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SYNTHESIS AND FUNCTIONALIZATION OF GOLD NANORODS FOR PROBING PLASMONIC ENHANCEMENT MECHANISMS IN ORGANIC PHOTOVOLTAIC ACTIVE LAYERS

by

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ABSTRACT OF THE DISSERTATION

Synthesis and Functionalization of Gold Nanorods for Probing Plasmonic Enhancement Mechanisms in Organic Photovoltaic Active Layers

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Incorporation of plasmonic nanostructures into organic photovoltaic solar cells (OPVs) is proposed to address photovoltaic losses within these devices, such as radiative and non-radiative charge recombination, and insufficient light trapping. Plasmonic nanostructures are sub-wavelength antennae that harness light energy through localized surface plasmon resonances (LSPRs), providing energy-specific light management through far-field Rayleigh-scattering. Furthermore, induction of LSPRs produces high electric fields local to the nanostructure, which have been shown to enhance absorption and emission in fluorescent organic molecules; both manifestations of plasmon resonance are expected to enhance OPV performance through increased light-trapping, and active layer absorbance or emission, respectively. Herein, we employ the aspect ratio-dependent longitudinal-LSPR (L-LSPR) of gold nanorods to investigate plasmonic enhancement in OPVs.

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In this dissertation, gold nanorods (Au NRs) are fabricated by a seed-mediated synthesis. Methods are developed to provide L-LSPRs between 667 nm and 1018 nm using identical growth conditions; altering aspect ratio is performed by controlling the introduction time of the co-surfactant benzyldimethylammonium chloride (BDAC) to the NR growth reaction. The time-dependent influence of BDAC on Au NR aspect ratio is most evident during early times of NR growth (0-20 minutes), directly correlating to growth stages which are susceptible to epitaxial micellar adsorption and passivation of the growing crystalline facets. Analysis of Au NR morphology indicate that increased aspect ratio is brought about through BDAC's inhibition of Au adatom adsorption to longitudinal facets, and a simultaneous increase in adatom adsorption to tip facets.

A series of Au NRs are then fabricated, functionalized, and dispersed within poly (3-hexylthiophene): phenyl-C₆₁-butyric acid methyl ester (P3HT: PCBM) bulkheterojunction active layers. Au NRs with L-LSPRs of varying spectral overlap with the absorption and emission bands of the electron donor's (P3HT) spectrum are prepared, in order to probe far-field and near-field enhancement mechanisms. OPV devices are fabricated from the nanoparticle-active layer composites, and their photovoltaic performance characterized. Substantial improvements in power conversion efficiency, up to 30%, are reported. Device performance increases with increasing L-LSPR wavelength. Evidence of plasmonic enhancements is not explicit; increased efficiency is attributed to improvements in molecular ordering of P3HT, as indicated by grazing incidence x-ray diffraction studies.

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rcw

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Key of Acronyms and Symbols

- 1. Au NR Gold Nanorod
- 2. BDAC Benzyldimethylcetylammonium chloride
- 3. BHJ Bulk Heterojunction
- 4. 5BSA 5-bromosalycilic acid
- 5. CTAB Cetyltrimethylammonium bromide
- 6. CTAC Cetyltrimethylammonium chloride
- 7. e⁻ Electron
- 8. E_g band-gap energy
- 9. ϵ Dielectric constant
- 10. EJ exajoules = 1×10^{18} joules
- 11. EQE External Quantum Efficiency
- 12. GHG Greenhouse Gas
- 13. h⁺ Positive charge-carrier, commonly known as a hole
- 14. HOMO Highest occupied molecular orbital
- 15. IQE Internal quantum efficiency
- 16. ITO Indium tin oxide
- 17. J_{sc} Short-circuit current
- 18. L/D Length / width = aspect ratio
- 19. L-LSPR Longitudinal localized surface plasmon resonance
- 20. LSPR Localized surface plasmon resonance
- 21. LUMO Lowest unoccupied molecular orbital

- 22. MWh Megawatt hour
- 23. NIR Near infrared
- 24. NP Nanoparticle
- 25. NR Nanorod
- 26. NREL National renewable energy laboratory
- 27. OECD Organisation for Economic Co-operation and Development
- 28. OPV Organic photovoltaic (solar cell)
- 29. P3HT Poly(3-hexylthiophene)
- 30. PCBM Phenyl- C_{61} butyric acid methyl ester
- 31. PCE Photo-conversion efficiency
- 32. PEDOT: PSS Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
- 33. Φ (Phi) Work function
- 34. PV Photovoltaic
- 35. PNP Plasmonic nanoparticle
- 36. PS Polystyrene
- 37. P_{th} Theoretical power output
- 38. SPR Surface plasmon resonance
- 39. TEM Transmission electron microscopy
- 40. T-LSPR Transverse localized surface plasmon resonance
- 41. U_{ads} Internal Energy of Adsorption
- 42. Voc Open circuit voltage

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Purpose and Scope of Work

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1.1 Introduction

Employing fossil fuels as our primary energy source has potentially induced irreversible, anthropogenic climate changes. Fossil fuel consumption releases greenhouse gasses (GHGs) such as carbon dioxide into the atmosphere, which consequently absorb infrared radiation and facilitate global warming¹. Increasing average global temperatures are expected to drastically change climate conditions, with detrimental effects on the global ecosystem and economy^{2,3}. In fact, current climate models predict that without significant effort toward mitigating GHG emissions, atmospheric levels will raise the average global temperature from 1.6 to 5 °C by the end of the century ^{2,3}. Predicted impacts of global warming include a 5 - 10% permanent loss in global domestic product due to decreased crop yields and water shortages, along with high extinction rates of land and sea-faring creatures (ca. > 20%) due to food shortages and ocean acidification, respectively³. Along with impending damages to the global ecosystem, fossil fuel sources are finite and are not expected to meet future energy demands. As of 2002, it has been illustrated that worldwide reserves of petroleum, natural gas, and coal are estimated to provide 98, 166, and 230 more years of energy production⁴.

Whether global warming and fuel reserve estimates are accurate, or the entire concept of anthropogenic climate change is valid, the global community cannot afford to gamble on the limits to our fuel supplies, or on changes to the global ecosystem; fossil

fuels are not a sustainable fuel source, and therefore, less harmful, more secure energy sources must be integrated into the global energy portfolio.

Amongst numerous sustainable energy technologies under development, photovoltaics remain one of the most appealing for grid-scale energy production. Photovoltaic (PV) devices use the sun's light energy to produce usable electricity; the allure of PV technology originates from the sun's ability to provide a relatively unlimited supply of light, as well as a high flux of light energy incident on the earth's surface. In fact, more sunlight energy hits the earth's surface in one and a half hours (~480 EJ) than worldwide energy consumption from all fuel sources during 2010 (~363 EJ) ^{5,6}. The potential impact of implementing a solar energy infrastructure is illustrated in estimations showing that the total power consumption of all countries within the Organisation for Economic Co-operation and Development (OECD), during the year 2010, could be provided by a 630,000 km² solar array operating at the highest known research cell efficiency ($\eta = 44.4\%$)^{*}. An area which is approximately the size of the state of Texas (678,048 km²), and is about 2% of the land area of all OECD countries combined⁺[1-5].

Despite the promise of PVs, their implementation as a major contributor to global energy production has not been realized; the lack of success in the marketplace is partially attributed to sociopolitical influences, but is mainly due to PV being less economical than current power sources (e.g. fossil fuels). For example, the levelized

^{*} The OECD consumes 3688 Mtoe/year of energy, which is equal to approximately 49 TW (3688 Mtoe/year * 4.1868 x 10^4 TJ/Mtoe * 1 year/3153600 seconds)^{2,3}. Using the solar flux incident on earth's surface (174.7 W/m²), which is calculated considering earth's curvature, as well as losses due to scattering and absorption, we can estimate the area of solar cells required for parity with the OECD's power usage. Using the highest reported research cell efficiency quoted by NREL, the area required to produce 49 TW is : 49 TW *(m²/174.7W)*(km/(1000m)²)= 2.8 x 10^5 km².

⁺ The solar panel installation to total OECD land area is as follows: (Area required for solar array/total area of OECD countries)*100%= $(6.78 \times 10^5 \text{ km}^2/3.43 \times 10^7 \text{ km}^2) \times 100\% = 1.98\%$

costs (in 2008 \$US per MW·h) for solar photovoltaic, next generation coal, and advanced combustion turbine plants coming online in 2016 are \$396.1, \$100.4, and \$139.5, respectively 10 .

Multifaceted research initiatives are focused on bringing PV costs to grid parity. These efforts include the utilization of low cost materials and fabrication techniques, as well as increasing PV module lifetime and durability ¹⁰⁻¹³. However, decreasing PV production costs and lifetime are not the only means of realizing PV integration into the global power grid; it is likely that creating market-viable PVs will also require advanced device engineering to increase photo-conversion efficiency. To date, PV devices are far from reaching theoretical efficiency limits due to the numerous charge-carrier losses that exist within the devices (vide infra).

Device performance is ultimately dependent on how well electrical charge carriers are generated and subsequently extracted from the solar cell, which is dependent on device materials, architecture, and engineering. The general architecture of a solar cell is shown in **Figure 1.1a**, where a semiconductor, otherwise known as a photo-active layer, is placed between two conductive electrodes, where one of the electrodes is made transparent to allow light to penetrate into the photoactive layer ¹⁰. Electrode materials are usually engineered with a disparity between their work-functions (Φ), in order to induce an intrinsic electric field within the device, and consequently direct charge carriers toward their respective electrodes ¹⁰. The mechanism of charge generation within, and extraction from, the solar cell is shown in **Figure 1b**. Light having energy higher than the semiconductor band-gap energy (E_g) will be absorbed to promote an electron (e⁻) across the band-gap, thereby creating an excited electronic state. Electron promotion to an excited energy level leaves behind a positively charged hole (h^+). This electron-hole pair, commonly known as an exciton for organic semiconductors, is Coulombicallybound. The bound charge carriers are subsequently separated by diffusion, guided by the device's internal electric field, and then extracted into an external circuit at the electrical contacts; in the case presented herein, the absolute value of the cathode's work-function (Φ_C) is less than that of the anode (Φ_A). Electrons and holes are consequently collected at the cathode and anode, respectively.



Figure 1.1 General architecture (a) and charge separation mechanism (b) within a solar cell where $|\Phi_C| < |\Phi_A|^{10}$.

Photovoltaic cells are primarily divided into two classes, according to whether the active layer is composed of organic or inorganic semiconductors. Inorganic solar cells employ a layered structure of n-type and p-type semiconductors such as polycrystalline silicon, crystalline silicon, CuInGaS, or CdTe¹⁴. Similarly, organic photoactive layers employ a variety of electron-donor and electron-acceptor small molecules or polymers. Inorganic solar cells currently exhibit higher power conversion efficiencies than organic

photovoltaics (OPVs). The highest research cell efficiencies reported by the National Renewable Energy Laboratory (NREL) for single-junction organic and inorganic cells are 11.1% and 28.8%, respectively ⁹. Although higher inorganic solar cell efficiencies create the perception of inorganic PVs being more market-viable, component toxicity (Cd), high fabrication and installation costs, along with the utilization of rare materials (Te & In) may limit the breadth of their applicability and global proliferation ¹⁰. Organic PVs, in contrast, are primarily composed of abundant elements such as carbon and sulfur ¹¹. OPVs can also be manufactured using inexpensive, continuous printing techniques, and can be easily integrated into consumer products such as windows or clothing due to their semi-transparency and flexibility ¹⁵. Moreover, OPVs have short energy payback times; albeit the current efficiency of OPVs is not economical, their promise for broad applicability and proliferation warrants further development ¹⁵.

Disparity in device performance between organic and inorganic PVs is largely attributed to the mechanisms by which charge carriers are generated, and subsequently extracted in each class of device. Absorption of a solar photon in inorganic active layers generates free electrons and holes, which are extracted under the device's intrinsic electric field ^{10, 14}. Ease of charge extraction is due to the high dielectric constant (ε) of inorganic materials, which imparts low electron-hole (e⁻-h⁺) binding energies on the order of a few meV; conversely, the 4 - 5x decrease in ε of organic semiconductors correlates to a significant increase in e⁻-h⁺ Coulombic attraction energy (0.1-1.4 eV) ^{16, 17}. Organic semiconductors also depart from inorganics in that the tightly bound exciton is localized to the semiconductor molecules. This localization, along with weak intermolecular interactions, decreases charge mobility, as opposed to the ease of charge transport within

an inorganic crystal lattice. High exciton binding energies and low mobility result in short charge-carrier lifetimes (< ns), and a small diffusion pathlength (~10 nm) before charge recombination occurs. Thus, efficient charge separation in OPVs imposes the requirement of nanometer-scale mixing between donor and acceptor species, in contrast to the comparatively simple p-n or p-i-n junction architectures which are suitable for inorganic PVs ¹⁴. Inefficient charge extraction in OPVs also limits the thickness of the active layer that can be used; thick active layers increase the charge-diffusion path length to the electrodes, and therefore increase the probability of charge recombination with increasing photoactive layer thickness. However, lowering active layer thickness proportionally decreases the amount of light-absorbing material. Therefore, a balance must often be struck between charge extraction efficiency and the device's cumulative absorbance, ultimately limiting device performance.

Theoretical efficiency calculations predict OPVs could approach the Shockley-Qeuisser efficiency limit of approximately 22-27% ¹⁸. However, current solar cell efficiencies have not come close to this limit due to the complexity of charge dissociation and extraction within OPVs ^{15, 18, 19}. Initial studies employing homojunction organic materials did not extend photo-conversion efficiencies beyond 0.1% ¹⁷. In 1986, Tang employed a bilayer hetero-junction of electron donor and acceptor materials, bringing OPV efficiencies up to ~ 1% ²⁰; Tang's discovery was a breakthrough, but OPV efficiencies were still far below what was necessary for the technology to be useful. It was not until the discovery of the dispersive (bulk) heterojunction (BHJ) in the mid-1990's, with device efficiencies quickly exceeding 4%, that the scientific community put much faith in OPVs ²¹⁻²⁴. The BHJ gains advantage over other active layer architectures (i.e., bilayer) in that the acceptor and donor are intimately mixed. Literature has shown that processing conditions can provide active layer microstructures with phase separated layers having domain sizes on the order of the exciton diffusion length ^{11, 12, 15, 17}. Benefits provided by this microstructure include a higher probability that excitons will diffuse to the donoracceptor (D-A) interface, due to the small domain pathlength, and a higher probability that charge-carriers will dissociate due to an increased D-A interaction area. BHJ active layers hold promise for the success of OPV technology, however, the complexity in BHJ microstructure engineering, and consequently exciton dynamics, bear many technological hurdles which must be overcome.

Numerous avenues to improve OPV device efficiency are being pursued, including the development of novel charge-carrier transport materials to facilitate charge exchange between active layer and electrodes, the development of new acceptor and donor molecules, new methods of active layer processing for microstructure optimization, as well as investigating molecular and nanoparticle additives for improving active layer microstructure and light management, respectively ^{13, 25-35}. Improvements in all components are necessary; yet enhancing photo-generation of charge carriers within, and their subsequent extraction from, the photoactive layer is arguably the most important, as the absence of such improvements would leave advances in other device components to lie fallow.

Amongst many challenges for enhancing the photovoltaic performance of active layer materials is the necessity for simultaneous tuning of photochemical stability, D-A intermolecular interactions to control active layer morphology, and D-A molecular orbital energy level alignment in order to maximize power conversion efficiency (vide infra)^{12,} ^{17, 36-41}. Optimizing all of these criteria is critical for high-efficiency devices. However, all of them are related to the molecular structure of the acceptor and donor materials, and are not necessarily in positive correlation with one another.

The photochemical stability of D-A active layers is of utmost importance for proliferation of the OPV technology: Modules that cannot perform beyond their energy payback lifetime are not viable. Numerous publications investigate the dependence of photochemical stability on molecular structure, and have found that the photochemical stability of semiconducting polymers is heavily dependent on the structure of the polymeric side chains ³⁹. Moreover, studies by Tromholt et al. and Hoke et al. show that photochemical instability of the acceptor increases proportionally with its electron affinity ^{37,40,42}.

Molecular orbital energy levels are also dependent on molecular structure, and heavily influence device performance. The theoretical power output (P_{th}) of PV solar cells is defined by the product of a solar cell's open-circuit voltage (V_{OC}) and the shortcircuit current (J_{SC})¹⁰. In organic PVs, V_{OC} is directly influenced by the relative position of the molecular orbitals of acceptor and donor ^{41,43,44}. An energy level diagram depicting charge generation, charge dissociation, and the estimation of V_{OC} for an organic BHJ is shown in **Figure 1.2**. In step (1) of Figure 1.2, a photon having energy above E_g is absorbed by the donor to produce a localized exciton. The exciton subsequently diffuses to the D-A interface, and is dissociated by electron transfer to the acceptor (step 2). Afterwards, charge carriers are transported to their respective electrodes, and extracted into an external circuit to perform work (step 3). It has been found that V_{OC} is proportional to the difference in energy between the HOMO of the donor, and the LUMO of the acceptor ⁴⁵⁻⁴⁷. Figure 1.2 also displays the importance of the D-A LUMO energy offset (ΔE_{LUMO}), where estimates show that effective charge dissociation at the D-A interface requires ΔE_{LUMO} to be greater than approximately a few hundred millielectronvolts ¹².



