field of organic-2D van der Waals heterojunctions, and will be of great use to the organic optoelectronics community in general.

8.3. Further Directions

We have demonstrated that multifunctional plasmonic metasurfaces can lead to enhanced absorption within thin amorphous semiconductors, such as conjugated polymers, and future work in our group will be conducted to verify whether these metasurfaces can lead to direct improvements in the photocurrent and open-circuit voltage, and ultimately the efficiency, of working photovoltaics. However, there are still many unresolved issues in implementing multifunctional plasmonic metasurfaces in large-area, low embodied-energy optoelectronic devices. One such issue returns to the energy payback time (EPBT) of BHJ-OPVs (Figure 1.5),
which was predicted to be as low as 1 day under certain conditions. Several of those conditions include: 15 % device efficiency, elimination of ITO and fullerenes, and solution-processing for all layers of the device. The multifunctional plasmonic metasurfaces were fabricated in this thesis using energy-intensive processes: vacuum deposition (Ag and AgNPA), chemical vapor deposition (MoS$_2$), RF O$_2$/Ar plasma (AgO$_x$). Development of solution-based processing techniques to fabricate these multifunctional plasmonic metasurfaces could help to achieve the EPBT of 1 day for high-efficiency BHJ-OPVs: the plasmonic metasurface can help push the efficiency close to 15 %, and using solution-processing for each of these layers could reduce the embodied energy in resulting devices. Nanoimprint lithography may be a crucial technology for solution-based fabrication of plasmonic metasurfaces.

Throughout Chapters 2 and 3, we made assumptions about the ηIQE of the BHJ-OPV devices studied in this thesis. Additionally, we only computed the $J_{sc}$ for devices employing plasmonic metasurfaces. Full 3D electrical simulations, which solve the drift-diffusion equations using the electrical properties of the materials and the optical generation rate (calculated using 3D FDTD or finite-element method electromagnetic simulations), would be of great benefit to understand the influence both the optical and electrical effects of employing plasmonic metasurfaces in BHJ-OPV devices. We expect that plasmonic metasurfaces will have a significant impact on the $FF$ of devices, since addition of metal to the active layer will likely change the $R_s$ and/or $R_{sh}$. It is currently not clear whether plasmonic metasurfaces will influence the $V_{oc}$: if the workfunction of metal electrodes is changed by addition of nanostructures, then the $V_{oc}$ will subsequently be changed. We expect that the workfunction will likely change upon addition of nanoparticles to metal electrodes, as described in Section 8.2.1. Further parameter optimization of the plasmonic metasurface structures introduced in Chapters 3, 4, and 7 could also be conducted to investigate which geometries giving rise to maximal efficiency enhancement in BHJ-OPV devices. These parameters could include: inter-particle spacing (or period); nanoparticle shape; metal oxide thickness; nanoparticle packing geometry; or use of different
types of plasmonic metasurfaces, such as nanoporous metal films or grating structures.

Parasitic absorption by the metal has been shown throughout this thesis to be detrimental to active layer absorption enhancement. If absorption by the metal nanostructures comprising the multifunctional plasmonic metasurfaces can be utilized, such as in hot carrier generation, then the efficiency enhancements may be able to be even greater. For example, hot hole transfer from a plasmonic metasurface to a conjugated polymer, such as P3HT, could be investigated using time-resolved pump-probe reflectometry. One could envision tuning one of the plasmonic resonances of an absorber-coated plasmonic metasurface system to a wavelength longer than the bandgap wavelength of the polymer (e.g., 800 nm for P3HT/metasurface), then pumping the system at the low-energy plasmonic resonance (e.g., 800 nm) and probing at the polymer’s positive polaron wavelength (e.g., 1000 nm). Because of the ubiquitous plasmon-exciton coupling in these absorber-coated plasmonic metasurface systems, the low-energy mode could lead to absorption enhancements through this hot hole transfer mechanism, whereas the high-energy mode could lead to absorption enhancements directly through enhanced carrier generation within the semiconductor. In addition, although we have exploited the macroscopic plasmonic properties of the AgNPA/Ag metasurfaces in this thesis, we have not considered other optical phenomena often observed in metasurfaces and metamaterials, such as negative refractive index and permeability, phase control, and optical cloaking. For example, metasurface mirrors, which flip the direction of the magnetic field instead of the electric field upon reflection, have been utilized in optoelectronic devices to optimize the standing wave profile (Figure 1.9a) in planar devices to maximize absorption. These properties can be explored in greater detail using multifunctional plasmonic metasurfaces to achieve even greater efficiency enhancements in optoelectronic devices.

Lastly, although this thesis was strongly focused on photovoltaic applications, the designed multifunctional plasmonic metasurfaces can also be employed in light-emitting devices, such as LEDs and lasers. A particularly interesting study would be to investigate the influence of
AIS on light emission, since typically PL and lasing occur at wavelengths red-shifted from the absorption band of the semiconductor, which is a similar wavelength as AIS. Investigating the influence of gain present within a conjugated polymer-coated plasmonic metasurface is also of potential interest. Since materials with gain have opposite trends in their material dispersion (i.e., they undergo normal dispersion in the wavelength regime within the full-width half-maximum of the gain transition and anomalous dispersion in wavelength regimes outside of this), it is expected that gain-induced scattering may occur (similar to AIS), but is likely to be blue-shifted from the gain transition wavelength. Whether gain-induced scattering occurs and how it influences stimulated emission from the conjugated polymer coating are still not known. Strong coupling between plasmons and excitons in conjugated polymers could also lead to nanoscale spasers, which are the surface plasmon analogue to lasers. Coupling surface plasmons to low-energy absorption features in conjugated polymers, such as any of the polaron or polaron-exciton transitions shown in Figure 1.2f,h, or to vibrational modes, could also be interesting from a fundamental physical perspective.
Appendix

A.1. Optical constants of all materials employed in simulations

For all simulations, the wavelength-dependent complex index of refraction ($\tilde{n} = n + ik$) of each material employed was required. The optical constants ($n$ and $k$) or complex relative dielectric permittivity ($\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$) were obtained from various sources and were either used directly or were digitized in OriginLabs.\textsuperscript{519} To convert between $\tilde{n}$ and $\tilde{\varepsilon}$, the following equations were used:

$$
\varepsilon_1 = n^2 - k^2
$$

$$
\varepsilon_2 = 2nk
$$

$$
n = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_i}{2}}
$$

$$
k = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_i}{2}}
$$

In order to simulate the electric field profile using Lumerical FDTD Solutions,\textsuperscript{317,349} the optical constants were fit to a polynomial equation, which was optimized in the software. The digitized literature values or the optical constants were input into the software for the fitting routine. The modeled optical constants were used in all simulations and are shown in Figures A1 - A9. Unless otherwise stated, the optical constants shown in Figures A1 - A9 were used for all optical simulations (FDTD and TMM) throughout the thesis. Whenever glass (SiO$_2$) substrates were employed in optical simulations, their $n$ and $k$ values were fixed at 1.52 and 0, respectively, throughout the visible spectrum.

A.1.1. Metals
Figure A1. Optical constants of noble (low-loss) metals: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were obtained from: Burkardt et al. for Al;\textsuperscript{2} an online Refractive Index database for Au and Cu;\textsuperscript{520} and Lumerical FDTD Solutions (Handbook of Optical Constants, Palik) for Ag.\textsuperscript{317}

Figure A2. Optical constants of lossy metals: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were obtained from: Burkardt et al. for Ca;\textsuperscript{2} an online Refractive Index database for Ni, Pd, and Cr;\textsuperscript{520}
Endriz et al. for Ba\textsuperscript{521} and Machorro et al. for Mg\textsuperscript{522}.

