

GOLD NANOSTARS: NEW SYNTHESSES AND APPLICATIONS IN
SERS AND PHOTOCATALYSIS

by

SUPRIYA ATTA

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ABSTRACT OF THE DISSERTATION

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By SUPRIYA ATTA

Dissertation Director:

Laura Fabris

Gold nanostars have received significant attention in different fields due to their unique optical and electrical properties. However, controlling the morphology (size and shape) and achieving high synthetic yields are still important challenges, even though several studies have already been reported on this topic. Moreover, it still remains challenging to achieve monodispersity and reproducibility. Finally, it is important to fabricate the gold nanostars in a way that allows us to fully exploit their tunable localized surface plasmon resonance (LSPR) bands and the high electron density localized at the tips.

In this dissertation, we design and synthesize a variety of gold nanostars with unique shape and surface properties to target specific applications in surface enhanced Raman spectroscopy (SERS) and photocatalysis, and by taking into consideration future biological applications, which is a major interest in our group. For instance, we developed a synthetic methodology to achieve gold nanostars with a unique 6-branched morphology, which possess narrow absorbance bands tunable from the visible to the short wave infrared. We investigated the role of various synthetic parameters (Triton X, ascorbic acid, AgNO_3 , and seeds) on the resulting shape of the gold nanostars, and revealed that the intermediate seed morphology determines the number and morphology of the branches obtained. For example, multiply-twinned and penta-twinned intermediate

seeds form multibranched stars and 6-branched nanostars respectively. The evolution of gold nanostars reveals that a common intermediate exists at a 5-minute time point, which is stabilized by increasing amounts of AgNO_3 . Therefore, the plasmon tunability (correlated to the morphological tunability) arises from the concentration of AgNO_3 . For example, at 100 μM AgNO_3 concentration, the LSPR band reaches its most redshifted position at 1071 nm, whereas a maximum at 734 nm is observed for 30 μM AgNO_3 . We developed a route for silica coating etching on gold nanostars that does not affect the morphology of the nanostar; this synthesis allowed us to investigate how the SERS enhancement depends both on the morphology of gold nanostars and the thickness of the surrounding silica shell. We used the chemoselective reagent NaBH_4 to etch the silica layer so that only sharp protruding tips of the nanostars were exposed. We correlated the Raman signal enhancements obtained experimentally by employing gold nanostars with different degrees of silica shell thickness with the field enhancements calculated employing 3D finite element models, obtaining excellent agreement and highlighting the role of both the amount of silica and the degree of gold tip exposure as the two main parameters influencing the intensity of the scattered fields. Similarly, we studied the role of a thin TiO_2 shell on the generation of hot electrons and their use in photocatalytic reduction reactions. We observed that when the gold nanostars are coated by a conformal crystalline TiO_2 layer, hot electrons are generated at the tips of the gold nanostars and can be injected into the semiconductor through the Schottky barrier between the Fermi level of the metal (Au) and the conduction band of the semiconductor (TiO_2), where they can be exploited to increase the performance of the photocatalyst (TiO_2). In model hydrogen evolution reactions (HER) we have observed that these nanostructures substantially outperform previously reported systems of hybrid gold

nanoparticle-TiO₂ photocatalysts, most importantly because of their ability to perform under broad illumination conditions, which is a promising alternative approach to efficiently obtain clean fuels from sunlight.

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DEDICATION

-This dissertation is dedicated to my family-

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Chapter 1

INTRODUCTION

1.1. Plasmonic Nanoparticles

Nanomaterials are basic building blocks: Nanospheres, nanorods, and nanostars, with dimensions varying between 1 nm and 100 nm, behave like whole units in terms of their optical and electrical properties, but they can be made to interact and acquire new interesting behaviors. They are different from bulk materials in physical and chemical properties due to their large reactivity, as a consequence to their high surface area. Noble metal nanoparticles have been used for more than 2000 years due to their fascinating appearance in the presence of visible light. The Lycurgus cup is one of the examples that best represents the optical properties of noble metal nanoparticles. The cup reflects green light (i.e. under daylight illumination) and appears red in transmission, such as when a source of light is inserted in it. It was discovered that the unique optical properties of the Lycurgus cup originate from the presence of silver and gold nanoparticles of ~ 70 nm diameter, with the color change due to the distinguishing optical property of metal colloids, named localized surface plasmon resonance (LSPR). The first scientific investigation and synthesis of these kinds of nanoparticles was carried out by Michael Faraday, who discovered how to synthesize the colloidal gold nanoparticles in a scientific way, i.e. by allowing the reduction of gold salt to be carried out by white phosphorous and the stabilization by carbon disulfide. Some years later in 1951, Turkevich *et al.* reported a well-known method for the synthesis of citrate-capped gold nanospheres, where the reduction of gold salt was realized by sodium citrate at high temperature.¹ In the last two decades, tremendous progress has been made with regard to the synthesis of nanoparticles and the understanding of the effect of the particle dimensions and morphology on the optical and electronic properties of these nanomaterials. As a consequence, a wealth of new applications opened up in the fields of photonics, catalysis, and biology.

1.2. The Localized Surface Plasmon Resonance (LSPR)

The important feature of metal nanoparticles is their optical property called the localized surface plasmon resonance (LSPR), which arises from the collective oscillation of free conduction electrons in the metal surface under light irradiation at a resonant frequency, as theoretically described by Mie.^{2, 3} Plasmons are generated when the electromagnetic radiation impinges on a metal surface, and a displacement of the electrons in the conduction band occurs, as a consequence of the fluctuating electric field. This results in an excess of positive charges that lead to the generation of a restoring force that recalls the displaced electrons to the centre of charge. The result of this charge oscillation is a dynamic dipole at the surface of the metal, which results in an amplification of the electric field associated with the incoming light, and a resonant absorption at the resonant frequency called localized surface plasmon resonance (LSPR), as shown in Figure 1.⁴

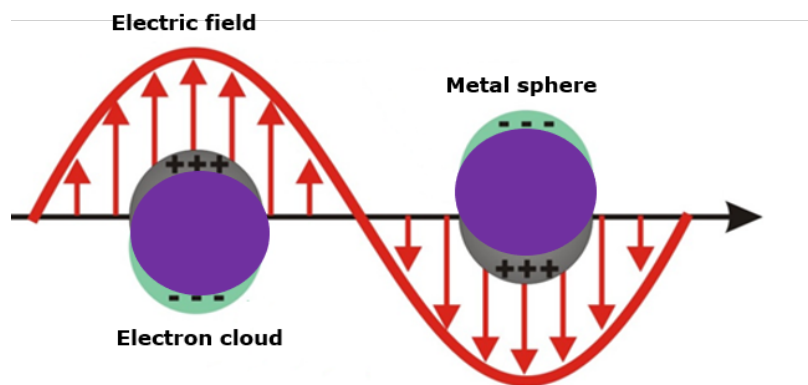


Figure 1.1. Schematic response of the free electrons cloud to resonant excitation.

LSPRs can be encountered in different positions of the electromagnetic field, ranging from ultraviolet (UV) to near infrared (NIR), depending on the particle size and shape.^{5, 6} For instance, spherical gold nanoparticles show only a single LSPR whereas gold nanorods show two different LSPR modes: A transverse surface plasmon resonance (TSPR) which corresponds to the light absorption and scattering along the short axis of the particle, and a

longitudinal surface plasmon resonance (LSPR) which corresponds to light absorption and scattering along the long axis of the particles. Besides the shape factor, the LSPR depends on dielectric medium surrounding of the nanoparticles. For example, the LSPR band of silica coated gold nanospheres red-shifts because of the higher dielectric function of silica with respect to vacuum or water, with a varying degree that depends on the silica shell thickness.⁴

1.3. Anisotropic Gold Nanoparticles

Despite the wide range of existing plasmonic nanomaterials based on silver,⁷ copper,⁸ and aluminum,⁹ the most commonly utilized material is still gold. Gold nanoparticles have been of particular interest and use in biological applications, as they are chemically inert, easy to fabricate, and non-cytotoxic.¹⁰⁻¹² Anisotropic gold nanoparticles such as rods, cubes, prisms, and stars have special interest over spherical nanoparticles, since the LSPR of spherical gold nanoparticles is limited to the visible region, whereas that of the anisotropic nanoparticles can be tuned from the visible to the NIR. Moreover, nanoparticles with sharp edges or protrusions (e.g. rods, stars), or in coupled configurations (e.g., dimers, aggregates, gaps) can further enhance the electric field at locations called ‘hot spots’.^{13, 14} Van Duyne, El-Sayed, Vo-Dinh, and Murphy were pioneers in developing modern concepts for anisotropic gold nanoparticles. A wide variety of wet chemistry-based synthetic methods were developed for synthesizing anisotropic gold nanoparticles. The formation of anisotropic nanoparticles involves mainly three steps.¹⁵ The first step is the formation of nuclei or tiny clusters consisting of few atoms. In the second step, the nuclei are grown into a well-defined structure called seed, which may consist of single-crystal, singly twinned, or multiply twinned structures. The third step is the formation of

anisotropic structures from isotropic seeds, which is the most important step, as it involves symmetry breaking.

1.4. Gold Nanostars

Gold nanostars are one of the most widely studied anisotropic gold nanostructure. Gold nanostars can be found called ‘branched’, ‘star-shaped’, ‘multipods’, ‘sea-urchin-like’ gold nanostructures. Gold nanostars have a central core from which multiple sharp spikes protrude, that act as ‘lightning rods’ to greatly enhance the local electromagnetic field. Gold nanostars also exhibit transverse and longitudinal plasmon bands, like gold nanorods, in the visible and the NIR region respectively. The longitudinal surface plasmon band is very sensitive towards the length and morphology of the spike. It becomes red shifted with increasing spike length. Liz-Marzán and Vo-Dinh were pioneers in developing modern concepts of seed-mediated gold nanostar synthesis. Gold nanostars are synthesized via two main pathways, namely, seeded and non-seed mediated. Seeded growth is a two steps process. In the first step, gold seeds are generated using a strong reducing agent like NaBH_4 , and then aged. After that, the gold seeds are introduced into a secondary growth solution containing additional gold salt, AgNO_3 , reducing agent, and surfactant. For non-seeded growth, the nanoparticles are synthesized in a one-pot synthesis where a seed is formed *in-situ*.

1.5. Seed mediated gold nanostars

Liz-Marzán and coworkers developed a method for high yield production of monodisperse gold nanostars.¹⁶ In this method, poly(vinylpyrrolidone) (PVP)-coated gold seeds are added to a growth solution of chloroauric acid (HAuCl_4) and PVP in N,N-dimethylformamide (DMF), where DMF acts as a weak reducing agent for the incomplete reduction of Au^{3+} to Au^+ , which leads to the formation of light-yellow ligand–metal charge

transfer Au^+ -DMF complexes, and PVP serves as a reducing agent for further reduction of Au^+ to $\text{Au}(0)$.^{17, 18} More importantly, PVP plays an important role for anisotropic deposition of gold atoms onto the gold seed surface to form and then stabilize the gold nanostar structure. Liz-Marzán and coworkers and Pu and coworkers further investigated that the seed morphology determines the branch number.^{19, 20} Khoury and Vo-Dinh then modified this protocol to enable size control of the stars to tune the plasmon resonance wavelength from the visible to the NIR.²¹ Alternatively, surfactant-based seed mediated gold nanostars were synthesized by using cetyltrimethylammonium bromide (CTAB) as surfactant. Interestingly, NaOH plays an important role to increase the monodispersity and reproducibility.^{22,23}

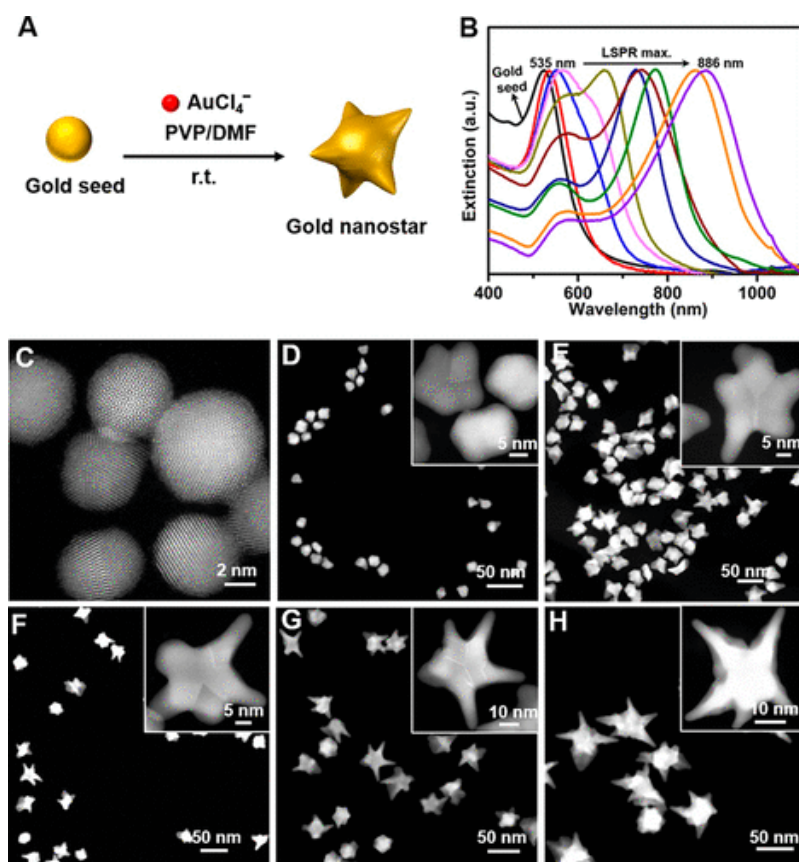


Figure 1.2. Schematic illustration of the synthesis of gold nanostars (A). Tunable extinction of gold nanostars was achieved by changing the concentration of seeds (B).

HAADF-STEM images of (C) gold seeds and the intermediate seeds (inset images) when the concentration of seeds were- (D) 0.84 nM, (E) 0.29 nM, (F) 0.218 nM, (G) 0.145 nM, and (H) 36.25 pM.²⁰ Copyright 2018, Inorganic Chemistry 2018, 57 (14), 8599-8607.

1.6. Non-seed mediated gold nanostars

Non-seed mediated gold nanostar synthesis is one of the special types of protocols that involves most commonly only two precursors- gold salt and a surfactant, which can act as a reducing and capping agent. Xie et al. were the first to develop a non-seed mediated synthesis procedure for gold nanostars using a biocompatible Goods buffer e.g. 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES),²⁴ acting as both reducing agent and surfactant. HEPES buffer contains two tertiary amines of the piperazine group to create cationic free radicals and reduce gold ions to form branched gold nanostars.²⁵⁻²⁷ The number of branches obtained using this protocol can vary from one to eight, growing selectively in the $\langle 111 \rangle$ directions. The branch formation in these gold nanostars can be kinetically controlled, as it depends on temperature and precursor salt concentration. The Odom group found that other Good's buffers such as 4-morpholinepropanesulfonic acid (MOPS) and 4-(2-hydroxyethyl)-1 piperazinepropanesulfonic acid (EPPS) can tune the branch number of nanostars.²⁷ Other factors that influence the growth of nanostars include the pH of the growth solution and the presence of halide ions.^{27, 28} Most recently, the Rodriguez-Fernández group reported another procedure for the seedless synthesis of multibranched hollow gold nanostars with a variable plasmon wavelength ranging from 700 to 2000 nm, which involves the addition of AgNO_3 into a solution of HAuCl_4 , and ascorbic acid in TX-100 solution.²⁹ The growth mechanism reveals that in-situ porous nanocage seeds were formed first and then gold atoms deposited on the seeds to form stars.