Figure 1.2 The energy level diagram depicts photo-generated charge separation at a semiconductor bulk-heterojunction interface ^{17, 44}.

Lastly, the molecular structures of both acceptor and donor dictate the nanoscale BHJ morphology. Therefore, detailed knowledge of the physicochemical interactions between acceptor and donor is required. For example, consider one of the most popular BHJ D-A pairings, which is phenyl- C_{61} -butyric acid methyl ester (PCBM) and poly(3-

hexylthiophene) (P3HT), respectively. Spin-casting the P3HT:PCBM BHJ, along with subsequent heat-treatment, creates a phase-separated blend, where P3HT ideally forms nanometer-scale crystalline domains, which are surrounded by flocculated PCBM clusters. The nanoscale morphology can be ideally described as bi-continuous where domains of each material have direct contact with themselves and each electrode, in order to facilitate charge transport to the electrodes from the D-A interface. It is serendipitous that the lack of miscibility of P3HT and PCBM creates a nanostructure that facilitates charge dissociation and transport. However, the balance of the physicochemical interactions that create optimized phase separation within the P3HT-PCBM BHJ are complex, and are not easily reproduced in systems employing different active layer materials.

The BHJ's nanostructured internal morphology is also sensitive to the relative concentrations of acceptor and donor, as well as the employed processing techniques (solvent, annealing conditions, chemical additives)^{11,41,48}. Numerous publications have shown that BHJ nanostructure and device performance are drastically influenced through changes in D-A composition and employment of different processing techniques. Illustrative work by van Bavel et al., who employed TEM tomography to analyze z-directional nanostructure variability of P3HT-PCBM BHJs, found that P3HT crystal size and morphology, as well as z-directional P3HT composition vary with the P3HT-PCBM ratio after thermal annealing ³³. Moreover, the BHJ morphology at each electrode interface also varies drastically with D-A composition.

The intricate balance of physical and chemical properties that contribute to fabricating effective BHJ active layers makes it difficult to quickly apply new materials. One must consider how optimizing a specific property of the active layer will affect the others. In fact, photo-conversion losses accrued within BHJ OPVs are largely attributed to exciton recombination mechanisms brought about by the complex BHJ nanoscale morphology. In considering excitonic losses in BHJs, it is illustrative to describe exciton creation and extraction in six fundamental steps, according to work by Schlenker et al.⁴⁴: (1) Absorption of a solar photon having energy equal to or above the semiconductor band-gap energy, with subsequent creation of a localized exciton. (2) The exciton then diffuses to the D-A interface through energy transfer pathways; exciton diffusion in organic media involves either intermolecular dipolar or electron exchange interactions. (3) Upon reaching the D-A interface, the exciton is quenched to produce a Coulombically-bound charge-transfer state. (4) The charge-transfer complex is then dissociated as fully ionized polaron species (e^{-} and h^{+}). (5) The electron and hole are then transported to oppositely charged electrodes through intermolecular self-exchange between localized hopping sites, and (6) the charge-carriers are collected from the BHJ by electrical contacts, and used to perform electrical work. Successful exciton diffusion, dissociation, and transport are therefore highly dependent on molecular conformational strain, molecular disorder (crystallinity), and the presence of impurities and trap states ⁴⁴.

Theoretical work by Kirchartz et al. adapted the Shockely-Queisser approach for estimating the performance of inorganic photovoltaics for OPVs, and predicted a maximum efficiency of >20%⁴⁹. They ultimately determined that amongst the exciton recombination loss mechanisms, such as insufficient transport to the D-A interface and

inefficient dissociation, the dominant loss mechanism was non-radiative exciton recombination which can occur at crystallographic defects and impurities within the absorber, at the D-A interface, or at the active layer-electrode interfaces; this further stresses complications brought about by the BHJ's morphology. Although increasing the D-A interfacial surface area is beneficial for increasing the probability of charge transfer, the D-A is also a recombination center.

Non-radiative charge-carrier recombination is one of five photonic loss mechanisms that contribute to significant photovoltaic loss in solar cells; the other sources of loss are attributed to a lack of effective light management within the solar cell, which can be divided into the three following categories: (1) re-radiation of absorbed photons through spontaneous emission; this process is entropically favored because the solid angle of light emission (~ 4π steradians) is much larger than the angle of incidence from which absorption can occur (~ 6 x 10⁻⁵ steradians)⁵⁰. (2) Incomplete light trapping within the solar cell results in photons taking a small pathlength within the photoactive layer, and escaping the device before they can be absorbed. (3) Thermalization losses from the absorption of photons having energy above E_g, where the excess energy is often dissipated as heat, and (4) lack of photon absorption due to the photon energy being less than E_g⁵⁰. Thermodynamic approximations of photo-conversion losses estimate that the contributions of light mismanagement and non-radiative recombination can account for up to 18% of all loss within solar cells (**Figure 1.3**)⁴⁷.



Figure1.3. Photo-conversion losses in OPVs according to the Shockley-Queisser analysis ⁴⁷.

Among the strategies that address the loss mechanisms outlined in Figure 1.3, insufficient absorption of sub-bandgap light and thermalization losses can be mitigated using multi-junction OPVs; each junction houses a different band-gap material, allowing a more complete capture of the incident spectrum ⁵⁰. The donor's band-gap is additionally tuned for optimum alignment with the most abundant photons above the band-gap energy, in order to prevent thermalization losses through non-radiative decay of excited states ⁵⁰.

Solutions that have been proposed to mitigate photonic losses attributed to nonradiative recombination and light mismanagement within organic solar cells are not as straightforward. Since OPVs employ thin active layers, typically on the order of 100 nm, to enhance charge collection, effective light management would require nanoscale photonic architectures to be integrated into the cell. For instance, surface reflectors and embedded scattering structures can be used to decrease the escape cone of light emitted from the active layer, and to increase the average light intensity within the active layer, respectively ⁵⁰. Losses due to non-radiative decay at carrier traps can also be mitigated by using sub-wavelength nano-photonic structures to increase the cell's radiative recombination quantum efficiency (QE), which is defined as $QE = R_{rad}/(R_{rad} + R_{nrad})$, where R_{rad} and R_{nrad} are the radiative and non-radiative recombination rates, respectively⁵⁰. The expectation of nano-photonic structures to increase OE is attributed to their ability to confine light within nano-scale volumes, which can couple to the local semiconductor, increase its photo-emission rate, and can thus be used to artificially enhance the local density of optical states, and bring about increases in R_{rad} within semiconductors having a low QE, and, in consequence, increase $V_{OC}^{50,51}$.

Plasmonic materials have received a considerable amount of attention as a potential means of addressing light management losses within solar cells (vide infra). Plasmonics deals with the physical manifestations of phenomena known as surface plasmon resonance and surface plasmon polaritons; surface plasmon resonances are coherent oscillations of conduction-band electrons within a material below its plasma frequency, which is induced upon interaction of the material's free electrons with the electric field of incident electromagnetic radiation ⁵². The incident electric field perturbs

conduction band electrons, and induces electron resonance which is subsequently damped by electron-electron collisions that have a characteristic collision frequency $\gamma = 1/\tau$, where τ is the relaxation time of the free electron gas, and is approximately 10⁻¹⁴ seconds at room temperature⁵².

Surface plasmon polaritons (SPPs) in thin films (thickness < 50 nm) are propagating, dispersive waves that are coupled to the free electrons of a conductor, and can propagate tens to hundreds of microns along the x-y plane of a metal-dielectric interface, with an evanescently decaying electric field that can extend up to 200 nm in the z-direction 52,54,55. The dispersion of SPPs in bulk materials, as well as the decay length of the SPP's electric field into the dielectric medium, is strictly dependent on the real dielectric constant of the dielectric (insulating) material, as well as the frequency dependent dielectric function of the conductor⁵². When discrete structures of materials that exhibit plasmonic behavior are reduced to sizes that are significantly smaller than the wavelength of light, the surface plasmons become localized, non-propagating excitations of the conduction-band electron cloud⁵². The excitation modes are described by the scattering of sub-wavelength conductive particles immersed within an oscillating electromagnetic field, and, unlike SPPs in bulk media, are highly dependent on the size and shape of the nanostructure. On the contrary, in analogy to SPPs, they show dependence on the dielectric function of the conductor and the dielectric constant of the surrounding insulator; these confined plasmons are known as localized surface plasmons (vide infra)⁵². Excitation of localized surface plasmons induces a resonance of the conductor's excited electron cloud, brought about by the restoring forces induced by the structure's surface curvature at high frequencies, as well as electron collisions, to create

an oscillating dipole; these resonances are known as localized surface plasmon resonances (LSPRs). Upon LSPR excitation, the resonating dipole creates enhanced fields both within the nanostructure, and in its external near-field. The electric near-field of LSPRs decays exponentially from the nanostructure's surface into the surrounding dielectric. These near-fields have been employed to couple to electronic states within semiconductors, when there exists spatial overlap with the region of electric fieldenhancement, and spectral alignment of the LSPR and the semiconductors absorption, in order to bring about an enhancement of the semiconductor's effective absorption crosssection. For application in OPVs, it is expected that near-field enhancement of the electron donor's effective absorption cross-section will result in enhanced exciton generation, and, in turn, increased photo-conversion efficiency⁵³. The plasmonic nearfields, as previously stated, can also couple to the semiconductor to enhance QE through increased R_{rad}; the increase in R_{rad} is mediated by the plasmonic modes' modification of the local density of optical states, meaning the energetic states that can be occupied by a photon, which introduces additional electromagnetic relaxation pathways for the excited electronic states within the semiconductor, and increases the radiative decay rate⁵¹.

For nanostructures made of Ag and Au, which are currently the two most widely employed metals for plasmonic applications, LSPRs can be excited by direct illumination with visible and near-infrared energy⁵². An advantage of employing plasmonic nanostructures over plasmonic thin-films is that the LSPR excitation energy can be tuned by altering the particle's morphology. Recent efforts in bottom-up synthesis have created a library of particle morphologies with LSPRs throughout the visible and NIR spectrum, ultimately providing access to energy-specific antennae that can harness and manipulate photon energy at size scales below the diffraction limit ^{54,55}. Harnessed photon energy is generally distributed within two processes: 1) a portion of the photon energy is absorbed by phonon modes within the material's crystalline lattice, leading to Joule heating of the particle, and 2) the light energy is directionally scattered to the external environment ^{54,} ⁵⁶. The ratio of scattered to absorbed photonic energy increases with particle size; specifically, the scattering (C_{sca}) and absorbance (C_{abs}) cross-section can be calculated for an isotropic structure according to equations 1.1 and 1.2, respectively, where $k = 2\pi/\lambda$, λ being the wavelength of incident light, α is the polarizability, **a** is the radius of the particle, ε is the frequency-dependent dielectric function of the conductor, and ε_m is the non-absorbing dielectric constant of the surrounding medium. Equations 1.1 and 1.2 illustrate that the magnitude of a particle's scattering and absorption cross-section are highly dependent on the size of the particle, where scattering scales as a^6 and absorption as \mathbf{a}^3 . Therefore, small nanostructures, where a $\ll \lambda$, will absorb more efficiently as they scatter. As the particle diameter approaches approximately 50nm, scattering becomes the more efficient extinction pathway, where the extinction cross-section (Cext) is the sum of the absorption and scattering cross-section terms $(C_{ext} = C_{sca} + C_{abs})^{52,56,57}$. Furthermore, equations 1.1 and 1.2 exhibit the dependence on the plasmonic particle's extinction on the dielectric function of the material, and the dielectric constant of the surrounding medium, where absorption and scattering are resonantly enhanced when the Frölich condition is met, specifically when $|\varepsilon + 2\varepsilon_m|$ is minimized; when Im(ε) does not vary much around the resonance condition, the Frölich condition simplifies to $Re[\varepsilon(\omega)] = -2\varepsilon_m$ 52,56,57

$$C_{\text{sca}} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2 \qquad 1.1$$

$$C_{abs} = kIm |\alpha| = 4\pi ka^3 Im \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|$$
 1.2

The above treatment for the wavelength-dependent extinction cross-section of a plasmonic nanoparticle surrounded by a dielectric medium is for isotropic particles such as spheres or cubes, which exhibit one LSPR mode; this is due to the particle's symmetry, which consequently produces the same LSPR resonance geometry independent of the particle's orientation to the incident electromagnetic radiation. However, anisotropic bodies can exhibit multiple LSPR modes. For example, nanorods have two dominant LSPR modes: One corresponding to electron resonance along the transverse surface of the nanorod, known as the transverse localized surface plasmon resonance (T-LSPR), and a second resonance mode corresponding to the LSPR along the longitudinal surface of the rod, which is known as the longitudinal surface plasmon resonance (L-LSPR)⁵⁸. These resonances are not mutually exclusive; each can be excited at the same time, or individually by altering the particle's position with respect to the direction of the incident light's electric field⁵⁹. The absorption and scattering crosssections of the plasmonic nanorods are therefore defined as the summation of the transverse and longitudinal resonance's contributions toward each extinction pathway, which are derived from Gans theory, and defined respectively in equations 1.3 and 1.4, where V is the unit volume of the nanoparticle, ε_m is the dielectric constant of the medium, ε is the dielectric function of the metal, and $n^{(i)}$ is the depolarization factor which is defined for the longitudinal and transverse axes of the nanoparticle in equations 1.5 and 1.6, respectively, where a, b, and c are the three axes of the rod-shaped

nanoparticle, a > b = c, and L/D is the aspect ratio (L/D = R = a / b) of the rod⁶⁰. Furthermore, the T-LSPR and L-LSPR will occur when $\varepsilon_1 = -(1-n^{(i)}) \cdot \varepsilon_m/n^{(i)}$, indicating the strong dependence of the L-LSPR frequency on L/D, and making them excellent candidates for applications which require energy-specific light management ⁵⁸. For investigating plasmonic near-field and far-field enhancement in OPVs, Au NRs can be advantageously employed given their the L-LSPRs strong dependence on aspect ratio, the high scattering cross-section of the L-LSPR for investigating far-field effects, and the enhanced electric near-fields at the nanorod tips for investigating near-field effects. The electric near-field enhancement of Au NRs is also an order of magnitude greater than that exhibited by spheres with decay lengths that scale with the size of the particle. Additionally, when considering Au NRs having the same volume, the electric near-field enhancement increase with aspect ratio, thereby increasing the potential volume with which the near-field can affect the surrounding media as L/D is increased.

$$C_{abs} = \frac{2\pi}{3\lambda} \varepsilon_{m}^{3/2} V \sum_{i} \frac{\varepsilon_{2}/(n^{(i)})^{2}}{\left(\varepsilon_{1} + \left[(1-n^{(i)})/n^{(i)}\right]\varepsilon_{m}\right)^{2} + \varepsilon_{2}^{2}}$$
 1.3

$$C_{sca} = \frac{8\pi^{3}}{9\lambda^{4}} \epsilon^{2}_{m} V^{2} \sum_{i} \frac{(\epsilon_{1} - \epsilon_{m})^{2} + \epsilon^{2}_{2}/(n^{(i)})^{2}}{(\epsilon_{1} + [(1 - n^{(i)})/n^{(i)}] \epsilon_{m})^{2} + \epsilon^{2}_{2}}$$
 1.4

$$n^{(a)} = \frac{2}{R^2 - 1} \left(\frac{R}{\sqrt{R^2 - 1}} \ln \frac{R + \sqrt{R^2 - 1}}{R - \sqrt{R^2 - 1}} - 1 \right)$$
 1.5

$$n^{(b)} = n^{(c)} = (1 - n^{(a)})/2$$
 1.6

Gold nanorods (Au NRs) have received a lot of attention in this regard, given the ease with which their L-LSPR is synthetically tuned ^{61,62}. Using bottom-up syntheses, Au

NR L-LSPRs can be tuned throughout a large portion of the visible, and well into the NIR region of the electromagnetic spectrum, simply by controlling their aspect ratio. While the L-LSPR is tuned through alteration of Au NR L/D, the rod diameter can be kept relatively constant ^{61,63,64}. Therefore, the T-LSPR position remains the same while the L-LSPR position is altered, allowing one to unilaterally experiment with a single LSPR energy. Moreover, additional versatility of Au NRs is brought about by the use of Au-S chemistry, thus providing the opportunity to functionalize Au NR surfaces with a desired chemistry.

The intention of this dissertation is to employ the unique properties of Au NR's longitudinal localized surface plasmon resonance to investigate plasmonic enhancement mechanisms in bulk-heterojunction photovoltaics.

It has been proposed that plasmonic nanoparticles (PNPs) may provide multimodal efficiency enhancement in photovoltaics ⁵⁷. The ability of PNPs to scatter specific photonic energies, and to simultaneously exhibit high local electric fields, are expected to mitigate photovoltaic losses from poor light management, and enhance photo-carrier generation; these enhancement effects are more commonly known as farfield and near-field enhancement, respectively ^{51,65}. Far-field effects are expected to increase the light intensity within the device's active layer. PNPs placed on the surface or within the active layer can scatter light, thereby increasing its pathlength within the active layer, and consequently increasing the probability of absorption, and subsequent exciton generation ⁶⁶. Near-field enhancement is attributed to the active layer's interaction with
the high electric near-field produced local to the particle. Recent literature shows enhanced exciton generation when the semiconductor is close to the nanoparticle, which has been attributed to the near-field enhancement of the affected semiconductor's absorption cross-section^{68,69,53}. Moreover, plasmonic nanostructures placed within the proximity of fluorescent organic molecules can enhance the radiative decay rate by more than a factor of 50, allowing plasmonic structures to possibly address charge-carrier losses from non-radiative decay at charge-carrier traps; a decay mechanism which Kirchartz et al. attributed to the D-A interface in BHJ active layers ^{49,69}.