### A.1.2. Organic materials

![Figure A3](image)

**Figure A3.** Optical constants of neat conjugated polymers: (a) real (n) and (b) imaginary (k) parts of the refractive index and (c) real (ε\textsubscript{1}) and imaginary (ε\textsubscript{2}) parts of the relative permittivity. Data were obtained from: Tammer and Monkman for MEH-PPV\textsuperscript{266}, Lin et al. for PCDTBT\textsuperscript{523} the thesis of Bernhauser for PTB7\textsuperscript{524} for P3HT, the optical constants were taken from Morfa et al.\textsuperscript{263} and were averaged over the in-plane and out-of-plane anisotropic optical constants as effects of optical anisotropy were not considered in this thesis. Note that the tail in the ε\textsubscript{2} for P3HT arose from the out-of-plane optical axis; the in-plane ε\textsubscript{2} reported by Morfa et al. had a sharper cut-off at 660 nm.
Figure A4. Optical constants of polymer:fullerene blends: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Monestier et al. for P3HT:PCBM,\textsuperscript{3} Nickel et al. for PCDTBT:PC$_{70}$BM,\textsuperscript{325} and Hedley et al. for PTB7:PC$_{70}$BM.\textsuperscript{526}

Figure A5. Optical constants of neat fullerene derivatives: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Azimi et al. for PCBM,\textsuperscript{527} and Klein et al. for PC$_{70}$BM.\textsuperscript{528}
Figure A6. Optical constants of transparent polymers: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from: Burkhardt et al. for PEDOT:PSS;\textsuperscript{2} and an online Refractive Index database for PMMA.\textsuperscript{520}

A.1.3. Inorganic semiconductors
**Figure A7.** Optical constants of \( p \)-type metal oxide interfacial layers: (a) real \((n)\) and (b) imaginary \((k)\) parts of the refractive index and (c) real \((\varepsilon_1)\) and imaginary \((\varepsilon_2)\) parts of the relative permittivity. Data were taken from: Gao et al. for Ag\(_2\)O;\(^{529}\) an online Refractive Index database for CuO;\(^{520}\) Kumagai et al. for NiO;\(^{530}\) and May et al. for MoO\(_3\).\(^{531}\)

**Figure A8.** Optical constants of \( n \)-type interfacial layers and ITO: (a) real \((n)\) and (b) imaginary \((k)\) parts of the refractive index and (c) real \((\varepsilon_1)\) and imaginary \((\varepsilon_2)\) parts of the relative permittivity. Data were taken from: Burkhardt et al. for ITO;\(^2\) the Handbook of Chemistry and Physics for LiF;\(^{532}\) and Postava et al. for ZnO.\(^{533}\)
Figure A9. Optical constants of monolayer MoS$_2$: (a) real ($n$) and (b) imaginary ($k$) parts of the refractive index and (c) real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the relative permittivity. Data were taken from Liu et al.$^{518}$

A.2. Appendix to Chapter 2

A.2.1. Equivalent circuit parameters

Table A1. Equivalent circuit parameters. Equivalent circuit parameters taken from the literature for similar device structures studied here. The average value was taken for the diode ideality factor.

<table>
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<tr>
<th>Structure</th>
<th>$R_s$ ($\Omega \text{cm}^2$)</th>
<th>$R_{sh}$ ($\Omega \text{cm}^2$)</th>
<th>$n$</th>
<th>Ref</th>
</tr>
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<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:1) /cathode</td>
<td>1.6</td>
<td>1423.79</td>
<td>1.74</td>
<td>Waldauf$^{531}$</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (4:1) /cathode</td>
<td>2.1</td>
<td>2.14</td>
<td>1.79</td>
<td>Schilinsky$^{534}$</td>
</tr>
<tr>
<td>“well-optimized devices”</td>
<td>2.5</td>
<td>1E6</td>
<td>1.72</td>
<td>Waldauf$^{535}$</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:0.6)/LiF/Al</td>
<td>2.87</td>
<td></td>
<td>1.8</td>
<td>Servaites$^{536}$</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:0.6)/Ca/Al</td>
<td></td>
<td></td>
<td></td>
<td>Eo$^{292}$</td>
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<tr>
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<td></td>
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<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:0.6)/Al</td>
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<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:0.6)/Au</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Device Configuration</td>
<td>Efficiency</td>
<td>Fill Factor</td>
<td>Reference</td>
<td></td>
</tr>
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<td>----------------------------------------------------------</td>
<td>------------</td>
<td>-------------</td>
<td>----------------</td>
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</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:0.6)/LiF/Al</td>
<td>4</td>
<td></td>
<td>Hau²⁷¹</td>
<td></td>
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<tr>
<td>ITO/ZnO/P3HT:PCBM (1:1)/MoOx/Al</td>
<td>8.46</td>
<td>4.4E3</td>
<td>Cheng³³⁷</td>
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</tr>
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<td>ITO/ZnO annealed/ P3HT:PCBM (1:1)/MoOx/Al</td>
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<td>7.77E4</td>
<td>Cho³³⁸</td>
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<td>ITO/ZnO/P3HT:PCBM /PEDOT:PSS/Ag</td>
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<td></td>
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<tr>
<td>ITO/ZnO/Rods/ P3HT:PCBM (1:1)/MoO3/ Al</td>
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<td>Reinhard³³⁹</td>
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<tr>
<td>ITO/ZnO / P3HT:PCBM (1:1)/ Ag</td>
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<td>591.7</td>
<td>Wang³⁴⁰</td>
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</tr>
<tr>
<td>ITO/ZnO O2 plasma etch/ P3HT:PCBM (1:1)/ Ag</td>
<td>1.5</td>
<td>731.4</td>
<td>Wang³⁴⁰</td>
<td></td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:1)/ Ca/ Ag</td>
<td>1.75</td>
<td></td>
<td>Schilinsky³²⁶</td>
<td></td>
</tr>
<tr>
<td>ITO/NiO/P3HT:PCBM / LiF/ Al</td>
<td>2.38</td>
<td></td>
<td>Servaites³²⁵</td>
<td></td>
</tr>
<tr>
<td>Average for conventional</td>
<td>4.51</td>
<td>-</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>Average for inverted</td>
<td>5.36</td>
<td>-</td>
<td>1.83</td>
<td></td>
</tr>
</tbody>
</table>
A.2.2. Transfer matrix method

To determine $J_{sc}$ for each OPV device configuration, the electric field must be calculated at each wavelength and on a finite spatial grid throughout the OPV device. When light is incident on the device, it undergoes a series of multiple reflections and transmissions as it propagates through each layer. One method of solving for the electric field throughout a stack of thin films was proposed by Heavens\textsuperscript{7} in 1955 and is called the transfer matrix method (TMM). This method was applied to OPVs first by Pettersson\textsuperscript{4} et al. in 1999 and later refined by Peumans\textsuperscript{5} et al. in 2003. A detailed description of the calculation can be found in their articles, but essentially the Fresnel reflection and transmission coefficients are used in a 2 x 2 matrix, which serves as the interface matrix, and the absorption coefficient and phase shift terms are lumped into a layer matrix. From these matrices, a transfer matrix is determined, and the transfer matrices of the corresponding layers are used to compute the final $\mathbf{E}$-field value. The TMM assumes that the materials are non-magnetic, \textit{i.e.} the relative permeability ($\mu_r$) for each material is 1, and that the materials are all linear, isotropic, and homogeneous. For this work, calculations were carried out in Matlab\textsuperscript{541} using code written by Burkhardt \textit{et al.}\textsuperscript{2}

A.2.3. Comparison of TMM to FDTD calculations

Table A2. Comparison of short circuit current density ($J_{sc}$) values calculated for BHJ-OPV devices containing various metal electrodes for inverted and conventional configurations using the TMM and FDTD methods. In all cases, the $J_{sc}$ obtained from the TMM was larger than that obtained from the FDTD method, although by less than 1\% in each case (calculated as $(\text{Conv} − \text{Inv}) / (\text{Conv} + \text{Inv}) / 2 \times 100\%$). The device configurations for these simulations were: ITO (100 nm)/ PEDOT:PSS (20 nm, conventional) or ZnO (20 nm, inverted)/ P3HT:PCBM (100 nm)/ Metal Oxide (20 nm, where appropriate)/ Metal (200 nm).