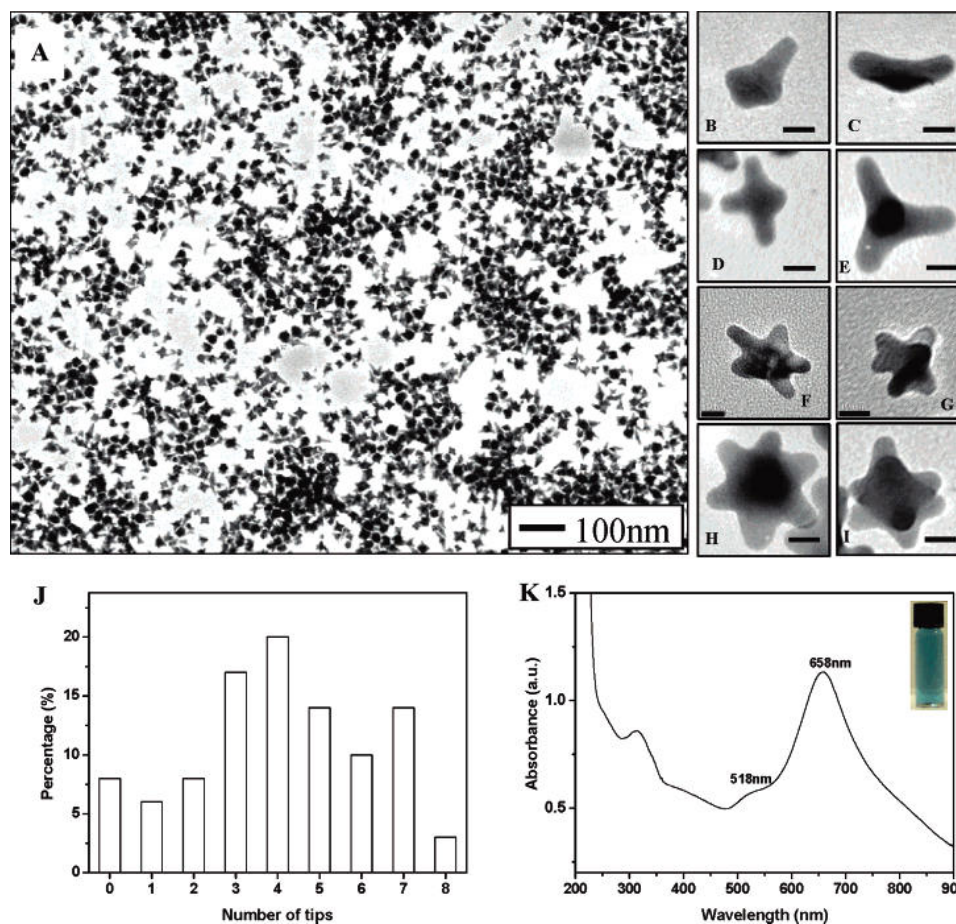


Figure 1.3. SEM image of gold nanostars indicates the polydispersity of branching of gold nanostars (A). Representative TEM images of branched gold nanostars with different number of tips: (B) one, (C) two, (D) three, (E) four, (F) five, (G) six, (H) seven, and (I) eight. Statistical distribution of gold nanostars (J). UV-vis spectrum of gold nanostars shows that the LSPR comes at 658 nm, and the color of the solution is green. Scale bars are 10 nm. Copyright 2007, Chemistry of Materials 2007, 19 (11), 2823-2830.

1.7. Surfactant free gold nanostars

Most of the reported surfactant-based gold nanostars are limited for biological applications as the syntheses were developed either in toxic organic solvents like DMF, which can denature proteins, or with surfactants like CTAB or PVP, which are toxic and difficult to exchange during biofunctionalization with proteins and/or oligonucleotides. Therefore, it

is necessary to develop a biocompatible route to synthesize monodisperse gold nanostars in water in order to avoid both the toxic surfactant and the organic solvent, leading to higher biocompatibility, easier surface functionalization, and higher surface area available for molecular recognition. Schutz et al. first developed the synthesis of seed mediated surfactant free gold nanostars. The synthesis involves addition of a hydroquinone solution to the growth solution containing 10 nm gold seeds, HAuCl_4 , and AgNO_3 . In surfactant-free nanostar synthesis, the seeds are generally citrate capped polycrystalline gold nanospheres synthesized by the citrate reduction method. However, the LSPR of these nanostars was limited to the visible region. This limitation was solved by Vo-Dinh and coworkers, who designed a seed-mediated silver-assisted wet chemistry method for gold nanostars with variable plasmon resonance from the visible to the NIR region. This synthesis involves simultaneous addition of AgNO_3 and ascorbic acid to an acidic mixture of 12 nm gold seeds and HAuCl_4 . However, the issues with the surfactant free gold nanostars are reproducibility and monodispersity. Ramsey et al. found that the low temperature (5 °C) is the most influential factor in producing reproducible and monodispersed gold nanostars.³⁰ Indrasekara et al. modified further the protocol to improve monodispersity and reproducibility of the nanostars where the AgNO_3 was added to the mixture of gold and an acidic gold chloride solution, and the ascorbic acid was introduced.³¹ The concentration of seeds and Ag^+ also have a substantial influence on branch density and the morphology of gold nanostars. The number of branches as well as their length are increased with increasing AgNO_3 concentration. However, the size of the seed doesn't influence the LSPR of the gold nanostars. The importance of hydrochloric acid (HCl) was also proven by replacing HCl with HNO_3 and observing only the formation

of nanospheres, meaning that chloride ions are also necessary for the formation of gold nanostars and influence the anisotropic growth.

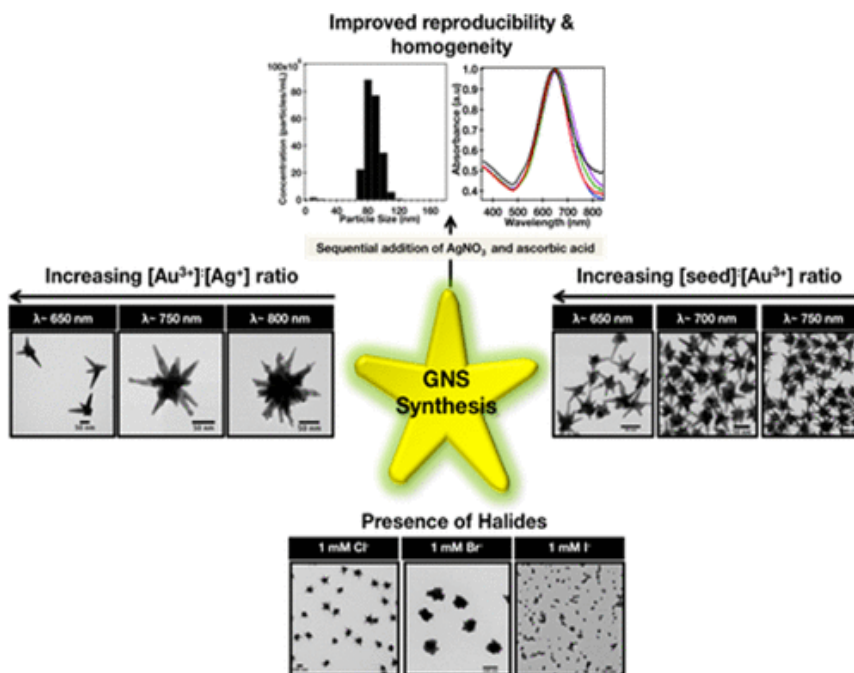


Figure 1.4. Highly monodispersed and reproducible surfactant free gold nanostars synthesis can be achieved by addition of $\text{AgNO}_3 \sim 5$ s later than ascorbic acid addition to the growth solution instead of addition of both ascorbic acid and AgNO_3 simultaneously. The morphology of the surfactant free stars depends on AgNO_3 , seeds, and halides. Copyright 2018, ACS Omega 2018, 3 (2), 2202-2210.

1.8. Surface Enhanced Raman Scattering

Raman spectroscopy is a spectroscopic technique to detect molecules based on their vibrational fingerprint. When a visible or NIR photon from the laser excitation source impinges on a molecule, the energy state of the molecule will be excited to a short-lived, virtual higher energy level, before the photon is emitted again and the molecule returns to its original state; this process is known as elastic scattering. When the molecules relax to either lower or higher energy levels, the events are known as Stokes and anti-Stokes

transitions, respectively. Stokes and Anti-Stokes transitions are collectively known as inelastic scattering, or Raman scattering. The Raman scattering pattern corresponds to characteristic transitions of a molecule, which can be useful as an analytical tool to detect the molecule. In most cases, the number of inelastically scattered photons is extremely small, which limits the trace detection of molecular analytes, especially those with small Raman cross sections. In 1977, the Van Duyne group observed that the Raman scattering intensity of an analyte molecule of pyridine increased by a factor of $\sim 10^6$ when the molecule was placed in close proximity to the surface of a nanostructured plasmonic Ag surface, and defined this phenomenon as the surface enhanced Raman scattering (SERS) effect.³² There are two theories generally accepted to explain the origin of SERS: The electromagnetic enhancement^{33,34} and the chemical enhancement.³⁵ In the electromagnetic field enhancement theory, when the incident light impinges on the surface, localized surface plasmons are excited and generate an intense scattered electric field near the metal surface, which leads to an amplification of the Raman signal of the analyte molecule in proximity to the metal. The second and less prominent mechanism is the “chemical enhancement”. It arises when metal-molecule charge transfer can take place.

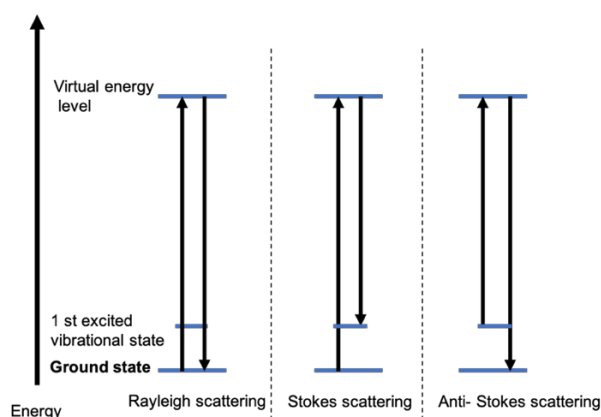


Figure 1.5. Rayleigh scattering- when there is no exchange of energy of the incident and emitted photons. Stokes scattering- when absorbed photon energy has less energy than the

emitted photon. Anti-Stokes scattering- when the absorbed energy has more energy than the emitted photon.

1.9. Plasmonic photocatalysis application

Photocatalysts are important to convert the energy of light into chemical energy. Most of the photocatalysts are semiconductor materials.^{36, 37} A well-known semiconductor material is TiO_2 .³⁸ There are three major steps in a typical semiconductor photocatalysis reaction. In the first step, electron-hole pairs generate by absorption of the incident light photons whose energy is larger than that of the semiconductor bandgap. In the second step, there occurs a photo-induced charge separation of the electron-hole pairs, where the electron moves to the conduction band of the semiconductor while the holes remain at the valence band. The crystallinity, size, and thickness of the semiconductor material show a great influence in this step as there is a possibility of recombination of the electrons and holes which can reduce the catalytic activity. The semiconductor materials should have high crystallinity to increase the charge separation and migration in order to obtain high photocatalytic efficiency. Similarly, the thickness of the semiconductor material should be small to obtain high surface area and reactive sites. In the third step, there occurs the chemical reaction at the semiconductor surface where electrons and holes carry out reduction and oxidation reactions, respectively. One of the main limitations in semiconductor photocatalysis is the recombination of electron-hole pairs. A large proportion of the electron-hole pairs recombine before reaching the semiconductor surface, which leads to no redox reactions at the semiconductor surface. One possibility to avoid the recombination would be to use of plasmonic noble metals and the synthesis of nanostructures with Schottky barriers at the metal-semiconductor interface. The use of nanostructured noble metals can improve the photocatalytic activity based on the excitation

of the LSPR and the generation of high numbers of hot electrons, i.e. electrons with high energies that, if captured before thermalization, contribute to enhancing the yield of the reduction reactions.

Direct electron transfer (DET) occurs when the electrons are promoted by light above the Fermi level and reach energy levels higher than that of the Schottky barrier. These electrons are called “hot” electrons. Hot electrons are generated by excitation at the specific LSPR frequency of the plasmonic metal. The Schottky barrier is formed at the interface between the plasmonic metal/semiconductor nanostructures and blocks the electron transfer from either way. When the hot electrons gain enough energy, they can overcome the Schottky barrier and be injected into the conduction band of the semiconductor. The DET mechanism was first proposed by Tian and Tatsuma, who observed an increment of photocurrent upon visible-light excitation of Au-TiO₂ photoelectrodes. For Au-TiO₂ system, the energy required to inject Au electrons from the Fermi level into the conduction band of TiO₂ is 0.96 eV. When the photocatalysts are exposed to water, the transferred electrons in the conduction band of TiO₂ reduce the protons into hydrogen, and the positive holes formed in the gold nanoparticles are scavenged by methanol, which is the sacrificial agent in the reaction.

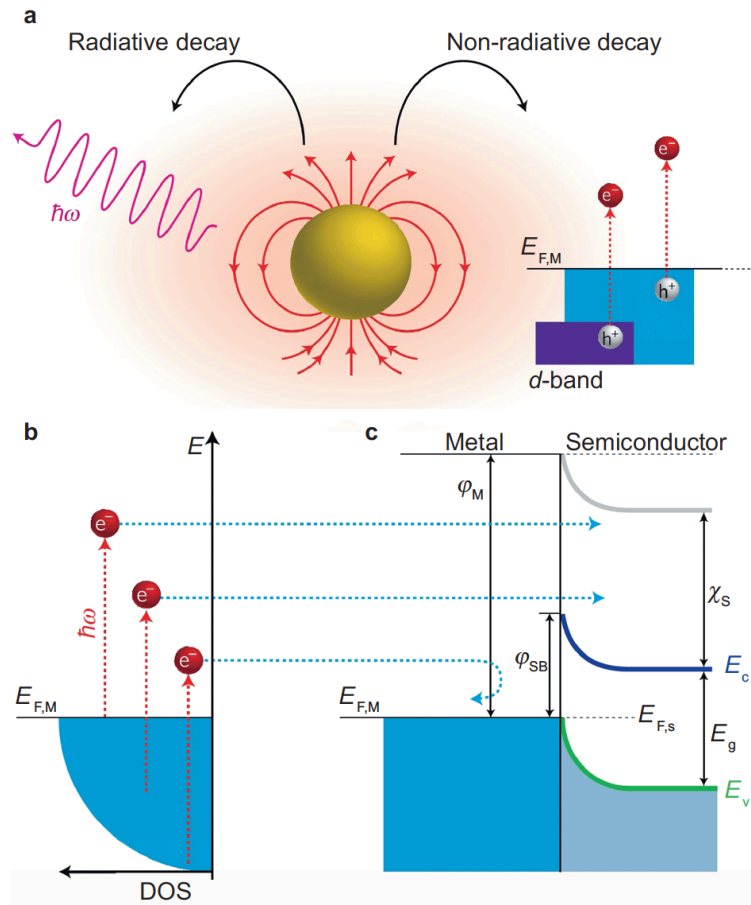


Figure 1.6. (a) LSPR can decay radiatively (which can emit as a photons) or non-radiatively (which can generate hot electrons). (b) The energies of hot electrons which have energies more than Fermi level. (c) The hot electrons can be injected into the conduction band of a semiconductor which have large energy to overcome the interface Schottky barrier.³⁹ Copyright 2014, Nature Photonics 2014, 8, 95.