Evidence of far-field enhancement has been demonstrated in recent work. Lee et al. have demonstrated that metallic nanoparticles embedded into the active layer primarily enhanced efficiency through far-field scattering ⁷⁰. Additionally, empirical work by Wang et al. saw BHJ OPV efficiency enhancement when incorporating poly(vinylpyrrolidone)-capped gold octahedra into the active layer ⁷¹. Similar work by Jankovic et al. observed OPV efficiency improvements through incorporation of silica-coated gold nanorods into BHJ OPV active layers, which they attribute to light trapping by the particles ⁷².

Near-field photovoltaic enhancement has also been investigated. Rand et al. showed increased e^-h^+ pair production in an organic dielectric placed within 10 nm of a Ag nanosphere array ⁶⁶. Furthermore, work by Shen et al. exhibited a near-field enhancement factor of 1.56 for 24 nm diameter silver nanoparticles in a P3HT : PC₆₁BM active layer ⁷³. Shen et al. also outlined the importance of the nanoparticle coating thickness on near-field enhancements, where nanoparticle coatings thicker than 5 nm were detrimental to near-field effects. Far-field and near-field enhancement pathways hold promise for addressing photovoltaic losses in OPVs. One approach towards maximizing far-field and near-field effects is to embed the PNPs into the active layer. Placing PNPs within the active layer would increase the interaction volume of the near-field in comparison to placing the nanoparticles at an active layer-electrode interface; the potential for optimizing far-field effects may also be realized because of the ability to incorporate more PNPs within the volume of the active layer than one could incorporate within an interface.

An additional advantage of incorporating PNPs within the active layer is their potential to influence the BHJs morphology, in order to provide an additional means of enhancing photo-conversion efficiency. The PNP's surface chemistry can be employed to interact with the BHJ materials to bring about favorable morphological changes such as increased donor crystallization and molecular ordering, or alteration of the D-A domain sizes, as has been presented in recent work^{74,75}. In 2008, Yuen et al. employed 1, 8-diiodooctane as a processing additive within the P3HT:PCBM OPV active layer that improved PCBM's solubility, and consequently P3HT's domain size which improved OPV efficiency from 3.4% to 5.1%⁷⁴. Similarly, Vohra et al. improved the molecular ordering of P3HT chains by introducing polystyrene in to the BHJ active layer blend, which resulted in phase segregated domains of polystyrene and P3HT, and consequently and enhanced self-assembly of P3HT⁷⁵. PNPs could therefore be applied in a similar fashion, but as optically active additives, as opposed to molecular species which only act to alter the BHJ morphology.

However, this approach is not without its limitations. The volume within the active layer that would be occupied by PNPs will require the removal of an equivalent

volume of photo-active material; therefore, the viability of this approach warrants that plasmonic enhancements outweigh photovoltaic losses accrued through the removal of photo-active material. Additionally, dispersion of colloidal particles within a polymer matrix is not trivial. Difficulty is mainly found in using the correct PNP ligand to ensure their compatibility with the bulk matrix, and thus favor dispersion of the nanoparticles within the BHJ. Poor interaction between particle ligands and host material will result in particle assembly, and possibly aggregation ⁷⁶⁻⁸⁰. Particle assembly often results in surface plasmon resonance hybridization between particles, which can completely alter their optical response⁸¹. Similarly, particles which are largely aggregated or coalesced undergo complete quenching of plasmonic properties⁸¹.

Despite the promising reports on nanoparticles incorporated into the bulkheterojunction, no work to date has shown sufficient evidence that discrete particles have been dispersed within the BHJ. Without characterization of the PNP-BHJ active layer, one does not know the degree of particle assembly or aggregation, and, consequently, the optical response expected from the plasmonic species. Therefore, efficiency enhancement data for plasmonic OPVs, alone, cannot elucidate enhancement mechanisms. To draw firm conclusions on specific enhancement mechanisms, PNP-BHJ active layer characterization will have to be correlated to device performance metrics, which will be addressed herein.

This work aims to study the influence on OPV photo-conversion efficiency of incorporating Au NRs into P3HT: PCBM BHJ active layers on OPV photo-conversion efficiency, and elucidate the means by which Au NRs bring about any changes in the BHJ active layer's photovoltaic properties. Au NRs were chosen because of their

tunable L-LSPR resonance, the alignment of which can be tuned to have varying degrees of spectral overlap with P3HT's absorption band, and for the fact that they exhibit the largest local fields in comparison to other Au nanoparticle morphologies, which provide unprecedented versatility for investigating plasmonic near-field and far-field photovoltaic enhancement. We expect that if far-field and near-field enhancements are significant, they will be most influential when the L-LSPR is resonant with the absorption band of P3HT. This dissertation therefore aims to make the following accomplishments:

- (1) Synthesize gold nanorods of varying aspect ratio with bottom-up techniques.
- (2) Functionalize gold nanorods with appropriate chemistry in order to disperse them within a P3HT:PCBM BHJ active layer.
- (3) Characterize the Au NR-BHJ composite's optical properties and the degree of Au NR dispersion within the BHJ matrix.
- (4) Fabricate Au NR-BHJ OPV devices to investigate the influence that Au NR incorporation and Au NR L-LSPR position have on photovoltaic efficiency.

Au NRs will be synthesized using an adapted seed-mediated synthesis⁸². This procedure allows one to systematically tune Au NR aspect ratio throughout the visible spectrum by simply altering the surfactant ratio of a binary surfactant growth solution. Additional advantage is gained from the ease with which Au NRs can be purified from byproducts through centrifugation or depletion-induced size segregation of particles, and functionalized through traditional nanoparticle place-exchange^{83, 84}.

Thiolated-polystyrene (PS) is chosen as the Au NR grafting layer for its ability to disperse Au NRs in traditional solvents used for casting BHJ active layers (e.g.,

chlorobenzene or dichlorobenzene) which is show herein, and the accessibility of a range of molecular weight (2500-50,000 Da), which provides the opportunity to tune the ligand shell thickness. PS-grafted Au NRs will be incorporated into the P3HT-PCBM solution from which the active layer is cast. From this solution, BHJ solar cells will be fabricated, and their performance metrics characterized.

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Overview of Experimental Methods and Instrumentation

~ II ~

2.1. Materials and Reagents

Cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC) benzyldimethylhexadecylammonium chloride (BDAC) were purchased from TCI America. Chloroauric acid, silver nitrate, sodium borohydride, potassium bromide, and L-(+)-ascorbic acid were purchased from Sigma-Aldrich. Hexane, 2-propanol, acetone, and methanol were all purchased from Fisher-Scientific. All chemicals were of analytical grade (purity > 98%) and were used without further purification. Deionized water (18 M Ω cm) was used in all experiments. Transmission electron microscopy was performed using holey Formvar grids from SPI supplies.

2.2. General Seed-Mediated Synthesis of Plasmonic Gold Nanorods

Gold nanorods were synthesized using an adapted seed-mediated procedure following work by Murphy et al. and Nikoobakht et al. ¹⁻⁴. This procedure first requires synthesis of crystalline gold nanospheres to act as the seeds for nanorod growth. Upon sufficient maturation of the seed, it is added to a nanorod growth solution. From procedures outlined by Murphy et al. and El-Sayed et al., Au NR growth is directed by the surfactant cetyltrimethylammonium bromide (CTAB). Nikoobakht et al. employed a binary surfactant growth solution of CTAB and benzyldimethylammonium chloride BDAC to increase Au NR aspect ratio, which is tunable through adjusting the CTAB to BDAC ratio. The specific synthetic procedures are described below.

2.2.1. Preparation of the Gold Seed

The seed solution was prepared by first adding 25 μ L of 0.1 M HAuCl₄ to 10 ml of a 0.1 M CTAB solution. This solution was sonicated at 30^oC for 30 minutes and allowed to cool to 25^oC. Afterwards, 60 μ L of ice-cold 0.10 M NaBH₄ were added to the stirring solution, resulting in the formation of a brown-yellow color. The brownish yellow color is indicative of gold spheres having a diameter less than 2 nm. Vigorous stirring of the seed solution was continued for 5 minutes, after which the solution was stirred at 25 °C until use.

2.2.2. Growth of Plasmonic Gold Nanorods

The growth solution is prepared by adding 500 μ L of 0.10 M HAuCl₄ (aq) to 100 mL of a 0.10 M CTAB (aq) solution, followed by 80 μ L of 0.10 M AgNO₃ (aq). The resulting mixture was sonicated at 30^oC for 30 min, and subsequently cooled back to 25^oC. To initiate Au NR growth, Au(III) was reduced to Au(I) through the addition of a 560 μ L of 0.10 M ascorbic acid (aq) to the growth solution. Complete reduction of Au(III) to the Au(I) is indicated by the color of the growth solution changing from dark yellow to colorless. Finally, 100 μ L of the seed solution were added to the growth

solution. The color of the solution changed over time according to the final aspect ratio (L/D) of the Au NR.

2.3. Purification of Gold Nanorods

2.3.1. Purifying Gold Nanorods through Centrifugation

Gold nanorods with L/D < 3 were centrifuged at 10,000•g for 60 min in a 50mL roundbottom centrifuge tube (Nalgene, Oak Ridge Style 3119)⁴. This centrifugation cycle produces two separate pellets in the centrifuge tube, one corresponding to nanorods, and the other to spherical or cubic impurities. The two pellets were then separated via pipette and the nanorods were dispersed in 0.1 M CTAB (aq).

2.3.2. Depletion-Induced Size and Shape Selection of Gold Nanoparticles

For higher aspect ratio nanorods (L/D > 3), BDAC was added to the postsynthetic growth solution, to a total surfactant concentration of 0.275 M 5 . The solution was incubated at room temperature for 48 hours. Completion of the purification process was apparent upon the nanoparticle solution changing color and having a decreased optical density, both from the aggregation of Au NRs. Afterwards, the supernatant was decanted from the aggregates at the bottom of the flask. The pellet containing purified nanorods was then dispersed in 0.1 M CTAB (aq).

2.4. Estimation of Gold Nanorod Concentration

Au NR concentration was estimated through the relationship between NR aspect ratio and its extinction coefficient developed by Nikoobakht et al., who employed Gans' adaption of Mie theory for spheroidal particles, and outlined the aspect ratio-dependent extinction coefficient. Data from Nikoobakht et al. are reproduced in **Figure 2.1**. The fitted regression line was used to estimate NR extinction cross-section upon quantifying NR aspect ratio through transmission electron microscopy. Determining the Au NR concentration was solely employed for estimating the proper conditions for ligand placeexchange, specifically to approximate the NP-thiolated ligand ratio; any error accrued by using this approximation of the Au NR extinction cross-section, due to the variation in the transverse and longitudinal dimensions between nanorods of the same aspect ratio, has not exhibited any significant effects (place-exchange yields or changes in particle morphology) on the ligand-exchange products (vide infra).



Figure 2.1 The dependence of Au NR extinction cross-section on its aspect ratio. Theoretical calculations by Nikoobakht et al. were performed at each NR's maximum extinction wavelength. Red trends indicate a 95% confidence interval ⁶.

2.5. Functionalization of Gold Nanorods with Thiolated Polystyrene

A stock solution of $5x10^{-4}$ M thiolated polystyrene (PS) (Mw=53,000, Polymer Source Inc.) was prepared in tetrahydrofuran (THF)⁷. Within a scintillation vial, 5 mL of the PS stock solution were mixed vigorously with 5 mL of a 3 nM NR suspension. The PS-functionalized gold nanorods immediately phase segregated from solution and were dried thoroughly on a hot plate. The functionalized nanorods were subsequently washed via suspension in toluene or chlorobenzene, followed by centrifugation at 6500•g for 20 minutes in order to remove excess PS. After decanting the supernatant from the washed NRs, the pellet containing purified PS-functionalized NRs was placed in a vacuum oven at 60°C for 12 hrs before blending with the BHJ solution.

2.6. Fabrication of Organic Bulk Heterojunction Solar Cells

Devices were fabricated on 1x1 inch pre-patterned indium tin oxide (ITO) on glass substrates (Luminescence Technology). Prior to fabrication, the ITO-coated glasses were cleaned by sequential sonication in detergent, deionized water, hexane, 2-propanol, acetone, and methanol. The final cleaning step was a UV ozone treatment for 20 minutes. A PEDOT:PSS layer (Clevios P, Heraeus) was spin-coated onto the slides, resulting in a film thickness of approximately 50 nm, as measured by profilometry. The film was dried at 160°C for 20 minutes, and the substrates were subsequently transferred to a nitrogenpurged glove box. The BHJ blend of poly-3-hexylthiophene (P3HT) and phenyl-C₆₁butyric acid methyl-ester (PC₆₁BM) (5:3, wt./wt.) was dissolved in chlorobenzene. Au NRs were taken from the dried pellet of the purified PS-grafted ligand exchange product, and blended into the BHJ solution at either 1 wt.% or 2 wt.% with respect to P3HT. The mixture was spin-cast on top of the PEDOT:PSS layer at a rate of 1500 rpm for 45 seconds. All devices were then covered by a 100 nm thick layer of Al through thermal evaporation under vacuum (BOC Edwards Auto 500), and subsequently annealed in an N₂ atmosphere at 158°C for 8 minutes.

2.7. Preparation of Transmission Electron Microscopy Samples

2.7.1. Casting Samples from Liquid Nanoparticle Suspensions

1 mL of Au NR solution was concentrated through centrifugation at 6500•g for 15 minutes. The supernatant was discarded, and the pellet dispersed in 1 mL 1 x 10^{-3} M CTAB (aq). Centrifugation was repeated, and the pellet dispersed in 100 µL of 1 x 10^{-3} M CTAB (aq). 5 µL of this solution was drop-cast onto a TEM grid, and allowed to dry for 24 hours under vacuum before use.

2.7.2. Preparing Samples of Bulk-Heterojunction Active Layers

BHJ solar cell active layers were extracted directly from OPV devices. Extraction of the BHJ thin film was performed by first sectioning the entire thin film into small squares by using a razor blade. The entire device was then gently submersed under pure water. Upon dissolution of the water-soluble PEDOT:PSS layer, the sectioned active layer pieces are suspended at the air-liquid interface. A TEM grid is then used to carefully capture the thin film through submersing the TEM grid into the water and raising it into contact with the floating thin-film.

2.8 Additional Instrumentation

UV-Vis-NIR spectra were acquired with a Cary 5000 spectrophotometer at room temperature using a quartz cell of 1 mm path length for liquid samples, and a standard glass slide mount for thin film samples, in the 300-1000 nm spectral region. Morphology and mean size of NPs were examined by TEM (Philips CM200 LaB₆ AT 200 kV or a Topcon 002B at 200 kV). Power conversion efficiency was measured under AM 1.5G solar irradiation (100 mW cm⁻²) using a xenon-lamp-based solar simulator (Oriel 81160) inside a nitrogen-purged, moisture-free glove box. The external quantum efficiency (EQE) as a function of wavelength was obtained with a photomodulation spectroscopic setup (Newport).

2.9. References

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~ III ~

Time-Dependent Susceptibility of the Growth of Gold Nanorods to the Addition of Co-Surfactant

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3.1 Introduction

Gold nanorods (Au NRs) have become a useful platform for investigating the application of plasmonic nanoparticles (PNPs) in many advanced technologies, including surface-enhanced Raman scattering-based chemical sensors, vectors for drug delivery, photo-thermal cancer therapy, chromatic polarizers and filters, optical switches, and as a potential means of enhancing photovoltaic solar cell efficiency ¹⁻¹⁰. Au NRs' versatility is due to their plasmonic properties which provide an energy-specific, electromagnetic extinction mechanism within the visible and near-infrared spectrum ¹¹⁻¹³. The longitudinal localized surface plasmon resonance (L-LSPR) of Au NRs, resulting from dipole resonance induction along the longitudinal axis of the rod, is highly sensitive to the rod's aspect ratio (L/D) ¹⁴. Thus, the L-LSPR band excitation energy, being easily tuned through synthetic control over the rod's L/D, provides access to harnessing light energy within the visible and near-infrared spectrum; this advantage makes Au NRs more versatile over other PNP morphologies, which have limited capabilities for tuning the extinction energy.

Bottom-up, synthetic procedures for single-crystalline Au NRs have become well established since the initial publications on the seed-mediated protocol by Murphy et al. and Nikoobakht et al. ^{11, 13, 15}. This method separates the nucleation and growth steps in order to control Au NR growth through employing specific chemical species in the growth solution. Gold seeds are synthesized in a surfactant solution, most often 0.1 M cetyltrimethylammonium bromide (CTAB), the molecular structure of which is shown in **Scheme 3.1a**. The seed solution is subsequently added to a growth solution containing 0.1 M CTAB to initiate the formation of NRs. Reagents, other than CTAB, that are added to the growth solution, which exhibit the most influence on Au NR growth, while providing the ability to tune Au NR L/D, include silver nitrate, benzyldimethylammonium chloride (BDAC), halides, and salicylic acid derivatives ^{9, 15-19} (**Scheme 3.1b**).