<table>
<thead>
<tr>
<th>Metal / Metal Oxide</th>
<th>$J_{sc}$ (mA/cm$^2$), TM</th>
<th>$J_{sc}$ (mA/cm$^2$), FDTD</th>
<th>Percentage Difference ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv.</td>
<td>Inv.</td>
<td>Conv.</td>
</tr>
<tr>
<td>Ag</td>
<td>12.5197</td>
<td>12.1399</td>
<td>12.4917</td>
</tr>
<tr>
<td>Al</td>
<td>12.2264</td>
<td>11.7084</td>
<td>12.1936</td>
</tr>
<tr>
<td>ZnO/Al</td>
<td>11.6768</td>
<td>11.5962</td>
<td>11.6513</td>
</tr>
</tbody>
</table>
The electric field ($E$) profiles were calculated as a function of thickness and wavelength using both TMM and FDTD methods for the planar devices. Using the $E$-field profiles, as well as Eq. (2.14), the $J_{sc}$ was calculated for 8 of the conventional and 8 of the inverted devices based on both methods, and the results are shown in Table A2. Note that for this comparison, 20 nm of metal oxide was used, backed by 180 nm of metal for each of the metal oxide-on-metal devices. From Table A2, it is evident that the most reflective metals (Ag, Al) result in the devices with the highest $J_{sc}$ values (12.14 mA/cm$^2$ and 11.71 mA/cm$^2$, respectively, based on inverted devices using the TMM calculation). The more absorptive and less reflective metals (i.e., the ‘lossier’ metals in the visible part of the spectrum - Cu, Au, and Ca) tended to have lower $J_{sc}$ values (10.58 mA/cm$^2$, 10.51 mA/cm$^2$, and 8.96 mA/cm$^2$, respectively, based on inverted devices using the TMM calculation). These trends held for both conventional and inverted devices, for both the TMM and FDTD methods.

For the devices that had a 20 nm metal oxide film supported by a metal layer, it was expected that the $J_{sc}$ would not vary very significantly from similar devices lacking the metal oxide, since oxides are mostly transparent as thin films. However, there were some notable differences between the $J_{sc}$ values for metal electrodes with and without a metal oxide layer. For ZnO/Al compared with bare Al, the $J_{sc}$ was not drastically different (11.60 mA/cm$^2$ and 11.71 mA/cm$^2$, respectively, based on inverted devices using the TMM calculation), differing by only 0.94 %, although for conventional devices the difference was closer to 4.5 %. However, for Ag$_2$O/Ag compared with bare Ag, the $J_{sc}$ difference was as large as 21.2 % (9.57 mA/cm$^2$ and

<table>
<thead>
<tr>
<th></th>
<th>10.7953</th>
<th>10.5788</th>
<th>10.7229</th>
<th>10.5152</th>
<th>0.6729</th>
<th>0.6030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>10.6978</td>
<td>10.5052</td>
<td>10.6733</td>
<td>10.4819</td>
<td>0.2293</td>
<td>0.2220</td>
</tr>
<tr>
<td>Au</td>
<td>9.1846</td>
<td>9.5689</td>
<td>9.1628</td>
<td>9.5475</td>
<td>0.2376</td>
<td>0.2239</td>
</tr>
<tr>
<td>Ag$_2$O/Ag</td>
<td>7.7507</td>
<td>8.0039</td>
<td>7.7023</td>
<td>7.9559</td>
<td>0.6264</td>
<td>0.6015</td>
</tr>
</tbody>
</table>
12.1399 mA/cm², respectively) for inverted devices based on the TMM calculation, and for CuO/Cu compared with bare Cu, the difference was as high as 24.3 % (8.00 mA/cm² and 10.58 mA/cm², respectively) for inverted devices based on the TMM calculation. In these cases, the metal oxide is acting as an optical spacer, serving to alter the interference patterns of the electric field. Here, given the chosen thickness, the optical spacers degrade the $J_{sc}$ of the devices; however, thickness optimizations could be performed in order for the optical spacers to improve the overall $J_{sc}$ relative to the bare metal devices.$^{180}$

In the final two columns of Table A2, percentage differences were calculated between the TMM and FDTD calculation methods for each of the 16 devices; this shows that the numerical results agree well with the analytical methods as all of the results agree within 1 %. For this comparison, a mesh step size in the $z$ - direction of 0.1 nm for both TMM and FDTD methods was required to obtain convergence between the 2 methods to within 1 %. This confirms the accuracy of the numerical FDTD method, but also highlights the strict requirements for the mesh step size to achieve accurate convergence between numerical and analytical results. For the simulations reported in Figure 2.5, a $dz$ step size of 0.9 nm was used; in this case, the planar, FDTD simulations agree within 6 % of the planar, TMM simulations. This step size was chosen based on the computational resources available; a smaller step size results with more accurate simulations, but is very computationally intensive when incorporating various nanophotonic structures. To further compare the similarities between the TMM and FDTD methods, fractional absorption spectra were generated for each of the different devices in the active layer (for the $dz$ stepsize of 0.1 nm) which are shown in Figure A10 for conventional (a, c) and inverted (b, d) configurations. The similarities between the absorption spectra calculated using the TMM and those calculated using the FDTD methods further confirms the accuracy of the FDTD simulations conducted for structures employing metallic nanostructures (Chapters 3-6).
Figure A10. Comparison of theoretical absorption spectra calculated using TMM (a,b) and FDTD (c,d) methods. Calculated fractional absorption spectra in the active layer for (a,c) conventional and (b,d) inverted device configurations for various electrode materials. FDTD method was performed using Lumerical FDTD Solutions. Devices studied here had a \(dz\) stepsize of 0.1 nm in order to achieve < 1 % difference between TMM and FDTD methods.

A.2.4. Correcting for substrate effects

This is the most accurate way of correcting for the multiple reflections that occur due to the glass because adding in a thin enough glass layer to the FDTD simulation and setting the background index to 1 would produce different optical interference effects within the thin glass layer than what would be expected from a thick glass substrate.