1.10. Dissertation Hypothesis and Overview

Gold nanostars have received significant attention in many applications due to their unique physical and chemical properties. Controlling their size and shape is important toward their wide application in many fields, such as surface enhanced Raman spectroscopy (SERS) for sensors, catalysis, and biological labeling. Driven by potential applications, our goal in this thesis centers on the synthesis and properties of gold nanostars.

Although some gold nanostructures like gold nanorods have been synthesized with tunable size and shape, it is challenging to synthesize anisotropic nanoparticles such as gold nanostars with high monodispersity, in particular with high aspect ratio features. Importantly, a full understanding of the growth mechanism of gold nanostars and the key shape determining parameters also remain limited. Our first objective of this dissertation was to develop strategies to investigate the growth mechanism of gold nanostars and achieve highly monodisperse and reproducible nanoparticles by varying the concentration of reagents (Triton X, ascorbic acid, AgNO_3 , and seeds). Then, our next goal was to apply the gold nanostars in different fields such as plasmonics and catalysis. SERS is one of the popular plasmonic applications of gold nanostars. However, there is a lack of a systematic investigation of how their morphology and surface functionalization can affect the SERS signals. Another aspect of this dissertation was to study the phenomenon of hot electron generation in gold nanostars and their use in photocatalysis, as our way to contribute to solving the current energy crisis. Photocatalytic H_2 production from water in presence of semiconductor materials has attracted global attention over the last few decades, because the chemical energy in H_2 can be stored. However, because of the wide band gap of the semiconductor materials, only UV light can be used for water splitting reaction. Unfortunately, UV light covers only 5% of the solar spectrum. To overcome these problems, a plasmon-induced water splitting system under broad spectrum irradiation using gold nanostars coated with conformal crystalline TiO_2 is presented in this study. The specific objectives that were undertaken in order to achieve this aim can be summarized as follows:

- Synthesis of 6-branched gold nanostars with tunable resonant modes.

- Mechanistic investigation of gold nanostar growth for better understanding of the origin of the plasmonic resonances, and their dependence on the nanoparticle morphology.
- Determination of the role of the reducing agent (ascorbic acid), surfactant (Triton X), AgNO₃, and seed concentration on gold nanostar synthesis and properties.
- Synthesis of tunable silica coatings on gold nanostars for investigation of morphology dependence of SERS signal enhancement.
- Design and development of a novel metal-semiconductor (Au-TiO₂) nanomaterial and investigation of the kinetics and mechanism of near infrared (NIR) photocatalytic water reduction reaction.

In summary, this PhD thesis was designed and implemented to contribute to the design of gold nanostars with tailored surface functionality, high colloidal stability, biocompatibility, and a substantial potential in SERS and photocatalysis.

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CHAPTER- 2

UNDERSTANDING the ROLE of AgNO₃ CONCENTRATION and SEED MORPHOLOGY to ACHIEVE TUNABLE SHAPE CONTROL in GOLD NANOSTARS

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Abstract

Gold nanostars are one of the most fascinating anisotropic nanoparticles. Nanostar morphology can be controlled by changing various synthetic parameters; however, the detailed growth mechanisms are not fully understood. Herein, we investigate this process in six-branched nanostars, focusing first on the properties of the single crystalline seed, which evolves to include penta-twinned defects as the gateway to anisotropic growth into 6-branched nanostars. In particular, we report on a high-yield seed-mediated protocol for the synthesis of these particles with high monodispersity in the presence of Triton-X, ascorbic acid, and AgNO_3 . Detailed spectroscopic and microscopic analyses have allowed the identification of several key intermediates in the growth process, revealing that it proceeds via penta-twinned intermediate seeds. Importantly, we report the first experimental evidence tracking the location of silver with sub-nanometer resolution and prove its role as stabilizing agent in these highly branched nanostructures. Our results indicate that metallic silver on the spikes stabilizes the nanostar morphology, and that the remaining silver, present when AgNO_3 is added at high concentration, deposits on the core and between the base of neighboring spikes. Importantly, we also demonstrate the possibility to achieve monodispersity, reproducibility, and tunability in colloidal gold nanostars that are substantially higher than previously reported, which could be leveraged to carry out holistic computational-experimental studies to understand, predict, and tailor their plasmonic response.

2.1. Introduction

Among the various types of gold nanoparticle systems providing features facilitating field localization, gold nanostars have been widely recognized owing to their tunable plasmon resonances, which have the potential to be extended from the visible to the infrared.¹⁻⁴ Generally speaking, there is a strong correlation between optical properties and morphology in plasmonic nanoparticles, with sharp edges and tips being further able to create localized electric field enhancement in proximity to the nanoparticle's surface. Due to the structure- and size-dependence of the localized surface plasmon resonance (LSPR) bands, morphological control during the synthesis is very important.⁵⁻⁶ For instance, we have observed how small differences in the shape and number of branches of a nanostar lead to drastic shifts in the LSPR band position and width, with highly branched nanostars being characterized by broad and blue shifted resonances.⁷ For this reason, an increasing number of synthetic procedures have been developed to control size and shape of plasmonic nanoparticles, among which both seeded and non-seed mediated methods have shown to afford morphological tunability.⁸⁻¹⁰ Importantly, it is crucial to obtain colloidal nanoparticles with high yield and reproducibility and large batch monodispersity. However, morphological control in gold nanostars is still not satisfactory.^{3, 11-12} To improve monodispersity and reproducibility in gold nanostars, it is necessary to develop a fundamental understanding of the role of the chemical variables and their impact on the growth mechanism, and to investigate the key factors affecting growth. One of the issues in achieving this goal is the difficulty to trap reaction intermediates due to the generally fast reaction kinetics for these particles, and to understand, as a consequence, how any ill-defined morphology can

affect the final products.¹³ One of the goals of this work was therefore to develop a fundamental understanding of the growth mechanism of these nanoparticles, and to identify a simple synthetic methodology that could yield highly monodispersed gold nanostars with consistent reproducibility.

The use of Ag^+ is common in seed-mediated syntheses of gold nanostars to tune spike morphology up to a certain length by gradually increasing AgNO_3 concentration in the growth solution.¹⁴ This phenomenon is similar to what observed in gold nanorods.¹⁵⁻¹⁷ However, while several mechanisms have been proposed to explain in detail the role of AgNO_3 , they are still highly debated despite the decade-long scientific efforts.¹⁶ For example, a face-specific cetyltrimethylammonium-Br- Ag^+ capping complex was hypothesized to be formed to block specific gold facets thus leading to the formation of nanorods.¹⁸ In another proposed mechanism, underpotential deposition (UPD) of monolayers or sub-monolayers of silver on the gold nanorod surface was invoked as the factor leading to anisotropic growth.¹⁹ In this mechanism, silver deposits on the surface of the nanorods and selectively blocks selected facets, such as the $\{110\}$, rather than others, for instance $\{100\}$ or $\{111\}$.²⁰ Unfortunately, while the presence of trace amounts of silver has been reported on the surface of the gold nanorods,²⁰⁻²² a mechanistic investigation on the role of AgNO_3 at different concentrations in the growth of gold nanorods or nanostars has not been carried out yet. In this respect, structural and elemental characterization could provide essential insight into the growth mechanism, ultimately allowing to improve the monodispersity and reproducibility of gold nanostars.

In this manuscript, we describe a novel type of gold nanostars, possessing only an average of 6-branches (see Figure S1 for the definition of average), and elucidate the role of the synthetic parameters in the surfactant-based seed-mediated protocol employed to synthesize them. We also propose a growth mechanism that focuses on the properties of the seeds and how they affect the final nanoparticle morphology. These nanoparticles show exceptionally high monodispersity compared to nanostar systems reported before,²³⁻²⁶ and can be synthesized with high reproducibility. The reduced number of spikes, whose length and shape can be rationally controlled, limits side-by-side spike cross-talk, thus reducing LSPR peak broadening, and enables establishing fundamental relationships between morphology and plasmonic properties, which has been not possible so far due to the irreproducibility of the traditional synthetic protocols for gold nanostars.²⁷ For these reasons, these nanoparticles represent the first example of branched nanostructure that can be synthesized by design to possess pre-determined physical and optical properties. Based on this potential, it is important to understand the role of the reagents and their interplay during nanostar growth. To address this need, we performed a systematic study to determine how the concentrations of the surfactant (Triton X), the reducing agent (ascorbic acid), and AgNO_3 , and their interaction with the evolving seeds affect the morphology, and thus the LSPR bands, of the resulting gold nanostars. By investigating the mechanism of gold nanostar formation in this surfactant-mediated synthesis, we propose a kinetically-controlled process as the basis of the growth.

2.2. Results and discussion

The two main recognized parameters affecting the growth of anisotropic gold nanostructures are the properties of the seeds and the concentration of AgNO_3 . In the specific synthesis explored in this work, investigating their interplay with the added surfactant (Triton X) and the reducing agent (ascorbic acid) also provides useful insight. To us however, the most important goal was to understand how seed evolution and silver concentration and position affect growth. Therefore, we first carried out the synthesis varying the concentrations of the four main reagents (i.e., Triton X, ascorbic acid, AgNO_3 , and seeds) and characterized the obtained nanoparticles to extrapolate trends to identify the optimal synthetic conditions to achieve 6-branched nanostars, the ideal starting point for a more in-depth analysis. In this seed-mediated synthesis, seed and growth solutions were prepared separately but with equal concentration of surfactant, starting from concentration values similar to what reported in the initial manuscript of Pallavicini et al. but departing from them to achieve monodispersity and eliminate byproducts.²⁸ By varying the concentration of the four variables independently, we have investigated and determined how to obtain highly monodispersed 6-branched gold nanostars. While we are aware that multiple parameter spaces could likely provide ideal conditions to achieve similar results, we deemed it beyond the scope of this work to search for additional concentration values, considering more important to instead focus on understanding the growth mechanism in this specific set of conditions. In Figure 2.1, we have investigated the role of Triton X and ascorbic acid by modifying their concentrations while keeping the concentration of AgNO_3 and seeds constant at 100 μM and 0.14 nM, respectively. We have examined four different concentrations of Triton X (0.01

M, 0.04 M, 0.15 M, and 0.3 M), and three different concentrations of ascorbic acid (0.8 mM, 1.6 mM, and 3.9 mM). In Figure 2.1, the concentration of Triton X varies along a column while the concentration of ascorbic acid is kept constant. For example, in column 1 of Figure 2.1, the concentration of Triton X was increased from 0.01 M to 0.3 M (0.01 M (1a), 0.04 M (1d), 0.15 M (1g), and 0.3 M (1j)), while the concentration of ascorbic acid was kept constant (0.8 mM). On the other hand, the concentration of Triton X was kept constant throughout a row while the concentration of ascorbic acid was varied. For example, in row 1 of Figure 2.1, the concentration of ascorbic acid was increased from 0.8 mM to 3.9 mM (0.8 mM (1a), 1.6 mM (1b), and 3.9 mM (1c)) while the concentration of Triton X was kept constant (0.01 M).

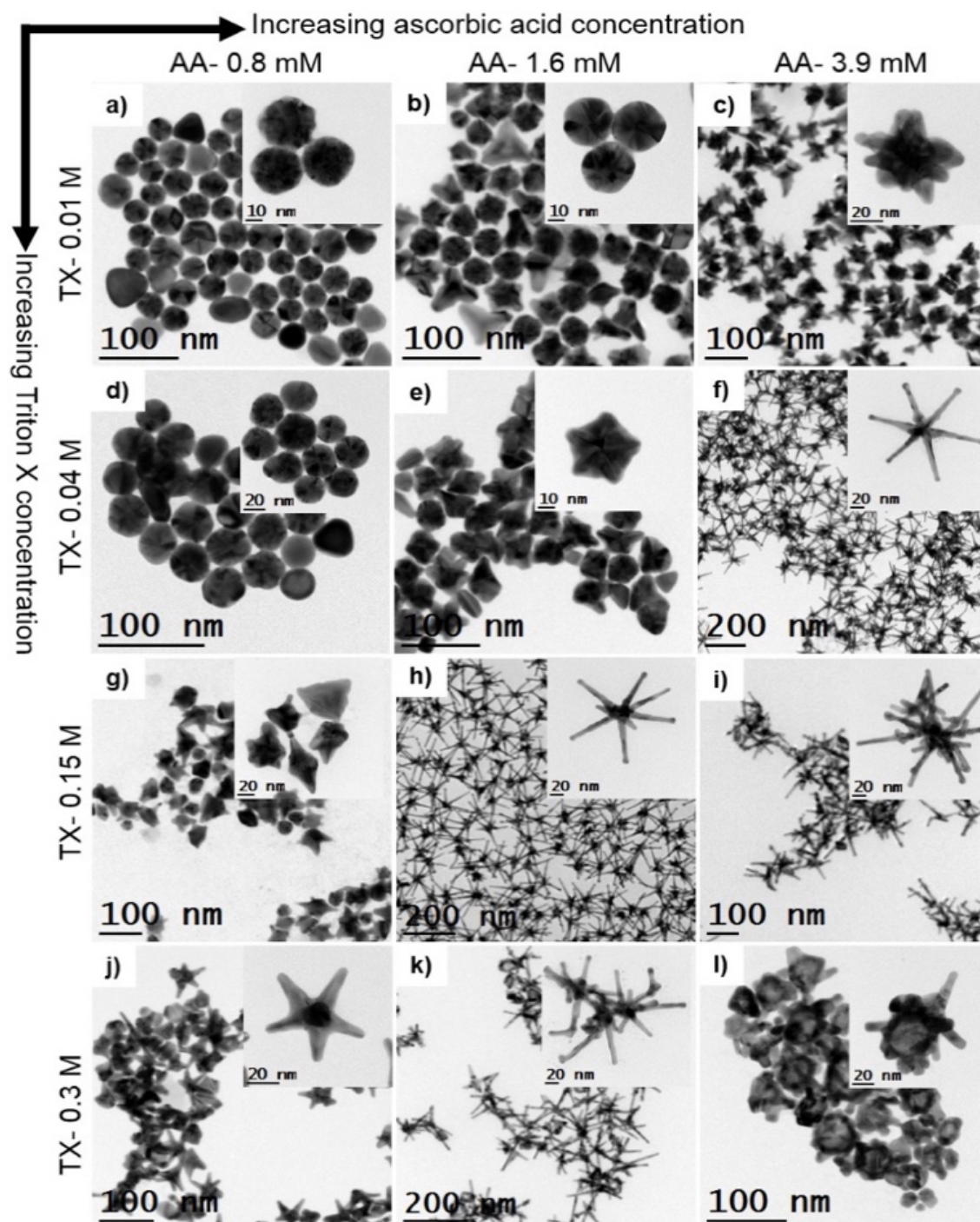


Figure 2.1. (a-l) TEM images of the gold nanoparticles where the concentration of the two chemical variables (Triton X and ascorbic acid) were progressively changed. In a column, the concentration of Triton X (TX) was varied from 0.01 to 0.3 M while

it was kept constant in a row. For example, the concentration of Triton X in column 1 were 0.01 M (a), 0.04 M (d), 0.15 M (g), and 0.3 M (j). On the other hand, the concentration of ascorbic acid was kept constant in a column while it was increased from 0.8 mM to 3.9 mM in a row. For example, the concentration of ascorbic acid in row 1 were 0.8 mM (a), 1.6 mM (b), and 3.9 mM (c). The concentrations of AgNO_3 (100 μM) and seeds (0.14 nM) were kept constant.