Scheme 3.1 Structures of hexadecyltrimethylammonium bromide (CTAB) and benzyldimethylammonium chloride (BDAC) in (a) and (b), respectively.

To date, the mechanism by which these reagents impose control over the gold crystal's morphology has not been determined. All species have the potential for epitaxial adsorption and passivation of low index crystalline gold facets, in order to bring about changes in the resultant Au NR morphology (vide infra). However, whether these species are directly interacting with the gold surface, or altering the activity of other surface-active agents is currently unknown. For example, Ag(I) inclusion into the growth solution has, on separate accounts, presented silver in elemental form, and as a Ag(I)Br⁻²-CTA⁺ complex on the Au NR surface; both species undoubtedly exhibiting different surface chemistry ^{9, 20-24}. Similarly, the halide series Cl⁻, Br⁻, and Γ have specific, marked effects on Au NR growth ^{9, 16, 18}. As previously stated, it is not known whether the halide's dominant action is through direct epitaxial adsorption to the growing gold crystal, or through inducing a change in the preferential adsorption behavior of micellar aggregates to growing crystalline facets. Both mechanisms are proven plausible in recent works ²⁵⁻²⁷.

In contrast, the surfactant's significance in affecting Au NR formation is revealed in computational work by Grochola et al., who used molecular dynamics simulations to show that anisotropic growth of Au NRs is facilitated through CTAB's epitaxial micellar adsorption, and subsequent passivation to developing, low-index gold facets ²⁸. Disparities found in the surface adsorption internal energy of CTAB to gold epitaxial surfaces were reported as follows: (110); $U_{ads} \approx -0.61 \text{eV} > (100)$; $U_{ads} \approx -0.356 \text{eV} >$ (111); $U_{ads} \approx -0.315 \text{eV}$. As a consequence, CTAB's passivation of (110) and (100) surfaces mediates anisotropic crystal growth through preferential reduction at (111) facets. Moreover, empirical evidence in separate accounts suggest that the micellar state, regarding micelle morphology and surface chemistry, strongly influences Au NR morphology ^{15, 19, 29}.

Nikoobakht et al. employed a CTAB-BDAC binary mixture in the growth solution to produce Au NRs having L/Ds between 4 and 10, ultimately extending the L-LSPR into the near-infrared region (λ ~1300nm)¹⁵. Similarly, Ye et al. used a growth solution consisting of CTAB and 5-bromosalicylic acid (5BSA) to increase the yield of rods, and provide access to L-LSPRs out to 1246 nm¹⁹. NMR spectroscopy by Ye et al. further revealed that the aromatic ring of 5BSA was intercalated into the palisade layer of the CTA⁺ micelle, whilst the carboxylic acid moiety remained in the hydrophilic micellar region. Intercalation of 5BSA into the CTA⁺ micelle imposes new electrostatic and geometric packing constraints, which affect micellization, micelle morphology, and ultimately the adsorption behavior of the micellar aggregate to epitaxial gold surfaces (vide infra). The micellar changes imposed by 5BSA are expected to be the driving force behind its ability to facilitate the tuning of Au NR L/D.

To illuminate the specific effects of surface-active species on Au NR development, one must first consider its growth mechanism. Recently, Park et al. were the first to track the entire Au NR growth process ^{29, 30}. In their analysis, Park et al. identified five distinct stages of Au NR growth subsequent to seed addition into the growth solution. Stages I (0-2 minutes) and II (2-5 minutes) of Au NR growth are characterized by: Stage I - isotropic growth of the seed crystal, primarily containing (100), (110), and (111) facets, to a critical radius (the critical radius being defined as the crystal size containing facets large enough to support micellar adsorption) which is able to support epitaxial micellar adsorption ($d_{micelle,CTAB}\sim 2.9$ nm), followed by Stage II -

preferential micellar adsorption and passivation of (100) and (110) facets. While stages I and II of Au NR growth are dominated by epitaxial micellar adsorption and facet passivation, stages III-V are characterized by development of the anisotropic crystal as a consequence of stages I and II. The validity of this growth mechanism is suggested in work by Murphy et al. who demonstrated that the addition of silver nitrate has the highest impact on Au NR morphology when added to the growth solution within 10 minutes of initiating NR growth ³¹.

Herein, we aim to elucidate the mechanism by which different additives modify Au NR L/D. According to the growth mechanism proposed by Park et al., altering the growth solution's micellar state should only be effective during growth stages I and II, which are dominated by epitaxial micellar adsorption and bilayer reconstruction. We added BDAC at different growth stages to understand how BDAC modulates the growth of Au NRs. Also, we compared results from the addition of BDAC with those from cetyltrimethylammonium chloride (CTAC) and CTAB, in order to determine the importance of surfactant headgroup chemistry, surfactant concentration, and counterion population on Au NR growth. In order to isolate the specific effect of the counter ion, control experiments are performed by the introduction of potassium chloride (KCI). Evidence is provided that show the addition of BDAC or CTAC to the growth solution changes Au NR L/D through modification of the thermodynamically favorable micelle morphology, which is dominant in controlling preferential micellar adsorption on the growing crystal surface, and thus controls the resultant Au NR morphology.

3.2. Experimental Methods

3.2.1. Materials.

Cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), and benzyldimethylhexadecylammonium chloride (BDAC) were purchased from TCI America. All other chemicals (HAuCl₄, AgNO₃, NaBH₄, potassium bromide, and L-(+)-ascorbic acid) were purchased from Sigma-Aldrich. All chemicals were of analytical grade (purity > 98%) and were used without further purification. Deionized Milli-Q water (18 M Ω cm) was used in all the experiments.

3.2.2. Preparation of the CTAB-Capped Gold Seed Solution

The seed solution was prepared by first adding 25 μ L of 0.1 M HAuCl₄ to 10 ml of a 0.1 M CTAB solution. This solution was sonicated at 30^oC for 30 minutes and allowed to cool to 25^oC. Subsequently, 60 μ L of ice-cold 0.10 M NaBH₄ were added to the stirring solution resulting in the formation of a brownish yellow solution. The brownish yellow color is indicative of gold spheres having a diameter less than 2 nm. Vigorous stirring of the seed solution was continued for 5 min. After the solution was stirred, it was kept at 25 °C.

3.2.3 Preparation of the Growth Solution

Nanorod (NR) growth solutions were prepared by an adaption of the traditional seed-mediated synthesis. First, 500 μ L of 0.10 M HAuCl₄ were added to 100 mL of

solution containing a known surfactant concentration, followed by 80 μ L of 0.10 M AgNO₃ solution. The resulting mixture was sonicated at 30^oC for 30 min, and subsequently cooled back to 25^oC. To initiate rod growth, Au(III) was reduced to Au(I) through the addition of a 560 μ L of 0.10 M ascorbic acid to the growth solution. Complete reduction of Au(III) to the Au(I) is indicated by the color of the growth solution changing from dark yellow to colorless. Finally, 100 μ L of the seed solution were added to the growth solution. The color of the solution changed over time according to the final L/D of the NR.

All the resulting solutions were centrifuged at 5600 • g for 30 min to remove surfactant in excess. The clear supernatant, mainly containing surfactants, was removed, and the concentrated nanoparticle solution was then collected and dispersed in deionized water. This process was repeated for further purification, however no size or shape exclusive purification was carried out.

3.2.4. Transient Influence of Surfactant, Surfactant Concentration, and Surfactant Counter-Ion on Au NR Growth.

In this set of experiments, Au NR synthesis was performed as previously described, using a 0.1 M CTAB concentration for both seed and growth solutions. Once the growth of NRs was initiated through addition of 100 μ L of seed to 100 mL of growth solution, seven 10 mL aliquots were prepared in scintillation vials. To each scintillation vial, an additional amount of CTAB, CTAC, or BDAC was added to achieve a final surfactant concentration of 0.225 M at time increments of 2, 5, 10, 20, 30, and 60 minutes after initiating NR growth. Each respective scintillation vial corresponds to one of the six

time increments. The remaining growth solution represents the control growth solution without co-surfactant. Upon the addition of co-surfactant, the growing NR solution was mixed vigorously using a vortex mixer to ensure complete surfactant dissolution within 10 seconds of its addition. Additionally, a 10 ml growth solution containing 0.1M CTAB and the co-surfactant was separately prepared, and 10 μ L of seed solution were added to represent the addition at 0 min. Each NR growth solution was allowed to mature for 48 hours before characterization with UV-Vis or transmission electron microscopy (TEM).

3.3. Results and Discussion

To check the possibility that increasing CTAB concentration can affect the formation of NRs, and alter L/D, a set of experiments was conducted by adding 0.125 M CTAB to the initial growth solution, containing 0.1M CTAB, at the time increments outlined in the Experimental Section. **Figure 3.1a** shows the UV-Vis-NIR spectra of the resulting Au NR solutions. **Figure 3.1b** focuses on the transverse peak. To enhance readability, the y-axis scale of Fig. 3.1b is magnified 5.6 times than that in Fig. 3.1a. Increasing the CTAB concentration at any time does not make significant changes in either transverse or longitudinal LSPR. The control solution, which only contains 0.1 M CTAB, shows the L-LSPR at 678nm. With the addition of more CTAB at different times, the L-LSPR shifted only a few nm, with no directionality. The degree of the shift was within the range that is observed in repeated experiments performed with a 0.1 M CTAB growth solution. Note that the solution from 0 min shows lower optical intensity, indicating a lower particle concentration. This can be ascribed to a higher growth solution

viscosity, which obstructs the initial growth from seeds. **Figure 3.1c** shows the size and L/D of the NRs obtained from analyzing TEM images. The typical NR dimensions from the control solution are shown after the value of 60min addition. **Figure 3.1d** is a representative NR image from the addition of more CTAB at 0 and 2min. As it is anticipated from the UV-Vis, there is no significant difference in the size of NRs synthesized by adding more CTAB (**Figure S3.1**).

Figure 3.2a shows the UV-Vis-NIR spectra of Au NRs grown from a 0.1M CTAB solution, with subsequent addition of BDAC to the growth solution, and **Figure 3.2b** focuses on the T-LSPR peak. In the resulting growth solution, the concentration of BDAC was 0.125 M, and the total surfactant concentration is 0.225 M. This concentration of BDAC (0.125 M) was chosen based on our previous experiments which showed this specific concentration ratio results in the formation of the longest rods (A.R \sim 6 to 7)³².



FIGURE 3.1 (a) UV-Vis-NIR spectra of Au NR solutions resulting from the addition of 0.125 M CTAB at incremental times, subsequent to the initiation of nanorod growth. (b) The change in the transverse plasmon resonance peak. The scale of the y-axis of Fig. 3.1b is magnified 5.6 times than that in Fig. 3.1a. (c) The time dependent alteration of nanorod length, diameter, and L/D. The values from control solution are shown in the right column (grey) for comparison. (d) TEM micrographs of Au NRs from the control solution (0.1 M CTAB) and the addition of 0.125 M CTAB at 0 and 2min. The scale bar =100nm.

The resulting Au NRs from the control growth solution, containing only CTAB, shows L-LSPR at 679nm and T-LSPR at 514nm. When BDAC was added before the addition of the seed solution, the L-LSPR appeared at 1028nm, and the T-LSPR at 514nm, with an additional peak around 560nm. Since the L-LSPR peak can be directly

correlated to L/D, red-shifts of the L-LSPR indicate that the addition of BDAC promotes the formation of higher L/D NRs ¹⁴. When BDAC was added at 2 min and 5 min, the peak slightly blue-shifted to 975nm. At 10 min, the peak became broad, with the appearance of a second peak around 800nm. At 20 min, the main peak now appeared at much short wavelength (729nm), but there was a small peak remaining around 1000nm. Upon BDAC addition at later time, at 30 min and 60 min, the L-LSPR peak was located at 708nm and 678nm, respectively, which are similar to the peak from the control solution.

In a typical CTAB-based seed-mediated synthesis, spherical polycrystalline particles (d~50nm, as seen in **Figure S3.2a**) are produced as byproducts, but the fraction of these particles is not significant (less than 5%). Therefore, the LSPR peak from these particles (supposed to be around 580nm) is negligible in the UV-Vis spectrum. Prior reports of Au NR synthesis, where BDAC was used as co-surfactant, show that nanocubes (edge length~20nm) were found as the dominant byproduct, along with the large spherical particles (**Figure S3.2b**)³³. The additional peak at 560nm arises from the existence of the nanocube byproduct. Thus, the concentration of nanocubes can be monitored through examination of this additional peak's intensity.

Fig. 3.2b shows the change in T-TSPR peak as a function of the time of BDAC addition. When BDAC was added earlier (< 10 min), the peak around 560nm became distinct. As BDAC was added at later times, the intensity of the additional peak around 560nm decreased. After 20 min, BDAC's influence on the formation of nanocubes decreases, and becomes negligible at longer times. This is also confirmed by





Figure 3.2 (a) UV-Vis-NIR spectra of Au NR solutions resulting from the addition of 0.125 M BDAC, at incremental times subsequent to the initiation of nanorod growth, are shown. (b) The change in the transverse plasmon resonance peak. The scale of the y-axis of Fig. 3.2b is magnified 5.6 times than that in Fig. 3.2a. (c) The time dependent alteration of nanorod length, diameter and L/D. The values from control solution are shown in the right column (grey) for comparison. (d) TEM micrographs of Au NRs from the control solution(0.1 M CTAB) and the addition of 0.125 M BDAC at incremental time. The scale bar =100nm.

BDAC's influence on L-LSPR and T-LSPR can be confirmed by size measurements. Fig. 3.2c presents the comparison of each sample's length, diameter, and L/D over all times of BDAC addition, which were measured based on TEM images shown in Fig. 3.2d. BDAC addition at earlier times (0-5 min) produces rods with a smaller diameter (~ 10-14 nm), and increased length, ranging between 66 and 73 nm. The L/D of these samples, relative to the control solution's NRs, are 1.6 - 2.5 times larger. At 10 minutes, the dimensions of the majority rod population were similar to those from the 5 min addition, but a small fraction (~30 %) of shorter NRs, with a larger diameter were also observed; these rods are responsible for the L-LSPR peak appearing around 800nm. At 20 minutes, the majority rods were shorter, with a small fraction (<10%) of longer NRs. The addition of BDAC at 30 min and 60 min results in short NRs, similar to ones from the control solution. It is also noteworthy that with the addition of BDAC at effective times, the shape of the rod's end becomes more truncated, having a flat (100) tip facet.

Based on our results, BDAC's effectiveness varies at different growth stages. The roman numerals at the top of Fig. 3.2c correspond to the Au NR growth stages defined by Park et al.²⁹. The addition of BDAC is most effective at growth stages I and II (~5 min). The results from the addition of BDAC during growth stage III shows the transition where the influence of added surfactant decreases. At later stages, the addition of BDAC has no significant effect on the growth of NRs.

Figures 3.3a and b show UV-Vis-NIR spectra of Au NR solutions resulting from the incremental addition of CTAC (0.125M). CTAC was selected to examine the influence of chloride as the surfactant counter-ion, for comparison with the results from using BDAC. When CTAC was added before the seed addition (t=0 min), the intensity of the L-LSPR dramatically decreased, while the T-LSPR became broad, showing a new peak around 560nm (Figure 3.3b). This indicates that the fraction of Au NRs was decreased. Instead, more spherical and cubical particles were formed. When CTAC was added after the seed addition, it was most effective during early stages of NR growth (2-10 min). At later time, the addition of CTAC does not significantly change the spectra. To approximate the fraction of rods and isotropic particles, the relative peak areas of the L-LSPR and the T-LSPR were calculated from the UV-Vis-NIR spectra (Figure 3.3c). From the Au NR control solution's UV-Vis spectrum, the relative peak area of L-LSPR was 95%, which is shown as a grey, dashed line (T-LSPR \sim 5%). When CTAC was added at earlier times, the relative peak area of the L-LSPR dropped to 80%. As the effect of CTAC diminishes at later times, the relative peak area became closer to 95% again.

Figure 3.3d shows TEM images of NRs resulting from the addition of CTAC. When added at earlier times (~10 min), CTAC induces the formation of more spherical particles than rods. However, the L/D of the NRs was similar to those from a CTAB growth solution, but with smaller transverse and longitudinal dimensions (**Figure S3.4**). Note that the size of rods obtained from the addition of CTAC at 10 min is much smaller than others. After 20 min, CTAC imposes negligible influence on Au NR growth.



FIGURE 3.3 (a) UV-Vis-NIR spectra of Au NR solutions resulting from the addition of 0.125 M CTAC at incremental time after the initiation of nanorod growth are shown. (b) The change in the transverse plasmon resonance peak. The scale of y-axis of Fig. 3.3b is magnified 5.6 times than that in Fig. 3.3a. (c) The time dependent alteration of relative peak area between the L-LSPR and T-LSPR. Values from the control solution are shown as a dashed line (grey) for comparison. (d) TEM micrographs of Au NRs from the control solution (0.1M CTAB) and the addition of 0.125 M CTAC at incremental time. The scale bar =100nm.

The consensus of both experiments is that the efficacy of each chemical stimulus

is highest during the earlier growth stages of Au NRs (growth stage I and II), which are

dominated by micellar adsorption and surface reconstruction, respectively. Based on these experimental results, it is possible to speculate that the co-surfactants enhance, or suppress, the directional growth of the particles by affecting micellar adsorption, thus altering surfactant-directed crystal growth.