Table A3. Substrate (glass) correction methods. The TMM, which corrects for the glass substrate in the calculation, is compared to the FDTD method using different procedures to correct for substrate effects. The first procedure does not include glass at all, and uses a background index, \(n_0\), of air (1.0). The second procedure uses \(n_0 = 1.52\) (that of glass), such that reflections at the air-
glass interface are ignored. The third procedure uses $n_0 = 1.52$, but includes a TM calculation of the identical device setup. The transmission coefficient through the glass-ITO interface is multiplied by the electric field intensity throughout the device in a similar way to how the TM method is computed.\textsuperscript{4,5} The fourth procedure uses an average value of this transmission coefficient, 0.8, which is averaged across the visible spectrum. The fifth procedure includes addition of a thin glass layer in the FDTD simulation, using $n_0 = 1.0$. In each simulation, the device structure was ITO (100 nm)/ PEDOT:PSS (20 nm)/ P3HT:PCBM (1:1, thickness indicated by $t_{AL}$/ Metal cathode (200 nm). $d\lambda$ represents the wavelength spacing used in the simulations. The correction procedures were compared for varying metal electrode, $t_{AL}$, addition of an electron transport layer ($ETL$) between the P3HT:PCBM and metal layers (thickness $t_{ETL}$), and $d\lambda$. For each simulation, the correction procedure most closely matching the TM method is shown in bold. The blue highlighted cells indicate the control in each comparison (Al cathode, $t_{AL} = 100$ nm, $d\lambda = 10$ nm, no ETL).

<table>
<thead>
<tr>
<th>Metal</th>
<th>TM Method (corrected for glass)</th>
<th>$n_0 = 1.0$</th>
<th>$n_0 = 1.52$, no correction</th>
<th>$n_0 = 1.52$, TM correction</th>
<th>$n_0 = 1.52$, ave T correction $\sim 0.8$</th>
<th>$n_0 = 1.0$, thin glass layer 100 (500) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$t_{AL} = 10$ nm, $t_{AL} = 100$ nm</td>
<td>11.7098</td>
<td>11.3416</td>
<td>18.3489</td>
<td>11.6618</td>
<td>11.7433</td>
</tr>
<tr>
<td>Ni</td>
<td>10.0829</td>
<td>9.6534</td>
<td>15.8592</td>
<td>10.0334</td>
<td>10.1499</td>
<td>10.2129</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$t_{AL}$ (nm)</th>
<th>$t_{AL} = 10$ nm, $t_{AL} = 100$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>8.486</td>
</tr>
<tr>
<td>150</td>
<td>11.0716</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ETL</th>
<th>Al cathode, $d\lambda = 10$ nm, $t_{AL} = 100$ nm, $t_{ETL} = 2$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>12.0766</td>
</tr>
<tr>
<td>ZnO</td>
<td>12.0652</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$d\lambda$</th>
<th>Al cathode, $t_{AL} = 100$ nm</th>
</tr>
</thead>
</table>
### A.2.5. Performance parameter data

Tables A4-A7. The following tables show the numerical results of the $J_{sc}$, $V_{oc}$, $FF$, and $\eta_p$ calculations for conventional and inverted devices having $S$-parameters of 1.0 and 0.1 for each metal electrode studied.


<table>
<thead>
<tr>
<th>$\phi$ (eV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$\rho_{sc}$</th>
<th>$r_s$</th>
<th>$r_{sh}$</th>
<th>$FF$</th>
<th>$\eta_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF/Al</td>
<td>2.6</td>
<td>14.0573</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.09</td>
<td>0.69</td>
</tr>
<tr>
<td>Ba/Al</td>
<td>2.7</td>
<td>13.4913</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.09</td>
<td>0.69</td>
</tr>
<tr>
<td>Ca/Al</td>
<td>2.87</td>
<td>13.0284</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.08</td>
<td>0.70</td>
</tr>
<tr>
<td>Mg/Ag</td>
<td>3.66</td>
<td>12.4752</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.08</td>
<td>0.70</td>
</tr>
<tr>
<td>ZnO/Al</td>
<td>4.0</td>
<td>14.0539</td>
<td>0.6</td>
<td>12.6713</td>
<td>0.74</td>
<td>0.11</td>
<td>0.65</td>
</tr>
<tr>
<td>Ag</td>
<td>4.26</td>
<td>14.1275</td>
<td>0.44</td>
<td>9.2923</td>
<td>0.68</td>
<td>0.14</td>
<td>0.57</td>
</tr>
<tr>
<td>Al</td>
<td>4.28</td>
<td>14.0706</td>
<td>0.42</td>
<td>8.8699</td>
<td>0.67</td>
<td>0.15</td>
<td>0.56</td>
</tr>
<tr>
<td>Cu</td>
<td>4.65</td>
<td>13.6302</td>
<td>0.05</td>
<td>1.0559</td>
<td>1.23</td>
<td>0.20</td>
<td>0.13</td>
</tr>
<tr>
<td>AgO/Ag</td>
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<td>14.0645</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>5</td>
<td>13.0355</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>Au</td>
<td>5.1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuO/Cu</td>
<td>5.3</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MoO3/Al</td>
<td>5.35</td>
<td>14.0513</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>

#### Table A5. Performance Parameter Data. Conventional, $S_e = 0.1$.

<table>
<thead>
<tr>
<th>$\phi$ (eV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$\rho_{sc}$</th>
<th>$r_s$</th>
<th>$r_{sh}$</th>
<th>$FF$</th>
<th>$\eta_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF/Al</td>
<td>2.6</td>
<td>14.0573</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.09</td>
<td>0.69</td>
</tr>
<tr>
<td>Ba/Al</td>
<td>2.7</td>
<td>13.4913</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.09</td>
<td>0.69</td>
</tr>
<tr>
<td>Ca/Al</td>
<td>2.87</td>
<td>13.0284</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.08</td>
<td>0.70</td>
</tr>
<tr>
<td>Mg/Ag</td>
<td>3.66</td>
<td>12.4752</td>
<td>0.7</td>
<td>14.7831</td>
<td>0.76</td>
<td>0.08</td>
<td>0.70</td>
</tr>
<tr>
<td>ZnO/Al</td>
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<td>0.6</td>
<td>12.6713</td>
<td>0.74</td>
<td>0.11</td>
<td>0.65</td>
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<tr>
<td>Ag</td>
<td>4.26</td>
<td>14.1275</td>
<td>0.44</td>
<td>9.2923</td>
<td>0.68</td>
<td>0.14</td>
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<td>Al</td>
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<td>8.8699</td>
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</tr>
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<td>Cu</td>
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<td>NiO/Ni</td>
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<td>MoO3/Al</td>
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<td>14.0513</td>
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<table>
<thead>
<tr>
<th>φ (eV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$\eta_p$ (%)</th>
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<tr>
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<td>2.6 14.1771</td>
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</tr>
<tr>
<td>Ba/Al</td>
<td>2.7 13.6524</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
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<td>2.87 13.2113</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Mg/Ag</td>
<td>3.66 12.6602</td>
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<td>0 0 0 0 0</td>
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<td>ZnO/Al</td>
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<td>0 0 0 0 0</td>
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<td>Ag</td>
<td>4.26 14.2625</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Al</td>
<td>4.28 14.1875</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Cu</td>
<td>4.65 13.7774 0.35 7.3916 0.63 0.21 0.49 39364.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$O/Ag</td>
<td>5 14.2090 0.7 14.7831 0.76 0.11 0.67 20928.57</td>
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<td></td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>5 13.2039 0.7 14.7831 0.76 0.10 0.68 18862.71</td>
<td></td>
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</tr>
<tr>
<td>Au</td>
<td>5.1 13.8289 0.7 14.7831 0.76 0.10 0.68 19755.57</td>
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<tr>
<td>Pd</td>
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<tr>
<td>CuO/Cu</td>
<td>5.3 13.6832 0.7 14.7831 0.76 0.10 0.68 19755.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoO$_3$/Al</td>
<td>5.35 14.1717 0.7 14.7831 0.76 0.10 0.68 20245.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A7. Performance Parameter Data. Inverted, $S_e = 0.1$.