TEM micrographs in Figure 2.1 reveal that the 6-branched morphology can be obtained only at ideal concentrations of both surfactant (Triton X) and reducing agent (ascorbic acid). In a column of Figure 2.1, when the concentration of Triton X was increased at a constant ascorbic acid concentration, the morphology changed from polyhedral nanoparticles to 6-branched stars. For example, in column 1 (Figure 2.1a, d, g, and j), the morphology of the nanoparticles changed from polyhedral to 6-branched stars at very high Triton X (0.3 M) and very low ascorbic acid (0.8 mM) concentration. However, the change in morphology from polyhedral to 6-branched stars was also observed at moderately high Triton X (0.15 M) and moderate ascorbic acid (1.6 mM) concentration in column 2 (Figure 2.1h), and at moderately low Triton X (0.04 M) and high ascorbic acid (3.9 mM) concentration in column 3 (Figure 2.1f). Interestingly, at a very low concentration of Triton X (0.01M) and very high concentration of ascorbic acid (3.9 mM) (Figure 2.1c) multibranched stars were formed, where multiple ($n \gg 6$) branches were grown from the central core. Complex hyperbranched nanoparticles, with multiple side branches on each of the six main branches (Figure 2.1k, and 2.1i), were formed when both Triton X and ascorbic acid concentration were higher than the ideal concentrations for 6-branched stars formation. Multibranched hollow gold nanoparticles were formed at a very high

concentration of Triton X and ascorbic acid (Figure 2.11); we are still investigating their mechanism of formation. We observed similar morphology changes from polyhedral to 6-branched stars to complex hyperbranched nanoparticles in a row when the ascorbic acid concentration was increased at constant Triton X concentration (Figure 2.1g-i).

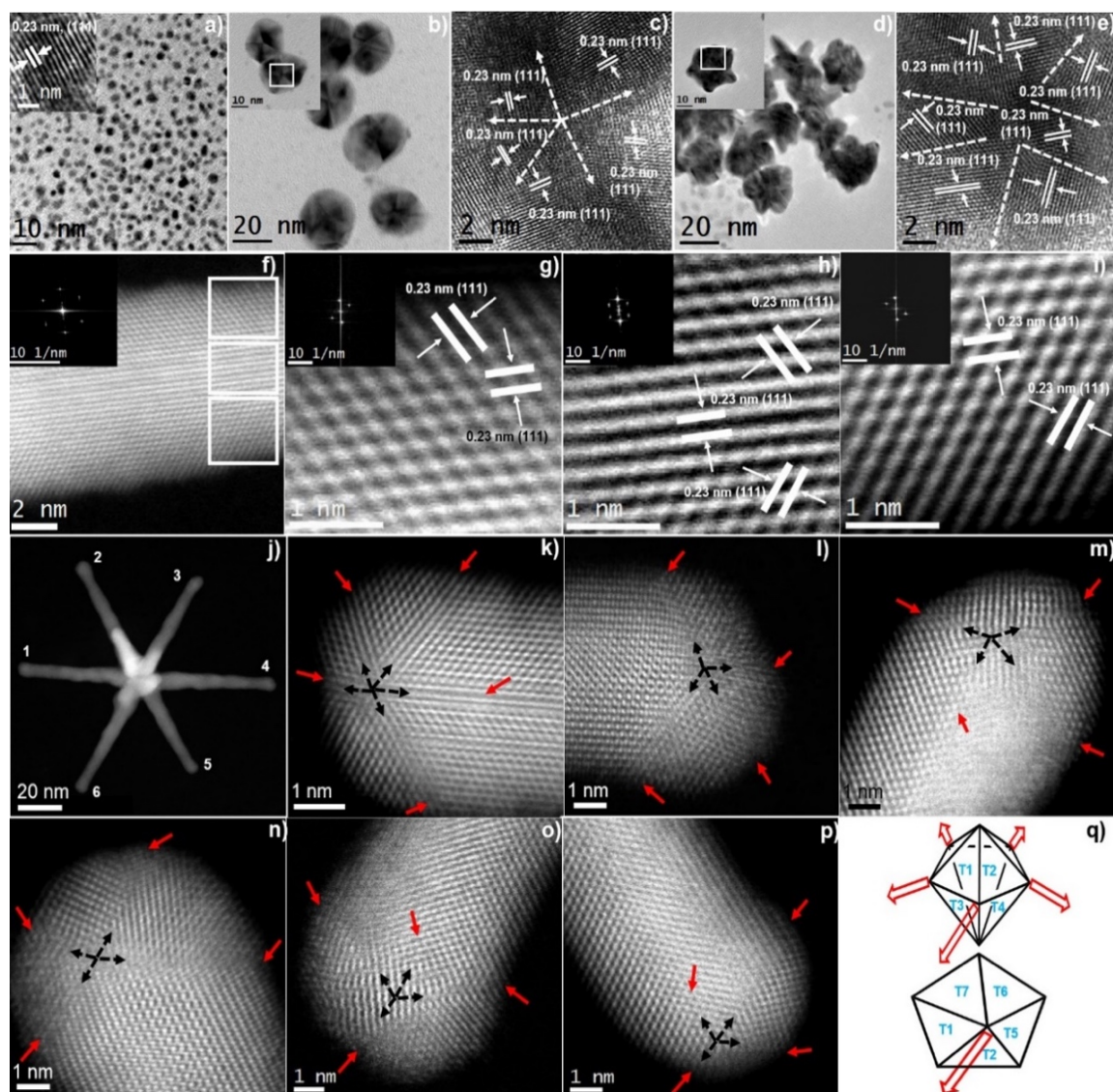


Figure 2.2. a) TEM micrographs of the seeds illustrating that their average diameter was 3 nm. HRTEM micrograph (inset) shows the single crystalline morphology of

the seed, with interplanar spacing characteristic of $\{111\}$ planes in FCC gold. (b-c) TEM and HRTEM micrographs of penta-twinned intermediate seeds of 6-branched stars. (d-e) TEM and HRTEM images of multiply twinned intermediate seeds of multibranched stars. (f-i) STEM images of the spike showing the presence of only a twin boundary where the FFT (inset) and lattice fringes represent $\{111\}$ planes reversely oriented with respect to a common twin plane. j) TEM image of the 6-branched stars. k) STEM micrograph of the tip showing five twinning planes, which indicates that the spike is forming on a twinning axis of a pentagonal unit. l-p) STEM micrographs of the tips shows four twinning planes, indicating that the spike is forming on a twinning axis of a tetrahedral unit. Red arrows show the twin planes. q) Representation of spike growth from decahedral seeds. Top image: Schematic side view identifying the spike growth directions on seeds such as that reported in Figure 2.7l. A maximum number of five spikes can grow along the equatorial directions identified by the red arrows, which are determined by four neighbouring facets (T1, T2, T3, and T4). Bottom image: Schematic top view representing the structure reported in Figure 2.S12, in which the spike growth is expected to occur from penta-twinned defects, in which five neighbouring facets are present (T1, T2, T3, T4, and T5).

At ideal ascorbic acid (and AgNO_3) concentrations for 6-branched nanostar synthesis, the final morphology of the particles depends strongly on the concentration of Triton X. We observed that multibranched stars were formed in the absence of Triton X (Figure 2.S2), while hyperbranched nanostars were formed at high Triton X concentration (Figure 2.1k). In agreement with previous reports, it appears that at very low concentration of Triton X, gold ions are not tightly bound

to the surface by the surfactant Triton X and can be easily reduced by ascorbic acid.²⁸ By increasing the surfactant concentration above the critical micelle concentration (CMC) of Triton X (0.3 mM), the number of Au-encapsulating Triton X micelles increases,²⁹ thus decreasing the amount of free Au ions. The reduction in available free Au ions leads to more controllable gold reduction and branch generation during the growth process. A similar effect has been observed in other surfactant-mediated gold nanostars syntheses, in which morphological changes from polyhedral to branched stars were also observed at increasing surfactant concentration.²⁶ For gold nanorods, it has been reported that a high concentration of surfactant (cetyltrimethylammonium bromide, CTAB) is necessary to achieve high aspect ratios, as high amounts of CTAB limit the number of free Au ions and reduce secondary nucleation events thus leading to the formation of longer nanorods.³⁰ However, because it is still unclear how micelle encapsulation for 6-branched nanostars occurs, we can only hypothesize that at extremely high concentrations of Triton X (>0.15 M) unzipping of the surfactant at the surface of the spikes may be taking place (mediated by the excess surfactant in solution) leading to the generation of secondary nucleation events on the spikes,³¹ and thus resulting in the formation of hyperbranched nanostars (Figure 2.1k).

Ascorbic acid can tune the morphology of the resulting nanoparticles as well, with higher amounts leading to the desired 6-branched nanostars. We believe this to be due to the increase in negative charge on the growing seeds due to excess ascorbic acid in the growth solution, resulting in the migration of gold atoms toward low surface energy facets, such as {111}, from high surface energy facets like {110}, or to an increase in crystal growth kinetics at higher ascorbic acid concentration.³²⁻³³

Clearly, additional experiments will be necessary to provide further evidence on the nature of the observed nanostar reshaping.

Having established the ideal parameter space for Triton X and ascorbic acid, we then focused our investigation on the determination of seed quality (size and crystallinity) (Figure 2.2). To avoid Ostwald ripening of the seeds on the grid during TEM analysis, we employed n-pentanethiol as a capping agent to quench the reaction and stabilize the seeds, as previously done to analyze the morphology of growth intermediates. HRTEM micrographs of the seeds disclose that most of the particles have single crystalline morphology, with an interplanar spacing of 0.23 nm, typical of (111) plane in FCC gold, and diameters of around 3 nm (Figure 2.2a). We have observed that at moderate ascorbic acid concentrations, ideal to produce 6-branched nanostars, the *in-situ* evolution of single crystalline seeds into five-fold twinned seeds occurs (Figure 2.2b). On the other hand, at very high ascorbic acid concentration the intermediate seed possesses multiple twin defects (Figure 2.2d), but these conditions do not lead to 6-branched nanostars, rather to multibranched particles. Therefore, although multiple nucleation centres at low surface energy {111} facets are necessary for spike growth, their identity and number are what determine the final nanostar morphology.

We also followed spike growth over time by TEM. It has been proposed that twinned seeds may be fundamental to ensure spike growth on nanostars,^{14, 34} however, the direct correlation between defect nature and nanostar morphology has never been shown. We have therefore carried out a detailed analysis of the crystallographic properties of the seeds to correlate them to the resulting nanostar product. The

morphology was investigated 10 s after addition of Triton X, ascorbic acid, and AgNO_3 for 6-branched stars and multibranched stars, leading to the products in Figure 2.2b and 2.2d. The morphology of the seed turned from single crystalline to twinned crystal, with all gold planes belonging to the $\{111\}$ family (Figure 2.2c, and 2.2e). To be specific, penta-twinned intermediate seeds were formed when the concentration of Triton X, ascorbic acid, and AgNO_3 were ideal for the formation of 6-branched stars (Figure 2.2b-c), whereas multiply twinned intermediate seeds having multiple $\{111\}$ facets were formed when the concentration of Triton X, ascorbic acid, and AgNO_3 were kept at values observed to produce multibranched stars (Figure 2.2d-e). The formation of multiple $\{111\}$ facets in a multiply twinned intermediate supports our hypothesis that at high ascorbic acid concentration multiple low energy facets $\{111\}$ are formed, whereas the reduction rate of gold (III) at 0.15 M Triton-X, 1.6 mM ascorbic acid, and 100 μM AgNO_3 leads only to the formation of penta-twinned defects. Interestingly, STEM micrographs of 6-branched nanostars show an anisotropic growth over the $\{111\}$ facets on either side of the twin boundaries for penta-twinned intermediate seeds (Figure 2.2f-i), which arises due to low twinning energy and angle strain.³⁵ The corresponding fast Fourier transform image further confirms that the two $\{111\}$ crystal facets are oriented with a common $\{111\}$ twin plane (Figure 2.2h). This is further confirmed by the STEM micrographs of the tips (Figure 2.2j-p) which provide a clear view of the crystallographic structure of the penta-twinned seeds from which the spikes were grown, as illustrated in Figure 2.2q. In comparing Figure 2.2j-p and 2.2q, one can observe that while in principle these particles should possess either five or seven spikes, the distribution reported in Figure 2.2q identified quite comparable numbers

of 5-, 6-, and 7-branched nanostars, with higher frequency of 6-branched nanostars. Further TEM tomography will allow us to better evaluate these numbers and clearly tease out the correlation between seed defects and spike numbers.

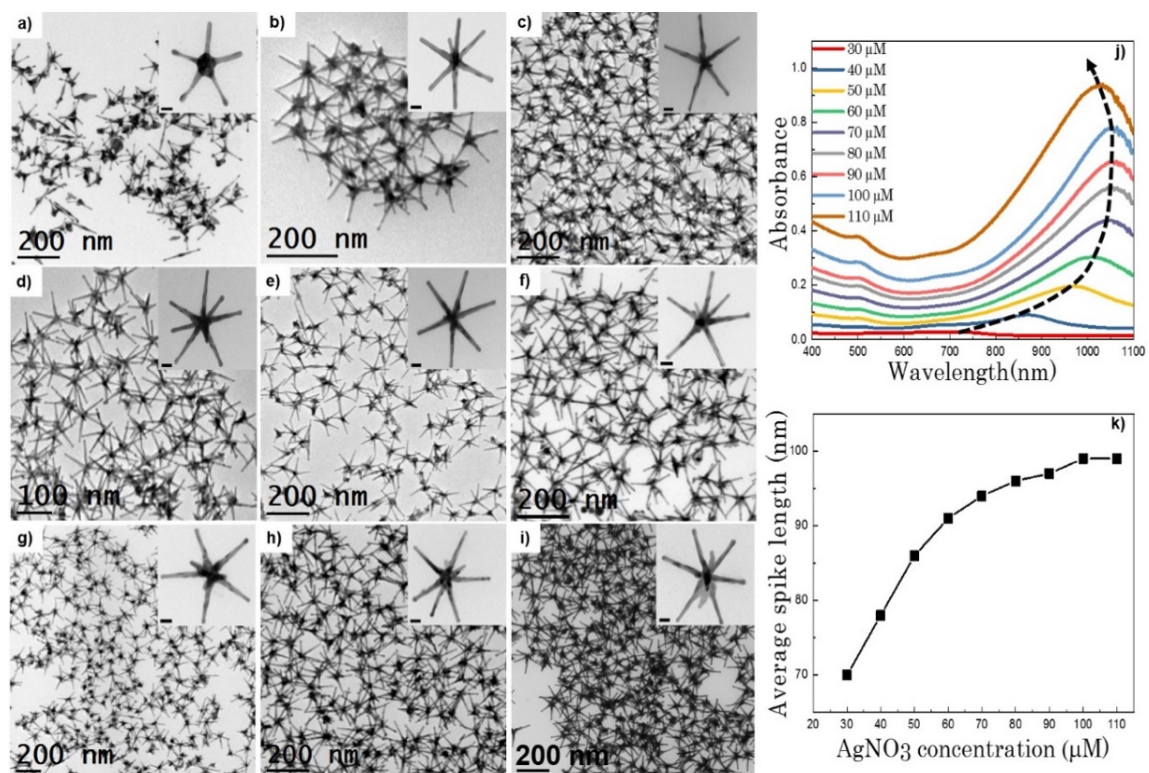


Figure 2.3. (a-i) TEM micrographs of nanostars formed under different AgNO_3 concentrations- 30 μM (a), 40 μM (b), 50 μM (c), 60 μM (d), 70 μM (e), 80 μM (f), 90 μM (g), 100 μM (h), and 110 μM (i). The concentration of other two chemical variables (ascorbic acid and Triton-X) were 1.6 mM and 0.15 M, respectively. Scale bars are 20 nm (inset). j) UV-vis spectra (normalized) for each of the colloidal dispersions which shows a gradual red shift with increasing AgNO_3 concentration as the spike length is increased, and blue shift after 100 μM AgNO_3 as silver is deposited on the core. k) Evolution of the average spike length as a function of AgNO_3 concentration.