In the case of BDAC, it has been known that the micellar structure of CTAB-BDAC mixed micelles is significantly different from that of CTAB. Park et al. observed that sphere-to-wormlike transitions in a CTAB-BDAC mixed solution (the mole fraction of BDAC ~0.5 to 0.55) occur at a higher concentration (0.5 M total surfactant concentration), as opposed to 0.3 M in a CTAB solution, thus indicating BDAC's apparent suppression of sphere-to-wormlike micellar growth ³³. Bakshi et al. observed that the relative viscosity of CTAB-BDAC binary mixtures dramatically decreased upon the introduction of BDAC into solution, and becomes even lower than that of a BDAC solution when the mole fraction of BDAC is about 0.4; this indicates that micelle size becomes smaller within the CTAB-BDAC binary solution. It was also confirmed that the mixed micelles are rich in BDAC ³⁴.

BDAC has also been known for having a smaller micelle aggregation number, compared to species having an equivalent alkyl chain length, due to the contributions of the bulky polar head group (benzyl moiety) providing additional hydrophobicity, and a higher head-group surface area, ultimately resulting in smaller micelles ³⁵⁻³⁷. Therefore, the micelle size of a CTAB-BDAC mixed solution is likely smaller than that of CTAB. The radius (R) and aggregation number (N) of a pseudo-spherical CTAB-BDAC mixed micelle was estimated based on a model developed by Israelachvili et al. ³⁸⁻⁴³ (supporting information). The estimation of $R_{CTAB-BDAC}$ and $N_{CTAB-BDAC}$ in CTAB-BDAC
mixed solution (CTAB: BDAC =1:1.25) yields 1.5 nm and 122, respectively, which is smaller than values reported for CTAB micelles in this solution condition ($R_{CTAB} \approx$ 3.1nm, $N_{CTAB} \approx$ 163).

The contribution of a smaller micelle toward increasing the L/D of Au NRs can be postulated by recalling the anisotropic growth processes of Au NRs in a CTAB solution. According to the growth mechanism proposed by Park et al., anisotropic growth only begins after the isotropic seed exhibits crystalline facets that are large enough to accommodate adsorption of CTAB micelles. In a typical CTAB based synthesis, this transition occurs for particles approximately 6 nm in diameter, which approximately corresponds to the size of a CTAB micelle in these solution conditions. Therefore, it is likely that in the binary CTAB–BDAC solution, the smaller micelles adsorb onto transverse (100) and (110) crystalline facets of younger (i.e. smaller) gold seeds, thus confining the transverse growth of the rods earlier on. Preferential micellar adsorption onto transverse (100) and (110) facets inhibits the adatom deposition of Au, which has been confirmed both empirically and computationally ^{28, 30}. Therefore, increasing L/D through the addition of BDAC can be due to enhanced confinement of transverse growth during earlier growth stages, compared to that seen with CTAB. Moreover, as transverse growth is confined, longitudinal growth is promoted.

The size measurements of the resulting rods confirm our speculation. When BDAC was added at effective timing, the diameter of the rod became smaller, and the length of the rod longer. For example, BDAC addition at 2 minutes yields rods which have a 36% decrease in diameter, and a 32 % increase in length, relative to the rods from the control growth solution. During growth stage III (10 and 20 min), the addition of BDAC results in a larger size distribution in diameter, which is from the existence of two morphologically disparate rod populations. At 10 min, the dominant population of rods is longer, with a smaller diameter (~13nm), resembling what is expected from a CTAB– BDAC solution. The less prevalent rods were shorter, with a larger diameter (~ 21 nm). At 20min, the dominant population of rods became shorter, and a small fraction of longer NRs were present. These results indicate that growth stage III is the transition point when BDAC's influence diminishes.

Accordingly, the truncated tips of Au NRs that are found from BDAC addition at earlier times, suggest that all (100) facets on the crystal, including the tip facet, are significantly passivated toward gold reduction. This behavior is exemplified in the TEM micrographs, and the quantification of Au NR tip curvature, from all times of BDAC addition, shown in **Figure 3.4a-c**. Au NR tip curvature is quantified as the relative curvature, C_R, by comparing the radius of curvature to the radius of the rod, which is close to 1 in the case of a tip having a sphero-cylindrical shape. C_R is low at early times of BDAC addition, indicating significant passivation of the (100) surface at the rod's tip. At times when the influence of BDAC is negligible, the tip curvature increases to what one would expect from a CTAB-based synthesis.

In the case of CTAC, addition before the seeds results in forming more spherical and cubical particles as byproducts, along with the formation of NRs; Au NR yields were primarily diminished during growth stages which are dominated by epitaxial micellar adsorption and reconstruction (Stages I and II). CTAC has the same hydrocarbon chain length as CTAB, thus the hydrophobic contribution to micelle behavior is not significantly altered. Therefore, the additional counter-ions (CI⁻) should be responsible

for the changes observed in NR morphology. The influence of the counter-ion on CTA⁺ micellar morphology was investigated by Velegol et al. and Magid et al., respectively ^{25, 27}. It was shown that Br⁻ exhibits a 5-fold increase in binding affinity to the CTA⁺ micellar surface over Cl⁻, which improves the electrostatic screening of the micelle's surface charge.



FIGURE 3.4 Comparison of nanorod tip morphology between CTAB (a) and CTAB-BDAC (b) based syntheses. The scale bar =20 nm. c) Quantification of the tip curvature at different times of BDAC addition.

As a result, the adsorption density of CTA^+ on silica surfaces is much higher (66%) when bromide is employed instead of chloride ²⁷. Additionally, bromide introduction into a CTA^+ -Cl⁻ solution displayed bromide's ability to displace Cl⁻ from the micellar surface. In a CTAB growth solution, the Br⁻ to CTA^+ ratio is 1. The adsorption density of CTA^+ micelles in the presence of bromide is high enough to preferentially passivate the transverse facets for anisotropic crystal growth. When 0.125 M CTAC is added to the Au NR growth solution, the Br⁻ to CTA⁺ ratio decreases to 0.44, while the Cl⁻ to CTA⁺ ratio is 0.56. Therefore, there is more chloride than bromide available per CTA⁺ molecule, resulting in a decreased adsorption density of CTA⁺. Anisotropic transition from spherical seed to rod occurs in early stages of growth (~5min) via dense micellar adsorption. Therefore, the addition of CTAC at these stages interrupts the seed's growth into rods.

Although we have discussed the counter-ion's potential to affect the growth solution's micellar behavior, direct adsorption of halides to developing crystal surfaces should be considered as a potential means of changing Au NR growth. All halides, except for F⁻, strongly adsorb to low-index gold surfaces (Au(111), Au(110), Au(100)) in the absence of surfactant ^{16, 44}. The associated bond energies of the halides to epitaxial gold surfaces relatively follow: $|\Delta G_{ads}^{Au}| = I^- > Br^- > Cl^-$. In the case of iodide, introduction at trace concentrations (~10 µM) into a CTAB-based synthesis completely suppressed Au NR formation; the resultant gold crystals existing as either prisms, or plate-like hexagonal and pentagonal particles, which strictly exhibited Au(111) facets ¹⁶.

To determine the role of Cl⁻, we conducted experiments introducing 0.0625 M and 0.125 M KCl as the chloride source. Using 0.0625 M KCl allows us to test the effect of chloride at the same ionic strength as the CTAB- CTAC system, while the introduction of 0.125 M KCl allows us to test the influence of an equivalent chloride concentration of the said system (supporting information). Interestingly, the UV-Vis spectra (shown in supplementary **Figure S3.5**) indicate that the introduction of 0.0625 M KCl induces at most 28 nm red-shift in L-LSPRs (a slight increase in A.R) at early times (0-20 min).

Increasing the KCl concentration to 0.125 M gives nearly identical results, exhibiting at most a 32 nm red-shift in L-LSPR.

The addition of KCl to the 0.1 M CTAB growth solution departs from the CTAB-CTAC system in that the Br⁻ to CTA⁺ ratio does not change. The excess of halide anions beyond the CTA⁺ concentration establishes a competition between Br⁻ and Cl⁻ for the adsorption sites on the CTA⁺ micellar surface. As previously discussed, Br⁻ exhibits higher selectivity for CTA⁺ micellar surfaces than Cl⁻, with a thermodynamic ion exchange ratio (Br/Cl) between 2 and 3; Cl⁻ is then acting solely to increase the ionic strength in instances where enough Br⁻ exists to saturate the surface adsorption sites on CTA⁺ micelles ²⁵. Therefore, the influence of BDAC and CTAC on Au NR growth is not attributed to the chloride concentration. Further evidence is provided showing that the introduction of 0.125M KCl before the initiation of nanorod growth had no significant influence on Au NR aspect ratio (Fig. S3.6).

3.4. Conclusions and Comments on Future Work

The time-dependent susceptibility of Au NR growth to the addition of cosurfactant was investigated. The influence of different co-surfactants on the resulting nanoparticle products is summarized in **Figure 3.5**. It is evident that BDAC incorporation into the growth solution has the most significant effect on increasing L/D. BDAC simultaneously inhibits transverse growth, and proportionally increases longitudinal growth, which our analysis suggests is due to BDAC facilitating the formation of smaller micelles. Consequently, unprecedented micellar passivation of smaller (110) and (100) crystalline facets is allowed, in order to bring about morphological modification at earlier stages of crystal growth. CTAC addition induces a significant change in opposing fashion through decreasing the fraction of NRs, while simultaneously increasing the fraction of byproducts. This effect can be ascribed to a deficiency in Br⁻, allowing chloride to disturb the favorable micellar state. Both increasing CTAB concentration and KCL addition resulted in minor changes in the final products, due to their mild influence on micellar state. Our studies demonstrate the importance of the growth solution's micellar state on Au NR growth. It is worth mentioning that each additive's influence is most drastic between growth stages I and II, and becomes negligible afterwards. As outlined by Park et al., stages I and II are dominated by epitaxial micellar adsorption, and subsequent surface reconstruction to passivate specific crystalline facets. Our results bolster the growth mechanism outlined by Park et al., proving nanorod growth is most susceptible to crystal habit modification during growth stages which are dominated by epitaxial micellar adsorption, surfactant bilayer reconstruction, and adatom reorganization.

Procedures developed herein will be applied to probing plasmonic nanoparticle enhancement mechanisms in organic photovoltaics. Au NRs will be synthesized having L-LSPRs that are within and outside of the BHJ donor's absorbance and emission, in order to probe the existence of plasmonic photovoltaic enhancement via SPR-enhanced exciton generation or BHJ photoemission.



FIGURE 3.5 The UV-Vis-NIR spectra and TEM images showing the effect of addition of 0.125 M CTAB, BDAC and CTAC to the growth solution of 0.1M CTAB. The scale bar =100 nm.

3.5. References

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3.6. Supplemental Information



Figure S3.1 TEM micrographs of Au NRs from the addition of 0.125 M CTAB at incremental time. The scale bar =100nm.



Figure S3.2. TEM micrographs of as-made Au NRs from (a) CTAB (0.1 M) solution and (b) CTAB-BDAC mixed solution(0.225 M) focused on the byproducts of the syntheses.



Figure S3.3. Comparison of nanorod purity (% rod content) for the addition of 0.125 M CTAB (green), CTAC (red), and BDAC (blue). Trend-lines serve solely as a guide to the eye.



Figure S3.4. The time dependent alteration of nanorod length and diameter upon adding 0.125 M CTAC.



Figure S3.5. KCl addition to growing nanorods. UV-Vis spectra of nanorods from the addition of 0.125 M (a) and 0.0625M (b) KCl at 2 (pink), 5 (maroon), 10 (blue), 20 (green), 30 (orange), and 60 (red) minutes after the initiation of nanorod growth are shown.

b)



Figure S3.6. Au NR growth in the presence of 0.225M CTAB (black trend line) and 0.125M KCl (blue trend-line) before the initiation of nanorod growth.

Estimation of Micelle Size within CTAB-BDAC Mixed Micelles

Empirical measurements of a_0 for CTAB and BDAC have been measured at $a_{0-CTAB} = 53.6 \text{ Å}^2$ and $a_{0-BDAC} = 132 \text{ Å}^2$ ^{1,2}. Similarly, calculation of v is done following developments by Tanford et al.(equation SE3.3), where n is the number of carbons in the hydrocarbon tail.

Micelle Diameter =
$$2R \approx \frac{3\nu}{a_0}$$
 (SE3.1)

Aggregation number (N)
$$\approx \frac{4\pi R^3}{3\nu}$$
 (SE3.2)

$$v = (27.4 + 26.9n) \text{\AA}^3$$
 (SE3.3)

To test the accuracy of our approach, we compare calculated and empirically determined values for CTA⁺ micelles. Park et al. measured the CTAB micelle diameter to be 6.2 nm in diameter using small-angle x-ray scattering (SAXS). Similarly, Aswal et

al. measured CTAC micelle dimensions using small-angle neutron scattering (SANS). As expected, they found that micelles become increasingly nonspherical as the surfactant concentration increases. For a micelle axial ratio of 1.18, the semiaxial measurements lie between 2.30 and 2.71 nm; the micelle diameter thus lies between 4.6 and 5.42 nm. Aswal et al. also determined that micelle size increases when using bromide as the counterion. Nevertheless, our calculation yields a CTA⁺ micelle diameter of 5.2 nm, which is well within empirical values. Similarly, the calculated aggregation number (N_{CTA}⁺= 153) differs by 6% from measured empirical values (N_{CTA}⁺= 163) proving our theoretical calculations are accurate. However, the reader is cautioned that all values depend on solution conditions, and our calculations only serve as example of the ideal changes from one system to another.

The BDA⁺ micelle diameter was calculated to be approximately 2.08 nm. Using equation SE3.4 to estimate the average a_0 within the mixed micelle, where χ_i and a_i are the mole fraction and a_0 of species **i**. For a system employing 0.125 M BDAC and 0.1 M CTAB, the weighted-mean a_0 is approximately 97 Å²; the estimated mixed micelle diameter is therfore 3 nm. Similarly, the mixed micelle aggregation number calculated to be 122.

$$\overline{a_o} = \frac{\sum_{i=1}^{n} \chi_i a_i}{\sum_{i=1}^{n} \chi_i}$$
(SE3.4)

Effective Ionic Strength Calculation of Au NR Growth Solutions.

In calculation of the effective ionic strength, we neglect contributions from silver nitrate, ascorbic acid, and gold tetrachloroaurate due to their concnetrations being more than 150x less than the employed additives (CTAC, CTAB, KCl). Similarly, the growth solution's surfactant concentration is well above the cmc; therfore, most surfactant moleculer are in micellar form. We thus consider the ionic strength to be dominated by the electrolytes introduced into the system from CTAB, CTAC, KCl, and BDAC; namely, chloride, bromide, and potassium.

Ionic strength is calculated using equation SE3.5 where C and Z are the concentration and ionic charge of species i, respectively. The Ionic strength of each experimental system is listed in Table ST3.1 below.

Ionic Strength (Z) =
$$\sum_{i=0}^{n} C_i Z_i^2$$
 (SE3.5)

System	Electrolytes Contributing to Ionic	Ionic Strength
	Strength	(M)
0.1 M CTAB + 0.125 M	0.1 M bromide + 0.125 M chloride	0.225
BDAC		
0.225 M CTAB	0.225 M bromide	0.225
0.1 M CTAB + 0.125 M	0.1 M bromide + 0.125 M chloride	0.225
CTAC		
0.1 M CTAB + 0.125 M	0.1 M bromide + 0.125 M potassium	0.350
KCl	+ 0.125 M chloride	
0.1 M CTAB + 0.0625 M	0.1 M bromide + 0.0625 M	0.225
KCl	pottasium + 0.0625 M chloride	

Table ST3.1. Ionic Strength of Gold Nanorod Growth Solutions

3.7. Supplemental References

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Gold Nanorod Enhanced Organic Photovoltaics: The Importance of Morphology Effects

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4.1 Introduction

Solar energy is one of the most abundant sources of alternative energy available. More solar energy irradiates the earth in one hour than human activity consumes in an entire year¹. Therefore, photovoltaic technology is currently undergoing significant growth, owing to the worldwide sensitivity to energy security and the importance of clean, renewable energy. Organic photovoltaic (OPV) systems represent a promising photovoltaic technology for light-to-electric conversion. Some of the advantages that are expected of OPVs include low cost of fabrication, ease of processing, mechanical flexibility, and lightweight modules. Unfortunately, the efficiency of thin film OPVs has substantially lagged behind that of inorganic PV technologies, thereby limiting their marketability due to a poor price-to-power output ratio. At present, the record power conversion efficiencies for OPV devices are recorded near 12%².

The most representative high performance OPVs reported in the literature have been fabricated using bulk heterojunction (BHJ) architectures, which are formed by spincasting a mixture of photosensitive electron donor and acceptor materials. This process creates a blended heterojunction of the donor and acceptor, with a high degree of interfacial surface area between each phase, at which photo-induced charge transfer occurs³. While a variety of materials have been investigated in BHJ films, P3HT/PCBM blends (poly-3-hexyl thiophene / phenyl- C_{61} -butyric acid methyl ester) represent the most well studied and reproducible system to date. The overall efficiency of an OPV device is highly dependent on the active layer film thickness⁴. A thinner active layer increases the excited state collection efficiency by lowering the probability of excited state recombination. However, light absorption, and subsequent exciton generation, is directly proportional to the active layer thickness. In other words, a thinner active layer has a lower absorption and thus limits the number of potential charge carriers that can be generated. Developing approaches to increase the effective absorption of light in thin films is a key challenge in the push to higher device efficiencies.