<table>
<thead>
<tr>
<th>φ (eV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$\eta_p$ (%)</th>
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</thead>
<tbody>
<tr>
<td>LiF/Al</td>
<td>2.6 14.1771</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Ba/Al</td>
<td>2.7 13.6524</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Ca/Al</td>
<td>2.87 13.2113</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Mg/Ag</td>
<td>3.66 12.6602</td>
<td>0</td>
<td>0 0 0 0 0</td>
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<tr>
<td>ZnO/Al</td>
<td>4.0 14.0857</td>
<td>0</td>
<td>0 0 0 0 0</td>
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<td>Ag</td>
<td>4.26 14.2625</td>
<td>0</td>
<td>0 0 0 0 0</td>
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<tr>
<td>Al</td>
<td>4.28 14.1875</td>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>Cu</td>
<td>4.65 13.7774 0.665 14.0440 0.75 0.11 0.66 20717.89</td>
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<td></td>
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<tr>
<td>Ag$_2$O/Ag</td>
<td>5 14.2090 0.7 14.7831 0.76 0.11 0.67 20928.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>5 13.2039 0.7 14.7831 0.76 0.10 0.68 18862.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>5.1 13.8289 0.7 14.7831 0.76 0.10 0.68 19755.57</td>
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<td>Pd</td>
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<td></td>
</tr>
<tr>
<td>MoO$_3$/Al</td>
<td>5.35 14.1717 0.7 14.7831 0.76 0.10 0.68 20245.29</td>
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A.2.6. Performance parameter comparison to literature values

Table A8. Performance parameters from literature. Performance parameters for BHJ-OPV devices reported in the literature for varying metal electrodes.

<table>
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<tr>
<th>Metal Electrode</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta_p$ (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PEDOT:PSS (35 nm)/ P3HT:PCBM 1:0.6 (220 nm)/ cathode</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>LiF (0.8 nm)/ Al</td>
<td>9.74</td>
<td>0.6</td>
<td>0.61</td>
<td>3.54</td>
<td>Eo$^{292}$</td>
</tr>
<tr>
<td>Ca (30 nm)/ Al</td>
<td>8.21</td>
<td>0.37</td>
<td>0.52</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>Mg (30 nm)/ Al</td>
<td>9.17</td>
<td>0.4</td>
<td>0.51</td>
<td>1.85</td>
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<tr>
<td>Al</td>
<td>9.27</td>
<td>0.52</td>
<td>0.53</td>
<td>2.54</td>
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<tr>
<td>Au</td>
<td>8.28</td>
<td>0.26</td>
<td>0.44</td>
<td>0.94</td>
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</tr>
<tr>
<td>ITO/PEDOT:PSS (30 nm)/ P3HT:PCBM 1:1 (270 nm)/ cathode; S ~ 0.1</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>9.04</td>
<td>0.403</td>
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<td>1.33</td>
<td>Reese$^{293}$</td>
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<td>Al</td>
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<td>0.42</td>
<td>0.382</td>
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<td>Mg:Ag (20 nm)/ Ag</td>
<td>10.3</td>
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<td>0.505</td>
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<td>LiF (0.6 nm)/ Al</td>
<td>10.42</td>
<td>0.58</td>
<td>0.573</td>
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<td>0.601</td>
<td>0.606</td>
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<td>Ba (20 nm)/ Al</td>
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<td>0.6</td>
<td>0.622</td>
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<tr>
<td>ITO/PEDOT:PSS (2 nm)/ MDMO-PPV:PCBM 1:1 (? nm)/ cathode; S ~ 0.1</td>
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</tr>
<tr>
<td>LiF (1 nm)/ Al</td>
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<td>0.47</td>
<td>0.2</td>
<td>Mihailetchi$^3$</td>
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<tr>
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<tr>
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<tr>
<td>Pd</td>
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<td>ITO/ZnONPs (50 nm)/ P3HT:PCBM (? nm)/ anode; S ~ 0.6</td>
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<tr>
<td>Pd</td>
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<tr>
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<td>negl.</td>
<td>negl.</td>
<td>negl.</td>
<td></td>
</tr>
<tr>
<td>ITO/ZnONPs (50 nm)/ P3HT:PCBM (? nm)/ PEDOT:PSS/ anode; S = 0</td>
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<td></td>
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<tr>
<td>Pd</td>
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<td>0.619</td>
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<td>Hau$^{298}$</td>
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<td>0.617</td>
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<tr>
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<td>0.616</td>
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<tr>
<td>Ag</td>
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<tr>
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<td>0.462</td>
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</tbody>
</table>
A.3. Appendix to Chapter 4

A.3.1. Additional data from period-dependent scattered-light simulations

Figure A11. Simulations for varying AgNPA period. Scattered-light simulations for varying AgNPA period for: AgNPA/Ag (a-c) with various coatings; AgNPA/glass with (f) and without (d) a P3HT coating; and glass NPA/glass with a P3HT coating (e). Spectra from (a,b,c,e) are the same data used for Figure 4.19 of the main text, except they have not been normalized or plotted as 2D contour plots.
Figure A12. $E_x$ and $E_z$ electric field amplitude profiles for the four modes described in Fig. 3 of the main text for five different periods, $\Lambda$, and for single AgNPs, with a dielectric coating having $n = 2.0$. The spectra and mode types are labeled in the top right panel.

Figure 4.19 showed the dependence of the simulated scattered-light spectra on array period for AgNPA/Ag metasurfaces with P3HT, PMMA, and no coating, as well as for the P3HT/glass NPA/glass case. The spectra were intensity-normalized to the LSPR peak to highlight the differences in peak position for the dispersive modes; Appendix Figure A11 shows the non-normalized spectra for each of these structures, in addition to bare and P3HT-coated AgNPA/glass. For all cases with P3HT present (Appendix Figure A11c,e,f), the AIS peak was
observed. The scattering intensity was, in general, much more intense for the AgNPA/Ag metasurfaces, with or without coatings, compared to the AgNPA/glass or glassNPA/glass surfaces.

Examination of the electric field amplitude profiles (Appendix Figure A12) for various array periods helped to identify the mode types. In particular, for Mode I and Mode IV, for a period of 120 nm, the $E_x$ fields showed that Mode I had more inter-particle coupling between the LSPRs of adjacent AgNPs compared with Mode IV, in which the LSPRs were more localized to individual AgNPs. As the period increased, Mode I started to resemble Mode IV more so, until by a period of 300 nm, Modes I and IV became degenerate. The single NP field profiles looked similar to the Mode IV field profiles and identical to the Mode I field profiles for a period of 300 nm, thus by 300 nm, the LSPRs of the particles were no longer coupled to one another.

A.3.2. Additional SPP field profiles
Figure A13. Field profiles for surface plasmon polariton simulations. (a) Schematic of back-scattered simulation setup, showing location of the back-scattered monitor (green dashed line). (b) Schematic of transmitted SPP simulation setup, showing location of the vertical monitor (green dashed line). Spectral in-plane ($|E_x|$) and out-of-plane ($|E_z|$) electric field magnitudes through (c-h) the back-scattered monitor and (i-n) the vertical monitor for: (c,d,i,j) P3HT:PCBM; (e,f,k,l) PTB7:PC$_{70}$BM; and (g,h,m,n) PMMA coatings.
Figure A14. Surface plasmon polaritons in the scattered field. Surface plasmon polariton (SPP) mode for P3HT/AgNPA/Ag (at 767 nm). The box in the center of each image contains the total field amplitude, and outside of that box is the scattered field amplitude. These simulations included only a cluster of AgNPs (7, in a hexagonal packing arrangement) which coupled light into the propagating SPP at the Ag-P3HT interface. (a) charge distribution; (b) $H_y$; (c) $E_x$; (d) $E_z$.