We have observed that polyhedral nanoparticles were formed in the absence of AgNO_3 , thus indicating that AgNO_3 is necessary for the formation of the desired 6-branched nanostars (Figure 2.S3). AgNO_3 concentration affects the stability of the particle as well, as we observed spherical impurities at or below $30\ \mu\text{M}$ AgNO_3 , likely due to nanostar reshaping. However, we have not seen the transformation from polyhedral nanoparticles to 6-branched stars by increasing the concentration of AgNO_3 at non-ideal concentrations of Triton-X and ascorbic acid (Figure 2.S4). We have investigated the effect of AgNO_3 when the concentrations of the other reagents are optimized to obtain highly monodisperse and reproducible 6-branched stars ($0.15\ \text{M}$ Triton X, $1.6\ \text{mM}$ ascorbic acid, and $0.14\ \text{nM}$ seeds) (Figure 2.1h). The concentration of AgNO_3 was increased in small increments of $10\ \mu\text{M}$ to determine the possibility of finely-tuning the morphology through AgNO_3 (Figure 2.3 and Figure 2.S5). The spike length increased rapidly by roughly $8\ \text{nm}$ by increasing AgNO_3 concentration in $10\ \mu\text{M}$ increments from 30 to $60\ \mu\text{M}$ AgNO_3 . Then it slowly increased by around $2\text{-}3\ \text{nm}$ by increasing the amount of AgNO_3 from 60 to $100\ \mu\text{M}$ in $10\ \mu\text{M}$ steps (Figure 2.3k and Figure 2.S6). This evolution was followed by monitoring the red-shift of the longitudinal LSPR band in the UV-Vis spectrum (Figure 2.3j and Figure 2.S5). The red-shift was also accompanied by a visible change in the solution color from blue to brown as the concentration of AgNO_3 increased. At AgNO_3 concentration higher than $100\ \mu\text{M}$, the spike length did not further increase (Figure 2.3j-k), rather a blue shift in the LSPR band, reported to indicate a shortening or thickening of the spike, was instead observed.^{6, 14} The blue shift of the LSPR at $110\ \mu\text{M}$ AgNO_3 concentration could also however be due to the deposition of atomic Ag on the core (vide infra), as the ascorbic acid in excess can

reduce remaining silver ions resulting in the nanostar core diameter to increase from 25 to 35 nm. Vo-Dinh and coworkers reported that silver overgrowth on gold nanostars is possible and can blue shift the plasmon resonance of the longitudinal mode.³⁶

To study the fate of silver and its role on the evolution of spike morphology, we first monitored the branch sharpness, which is the ratio between the spike widths at core and tip, observing that it increased from 1.2 to 1.9 (Figure 2.S7) with increasing AgNO_3 concentration from 30 μM to 100 μM , possibly due to the migration of gold atoms from the tip toward the core. This result further motivated us to study the evolution of the spike morphology. Spike growth was investigated in detail by arresting the reaction at different time points and examining the intermediates via TEM to correlate morphology evolution to LSPR position, when the concentration of Triton X, ascorbic acid, and AgNO_3 were 0.15 M, 1.6 mM, and 30 μM respectively (Figure 2.3 and Figure 2.S8). TEM micrographs (Figure 2.3a-l and Figure 2.S8a-l) at different time intervals reveal that the branches grew gradually and reached maximum length (100 nm) after 5 minutes. After that, they shrank, and the process was completed after 12 hours, with an overall shrinking in spike length by 30 nm, from 100 nm (5 min) to 70 nm (12 hours). The time-dependent evolution of this reaction was monitored by UV-Vis spectrophotometry (Figure 3m), which elucidated that the LSPR band gradually red shifted as the spike length increased between 30 seconds and 5 minutes. The LSPR band reached its maximum redshift to 1071 nm after 5 min, then blue shifted from 1071 nm to 734 nm after 12 hours. The blue shift was associated to the migration of gold atoms from high energy sites on the tip toward lower energy ones at the core, resulting in a decrease in spike

length from 100 nm to 70 nm. The LSPR shift was also accompanied by a visual color change in the solution from blue to green to brown to blue, as observed before for the growth of multibranched gold nanostars and gold nanorods when the spike length was reduced in the late stages of the reaction.^{4, 17, 22, 37}

The nanostars morphology at 30 μM AgNO_3 concentration for a given growth time was further investigated by STEM (Figure 4n-p) to study spike morphology in detail. STEM micrographs revealed that the gold nanostars grown for 5 minutes contained spherical penta-twinned tips where twin boundaries having $\{111\}$ facets bridging the sides with the tips can be observed (Figure 2.4n). However, after 6 hours the tip was observed to be less spherical (Figure 2.4o) and to become oblate after 12 hours, with no clearly distinguishable facets detectable, as the penta-twinned morphology of the tips disappeared after 6 hours. (Figure 2.4o-p). We believe that the driving force for these morphological changes is the surface energy minimization that is achieved by removing reactive edge atoms located at the twin boundaries of highly faceted penta-twinned spikes.^{15, 38}

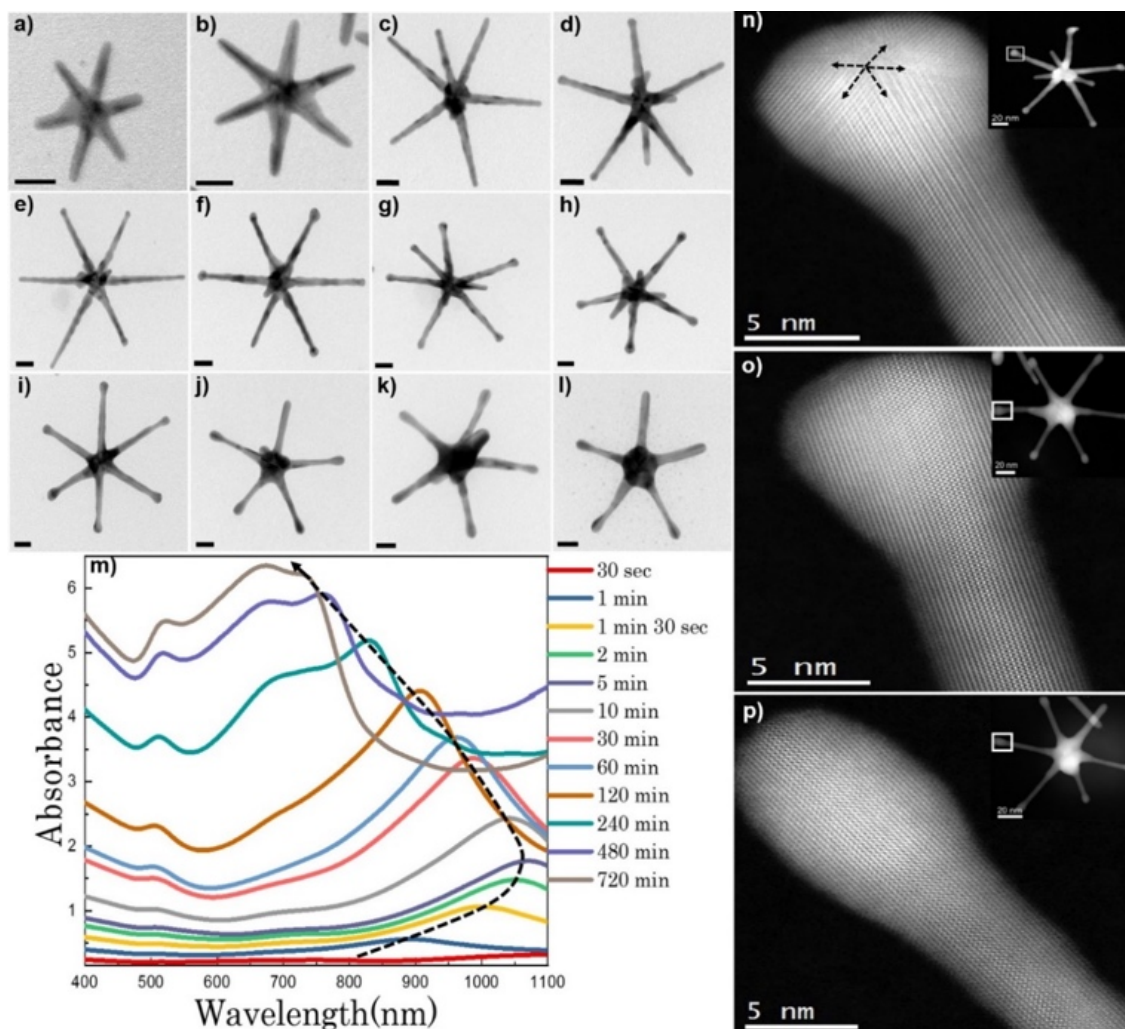


Figure 2.4. a-l) TEM micrographs of gold nanostars when the concentrations of the growth solution are- Triton-X-0.15 M, ascorbic acid- 1.6 mM, and AgNO_3 - 30 μM for which growth was arrested at the indicated reaction times (30 sec (a), 1 min (b), 1 min 30 sec (c), 2 min (d), 5 min (e), 10 min (f), 30 min (g), 60 min (h), 120 min (i), 240 min (j), 480 min (k), and 720 min (l)). m) Corresponding UV-vis spectra (normalized) taken from each aliquot sample which indicates that an initial red shift of the longitudinal plasmon peak occurred, which reversed after 5 minutes, and was followed by a permanent blue shift. Scale bars are 20 nm. (n-p) STEM micrographs

of the spike at 5 min (n), 240 min (o), and 720 min (p) showing the morphology from twinned spherical tip to oblate tip.

To gain further insight into the evolution of the spikes, we have investigated in detail the changes in overall nanostar morphology at the 5-minute (Figure 2.S9) and 12-hour (Figure 2.2b-d, 2.2f, and 2.2h) marks, by varying the concentration of AgNO_3 , starting from the observation that maximum spike length is reached after 5 minutes and the minimum after 12 hours, for reactions with $30\ \mu\text{M}$ AgNO_3 . We have used five different additional concentrations of AgNO_3 ($40\ \mu\text{M}$, $50\ \mu\text{M}$, $60\ \mu\text{M}$, $80\ \mu\text{M}$, and $100\ \mu\text{M}$), and observed that the spike length is maximized after 5 minutes ($100\ \text{nm}$) for all AgNO_3 concentrations, with additional substantial shape reconstruction occurring at the 12-hour time point. For nanostars synthesized with $30\ \mu\text{M}$ AgNO_3 the shape reconstruction was substantial, with spike length reduction from $100\ \text{nm}$ to $70\ \text{nm}$ and loss of the sphere at the tip (Figure 2.4n-p). However, the extent of deformation decreased with increasing the concentration of AgNO_3 from $30\ \mu\text{M}$, becoming the lowest for nanostars synthesized at $100\ \mu\text{M}$ AgNO_3 (Figure 2.S9a-f). For instance, while a $341\ \text{nm}$ blue shift was observed for $30\ \mu\text{M}$ AgNO_3 stars, only a $6\ \text{nm}$ blue shift was observed for $100\ \mu\text{M}$ AgNO_3 stars (Figure 2.5a-f). We also observed visually that the color did not change from brown to blue when the concentration of AgNO_3 was kept at $100\ \mu\text{M}$ AgNO_3 . These results led us to postulate that the 5-minute morphology might be the kinetically trapped version of the thermodynamically-stable 12-hour morphology, and that deposited Ag atoms might reduce significantly the atom diffusion typically observed for highly energetic gold facets on gold nanoparticles. These observations also established the added important role for AgNO_3 (i.e. to stabilize the nanostar shape and size) beyond the

well-known shape-inducing role. We attribute the shape reconstruction observed at longer reaction times for low AgNO_3 concentration to the fact that the highly energetic gold atoms at the tips can easily diffuse along the spike migrating to more energetically favourable positions on the nanostar, such as the base of the spike. However, when the concentration of AgNO_3 was 100 μM , the Ag atoms appeared to stabilize the highly energetic gold atoms, thus inhibiting their diffusion toward the core. A similar result was reported by Tong et al., who observed a blue shift of the longitudinal plasmon peak of gold nanorods when they kept from 2 hrs. to 13 weeks.¹⁵ The possible reason behind the stability gained at above 30 μM AgNO_3 concentration is that the presence of submonolayer silver atoms act as a protective agent for the underlying the gold atoms in form of Au-Ag(UPD)-Cl on the surface of the nanoparticles.³⁹⁻⁴⁰

We have investigated further the role of Ag by using scanning transmission electron microscopy-efficiency energy dispersive X-ray spectroscopy (STEM-EDS), to determine whether or not Ag exists as adsorbed species on the Au surface or becomes fully alloyed to Au on the nanostar spike. We also wanted to ascertain whether or not the deposition of increasing amounts of silver at high concentrations of AgNO_3 is responsible for the observed morphology stabilization and LSPR blue shifts. Figure 6 shows the STEM image of 6-branched gold nanostars having three different AgNO_3 concentrations (30, 100, and 110 μM) along with corresponding STEM-EDS map showing the gold signal (red scale) and the silver signal (blue scale), which reveal that silver was alloyed with gold in the nanostars. Moreover, we have observed that the relative silver signal increased with increasing AgNO_3 concentration, going from 3.86% (2.21% at core, and 5.51% at spike) to 14.66%

(13.87% at core, and 15.45% at spike) when the concentration of AgNO_3 was increased from 30 μM to 100 μM , and even further increased to 16.45% (18.94% at core, and 13.97% at spike) when the concentration of AgNO_3 was 110 μM . Interestingly, the line-scanned EDS elemental profiles of the spike and the core of 30 μM AgNO_3 showed that the amount of Ag was uniform throughout the spike and the core and (Figure 2.6a'-b'), While it was higher at the side wall of the spike for 100 μM AgNO_3 , which supports our hypothesis that a submonolayer of silver stabilizes the surface Au atoms (Figure 2.6c'-d'). Moreover, silver deposition increased at core when the concentration of AgNO_3 was 110 μM (Figure 2.6e'). This growth mechanism also supports the observed patterns in gold nanorod growth, where silver deposits on the side wall of the rod rather than the tips.²⁰ We further carried out an area scanned analysis of the EDS map to obtain more information about the amount of Ag present on the gold nanostars (Table 2.S1). Area scan results of the spike at 30 μM AgNO_3 show 3.28% (A1), 8.84% (A2), and 4.12% (A3) of Ag present at the tip, side wall, and middle portion of the spike, respectively, which reveals that the amount of Ag was almost uniform on the spike. On the other hand, the amount of Ag was significantly lower at the core (A4, 2.46 % Ag). However, we have seen an increase in the amount of Ag at the side wall of the spike of the stars at 100 μM and 110 μM AgNO_3 (36.87% for 100 μM (A7) and 33.70% for 110 μM (A15)) compared to the middle portion of the spike (23.61% for 100 μM (A8) and 13.78% for 110 μM (A16)). Interestingly, we have seen that the amount of Ag increased at core when the concentration increased from 100 μM (8.34 % Ag (A10)) to 110 μM (25.05 % Ag (A13)) which supports our hypothesis that the observed LSPR blue shift is also due to Ag deposition at the core (Figure 2.3).