A recent approach towards improving light absorption within the polymer thin film is the incorporation of metal nanoparticles within the organic device architecture because of the potential for plasmonic enhancement effects⁵. The field of nanoparticle plasmonics has been incredibly active in the past two decades, leading to the discovery of some very interesting phenomena, and the development of applications related to light manipulation and confinement ⁶⁻⁸. The electric field component of incident electromagnetic radiation can excite the sea of conduction band electrons associated with the metal particle at a resonant mode which causes the electrons to oscillate coherently on the surface of the particle; this phenomenon is referred to as a localized surface plasmon resonance (LSPR). This resonant mode behaves much like an antenna, focusing the energy to a sub-wavelength dimension⁸. A portion of this energy is re-radiated to the environment in a range of directions dictated in part by the shape of the particle while the remaining energy is dissipated as heat. This ratio of scattered / absorbed energy, which is referred to as the particle's albedo, is dependent on several factors, such as the size of the particle and the dielectric environment⁹.

The general set of phenomena categorized as plasmon enhancement in OPV devices involves several mechanisms that are related, but physically distinct. The most widely observed effect is the increase in beneficial far-field scattering from the nanoparticles at the LSPR frequency, which have an extraordinary large scattering crosssection compared to their geometric cross-section^{8,10-12}. Far-field scattering is from plasmonic nanostructures distributes the scattered light in many directions, especially for anisotropic species which exhibit morphology-dependent scattering geometry, and enhances the thin-film OPV device by redirecting normally incident light through the film, so that the light has an longer average effective pathlength, thereby leading to a higher probability of photon absorption within the film; this process is a linear effect (neglecting losses due to the nanoparticle absorption). A second enhancement mechanism from the localized plasmonic modes is surface enhanced absorption, which is a near-field effect involving spatial overlap of the concentrated evanescent field at the nanoparticle surface and a nearby organic chromophore¹³⁻¹⁵. This effect has been proposed to be nonlinear because it is related to the square of the concentrated field ¹⁶.

A variety of strategies have been used to incorporate plasmonic nanostructures into organic PV devices, such as placing nanoparticles at the electrode / polymer interface, incorporating particles within a charge blocking polymer layer, and mixing nanoparticles directly into the active BHJ film^{10-15,17}. The majority of these studies utilize isotropic or nearly isotropic nanoparticles (spheres, octahedra) of various sizes, with a few groups using anisotropic particles ^{12, 17-23}. The nanoparticles have been reported to affect both the overall photo-conversion efficiency of a photovoltaic device, and some of the more specific photo-physical properties of the organic layers ^{13, 17, 18, 23-27}. In most cases, these effects are beneficial, with a few exceptions where the conversion efficiency is reported to degrade when metal nanoparticles are incorporated into the device ²⁸. In nearly every report, the effects are attributed to the induced localized plasmon modes of the nanoparticles, although these mechanisms are not always clearly differentiated between near-field and far-field effects, primarily due to both enhancement pathways' potential to increase photo-conversion efficiency through enhancing the absorption of the BHJ active layer. In addition to the plasmonic effects, secondary effects of colloidal nanoparticle integration on the OPV performance are also likely, but are not readily discussed in the literature. Such effects are polymer morphology changes, conductivity improvements, electrode work function modification, and changes to excited state lifetimes in the organic molecules ^{17, 22, 29, 30}. These effects, induced by blending metal nanoparticles into the BHJ film, are only fleetingly addressed in the literature as minor consequences and are proposed to play trivial roles in altering device performance.

In this work, we demonstrate that nanoparticle incorporation into the BHJ can significantly alter the active layer's morphology, with parallel enhancements in device performance. The nanorods are treated with a sophisticated ligand exchange protocol to solubilize the rods in organic solvents, and render them compatible with the aromatic BHJ active layer. The effects of nanorod concentration and aspect ratio on the device performance are investigated and significant improvements in the photo-conversion efficiency (PCE) are observed. Using a combination of electron microscopy and device characterization, the different effects induced by the presence of the particles are discussed, including plasmonic mechanisms and morphological changes to the BHJ film. Based on these observations, the majority of the performance enhancement in the OPV devices studied here is attributed to nanoparticle-induced morphology changes in the BHJ film, which substantially increase the absorption of the P3HT, and enhance internal quantum efficiency processes; negligible effects from plasmonic enhancement mechanisms are observed.

4.2. Experimental Section

4.2.1. Materials

Cetyltrimethylammonium bromide (CTAB) and benzyldimethylhexadecylammonium chloride (BDAC) were purchased from TCI America. All other chemicals (HAuCl₄, AgNO₃, NaBH₄, potassium bromide, and L-(+)-ascorbic acid) were purchased from Sigma-Aldrich. All chemicals were of analytical grade (purity > 98%) and were used without further purification. Deionized water (18 M Ω cm) was used in all the experiments.

4.2.2. Instrumentation

UV-Vis-NIR spectra were acquired with a Cary 5000 spectrophotometer at room temperature using a quartz cell of 1 mm path length in the 300-1000 nm spectral region. Morphology and mean size of NPs were examined by TEM (Philips CM200 LaB6 AT 200 kV or a Topcon 002B at 200 kV). For each sample, the size of at least 300 particles was measured to obtain the average size and size distribution.

4.2.3. Synthesis, Purification, and Functionalization of Gold Nanorods

Gold nanorods (Au NRs) having aspect ratios (AR) of 2.15, 2.5, and 3.3 were synthesized according to procedures adapted from the traditional seed-mediated methods, developed in separate efforts by Park et al., Nikoobakht et al., Gole et al., and Sharma et al.³¹⁻³⁵.

4.2.3.1. Synthesis of the Spherical Gold Seed

First, 25 μ L of aqueous 0.1 M gold tetrachloroaurate trihydrate (HAuCl₄•3H₂O) were added to 10 mL of aqueous 0.1 M cetyltrimethylammonium bromide (CTAB). This solution was subsequently sonicated for 30 min at 30°C, and then cooled down to 25 °C. Under vigorous magnetic stirring, the nanoparticle seed was formed through the addition of 60 μ L of ice-cold 0.1 M sodium borohydride (NaBH₄), upon which the solution turned a yellow-brown color, which indicates the presence of gold spheres approximately 2 nm in diameter. These seeds were aged under stirring for exactly 5 min before use.

4.2.3.2. Synthesis of Gold Nanorods Having Aspect Ratio 2.15 and 2.5

To 50 mL of 0.1 M CTAB (aq), 2.5 mL (250 μ L) of 0.1 M HAuCl₄ (aq) were added followed by 400 μ L (40 μ L) of 0.1 M AgNO₃ (aq). (Values stated in parentheses represent the corresponding reagent volumes required for the synthesis of aspect ratio 2.5 NRs.) This growth solution was sonicated for 30 min at 30 °C, and subsequently cooled to 25°C. Upon reaching 25°C, 2.8 mL (280 μ L) of 0.1 M L-(+)-ascorbic acid (aq) were added. Once the solution turned from yellow to colorless, indicating the reduction of Au (III) to Au (I), 500 μ L (50 μ L) of the seed solution were added under mild mixing. Each growth solution was aged for 48 hours at 25°C to ensure completion of NR growth.

4.2.3.3. Synthesis of Gold Nanorods Having Aspect Ratio 3.3

The NR growth solution in this synthesis employs a binary surfactant mixture composed of 0.062 M benzyldimethylammonium chloride (BDAC) (aq) and 0.1 M CTAB (aq). To 50 mL of the surfactant mixture was added 250 μ L of 0.1 M HAuCl₄ (aq), followed by 40 μ L of 0.1 M AgNO₃ (aq), and subsequent sonication for 30 minutes at 30 °C. The solution was then cooled to 25°C, followed by the addition of 300 μ L of 0.1 M ascorbic acid (aq). Once the solution turned from yellow to colorless, 50 μ L of the gold seed were added under stirring. The gold nanorod suspension was aged 48 hours before purification.

4.2.3.4 Nanorod Purification

Purification was performed using centrifugation and depletion induced segregation ³⁵. Gold nanorods with L/D 2.15 and 2.5 were centrifuged at 10,000•g for 60 min. This centrifugation cycle produces two separate pellets in the centrifuge tube, one

corresponding to nanorods, and the other to spherical and cubic impurities. The two pellets were then separated via pipette and the nanorods were dispersed in a 0.1 M CTAB (aq). For L/D 3.3 nanorods, BDAC was added to the post-synthetic growth solution to yield a total surfactant concentration of 0.275 M. Depletion force-mediated reversible aggregation of NRs from byproduct morphologies (spheres and cubes) was run for 48 hours. Afterwards, the supernatant was decanted from the pellet. The pellet containing purified nanorods was then dispersed in 0.1 M CTAB (aq).

4.2.3.5 Functionalization of Nanorods with Thiolated Polystyrene

A stock solution of 5×10^{-4} M thiolated polystyrene (PS) (Mw=53,000, Polymer Source Inc.) was prepared in tetrahydrofuran. Within a scintillation vial, 5 mL of the PS stock solution were mixed vigorously with 5 mL of a 3 nM NR suspension. The PSfunctionalized gold nanorods immediately phase segregated from solution and were dried thoroughly on a hot plate. The functionalized nanorods were subsequently washed via suspension in toluene or chlorobenzene, followed by centrifugation at 6500•g for 20 minutes in order to remove excess PS. After decanting the supernatant from the washed NRs, the pellet containing purified PS-functionalized NRs was placed in a vacuum oven at 60°C for 12 hrs before blending with the BHJ solution.

4.2.4. Bulk Heterojunction Solar Cell Fabrication

The devices were fabricated on 1x1 inch pre-patterned indium tin oxide (ITO) on glass substrates (Luminescence Technology). Prior to the fabrication process, the ITO glasses were cleaned by sequential sonication in detergent, deionized water, hexane, 2propanol, acetone, and methanol. The final cleaning step was a UV ozone treatment for 20 min. A PEDOT: PSS layer (Clevios P, Heraeus) was spin-coated onto the slides resulting in a film thickness of about 50 nm, as measure by profilometry. The film was dried at 160°C for 20 min and the substrates were transferred to a nitrogen-purged glove box. The BHJ blend of poly-3-hexylthiophene (P3HT) and phenyl-C₆₁-butyric acid methyl-ester (PC₆₁BM) (5:3, wt./wt.) was dissolved in chlorobenzene. Gold nanorods were blended into the BHJ solution at either 1 wt.% or 2 wt.% with respect to P3HT. The mixture was spin casted onto the PEDOT: PSS coated substrate at a rate of 1500 RPM for 45 s. All devices were covered by a 100 nm thick layer of Al through thermal evaporation under vacuum, and subsequently annealed at 158°C for 8 min.

Power conversion efficiency was measured under AM 1.5G solar irradiation (100 mW cm⁻²) using a xenon-lamp-based solar simulator (Oriel 81160) inside a nitrogenpurged, moisture free glove box. The external quantum efficiency (EQE) as a function of wavelength was obtained with a photomodulation spectroscopic setup (Newport). UVvisible spectra were acquired with a Cary 5000 UV-visible-near IR spectrophotometer, and gold nanorod morphology was examined by Transmission Electron Microscopy (TEM) (Philips CM200 LaB₆ AT 200 kV).

4.3 Results and Discussion

Gold nanorods (Au NRs) were functionalized with thiolated polystyrene (PS) and incorporated into the BHJ layer of organic photovoltaic devices at two loading concentrations (1% and 2% Au / P3HT by weight). The aspect ratios (L/D) of the NRs were 2.15, 2.50, and 3.30; the respective average lengths/widths were 38/18 nm, 43/18

nm, and 49/15 nm, measurements which were taken over at least 300 particles (histograms of the size distribution are provided in the supporting material). Representative TEM images of the rods drop-cast from solution are shown in **Figures 4.1A-C**. The aqueous phase extinction spectra are shown in **Figure 1D**, where the transverse resonance bands appear around 530 nm and the longitudinal resonance bands occur at longer wavelengths, the position of which is dependent on L/D ³¹⁻³⁵. The aspect ratios were systematically varied in order to tune the longitudinal localized surface plasmon resonance band (L-LSPR) between partial overlap (AR 2.15: $\lambda_{ex} = 638$ nm) and no overlap (AR 3.3: $\lambda_{ex} = 780$ nm) with the P3HT absorption bands, shown as the shaded area in Figure 1D. Detailed characterization of the NRs via TEM indicates that there is no significant variation in the volume or NR surface area with aspect ratio (less than 10% variation; see supplemental information).

Careful selection of the Au NR ligand was taken to ensure fine dispersion of the particles throughout the BHJ, thus avoiding the formation of high-order aggregates. Finely dispersing Au NRs within a polymer matrix requires that the matrix sufficiently wets the particle's polymer brush. This requires that the matrix and brush are chemically compatible, and that the loss of conformational entropy of brush molecules, upon inter-digitation with matrix chains, remains low.

Hore et al. showed that polystyrene-grafted Au NRs overcame these energetic constraints, becoming finely dispersed within a polystyrene matrix, when the brush's degree of polymerization (N) was at least twice that of the matrix (P) ³⁶. However, Hore et al. used identical chemistry for the brush and matrix to avoid chemical incompatibility. The polystyrene brush and P3HT matrix used in these experiments introduces chemical

incompatibility, and favors particle aggregation within the BHJ. Hildebrand and Hanson solubility parameters can be used to roughly approximate compatibility between chemical species, where chemical species sharing identical solubility parameter values are likely compatible. Hanson solubility parameter values for P3HT, PCBM, and polystyrene are approximately 19.1 MPa^{1/2}, 21.7 MPa^{1/2}, 20.64 MPa^{1/2}, respectively ^{37,38,39}. The variation of more than 1 MPa^{1/2} indicated that there is likely some incompatibility between these species.



Figure 4.1. (A), (B), and (C) show TEM images for gold nanorods with aspect ratio: 2.15, 2.5, and 3.3, respectively. Scale bar is 25 nm. (D) UV-visible extinction spectra of

gold nanorods with various aspect ratios in aqueous phase. The gray shaded area in (D) is the normalized absorption of the P3HT: PCBM BHJ film.

Results for the grafting of Au NRs with PS, and their incorporation into P3HT: PCBM BHJs are shown in **Figure 4.2 a-d**. Successful grafting of the Au NR surface with PS is indicated by the aqueous-to-organic phase transfer, Figure 4.2a. The 45 nm red-shift in L-LSPR upon phase transfer is expected due to the change in the bulk medium's refractive index ($\Delta n \approx n_{chlorobenzene}-n_{water} = 0.191$), due to the Frölich condition's dependence on ε_m (chapter 1), which induces a red-shift in LSPR with increasing ε_m , and thus increasing refractive index ⁴⁰. TEM micrographs in Figure 4.2b and c show no change in morphology between as-synthesized and PS grafted Au NRs, respectively.

PS-grafted NRs were then mixed into a chlorobenzene solution containing a 5:3 w/w ratio of P3HT to PCBM. Thin films were then spin-cast onto a PEDOT-PSS-coated ITO substrate, in order to test whether the polystyrene shell provided sufficient dispersion of the particles within the BHJ. Figure 4d exhibits TEM micrographs of the BHJ films. The particles are well dispersed, showing minimal flocculation. Particles are mostly found as monomers, dimers, and trimers with a measured inter-particle spacing for flocculated particles in a side-to-side configuration of 12 +/- 3nm, indicating that the PS shell is approximately 6 nm thick (supplemental information).

A variety of PS-grafted Au NR aspect ratios were then incorporated into active layers within OPV cells. **Figures 4.3A and B** show representative TEM images of the BHJ films, where nanorods of L/D = 2.15 and 3.30 were incorporated at a 2 wt. % loading. To prepare the BHJ films for TEM imaging, previously reported techniques were

used to float the organic layer off of the device substrate onto an aqueous / air interface, where the film was subsequently transferred to a TEM grid, and allowed to dry 41 .



Figure 4.2 The incorporation of Au NRs into Bulk Heterojunction Thin-Films. Successful grafting of the NR surface with thiolated polystyrene (PS) is indicated by particle dispersion in chlorobenzene after place-exchange in the aqueous solution (a). TEM micrographs of NRs before and after PS grafting is shown in (b) and (c), respectively. Nanorods (2 wt. NRs with respect to P3HT) dispersed within a P3HT: PCBM BHJ thin-film is shown in (d). Length of the scale bars in (b) and (c) are 50nm, and 500nm in (d).

Characterization of the particles embedded within the BHJ films indicates that

large scale agglomeration was avoided during casting, which is presumed to be a

kinetically trapped state given the expected incompatibility between PS and P3HT, although a notable fraction of the nanorods tended to form dimers or trimers with a preferred side-to-side orientation. The particle aspect ratio had a slight effect on the degree of agglomeration in the BHJ films. The least agglomeration occurred with low aspect ratio (L/D = 2.15) particles, where nearly 30% of the particles were isolated, and another 40% of particles were found in dimers. There were no agglomerates in the films with L/D = 2.15 nanorods larger than 5 nanoparticles observed. The high aspect ratio particles (L/D = 3.30) were found to agglomerate to a larger degree, where 25% of the particles were isolated in the BHJ film, another 25% formed dimer or trimer groups, and the remaining 50% of the particles were found in groups of 4-10 particles. This is likely due to the increased depletion-attraction forces between higher aspect ratio nanorods, brought about through the increased surface area of interaction of a longer rod's longitudinal surface ⁴². The overwhelming majority of particle-particle interactions appeared to be side-to-side, accounting for nearly 2/3 of all interactions over the films. A histogram depicting these results is shown in Figure 4.3C. Most of the rods in the films are lying in the plane of the film surface, which can be observed from the TEM images taken of the rods in the BHJ films, although the rods are not necessarily co-planar. Tilted TEM imaging indicated that there was variation of particle position in the z-direction (not shown).