Appendix Figure A13a,b shows schematics of the two different types of field profiles
being compared in Fig.5b-d of the main text and Appendix Figure A13c-n: the back-scattered simulations (Appendix Figure A13a) and the transmission through the vertical monitors (Appendix Figure A13b), where the scattered light was collected through the polymer and metal films and just above the sample surface in the y-z plane. From the spectrally-resolved back-scattered electric field profiles (Appendix Figure A13c-h), it was observed that the LSPR peaks (~350 - 500 nm) in the back-scattered monitor were dominated by the in-plane ($E_x$) component of the electric fields, which was expected for a transverse LSPR. The two components of the long wavelength peak (plasmon-AIS at the absorption edge and SPPs at longer wavelengths) were observed to each be dominated by different field components: the plasmon-AIS peaks (650 nm for P3HT:PCBM, Appendix Figure A13c; 730 nm for PTB7:PC$_{70}$BM, Appendix Figure A13e) were dominated by the $E_x$ component, and the SPP modes were relatively broadband and dominated by the out-of-plane ($E_z$) component (Appendix Figure A13d,f,h). Note that for PMMA, the plasmon-AIS component was not observed due to lack of an absorption edge within the spectral range, and the broadband $E_z$ component had an onset overlapping the LSPR peaks of the AgNPA/Ag.

The spectrally-resolved vertically-oriented electric field profiles (Appendix Figure A13i-n) gave further support for understanding the two components of the long wavelength mode. For the plasmon-AIS peak (Appendix Figure A13i,k), the fields were located away from the Ag-polymer interface, and were localized closer to the polymer-air interface. The fields of the SPP modes (Appendix Figure A13j,l), i.e., the $E_z$ component, were confined tightly to the Ag-polymer interface, although the fields leaked out of the polymer, especially at the longest wavelengths. Since the LSPR peak was observed for the PMMA coating (Appendix Figure A13m) but not for the P3HT:PCBM or PTB7:PC$_{70}$BM coatings (Appendix Figure A13i,k), it was expected that the LSPR was absorbed by the conjugated polymer:fullerene films efficiently. The same was expected for the SPP modes: the PMMA-coated AgNPA/Ag vertical monitor showed that the broadband SPPs were detected 100 nm away from the AgNPs in the plane of the PMMA-Ag.
interface (see Figure 4.6 for GUI image of setup), suggesting that the same modes were supported by the conjugated polymer:fullerene coatings, but wavelengths within the absorption bands of the coatings were absorbed.

Furthermore, the scattered fields observed outside of the TFSF source (see Figure 4.6 for GUI image of setup) for P3HT/AgNP cluster/Ag at 767 nm showed propagating SPP behavior (Appendix Figure A14). Charge density oscillations were observed on the surfaces of the Ag film \((z = 0 \text{ and } z = -50 \text{ nm})\) with \(x\)- and \(z\)- polarized electric fields and \(y\)-polarized magnetic fields, which are requirements for SPPs. Thus, at these long wavelengths, the AgNPs acted as near-field in-couplers of the SPPs on the coating-Ag interface (with the near-field excitation having fields shown in Figure 4.22e). Experimentally, the SPPs could have occurred in regions between patches of AgNPs and could have been out-coupled for the amorphous organic coatings by surface roughness in the Ag or coating films, or grain boundaries.

**A.3.3. Full spectra for angle-dependent scattered-light spectra**
Figure A15. Angle-dependent scattered-light spectra. Angle-dependent scattered-light spectra for all substrates coated with: (a) P3HT; (b) PCDTBT; (c) PTB7; (d) PMMA; (e) P3HT:PCBM; (f) PCDTBT:PC$_{70}$BM; (g) PTB7:PC$_{70}$BM; (h) nothing (bare substrates). The numerical aperture increased with increasing objective magnification, thus changing the angle of incidence and extending the collection cone of scattered light (see Methods).

A.3.4. GIWAXS and GISAXS from absorber-coated plasmonic metasurfaces
Figure A16. 2D GIWAXS profiles for all coatings and substrates used in this study. Note that all measurements were acquired using the same incident angle and acquisition time (see Methods).

2D GIWAXS profiles are shown in Appendix Figure A16 for the polymer and polymer:fullerene blends coated on glass, planar Ag, and AgNPA/Ag substrates, where each of the dominant scattering peaks are labeled. For neat P3HT, the (100) and higher order reflections had mostly out-of-plane ($q_z$) character, while the (010) reflection had a slight preference for the in-plane ($q_r$) direction, although it was largely isotropic. This is typical for P3HT films spin-coated from chlorobenzene solutions\textsuperscript{113,114,357,542} and indicates that P3HT took a mostly edge-on molecular orientation. The isotropic (111) and (200) reflections from the underlying Ag film and the embedded AgNPs were also evident in the 2D profiles ($q \sim 2.68$ Å\textsuperscript{-1} and 3.10 Å\textsuperscript{-1}, respectively) for the Ag and AgNPA/Ag substrates. For P3HT:PCBM, there was a reduction in the spread of the (100) and higher order peaks in the $q_r$ direction, indicating that the P3HT
molecules in the blend were preferentially oriented in the edge-on configuration, although the overall intensity of the peaks was lower compared to the neat P3HT film. The presence of the isotropic PCBM reflection at $\sim 1.4 \, \text{Å}^{-1}$ indicates that the P3HT and PCBM were well-mixed.$^{543}$

For neat PCDTBT, an almost completely amorphous polymer, the scattering peaks were very low in intensity, although the (100) and (010) reflections were still observed. In the PCDTBT:PC$_{70}$BM blend, the reflections from PCDTBT were not readily apparent, although the isotropic PC$_{70}$BM reflections were still observed. A similar trend was observed for neat PTB7 and PTB7:PC$_{70}$BM, although the (100) and (010) reflections observed for PTB7 were stronger than those observed for PCDTBT. The (010) reflection for PTB7 had a strong out-of-plane component, suggesting that the $\pi-\pi$ stacking direction favored the out-of-plane direction and that the PTB7 molecules took a face-on orientation as others have reported.$^{270,544}$

As evidenced from Appendix Figure A16, there was no dramatic change in the alignment of polymer molecules between varying substrates (i.e., P3HT remained edge-on, PTB7 remained face-on between the 3 substrates). From the 2D plots, it was observed that there was very little change between the glass and planar Ag substrates for each of the coatings, except for the presence of the Ag (111) and (200) isotropic rings for the Ag substrates. The polymer peaks were all less intense for the neat polymer coatings in the presence of the AgNPA/Ag substrates, as described in the main text and the subsequent section.
Figure A17. 2D GISAXS profiles for all coatings and substrates used in this study which were useful for ensuring the AgNPA was being probed by the X-rays in the GIWAXS measurements (Appendix Figure A16). Note that all measurements were acquired using the same incident angle and acquisition time (see Methods).