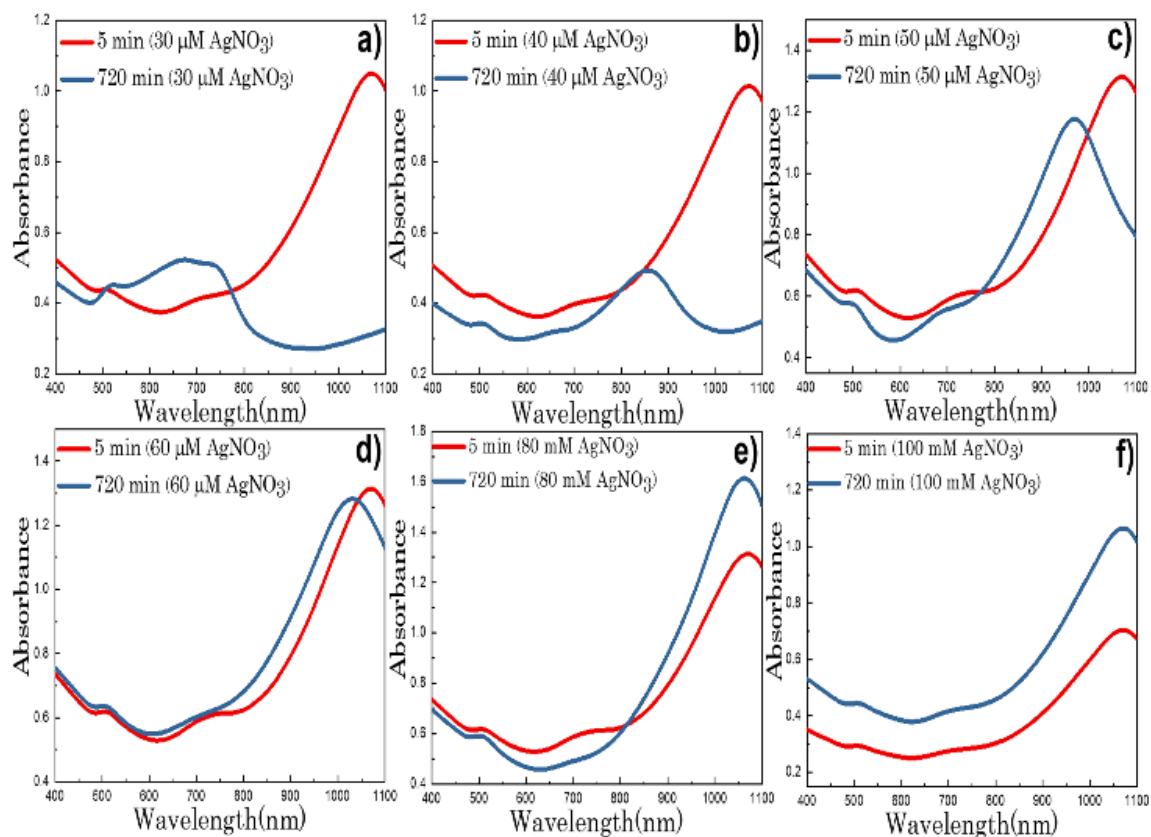


Figure 2.5. (a-f) UV-Vis spectra of 6-branched gold nanostars formed after 5 min and 720 min reaction time under different AgNO_3 concentration-30 μM (a), 40 μM (b), 50 μM (c), 60 μM (d), 80 μM (e), and 100 μM (f). UV-Vis spectrum shows a 341 nm, 212 nm, 99 nm, 42 nm, 12 nm, and 6 nm blue shift for 30 μM , 40 μM , 50 μM , 60 μM , 80 μM , and 100 μM AgNO_3 respectively.

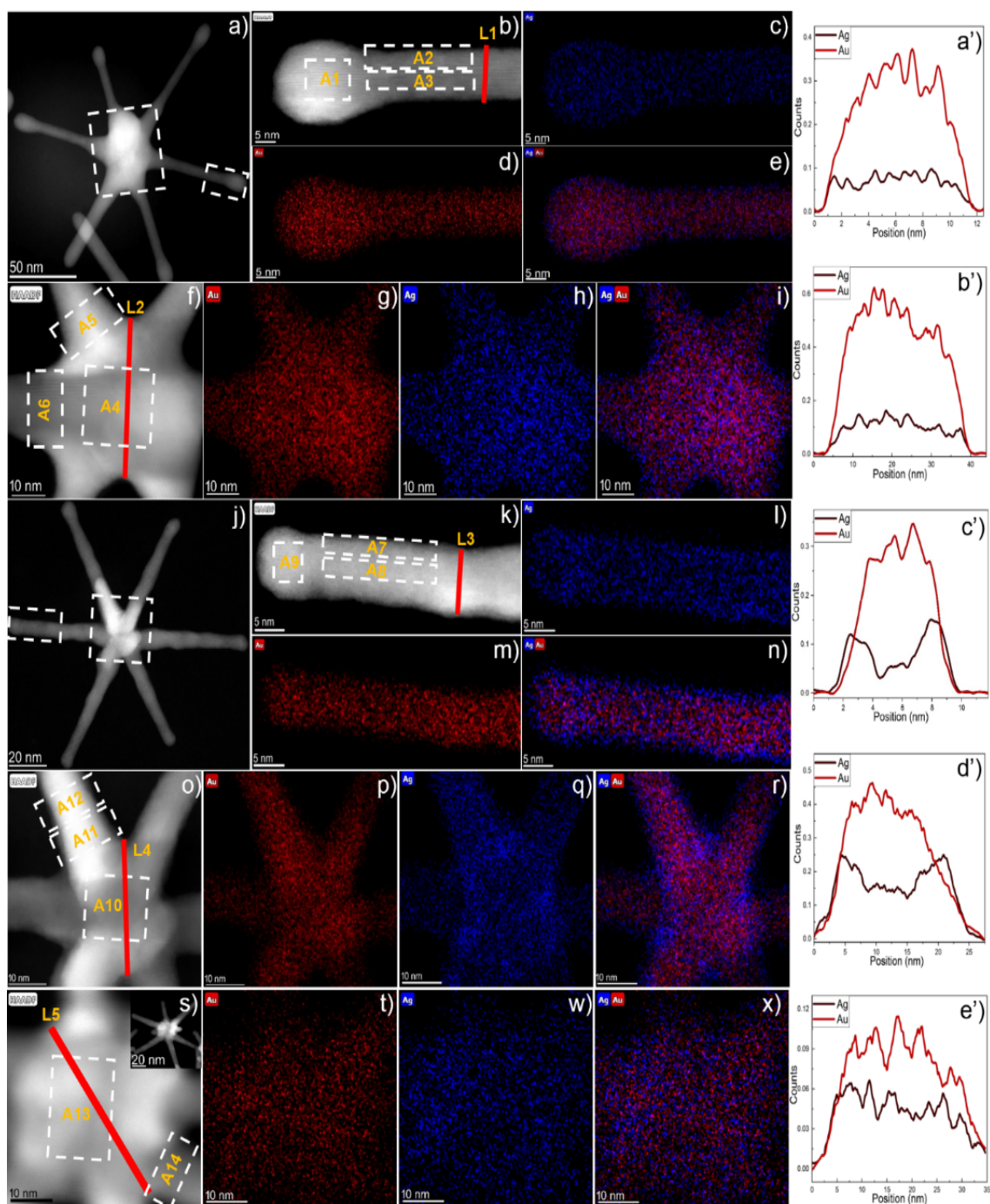


Figure 2.6. (a) TEM micrograph and (b-i) HAADF-STEM micrograph and elemental maps of the spike (b-e) and the core (f-i) of 30 μ M AgNO₃ after 12 hours. (j) TEM micrograph and (k-r) HAADF-STEM micrograph and elemental maps of the spike (k-n) and the core (o-r) of 100 μ M AgNO₃ after 12 hours. (s-x) HAADF-

STEM micrograph and elemental maps of the core of 100 μM AgNO_3 after 12 hours. (a'-e') Line scan elemental profiles of 6-branched nanostars at 30 μM (spike a', and core b'), 100 μM (spike c', and core d'), and 110 μM (core e') which reveal that Au and Ag are miscible in all samples. At increasing AgNO_3 concentrations, metallic Ag first saturates deposition sites along the side wall of the tips, and then proceeds to deposit at the core.

The concentration of seeds to be added to the growth solution is also a very important parameter to monitor, as the seed is the primary nucleation center from which the spikes are formed. Moreover, it is reported that multibranched hollow gold nanostars can be formed in the absence of seeds.¹⁰ We have determined the concentration of seeds following a reported method,⁴¹ and investigated their effect by increasing their concentration from 0.02 nM to 0.14 nM, in 0.04 nM increments (Figure 2.7a-d and Figure 2.S10). We determined that 0.14 nM is the smallest amount of seeds necessary to achieve 6-branched stars with high monodispersity (Figure 2.7d), which is associated to both spike number and spike length reduction (Figure 2.7a-d). On the contrary, multibranched stars were formed at 0.02 nM seed concentration (Figure 2.7a). Interestingly, the spike number never increased above six by increasing the concentration of seeds above 0.1 nM (Figure 2.7c). The high sample monodispersity achieved for 0.14 nM seeds was evidenced in the UV-Vis spectra reported in Figure 2.7e in the form of narrower LSPR bands (green curve) compared to what observed at lower seed concentrations. During the growth process, the availability of free gold atoms is very high when the concentration of seeds in the growth solution is low. These gold atoms can easily associate to the seeds and generate nucleation centers in high numbers, thus leading to the formation of

multibranched stars. However, the availability of free gold atoms saturates at or above 0.1 nM seed concentration, thus leading to nanostars with fewer spikes and shorter spike lengths, as larger amounts of seeds at equal Au concentration create more primary growth centers. A similar observation was reported by Barbosa et al. who noted that the branching of PVP-capped gold nanostars increased by decreasing seed concentration in the growth solution.⁴²

One of the most interesting aspects of this synthesis is the possibility to leverage the interplay between Triton X, ascorbic acid, and seeds to modify the number of branches in the nanostars. For instance, in Figure 1 we have seen that the number of branches can be increased by either decreasing Triton X (Figure 2.1c, and 2.1f) or by increasing ascorbic acid (Figure 2.1g, and 2.1h) at constant seed concentration. In Figure 2.7 (7a-d) the number of branches was increased by decreasing the seed amount when the other variables were kept constant. To examine how these three variables are connected to each other, we ran two additional control experiments starting from the multibranched stars reported in Figure 7a and 7b. These nanoparticles were synthesized in conditions ideal to specifically obtain multibranched stars (0.15 M Triton X, 1.6 mM ascorbic acid, 100 μ M of AgNO₃, and either 0.02 nM or 0.06 nM seeds). In our first control, we increased the concentration of Triton X from 0.15 M to 0.3 M, while the other concentrations were kept constant, and observed that in both cases the morphology changed from multibranched to 6-branched stars (Figure 2.7f-g). In the second control experiment, we decreased the concentration of ascorbic acid from 1.6 mM to 0.8 mM keeping the other variables constant. In these conditions we did observe a decrease in the number of branches with decreasing ascorbic acid concentration (Figure 2.7h-i), but

this was not sufficient to produce 6-branched nanostars at 0.02 nM seed concentration (Figure 2.7h). These results show that the basic process of forming the 6-branched stars can be tweaked by independently modifying the concentration of Triton X, ascorbic acid, and seeds, which provides a useful knob to rationally tuning morphology.

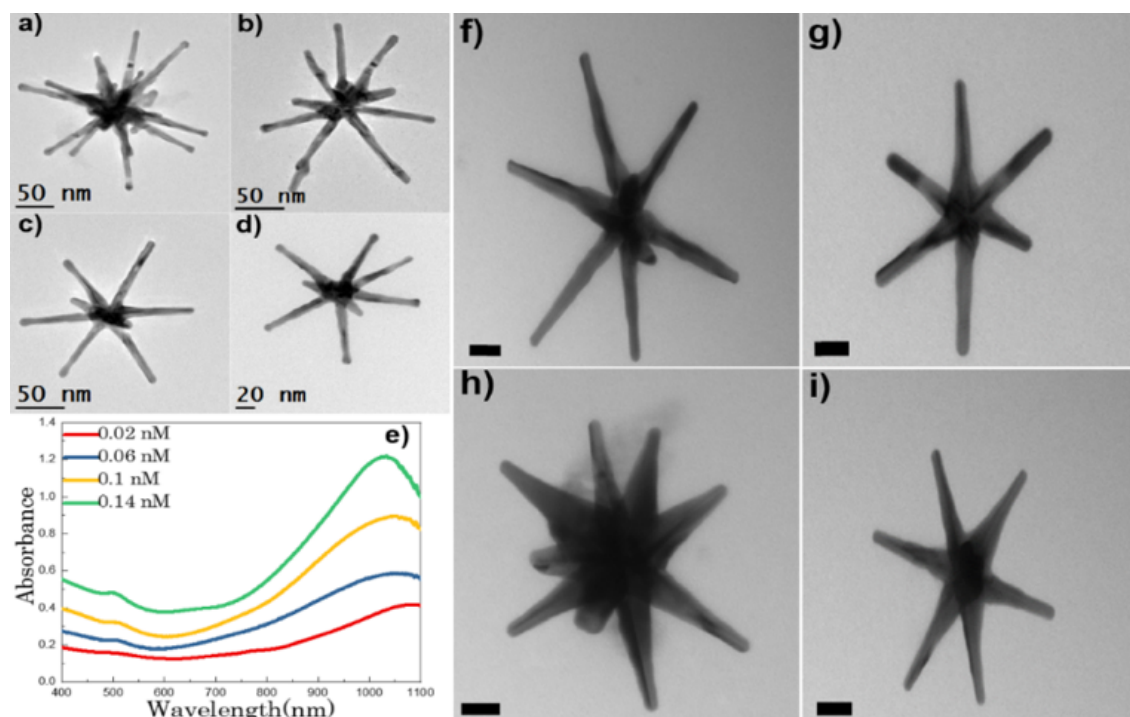


Figure 2.7. (a, d) TEM micrographs of gold nanostars synthesized by adding different amounts of seeds (0.02 nM (a), 0.06 nM (b), 0.1 nM (c), and 0.14 nM (d)) to the growth solution containing 0.15 M Triton X, 1.6 mM ascorbic acid, and 100 μ M of AgNO_3 . (e) UV-Vis spectra (normalized) of the nanostars at different concentration of seeds showing a blue-shifted narrower LSPR band with increasing seed concentration, which indicates that lower branching and higher monodispersity of the stars can be achieved at 0.14 nM seeds concentration. (f, g) TEM micrographs

of gold nanostars synthesized by adding different amounts of seeds (0.02 nM (f), and 0.06 nM (g)) to the growth solution containing 0.3 M Triton X, 1.6 M ascorbic acid, and 100 μ M of AgNO₃. (h, i) TEM micrographs of gold nanostars synthesized by adding different amount of seeds (0.02 nM (h), and 0.06 nM (i)) to the growth solution containing 0.15 M Triton X, 0.8 mM ascorbic acid, and 100 μ M of AgNO₃. A decrease in spike number from figures a and b is evident. At low ascorbic acid concentration (h and i) 6-branched nanostars cannot be obtained at low seed concentration, as opposed to the other conditions. Scale bars are 20 nm in figures f-i.