Figure 4.3. HAADF-TEM images of PS-grafted gold nanorods dispersed in the BHJ film of organic photovoltaic devices for gold nanorods of aspect ratios 2.15 (A) and 3.30 (B). The scale bar is 500 nm and applies to both (A) and (B). The loading amount of gold nanorods was 2 wt. % for both images. (C) Bar graph illustrating the changes in nanoparticle agglomeration behavior within the BHJ film as the aspect ratio is increased.

Organic bulk heterojunction photovoltaic devices were fabricated from the nanorod embedded films imaged in Figure 4.3. The J-V curves for devices fabricated with each L/D of gold nanorods incorporated in the films, at 1wt. % and 2wt. % relative to P3HT, are provided in Figures 4.4A, B, and C. Previous investigations indicated that 2wt. % was the optimum loading concentration for L/D = 2.50 nanorods (results not shown), which is consistent with other reports¹⁷. Therefore, we investigate maximum loading percentages of 2wt. % herein. For each aspect ratio, the J_{SC} increases as the nanoparticle loadings are increased, while the V_{OC} and fill factor (FF) remain relatively constant for all devices. This effect results in a substantial increase in device efficiency. The device performance values are averages of multiple (>10) devices with deviations less than 5%, and the J-V curves in Figure 4.4 are representative of the devices. A summary of the important J-V characteristic values is provided in **Supporting Table ST4.2**. The largest efficiency improvement observed was a 30% enhancement, which was achieved using nanorods of aspect ratio 3.30 at a 2wt. % loading. For every aspect ratio, the initial increase in device performance (the change between the control and the 1% wt loaded films) is much greater than that seen when the Au NR loading is doubled (from 1wt. % to 2wt. %). While doubling the amount of rods does result in increased J_{SC} and PCE for all aspect ratios, it is to a lesser extent than the initial change, which is illustrated in Figure 4.4D.

As nanorod aspect ratio increases, parallel increases in device performance are observed, as shown in **Figure 4.5A**. Representative optical extinction spectra of the BHJ films taken from each Au NR aspect ratio, at a particle loading of 2 wt. %, is shown in

Figure 4.5B, which indicate an increase in extinction as the Au NR aspect ratio increases.



Figure 4.4. Effects of gold nanorods on the performance of the polymer solar cells. J-V curves of OPV devices with nanorods of aspect ratio (AR) of 2.15 (A), 2.5 (B), and 3.3 (C) incorporated into the BHJ film at 1 and 2 wt. % loading. With each aspect ratio, the efficiency improves as the loading of the nanoparticles increases up to 2wt. %. Higher loadings were seen to reduce device performance in preliminary studies. (D) Comparison of the short circuit current density (J_{SC}) and photo-conversion efficiency (PCE) of devices with gold nanorods of several aspect ratios cast within the bulk heterojunction layer of an organic photovoltaic device, at the stated loadings.

It should be noted that Figure 4.5B displays extinction, where the intensity is a

combination of absorption (by the film and the particles) and scattering (predominately
by the particles at their LSPR frequencies, film roughness, and variations in BHJ crystallinity). The BHJ/PEDOT: PSS film thickness remained constant at 160 nm for all of these devices. There are two distinct regions of increased extinction in these films. The most prevalent is observed in the region between 400 nm and 600 nm, where the absorption bands of P3HT, and the transverse plasmon bands of the nanorods co-exist. The second region is between 600 nm and 800 nm, where the longitudinal plasmon resonance of the nanorods resides. There is little to no absorption in the BHJ film above 800 nm. In order to associate these optical changes to those seen in the device photoconversion efficiency plot shown in Figure 4.5A, we measured the external quantum efficiency (EQE) of each device (Figure 4.5C). There is a comparable increase in the EQE with those seen in the optical extinction shown in Figure 4.4B (between 400-600 nm). However, the minor rise in EQE between 600-800 nm does not correlate with the increase in extinction within this region. This may indicate that plasmonic enhancement may be contributing to the small increase in EQE within this region; however, firm conclusions cannot be made since we do not know the dominant plasmonic response of the Au NR aggregates within the cells. Furthermore, the increase in refractive index of the PS shell and the P3HT matrix will work to red-shift the L-LSPR modes, but side-toside assembly of Au NRs blue-shifts their L-LSPR⁴³. Therefore, it is hard to estimate where we would expect the L-LSPR to lie. Albeit, based on these results, the majority of the photo-conversion efficiency improvement, when gold nanorods are embedded within the BHJ films, originates in the 400-600 nm region. This enhancement may also be due to plasmonic enhancement if the dominant plasmonic response of the Au NR assemblies lies within this region. However, we would expect an increase in EQE in the spectral

region of the plasmon resonance, and the EQE spectra of the experimental Au NR cells do not indicate significant asymmetry in comparison to the control ¹⁷.

We postulate that, since the increases in EQE are coincident with the increases in P3HT the significant source of the increased EQE in Figure 4.5B is due to increases in the P3HT absorption upon Au NR incorporation, given that the increase in EQE is spectrally coincident with the increased absorption of the BHJ. The smaller increase in EQE between 600-800 nm is not proportional to the extinction increase in this region. It is likely that the rise in extinction between 600-800 nm in Figure 4.5B is primarily due to the longitudinal plasmon resonance of the rods. The increased extinction at longer wavelength is much broader than that of the rods in solution, which is attributed to the increase in refractive index of the BHJ matrix ($n \approx 1.7$, see supplemental information). Thus, scattering of light (far-field plasmonic effects) by the longitudinal plasmon modes of the rods throughout the film in this region potentially contributes to the small rise in EQE value of the weak P3HT absorption peak at 700nm, which is seen in the inset of Figure 4.5C, but cannot be strictly confirmed within this data set.



Figure 4.5. (A) Comparison of the device performance (J-V curves) of three devices with various gold nanorod aspect ratios loaded at 2wt. %. (B) Extinction spectrum of BHJ films used in the devices shown in A. (C) External Quantum Efficiency (EQE) of the four devices shown in A and B.

However, to understand the mechanism for the enhanced absorption, and hence efficiency, in the spectral region from 400-600 nm, we consider two possible general mechanistic pathways: 1) Plasmon enhanced absorption mechanisms and 2) absorption enhancement due to changes in the BHJ morphology. Plasmon enhanced absorption could be due to either far-field scattering, which could lead to increases in the effective optical path length of the light, or to near field effects. In the wavelength region between 400-600 nm, the transverse mode is active but it is unlikely to scatter a significant amount of light into the far field because the rod dimension associated with this mode is less than 20 nm, which results in a very small particle albedo for this mode ⁴³. Therefore, the only legitimate plasmon enhancement mechanism in this spectral region of our system would be near-field induced absorption enhancement. The intensity of the transverse plasmon resonance remains constant as L/D is increased, and is expected to have an equivalent contribution in all samples ⁴⁴. The near-fields produced from the L-LSPR are expected to induce the highest enhancement when the L-LSPR frequency is aligned with P3HT's absorption spectrum. Therefore, the lowest L/D would provide the highest enhancement. However, in all of our studies, the film extinction, the device efficiency, and the device EQE increase with increasing L/D, indicating that near-field effects are not likely responsible for the enhanced P3HT absorption, or the device efficiency enhancement in the spectral region between 400-600 nm. This is not unexpected since the P3HT absorbing polymer is at least 6 nm away from the nanorod surface due to the thick polystyrene shell. It is well known that the evanescent near-field decays exponentially away from the particle surface, which would significantly reduce the volume of active layer affected by the near-field. With these considerations, it is unlikely that plasmonic enhancement mechanisms are responsible for the significant improvement in device performance, or enhanced P3HT absorption, when Au NRs are embedded within the BHJ film.

An alternative explanation for the enhanced P3HT absorption and device performance is nanoparticle-induced morphological changes in the BHJ film. Morphology effects are well known to substantially influence device performance. It is well documented that the alignment of the P3HT crystallites within the BHJ film can have a significant effect on both the absorption efficiency and charge mobility throughout the device ^{45,46}. Moreover, the incorporation of nanoparticles into organic thin films often results in substantial morphology changes^{47,48}. However these effects have not been widely considered in the case of plasmonic nanoparticles within organic BHJs. **Figure 4.6** shows the effect of varying the aspect ratio, and loading of Au NRs in the active layer, on the P3HT chain orientation. With increases in either the loading weight or the aspect ratio of the nanorods, the [100] / [020] peak ratio increased. Since [100] and [020] reflections are orthogonal, the increase in the [100]/[020] ratio indicates that the alignment of the P3HT crystallites is beneficially altered upon the introduction of Au NRs. Nanorod induced selectivity of the [100] P3HT orientation could have multiple benefits in an OPV device, including better overlap of the P3HT transition dipole with the incident electric field, leading to an increase in absorption, or internal quantum efficiency improvements such as increased charge carrier mobility throughout the active laver ^{45,46,47,49}.

Assuming that the increase in extinction seen in Figure 4.5B is predominantly due to an increase in the P3HT absorption, a predicted increase in the short-circuit current can be calculated. We followed the analysis performed by Kim et al.⁴⁶, comparing the predicted J_{SC} values derived from the device absorbance, Figure 4.5B, to the empirically derived J_{SC} from device J-V characterization, Figure 4.5A. The integrated product of the wavelength-dependent absorbance of the film, A (λ), and the AM1.5G solar spectrum b (λ) was calculated to give the maximum short-circuit current expected when assuming the internal quantum efficiency (IQE) is 100%, (See supplemental information).



Figure 4.6. (A and B) Grazing Incidence Wide Angle X-Ray (GIWAX) diffraction of the 1% wt. and 2% wt. nanorod-loaded BHJ films as a function of aspect ratio, respectively shown with the control (no nanorod) films. (C) Comparison of the ratio of the 100 P3HT peak area to the 020 P3HT peak area as a function of nanorod loading ratio. The increase in the ratio indicates greater preference of the 100 stacking in P3HT.

The calculated and empirical values of the J_{SC} were compared by normalizing the calculated J_{SC} values to the measured control device J_{SC} without any nanorods as shown in Figure 6. In this analysis, if the IQE of the devices remained constant as gold nanorods are incorporated into the BHJ films, the data points in **Figure 4.7** would reside along the y=x line (solid green), indicating that the change in the measured J_{SC} has a 1:1 correlation

with changes in the film absorbance. Deviation from the y=x line indicates changes in the measured J_{SC} that are not accounted for merely by changes in film absorption, and are therefore related to changes in the internal charge collection processes (IQE) such as charge mobility, recombination rates, and charge collection efficiency. Values below the y=x line signify an increase in IQE while deviations above indicate a decrease in the IQE. Here we observe a deviation below the y=x line corresponding to improvements in the device IQE when nanorods are incorporated into the BHJ. The IQE improvement likely arises from increased charge mobility in the polymer, due to the higher [100] selectivity when Au NRs are present. It is interesting to note that the IQE appears to increase with increasing loading of the nanorods, however it remains constant as the aspect ratio is increased (slope =1 for both the 1wt. % and 2 wt.% loadings). This suggests that the nanorods simultaneously act to increase the P3HT charge carrier mobility, as well as the P3HT chain orientation, with increasing L/D leading to higher absorption. It should be noted that intrinsic losses from the nanoparticles from plasmonic relaxation and intraband absorption are not accounted for in this analysis. These effects likely decrease device efficiency, since the energy would be lost as heat. In spite of these losses, however, the morphological changes induced in the film through the incorporation of Au NRs cause a substantial increase in both the efficiency and IQE of the devices.



Figure 4.7. Comparison of the empirically derived J_{SC} to the calculated J_{SC} maximum from the extinction spectra of the films analyzing changes in internal quantum efficiency of OPV devices with gold nanorods embedded. The data is normalized to the control devices without nanorods. Deviation of the data points below the x=y line indicate an overall increase in IQE for nanorod/OPV devices. The apparent fitting of each loading weight of nanorods to a line with slope = 1 indicates the IQE is constant for devices with constant nanorod loading, irrespective of aspect ratio.

4.4 Conclusion

Substantial enhancement of up to 30% in the performance of organic photovoltaic devices was observed when thiolated polystyrene-coated gold nanorods were incorporated into the BHJ active layer. Device efficiency was studied as a function of both loading weight and aspect ratio of the nanorods. The nanorod distribution within the film was analyzed using transmission electron microscopy, and the effects of the rods on the P3HT domain morphology were determined using wide angle X-ray scattering. It was

determined that the majority of the enhancement can be attributed to nanoparticleinduced morphology changes in the BHJ, most likely to the P3HT crystalline domains. Plasmonic effects, both far-field (linear scattering) and near-field were not observed to any significant extent, thus highlighting the importance of nanoparticle-induced morphological effects in organic photovoltaic devices.

4.5. References

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4.6. Supplemental Information

Estimation of Ligand Shell Thickness: 200 measurements of Au NR interparticle spacing was performed using the TEM micrographs of the BHJs employed in these experiments. The average inter-particle spacing was calculated to be 12 +/- 3nm.

Estimation of PS-Functionalized Particle Volume: Estimation of the PSfunctionalized particle volume was done assuming a sphero-cylindrical NR morphology; this allows the geometrical separation of the NR body into 2 hemispherical caps and 1 cylindrical body. The volume of the 2 hemispherical caps and cylindrical body are calculated as shown in equations SE 4.2 and 4.3, respectively. Herein, it is assumed that r_{cap} is equal to $r_{cylinder}$ (**Figure S4.1**). Furthermore, the cylinder height (h) = (NR length -2 r_{cap}), and the radius values were increased by 6 nm to account for the PS ligand shell. The values used for these calculations were taken from the corresponding average values taken from at least 300 measurements of each NR population using ImageJ software.

$$2V_{cap} = V_{sphere} = (4/3)\pi(r_{cap})^3$$
 SE4.2

$$V_{cylinder} = \pi (r_{cylinder})^2 h$$
 SE4.3



Figure S4.1. Estimation of NR volume and surface area. The sphero-cylindrical morphology of NRs using our synthetic protocol is shown (a) along with geometrical considerations made to calculate NR volume (b).

Similarly, NR surface area was estimated by equation SE 4.4. The calculated volume and surface area values for aspect ratio 2.15, 2.50, and 3.30 nanorods are tabulated in

Nanorod Surface Area =
$$4\pi (r_{cap})^2 + 2\pi r_{cylinder}h$$
 SE4.4

Supplemental Table ST4.1.

Aspect Ratio	Width (nm)	Length (nm)	Volume (nm ³)*	Surface Area (nm ²)*
2.15	18	38	(18639)	(4700)
2.50	18	43	(22240)	(5178)
3.30	15	49	(24066)	(5371)

* Values in parentheses include the 6nm polystyrene brush.

Table ST4.1. Measurements of width, length and calculated volume and surface area of nanorods from transmission electron micrographs cast from aqueous solution.



Figure S4.2. (A-C) Histograms of as-synthesized nanorods analyzed from TEM micrographs that were later incorporated into plasmonic/BHJ films after counting 200+ nanorods from each synthesis. Average aspect ratios of the samples were 2.15, 2.50, and 3.30, respectively.

Device	V _{oc} (V)	J _{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	0.66	6.97	66	3.01
Au NRs AR2.15 1wt%	0.66	8.10	62	3.31
Au NRs AR2.15 2wt%	0.64	8.35	63	3.40
Au NRs AR2.50 1wt%	0.65	8.20	64	3.42
Au NRs AR2.50 2wt%	0.65	8.87	63	3.63
Au NRs AR3.30 1wt%	0.65	8.43	67	3.67
Au NRs AR3.30 2wt%	0.65	9.08	66	3.89

Table ST4.2. Photovoltaic characteristics of OPV devices incorporating gold nanorods in BHJ layer with various concentrations and aspect ratios. The uncertainty in each measurement is less than 5% of the value.

More on the extinction spectra in Figure 4.5: The weak extinction signal of the rods compared to the P3HT absorption is expected due to the low particle number density in the films, measured to be approximately7.5 particles/ μ m². The variation in the spectra, including a broadening of the resonances, is due to the variation in nanorod agglomeration when incorporated in the BHJ films, as outlined in Figure 4.4C. The broad absorption peaks from 425-625 nm are due to the semi-crystalline regio-regular P3HT (Fig.S4.3). The shoulders in the extinction spectra of the BHJ films loaded with nanorods

on the red side of the P3HT absorption band (~ 700 nm) are attributed to the L-LSPRs of the incorporated nanorods. The LSPRs of the nanorods red-shifts with the increasing AR when the rods are embedded within the BHJ (as is the case in solution), but the bands are more broad and red-shifted in comparison with the solution based extinction measurements given in Figure 4.1A. This shift and spectral broadening is attributed to the higher dielectric environment of the BHJ ($n \approx 1.7$) compared to water ($n \approx 1.33$) and the small scale agglomeration when the nanorods are embedded in the films (**as discussed above, S4.4**). For completion, the extinction spectra of the 1wt. % nanorods are provided in **Figure S4.3**.