Although complete analysis of the grazing-incidence small-angle X-ray scattering (GISAXS) measurements is beyond the scope of this work, the GISAXS data was still very useful for ensuring the AgNPA was being probed by the X-rays in the GIWAXS measurements (Appendix Figure A17). Since the alignment for the samples only needed to be done once for each individual GIWAXS/GISAXS measurement, confirmation of the AgNPA in the GISAXS data ensured that the AgNPA regions were probed in the GIWAXS data. The presence of the AgNPA was evidenced for all coated metasurfaces by the wide spread in the $q_r$ direction for the AgNPA/Ag substrates relative to the Ag or glass substrates.
Figure A18. Grazing-incidence wide-angle X-ray scattering line scans. 1D GIWAXS line scans extracted from the 2D data for the in-plane (q_r) direction (extracted at q_z = 0; top row for each panel) and the out-of-plane (q_z) direction (extracted at q_r = 0; bottom row for each panel) for: (a) P3HT; (b) PCDTBT; (c) PTB7; (d) P3HT:PCBM; (e) PCDTBT:PC_{70}BM; (f) PTB7:PC_{70}BM. Note that the arrows in each scattering profile represent the observed peaks: green - (100); violet - (010); orange - Ag (111); pink - PCBM. Three different plots were used for three different q ranges to allow different intensity scales to be used so that the prominent peak(s) in that q range could be clearly displayed.

Line scans were taken from the 2D GIWAXS profiles (Appendix Figure A16) for all coatings and substrates in both the in-plane (q_r) and out-of-plane (q_z) directions (Appendix Figure A18). The higher intensity of the metal peaks for the AgNPA/Ag metasurfaces compared to the planar Ag substrates gave further support that the X-rays were probing regions with the AgNPAs. It was observed that for P3HT, the (100) and (010) in- and out-of-plane peaks were all lower in intensity for the AgNPA/Ag metasurface compared to the planar substrates (Appendix Figure A18a); for PCDTBT, the (100) in-plane and (010) in- and out-of-plane peaks were lower in
Intensity for the AgNPA/Ag metasurface compared to the planar substrates (Appendix Figure A18b); and for PTB7, the (100) in-plane and (010) out-of-plane peaks were lower in intensity for the AgNPA/Ag metasurface compared to the planar substrates (Appendix Figure A18c). This suggests, as described in the main text, that the AgNPAs reduced the crystallinity of the neat polymers.

For P3HT:PCBM, although the P3HT (100) out-of-plane peak was larger in intensity, the P3HT (100) and (010) in-plane peaks were less intense for the AgNPA/Ag metasurface compared with the planar substrates (Appendix Figure A18d). This suggests that for P3HT:PCBM, the P3HT molecules became more oriented in the edge-on direction (i.e., a greater edge-on to face-on ratio) for the AgNPA/Ag metasurface compared with the planar substrates. For PCDTBT:PC$_{70}$BM, no polymer scattering peaks were observed (Appendix Figure A18e). For PTB7:PC$_{70}$BM, the PTB7 (100) in-plane and (010) out-of-plane peaks were more intense for the AgNPA/Ag metasurface compared to the planar substrates, suggesting an overall increase in the crystallinity of the PTB7 in the blend in the presence of the AgNPA (Appendix Figure A18f).
**Figure A19.** Intensity of out-of-plane (100) peak for P3HT on various substrates for the raw data ($I_{100}$) and normalized to account for the volume of P3HT present in the region probed ($I_{100}^{\text{norm}}$).

Since the intensity of all of the polymer scattering peaks were reduced for the neat polymers coated on the AgNPA/Ag metasurfaces, we wanted to verify that this was indeed a reduction in the crystallinity of the polymers and was not an effect of probing a smaller volume of polymer due to the presence of the AgNPs. For this type of polymer-metal composite, we normalized the intensity of the (100) out-of-plane peak for each substrate type for P3HT (as a test) to the volume of polymer probed in the region. This was done using the following equation:

$$\% \text{ polymer crystals} = \frac{A_{100}}{A_{100} + A_{\text{metal}}}$$

where $A_{100}$ was the area of the P3HT (100) peak and $A_{\text{metal}}$ was the area of the Ag (111) peak. The volume percent of polymer crystals ($\% \text{ polymer crystals}$) in the region probed was then used to normalize the intensity of the P3HT (100) peak ($I_{100}$) to obtain $I_{100}^{\text{norm}}$:

$$I_{100}^{\text{norm}} = \frac{I_{100}}{\% \text{ polymer crystals}}.$$

Appendix Figure A19 shows all of these parameters, and the normalized P3HT (100) peaks. As observed from Appendix Figure A19a, normalizing the (100) peak to the volume of polymer in the probed region still cannot account for the decrease in the intensity of the (100) peak in the presence of the AgNPA/Ag metasurface; thus, it was still concluded that the AgNPA reduced the crystallinity of the neat conjugated polymers.

**A.3.5. Additional absorption simulations for coated AgNPA/Ag metasurfaces**
Figure A20. Simulated absorptance enhancement factors. Simulated absorptance enhancement factors (solid lines) in (a) the coating layer and (b) the AgNPA/Ag metasurface for the polymer:fullerene coatings on AgNPA/Ag relative to polymer:fullerene-coated planar Ag substrates. Note that for the equivalent-volume planar simulations, the polymer:fullerene film thickness was 67.9 nm, whereas for the equivalent-thickness planar and AgNPA/Ag simulations, the polymer:fullerene film thickness was 80 nm. The simulated scattered-light spectra are overlaid for the coated AgNPA/Ag metasurfaces (dashed lines).

For the planar Ag reference simulations, we have conducted both equivalent thickness and equivalent volume comparisons, where either the thickness or the total volume of the coating were fixed between the planar Ag and AgNPA/Ag simulations. For the equivalent thickness simulations, the coating thickness was fixed at 80 nm. For the equivalent volume simulations, the volume of the coating on the AgNPA was first determined by calculating the total volume of one unit cell simulated (coating + AgNPs), then subtracting the volume of the AgNPs in one unit cell. The volume of a paraboloidal AgNP ($V_p$) is given by:
\[ V_p = \frac{1}{2} \pi r^2 h \]

where \( r \) is the base radius and \( h \) is the maximum height of the paraboloid. For the AgNPs defined above, this volume was calculated to be 47,1238.90 nm\(^3\), for 2 AgNPs/unit cell. This volume was subtracted from the total volume of the unit cell of the coating layer (150 nm \( \times \) 260 nm \( \times \) 80 nm = 3,117,696 nm\(^3\)) to give the total volume of the absorber coating only (\( V_{\text{equiv}} \): 2,646,457.10 nm\(^3\)).

\( V_{\text{equiv}} \) was then used to determine the thickness of the coating used for the equivalent volume planar simulations, 67.9 nm. Enhancement factors were reported for both equivalent thickness and equivalent volume comparisons in Figure A20. In general, the absorption enhancement in the coating was larger for the equivalent thickness comparison than for the equivalent volume comparison, which we attribute to differences in thin-film interference effects between the 80-nm-thick coating and the 67.9-nm-thick coating. For wavelengths greater than the absorption edge of the coating, the equivalent volume comparisons showed greater enhancement than the equivalent thickness comparisons. However, when integrated over all wavelengths and weighted by the AM1.5 solar spectrum, the absorptance enhancement was larger for the equivalent thickness comparisons than the equivalent volume comparisons, with enhancement factors ranging from 2.2 - 7.0 % for equivalent volume cases (compared to 7.5 - 12 % for equivalent thickness cases). Thus, the metasurfaces have a greater impact on increasing absorptance when the coating thickness is constant between the planar reference and the metasurface.