2.3. Conclusion

In this study, we have reported a detailed systematic study of the seed-mediated growth mechanism of 6-branched gold nanostars. The interplay of various synthetic parameters (Triton X, ascorbic acid, AgNO₃, and seed concentrations) is shown to influence the growth and final morphology of stars. After extrapolating the fundamental growth parameters, a identifying the ideal parameter space for Triton X, ascorbic acid, AgNO₃, and seeds to yield to the expected 6-branched products, we explored in detail the role of the nature of the seeds and the concentration of AgNO₃. Analysis of the kinetic data and microscopic images reveals that during this synthesis the single crystalline seeds transform into two different types of intermediate seeds – multiply-twinned intermediate seeds for multibranched stars and penta-twinned intermediate seeds for 6-branched stars. Moreover, the evolution of the spikes of 6-branched stars shows that the shape and size of the spikes are highly dependent on AgNO₃ concentration, proceeding via a common intermediate

having maximum spike length (100 nm), with final spike length determined by the amount of AgNO_3 in solution. We have demonstrated the important role of silver in the stabilization of the evolving crystal, confirmed by the observation that at low AgNO_3 concentrations kinetically-trapped nanostars, at 5-minute time points, evolve substantially before reaching thermodynamic equilibrium at 12 hours. Most importantly, the presence of metallic silver both at the side walls of the spikes (at low AgNO_3 concentration) at also at the core (at high AgNO_3 amounts) reveals in detail the importance of this reagent in tuning nanostar morphology: Increasing amounts of deposited silver appear to stabilize the five-fold twinned morphology, which would instead be lost at low Ag concentrations due to the substantial strain present in highly-curved twinned regions. These nanostars display high monodispersity, batch-to-batch reproducibility, and plasmon tunability between the visible and the short-wave infrared, which could prove extremely useful in several quantitative applications or fundamental studies for which the rational design of multibranched nanoparticles is necessary. Looking ahead, it is possible to envision how this synthesis could lend itself as a model for the implementation of machine learning tools in materials design.

2.4. Experimental section

2.4.1. Materials

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3 ; 99.995%), L(+)-ascorbic acid, sodium borohydride (NaBH_4), and TritonX-100 were purchased from Sigma-Aldrich. All these chemicals were used without further purification.

Ultrapure MilliQ water (18.2 M Ω .cm) was used in all syntheses. All glassware was aqua regia cleaned before each synthesis.

2.4.2. Instrumentation

Absorption spectra were collected on a Thermo Scientific Evolution 300 UV-Visible spectrophotometer using a quartz cuvette with 1 cm path. Nanoparticle morphology was determined using a Topcon 002B TEM. HRTEM analysis was performed on a JEOL 2010 F high-resolution transmission electron microscope. The particle sizes (spike length, spike width) were analyzed using ImageJ. Particle morphology was analyzed using Gatan DigitalMicrograph (TM) 3.11.1 for GMS 1.6.1. The values of average d spacing were obtained from Fourier transform analysis of high-magnification images.

STEM were obtained using a FEI Titan Themis transmission electron microscope (TEM) operated at 200kV. Energy dispersive X-ray spectroscopy maps (EDX maps) were obtained in scanning mode of TEM (STEM). The point resolution in this aberration-corrected mode is 0.08nm. 1nm resolution EDX maps with an average beam current of 100pA are routine with this microscope.

2.4.3. Synthesis of 6-branched Gold Nanostars

The synthesis of 6 branched gold nanostars was first proposed by Pallavicini et al.²⁸ However, their nanoparticles did not display sufficient purity and monodispersity. We therefore modified and varied the synthetic parameters to achieve high monodispersity and tunable morphology. Briefly, the seed solution was prepared by

addition of a freshly prepared ice-cold solution of NaBH_4 (0.6 ml, 0.01 M) into a solution mixture of HAuCl_4 (10 ml, 0.25 mM) and Triton X, whose concentration was ranging from 0.01 to 0.3 M. The solution turned immediately from pale yellow to orange after addition of NaBH_4 . The mixture was stirred for 2 minutes and aged for 10 minutes at 4°C before use.

The growth solution was prepared by adding 0.4 ml of 25 mM HAuCl_4 solution to a 20 ml Triton-X solution where the concentration of Triton-X was the same for both the seed and growth solutions. This step was followed by addition of ascorbic acid (ranging from 0.8 to 3.9 mM), AgNO_3 (ranging from 30 to 110 μM), and Au seeds (ranging from 0.02 nM to 0.14 nM) to the growth solution. The solution was stirred for 12 hours and then centrifuged at 4,000 g for 10 min and dispersed with 5 ml of Ultrapure MilliQ water (18.2 $\text{M}\Omega\cdot\text{cm}$).

2.4.4. Arrested Growth Studies

We have observed that n-pentanethiol works best to trap reaction intermediates compared to the more commonly used mPEG-SH (MW 5000), as we observed surface modifications and nanoparticle restructuring using the latter. Briefly, an aliquot (1 ml) of growth solution at the desired time was added to the solution of 1 ml 8.4 mM n-pentane in ethanol. Then, the solution was mixed well and centrifuged at 8000 g for 10 minutes. UV-Vis and TEM analysis of the particles were performed immediately after re-dispersion of the particles in 500 μL of MilliQ water.

2.5. Supporting Information

2.5.1. Statistical Analysis and Nomenclature

This novel type of gold nanostar was defined 6-branched stars because the majority of the product has six branches. We have investigated the distribution of the stars when the concentrations of the variables are 0.15 M (Triton X), 1.6 mM (ascorbic acid), 100 μ M (AgNO_3), and 0.14 nM (seeds). The analysis shows that the product was a mixture of branched nanoparticles with one to eight spikes and ~1% spherical nanoparticles. We counted the number of spikes over hundreds of particles. There is a possibility of spike number underestimation as we analyzed three dimensional stars in two dimensional TEM micrographs. The histogram shows that 38 % of the stars have six branches (**Figure 2.3d**).

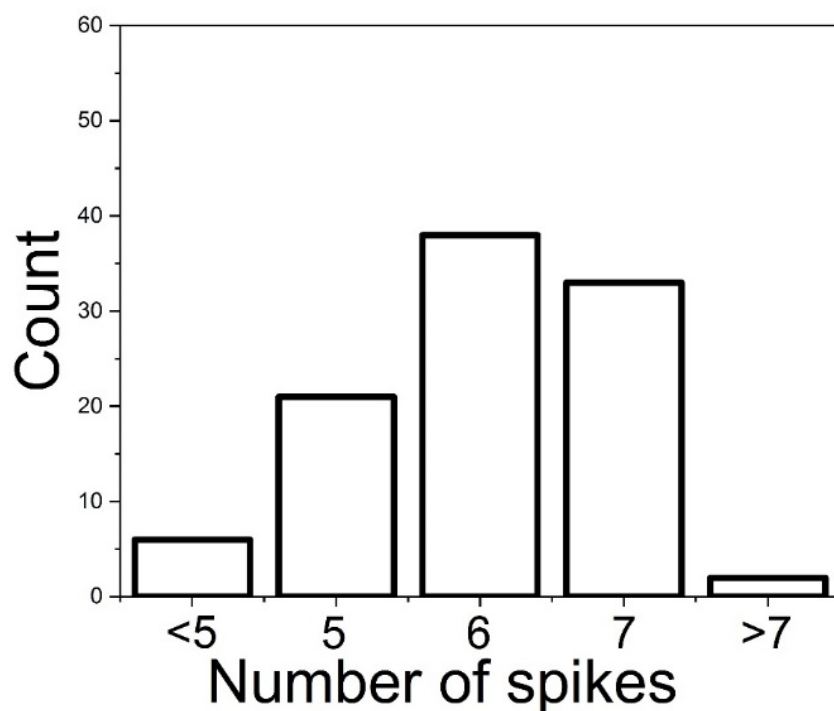


Figure 2. S1. Statistical analysis reveals that around 38 % of these stars are 6-branched stars, 33 % of these stars are 7-branched stars, 21 % of these stars are 5-branched stars, 6 % of these stars have less than 5 branches, and 2 % of these stars have more than 8 branches.

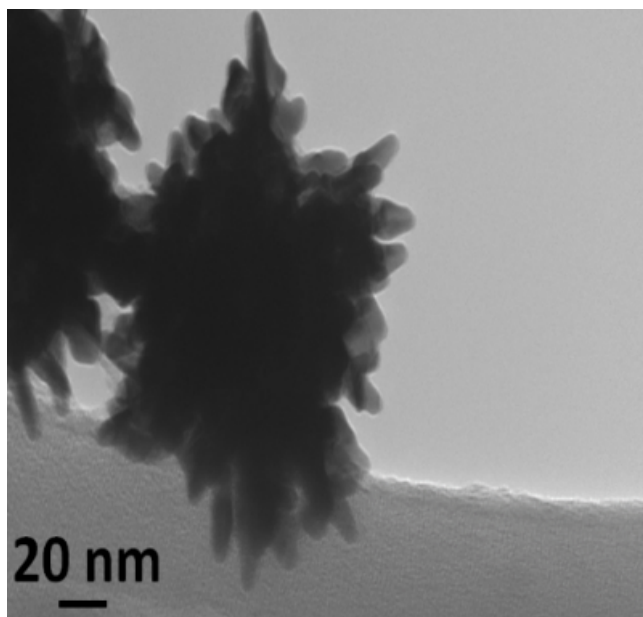


Figure 2. S2. TEM micrograph of gold nanostars obtained in the absence of Triton X, where the concentration of the other variables was 1.6 mM (ascorbic acid), 100 μ M (AgNO_3), and 0.14 nM seeds.

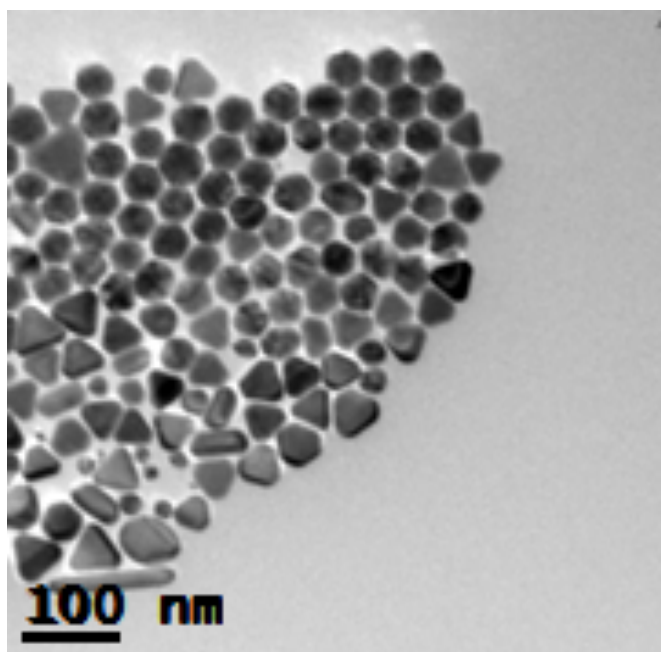


Figure 2. S3. TEM micrograph of polyhedral gold nanoparticles formed in the absence of AgNO_3 . The concentrations of the other variables, Triton-X, ascorbic acid, and seeds, were 0.15 M, 1.6 mM, and 0.14 nM respectively.

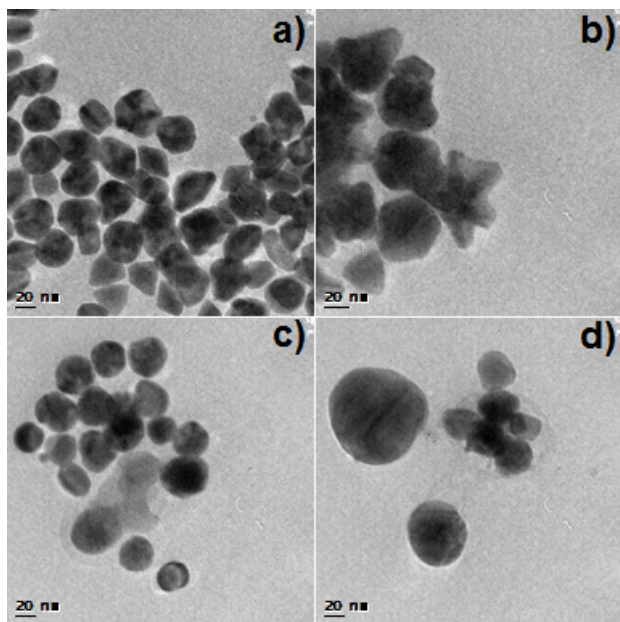


Figure 2. S4. TEM micrographs of gold nanoparticles formed under different concentrations of AgNO_3 (25 μM (a), 50 μM (b), 100 μM (c), and 150 (d)). The concentrations of the other variables Triton-X, ascorbic acid, and seeds were kept constant, at 0.15 M, 0.8 mM, and 0.14 nM respectively.

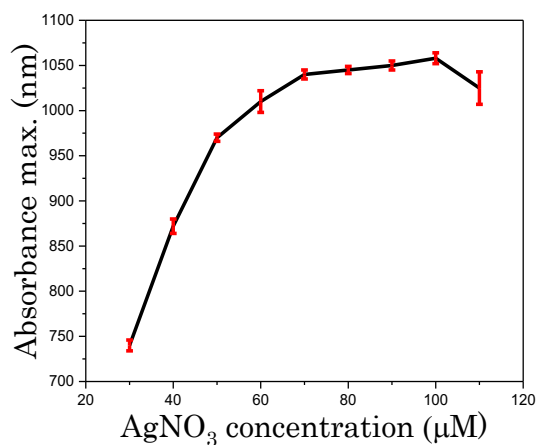


Figure 2. S5. Evolution of the LSPR position with AgNO_3 concentration (30 μM , 40 μM , 50 μM , 60 μM , 70 μM , 80 μM , 90 μM , 100 μM , and 110 μM) at constant concentration of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM).