Figure S4.3. Extinction spectra of control and 1wt. % loaded nanorod samples in BHJ films.

Details on the IQE analysis in Figure 4.7: The calculation was performed using Equation SE4.5:

$$\int_{350}^{625} A(\lambda) b(\lambda) d\lambda \qquad SE4.5$$

where $A(\lambda)$ is the wavelength-dependent absorbance of the film, and $b(\lambda)$ is the AM1.5G solar spectrum. The integrated product was calculated to give the maximum short-circuit current expected assuming the internal quantum efficiency (IQE) to be 100%. This region (excluding wavelengths above 625 nm) was chosen because at wavelengths above 625 nm scattering from the L-LSPR resonance dominate the extinction response of the film, and would contribute to significant error in the calculation. From the EQE measurements in Figure 4.5C, it is evident that only a minute fraction of the converted energy occurs at wavelengths greater than 625 nm, and the difference in the EQE above 625 nm in the samples is nearly insignificant. Therefore, to minimize the error in the calculation, 625 nm was chosen as the upper limit for the integration.

4.7. Supplemental Information References

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Remarks on Moving Forward

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5.1. Discussion

The results presented herein elucidate important themes in both surfactantmediated crystalline nanoparticle synthesis and the incorporation of plasmonic nanoparticles within the active layer of OPVs. Regarding surfactant-mediated crystalline nanoparticle synthesis, the dependence of particle morphology upon introduction of a cosurfactant to the growth solution, as well as the time-dependent nature of the cosurfactants efficacy, highlight the importance of the growth solution's micellar state in guiding nanoparticle growth; the composition, size, and surface chemistry of micelles define their ability to passivate growing epitaxial surfaces, as well as their selectivity towards these surfaces. Through understanding how mixed micelle composition defines micellar interactions with crystalline surfaces, correlations between micellar composition and resultant nanoparticle morphology are also possible. To date, numerous binary surfactant systems have been used to create a library of nanoparticle morphologies^{1,2}. In the case of gold nanorods, the tunable nature of the aspect ratio, and control of the crystallographic facets that the Au NR product presents, has been demonstrated by simply altering the co-surfactant employed with CTAB. However, work to elucidate the effect of each co-surfactant on the growth solution's micellar state, and the corresponding micellar surface activity, are lacking; the absence of such data limits the experimentalist to using previously investigated reagents, and provides no means of making confident

hypotheses about a new surfactant's potential to alter crystal morphology. Without pursuing the underpinnings of surfactant-mediated nanoparticle growth, the full potential of bottom-up synthetic nanoparticle synthesis cannot be realized.

In attempting to understand the role that co-surfactant chemistry has on Au NR growth, investigations should be focused on how the co-surfactant influences the host surfactant's micellar morphology and epitaxial passivation of a specific surface of interest (i.e. Au), as the latter is directly dependent on the former. Focused investigations should first aim to elucidate the molecular interactions which define the co-surfactant's influence on CTAB; specifically: (1) Does the co-surfactant change the micellar growth horizons of CTAB, and, if so, how is this brought about? Is it the co-surfactant's tail or head-group chemistry working to alter the micelle's aggregation number, size, or morphology? Furthermore, how do the head-group interactions influence the mixedmicelle's surface chemistry? (2) How do these changes, if any, alter the micelle's ability to passivate epitaxial Au surfaces towards adatom adsorption to the growing NR? Are changes in the micelle size and morphology allowing the passivation of the growing crystalline facets at earlier stages of growth as indicated herein, which would lead to the conclusion that geometrical constraints on surfactant self-assembly, that are imposed by the co-surfactant, are dominant in altering Au NR growth; or is the co-surfactant altering the crystal habit through some other means, such as soft epitaxial adsorption that is mediated through co-surfactant's head-group chemistry. It has been demonstrated in computational studies by Heinz et al. that certain pendant moieties on surfactants, such as the phenyl ring found on BDA⁺'s ammonium head-group, show preference for epitaxial adsorption onto Au surfaces having an appropriate inter-atomic spacing³.

However, one cannot determine the specific means of epitaxial passivation without knowing whether the surfactant's head-group moieties are intercalated within the oily core of the micelle, or show preference towards interaction with the external environment.

In the case of the CTAB-BDAC binary system, understanding both the concentration-dependent influence that BDAC has on CTAB micelle morphology and micellar passivation of epitaxial gold surfaces, as well as determining which surfactant head-group chemistry is expressed at the mixed micellar surface, and how this chemistry determines the micelle's proclivity toward epitaxial adsorption onto Au surfaces, are equivalently warranted; knowing micelle morphology and size will aid in determining the magnitude of any geometrical and thermodynamic constraints that the co-surfactant is contributing, and subsequently the impact that these changes exhibit on the Au NR morphology(vide supra). Similarly, determining the chemistry which is expressed at the mixed-micelle's surface would indicate the potential for soft-epitaxial adsorption of molecular moieties to contribute to the selective passivation of Au crystalline surfaces.

In a broader sense, further characterization of the means with which BDAC alters the Au NR growth solution's micellar state can be applied to the many other cosurfactant's that have been employed in Au NR synthesis such as BDAC and salicylatebased sodium salts^{1,2}; the investigation strategy developed for understanding the BDAC-CTAB growth solution's ability to alter Au NR L/D could be directly applied to understanding other CTAB/co-surfactant systems. Ideally, the proposed investigation would elucidate the dominant contributions of the co-surfactant in altering the micellar state of the growth solution, and how these conditions specifically affect Au NR morphology, regarding both aspect ratio and the crystalline facets that the final product exhibits. From this, the experimentalist may be provided the opportunity to make educated hypotheses about the influence of co-surfactants that have not been investigated, simply by examining the surfactants molecular structure and physical properties.

Separately, enhancement of OPVs through PNP inclusion into the active layer holds promise for highly efficiency devices. The results achieved in these experiments did not indicate that plasmonic enhancement mechanisms significantly contributed toward enhancing solar cell performance; by no means does this work discount previous studies showing far-field and near-field enhancements, but only suggests that other means of incorporating PNPs into the photo-active layer may be necessary to do so. Additionally, this work illuminates the potential to favorably alter the BHJ's microstructure through addition of polymer-grafted nanoparticles, and broadens the applicability of PNPs in the sense of improving OPV photo-conversion efficiency through plasmonic and morphological enhancements of the BHJ active layer's properties.

The mechanisms behind Au NR-facilitated P3HT ordering have not been determined, and certainly warrant further investigation. It is likely that the polystyrene layer on the nanoparticle provides favorable interaction with P3HT, thereby optimizing molecular alignment. However, it may be that the incorporation of an anisotropic nanostructure can influence the BHJ's morphology. If efforts are made to determine whether it is the incorporation of anisotropic nanostructures, or the Au NR surface chemistry, that is optimizing BHJ microstructure, there lies potential for developing new platforms for enhancing BHJ microstructure, and consequently improving photoconversion efficiency. Although plasmonic enhancement of OPV photo-conversion efficiency was not obviously indicated in these studies, it does not remove the possibility for Au NRs to be applied toward such means. As before, it has been indicated in previous studies that PNPs, as well as their organic ligand shell, may act as photo-generated charge recombination centers if not properly insulated from the active layer materials (vide supra). Investigation into whether PS-capped Au NRs are acting as charge recombination centers is possible through the use of different materials to encapsulate the Au NRs. For example, Jankovic et al. employed silica encapsulated Au NRs in a similar study, where plasmonic enhancement of OPV performance was indicated. Silica's refractive index (n \approx 1.458 at room temperature) is very close to that of water (n \approx 1.333 at room temperature), allowing one to encapsulate Au NRs within a silica shell without drastically altering its L-LSPR frequency⁴. Therefore, one does not have to consider the L-LSPR's shift due to either the dielectric behavior of the ligand shell or active layer species.

Future work should also include the determination of the Au NRs optical response within the BHJ active layer. Utilizing a polystyrene ligand shell on the Au NRs induced varying degrees of aggregation within the BHJ; since the aggregation order and geometry varied within each sample, one cannot easily predict where the Au NR's L-LSPR will reside due to plasmonic hybridization, which is undoubtedly observed at the inter-particle spacing presented in these samples⁵. Furthermore, the Au NRs in these experiments were capped with polystyrene, having an index of refraction between 1.55-1.59, and the PSgrafted particles were placed within a BHJ, which has a wavelength-dependent refractive index above 1.75 within spectral region of ~ 450 - 1100 nm⁶. The increase in refractive index of both the ligand shell will red-shift the L-LSPR approximately 45 - 50 nm as seen before. Additionally, the near-field decay length of Au NRs is proportional to its size, indicating that the L-LSPR is likely to extend beyond the ligand shell, and thus have its resonance frequency altered by the BHJ as well⁷. Therefore, with the various Au NR assemblies seen within these samples, which can red-shift or blue-shift the L-LSPR, depending on whether the aggregates are assembled end-to-end or side-to-side, coupled with the red-shift of the L-LSPR upon grafting the Au NRs with PS and incorporating them into the BHJ, further characterization of the Au NR's optical properties within the BHJ are necessary, and could simply be done through dark field scattering characterization of the plasmon resonance modes of the Au NRs, and their respective assemblies, within the BHJ films⁷.

In the application of Au NRs for probing plasmonic enhancement effects in OPV active layers, assuming that we can employ the correct core-shell Au NR nanostructure which promotes plasmonic enhancement of OPV photo-conversion efficiency, the question is raised: how would one deconvolute near-field from far-field effects, given that both enhancement mechanisms will show their greatest effect when the spectral overlap between the L-LSPR and the absorption region of the BHJ's electron donor is greatest? This issue can simply be addressed through employing a shell for the Au NR, such as silica, whose thickness can be tuned beyond the near-field decay length of the Au NP ^{4,8}. One could then vary the shell thickness of an identical nanostructure, and correlate any changes in the enhancement with that of the shell's thickness. If plasmonic enhancement decreases with increasing shell thickness, near-field effects are predominant. Conversely, if no changes are seen with shell thickness, far-field scattering would be expected to be the dominant plasmonic enhancement pathway.

Arguably the most prominent conclusion from the experiments involving Au NRs into OPV active layers is that Au NRs can induce preferential alignment of P3HT, indicating the potential of plasmonic nanostructures to enhance organic photovoltaic efficiency through plasmonic and morphological effects. Our results indicate that incorporating PS-capped Au NRs has a dramatic influence on the BHJ morphology, where enhanced alignment of P3HT chains brought about a photovoltaic efficiency enhancement of up to 30% within this experimental set. It is not known whether it is the anisotropic morphology of the Au NRs or the polystyrene surface chemistry that is altering the alignment behavior of P3HT. However, recent studies by Vohra et al. indicate that the P3HT-PS interaction can lead to increased ordering of P3HT in BHJ solar cells, and that the ordering seen herein is likely due to the P3HT-PS interactions⁹.

Future work to investigate whether molecular interactions between P3HT and polystyrene, or simply the presence of anisotropic nanostructures within the BHJ are inducing the molecular ordering of P3HT, should include experiments specifically aimed toward studying the influence of nanostructure size, morphology, and the physicchemical properties of the nanostructure's surface chemistry on P3HT's crystallinity.

Determining the influence of anisotropic nanostructures on the BHJ's morphology warrants the removal of any organic ligand shell on the nanostructure's surface, which could be accomplished using a silica shell, as was proposed before, to differentiate between near-field and far-field plasmonic effects. However, recent reports on incorporating Au NR/silica core-shell structures into BHJ active layers have concluded that this requires the functionalization of the surface of the silica shell with an organic ligand such as octadecyltrimethylsilane⁴. Although octadecyltrimethylsilane has a relatively short alkyl chain (C_{18}) in comparison to PS, physical interactions with the BHJ materials are still expected, and thus this system may not provide the ideal conditions for a control experiment versus the PS-Au NRs.

In the event that an organic ligand is required to disperse Au NRs within the BHJ, it must be judiciously chosen in order to minimize chemical incompatibility and entropic losses due to matrix-ligand interpenetration upon successful mixing¹⁰. In the ideal case, one would employ the same chemistry for the ligand and BHJ matrix, while also determining the correct molecular weight of the two species, following work by Hore et al., in order to finely disperse the particles throughout the active layer¹⁰.

As previously stated, it is likely that the intermolecular interactions between PS and P3HT are inducing the molecular ordering of P3HT in our sample set, and consequently enhancing OPV photo-conversion efficiency; investigating the impact of NP surface chemistry on BHJ morphology should be approached by studying the influence of the nanostructure's curvature, as well as the ligand's molecular weight and chemistry on the BHJ's morphology, as all of these will dictate PS's grafting density, brush morphology, and thus the interactions with the BHJ matrix.

Nanoparticle surface curvature is a critical parameter in determining the interactions of the ligand brush with the BHJ matrix. Surface curvature influences the ligand's grafting density, which in turn dictates brush conformation, and ultimately the BHJ matrix-brush interaction^{10,11}. In the case of Au NRs, it is difficult to determine the influence of surface curvature given the relative lack of curvature along the longitudinal faces, and the disparate curvatures of the spherocylindrical tips and transverse surface;

thus in these studies it would be most appropriate to employ isotropic structures such as gold nanocubes are nanospheres. In this experimental regime, the curvature of the nanostructure is consistent, where nanocubes exhibit planar crystalline facets, acting as a surface with little, or no curvature, and nanospheres can be employed to investigate curvature-dependent phenomena, where the surface curvature can be altered simply through synthetically changing the sphere's diameter. While investigating the influence of particle morphology, one should employ the same ligand throughout all experiments since the interest in surface curvature is due to its effect on the brush's grafting density and conformation. Thus, any influence of the grafted NPs curvature on BHJ morphology would also have to be correlated to the grafting density of the brush.

The chemistry and degree of polymerization of the brush also dictate how the NP's ligand layer will interact with a polymer matrix¹⁰. In cases where the brush's chemistry yields favorable interactions with P3HT, the brush will be well extended, allowing interpenetration of the brush and matrix polymer chains; in this case, the brush's degree of polymerization has considerable impact on matrix-brush interactions¹⁰. When brush-matrix interactions are unfavorable, as is likely for PS given that spontaneous phase separation occurs between bulk PS and P3HT, the NPs polymer brush will be collapsed; the two different brush states will determine whether a polymer weld will occur between the brush and matrix, and therefore determine whether the NPs presence affects the matrix. Additionally, the brush's molecular weight will determine brush size and volume, and also influence its interactions with the matrix^{11,12}.

In studying the influence of brush chemistry, one would preferably employ an isotropic nanostructure such as a nanosphere, where the curvature of the experimental

sphere samples would ideally be comparable to the surface curvature exhibited by the Au NR transverse surface and tip. Brush chemistry would then be varied from the same molecular species as that of the BHJ matrix, to chemistries which are incompatible with the BHJ; such studies would provide insight into the brush's conformational state, and therefore into its intermolecular interactions with the BHJ matrix, the BHJ's morphology, and into its consequential effect on photo-conversion efficiency.

Throughout these studies we have explored the time-dependent influence of cosurfactant addition to a seed-mediated Au NR synthesis, and the potential for Au NRs to induce plasmonic and morphological enhancement effects in BHJ-OPV active layers. In our investigations of Au NR synthesis, we have elucidated the importance of the micellar state, with respect to epitaxial adsorption and surfactant adsorption density, and the dependence of these phenomena on the molecular structure and physical properties of the co-surfactant, in modulating the morphology of Au NRs; modulating morphology in this case not only refers to the apparent size, shape, and L/D of the Au NR, but also the crystalline facets that they exhibit.

However, the importance of the co-surfactant's structure and properties must be further investigated. If parallel investigations are made into the specific changes that various co-surfactants induce on the micellization of CTAB, on its epitaxial adsorption behavior onto Au surfaces, and on the correlated alterations in Au NR morphology, the dominant mechanisms of how the binary surfactant changes morphology can be determined. Advances towards these ends may provide the experimentalist with the means of selectively tuning NP morphology through employing surfactant mixtures with known epitaxial adsorption behavior. Through our investigation on the use of Au NRs to investigate plasmonic and morphological enhancement mechanisms in BHJ OPVs, we have found no obvious indication of plasmonic enhancement. This may be due to our employment of an organic ligand shell, which can provide a charge-recombination pathway, or the assembly of the Au NRs shifting the plasmon resonance outside of P3HT's region of absorption. Future investigations should employ Au NRs with an insulating shell such as silica to determine if plasmonic enhancements are seen, and elucidate near-field and far-field effects by tuning the shell thickness beyond the decay length of the plasmonic near-field, of course, in the event plasmonic enhancement is evident.

We have discovered that PS-grafted Au NRs can beneficially align P3HT domains to increase the BHJ active layer's absorbance, EQE, and IQE, ultimately resulting in a 30% enhancement of photo-conversion efficiency. These experiments, however, do not indicate the mechanism by which molecular ordering of P3HT is brought about, whether it is the incorporation of an anisotropic nanostructure, or the PS-P3HT interaction. Therefore, further investigation should elucidate the dependence of BHJ active layer morphology on the size, shape, and curvature of the nanostructure, as well as exploring the impact of the NP's brush chemistry, grafting density, and brush's conformational state.

5.2. References

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