Figure A20b shows the simulated absorption in the Ag and AgNPA/Ag layers for the absorption enhancement simulations discussed in the main text. It was observed that there was an overall increase in the absorptance in the AgNPA/Ag compared to the planar Ag substrates for all coatings and wavelengths, but the enhancement was most pronounced in the regions of the LSPR and the plasmon-AIS peaks. Thus, these modes are useful for enhancing absorption in the metal, which could be beneficial for hot electron generation or photothermal therapy.
A.4. Appendix to Chapter 6

A.4.1. Pump-probe stability measurements and blanks

Figure A21. Examples of raw pump-probe signals from P3HT:PCBM coated on a Ag metasurface for a pump wavelength of 400 nm and probe wavelengths of a) 1000 nm and b) 1150 nm. The raw signal measured at the lock-in amplifier, in Volts, is the $\Delta R$, which is divided by the reflectance (R) at the probe wavelength in the ground state (i.e., without pumping). The signals each represent a single scan, with the color of the scans ranging from violet through red (following the visible spectrum) for increasing time of scan (i.e., first scan is purple, last scan taken is red). The thick black line shows the average of all measurements. This demonstrates the stability of the P3HT:PCBM film over the course of the measurements under photoexcitation.
Figure A22. ps-scale transient pump-probe reflection measurements from bare Ag and plasmonic metasurface and from MoS\textsubscript{2}/Ag and MoS\textsubscript{2}/metasurface using pump and probe wavelengths of 400 nm and 1000 nm, respectively. The $\Delta R$ value was the value obtained directly from the lock-in amplifier during the pump-probe measurement (\textit{i.e.}, not normalized to the reflection, $R$, from the probe alone). No signal was observed for all delay times.

A.4.2. Pump-probe dynamics at ps-time scales
There were negligible differences in the normalized decay dynamics for P3HT:PCBM on the various substrates for all pump and probe wavelengths within the ps-time scale (Figure A23). This implies that the recombination mechanisms were unchanged between the various substrates, and only the population of excited states (excitons and polarons) were influenced. The $\Delta R/R$ curves were fit with exponential decay functions, and the parameters are reported in Table A9.

Table A9. Decay parameters obtained from fitting ps-scale $\Delta R/R$ curves to the following equation: $\Delta R/R = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + C$, where $t$ is the decay time, $A_1$ and $A_2$ are the
amplitudes of the components of the decay, \( \tau_1 \) and \( \tau_2 \) are the lifetimes of the components of the decay, and \( C \) is a constant for the excited states that did not decay within the time range (12 ps). The amplitude values are reported as normalized percentages (i.e., \( A_i/(A_1 + A_2 + C) \times 100\% \)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1, \text{ ps } (A_1) )</th>
<th>( \tau_2, \text{ ps } (A_2) )</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>0.41 (43%)</td>
<td>3.19 (14%)</td>
<td>long (43%)</td>
</tr>
<tr>
<td>P3HT:PCBM/metasurface</td>
<td>0.43 (53%)</td>
<td>3.71 (11%)</td>
<td>long (37%)</td>
</tr>
<tr>
<td>P3HT:PCBM/MoS(_2)</td>
<td>0.52 (36%)</td>
<td>6.16 (13%)</td>
<td>long (51%)</td>
</tr>
<tr>
<td>P3HT:PCBM/MoS(_2)/metasurface</td>
<td>0.47 (47%)</td>
<td>5.06 (12%)</td>
<td>long (41%)</td>
</tr>
</tbody>
</table>

- **pump = 400 nm**
- **probe = 1000 nm (polaron + exciton peak)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1, \text{ ps } (A_1) )</th>
<th>( \tau_2, \text{ ps } (A_2) )</th>
<th>( C )</th>
</tr>
</thead>
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<tr>
<td>P3HT:PCBM</td>
<td>0.71 (45%)</td>
<td>(0%)</td>
<td>long (55%)</td>
</tr>
<tr>
<td>P3HT:PCBM/metasurface</td>
<td>0.70 (37%)</td>
<td>(0%)</td>
<td>long (63%)</td>
</tr>
<tr>
<td>P3HT:PCBM/MoS(_2)/metasurface</td>
<td>0.44 (40%)</td>
<td>(0%)</td>
<td>long (60%)</td>
</tr>
</tbody>
</table>

- **pump = 800 nm**
- **probe = 1000 nm (polaron + exciton peak)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1, \text{ ps } (A_1) )</th>
<th>( \tau_2, \text{ ps } (A_2) )</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
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<td>P3HT:PCBM</td>
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<td>4.71 (21%)</td>
<td>long (7%)</td>
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<tr>
<td>P3HT:PCBM/metasurface</td>
<td>0.47 (75%)</td>
<td>5.17 (18%)</td>
<td>long (7%)</td>
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<tr>
<td>P3HT:PCBM/MoS(_2)</td>
<td>0.52 (65%)</td>
<td>4.63 (25%)</td>
<td>long (10%)</td>
</tr>
<tr>
<td>P3HT:PCBM/MoS(_2)/metasurface</td>
<td>0.52 (65%)</td>
<td>4.62 (25%)</td>
<td>long (10%)</td>
</tr>
</tbody>
</table>

- **pump = 400 nm**
- **probe = 1150 nm (exciton peak)**

### A.4.3. Fitting analysis for pump-probe dynamics at ns-time scales
Figure A24. Fitting analysis for ns-scale transient pump-probe reflection measurements from a) P3HT:PCBM (constant fit); b) P3HT:PCBM with the metasurface (single exponential decay fit); c) the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer (single exponential decay fit); d) the hybrid P3HT:PCBM/MoS\textsubscript{2} active layer with the metasurface (double exponential decay fit). The decay times and amplitudes are shown in Table 6.1.

There were significant differences in the $\Delta R/R$ dynamics over the ns-time scale. For P3HT:PCBM alone, no decay was observed within 800 ps, so the dynamic curve was fit to a constant value, suggesting all charges lasted much longer than 800 ps. For P3HT:PCBM on the metasurface, the best fit to the data was obtained when the long time constant value ($C$) was fixed.
to zero; thus the decay shows that within ~7 ns, all charges should returned to the ground state. The hybrid P3HT:PCBM/MoS$_2$ was fit with a single exponential decay, having a decay time of ~160 ps with a significant fraction of the charges lasting for times much longer than 800 ps. For the hybrid P3HT:PCBM/MoS$_2$ with the metasurface, the best fit was obtained using a double exponential decay with a fixed long time constant value ($\tau$) \textit{i.e.} combination of the decay components from P3HT:PCBM/MoS$_2$ and P3HT:PCBM/metasurface). The fast component had a decay time of ~70 ps, and the slow component had a decay time of ~3 ns. As reported in the main text, these decay components are faster than those for either P3HT:PCBM/MoS$_2$ or P3HT:PCBM/metasurface, supporting the hypothesis that the hybrid P3HT:PCBM/MoS$_2$ with the metasurface had the largest population of P3HT polarons within this time scale. It is interesting to note that in the presence of the metasurface (with or without MoS$_2$), the decay was significantly faster, with all charges returning to the ground state in under 7 ns based on the fitting to the 800 ps time scales. Pump-probe measurements at longer time scales (ns - $\mu$s) would be of interest to determine if the excess polarons produced for the hybrid P3HT:PCBM/MoS$_2$ with the metasurface survive long enough to be collected at the electrodes.

\textbf{A.4.4. Variability in microscope-coupled extinction measurements}
Figure A25. Individual microscope-coupled extinction measurements from: a) P3HT:PCBM; b) P3HT:PCBM with the plasmonic metasurface; and c) the hybrid P3HT:PCBM/MoS$_2$ active layer with the plasmonic metasurface. Although the spot size was roughly 5 µm$^2$, the spectra acquired from these regions were quite reproducible, with the spot-to-spot variability within each sample being smaller than the difference between the three samples themselves. Note that the averages shown here are the same ones plotted in Figure 6.11a.
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