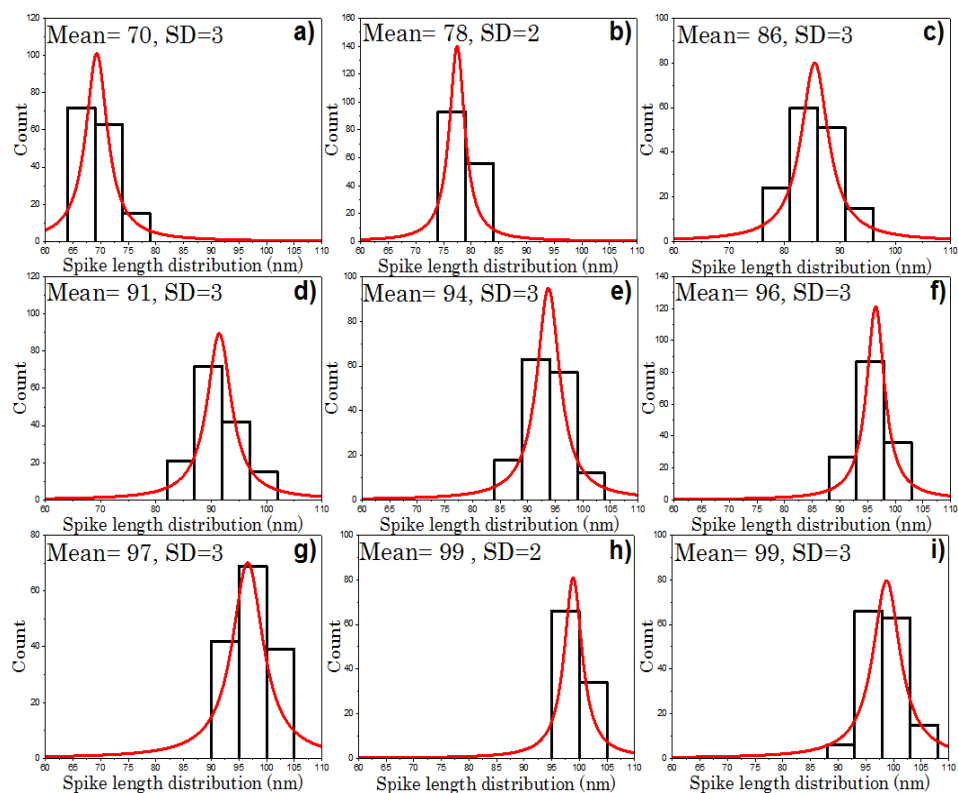


Figure 2. S6. Statistical analysis of the spike length (the distance measured from the core to the tip) of 6-branched nanostars when the concentration of AgNO_3 was varied from 30 μM to 110 μM (30 μM (a), 40 μM (b), 50 μM (c), 60 μM (d), 70 μM (e), 80 μM (f), 90 μM (g), 100 μM (h), and 110 (i)) while the concentrations of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM) were kept constant.

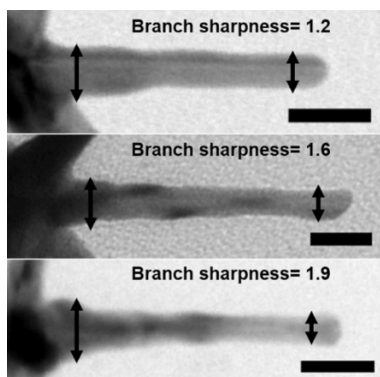


Figure 2. S7. Detailed TEM micrographs of spikes having aspect ratios (the ratio of width at core and tip of a spike) of 1.2 (40 μM AgNO_3), 1.6 (60 μM AgNO_3), and 1.9 (100 μM

AgNO_3). The concentration of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM) were kept constant. Scale bar is 20 nm.

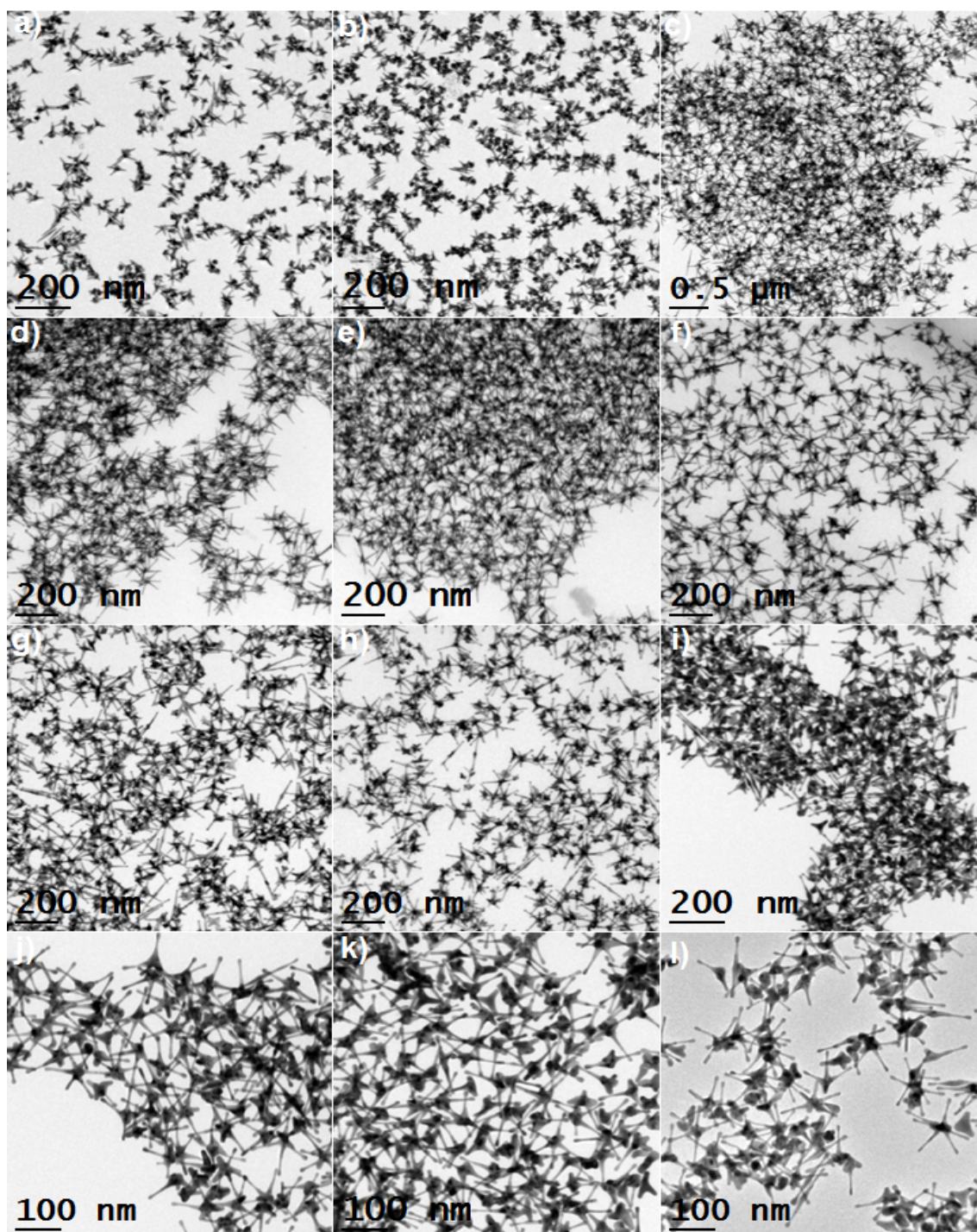


Figure 2. S8. (a-l) TEM micrographs with many stars at different time interval- 30 sec (a), 1 min (b), 1 min 30 sec (c), 2 min (d), 5 min (e), 10 min (f), 30 min (g), 60 min (h), 120

min (i), 240 min (j), 480 min (k), and 720 min (l) when the concentrations of Triton X, ascorbic acid, AgNO_3 , and seeds were kept at 0.15 M, 1.6 mM, 30 μM , and 0.14 nM respectively. These micrographs portray the consistently high monodispersity of these nanostar batches.

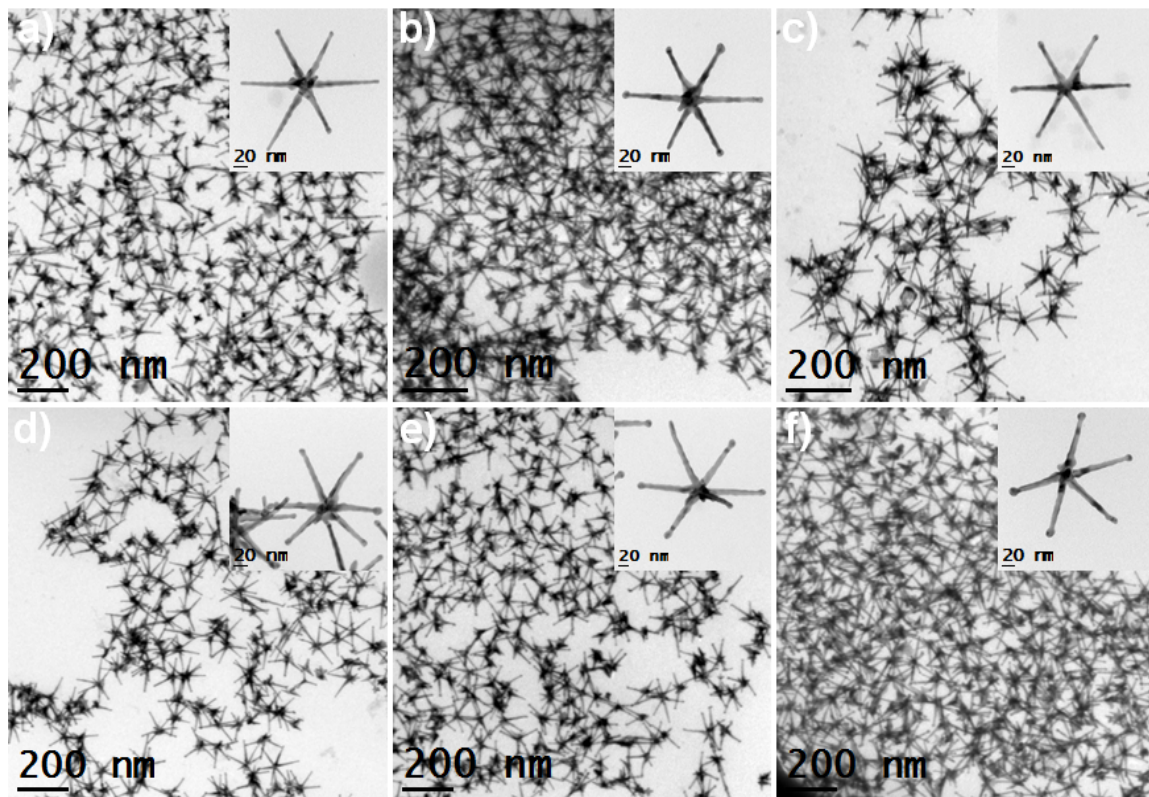


Figure 2. S9. (a-f) TEM micrographs of 6-branched gold nanostars formed after 5 min reaction time under different AgNO_3 concentration-30 μM (a), 40 μM (b), 50 μM (c), 60 μM (d), 80 μM (e), and 100 μM (f) while the concentrations of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM) were kept constant.

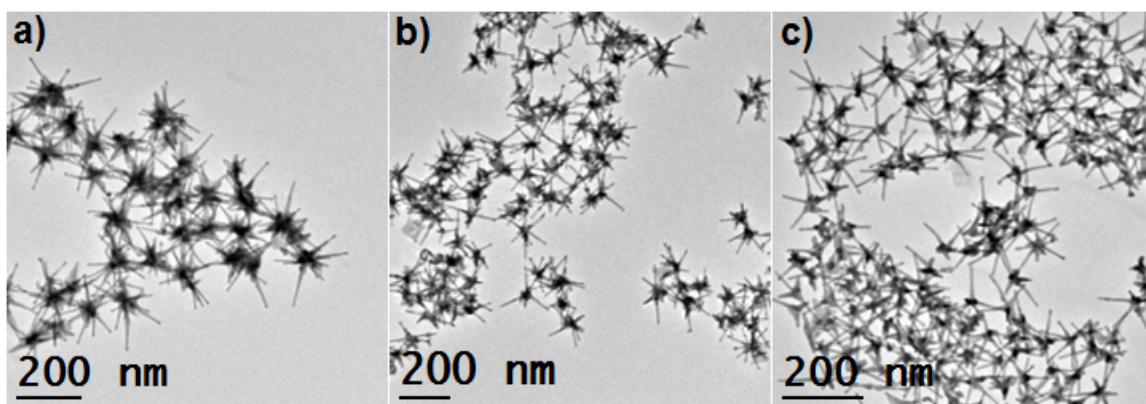


Figure 2. S10. (a-c) TEM micrographs of gold nanostars obtained starting from different amounts of seeds (0.02 nM (a), 0.06 nM (b), and 0.1 nM (c)) added to the growth solution containing 1.5 M Triton X, 1.6 mM ascorbic acid, and 100 μ M of AgNO_3 .

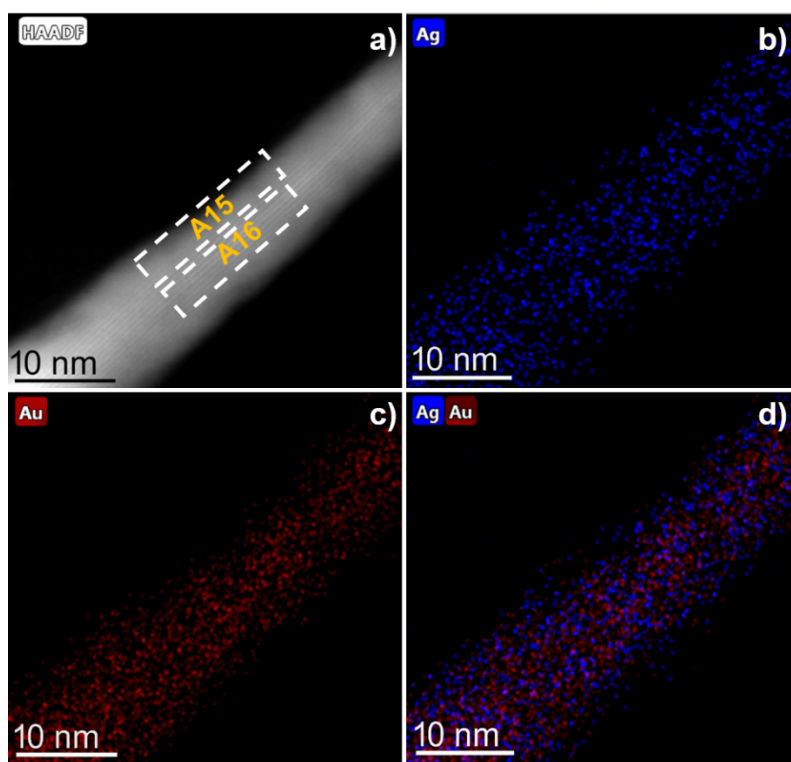


Figure 2. S11. HAADF-STEM image and elemental maps of the spike (a-d) for 110 μ M AgNO_3 concentration after 12 hours.

Area	Element	Atomic Fraction (%)	Atomic Error (%)
A1	Ag	3.28	0.56
	Au	96.72	17.90
A2	Ag	8.84	1.47
	Au	91.16	16.44
A3	Ag	4.12	0.72
	Au	95.88	17.68
A4	Ag	2.46	0.40
	Au	97.54	18.12
A5	Ag	5.66	1.05
	Au	94.34	17.31
A6	Ag	4.94	0.99
	Au	95.06	17.55
A7	Ag	36.87	4.79
	Au	63.13	10.07
A8	Ag	23.61	3.39
	Au	76.39	12.82
A9	Ag	12.17	2.05
	Au	87.83	15.65
A10	Ag	8.34	1.29
	Au	91.66	16.52
A11	Ag	13.04	1.95
	Au	86.96	15.30
A12	Ag	17.62	2.55
	Au	82.38	14.15
A13	Ag	25.05	4.30
	Au	74.95	13.28
A14	Ag	18.70	3.51
	Au	81.30	14.62
A15	Ag	33.70	10.02
	Au	66.30	16.89
A16	Ag	13.78	2.56
	Au	86.22	15.56

Table 2. S1. Area scan elemental profile of 6-branched stars at 30 μM , 100 μM , and 110 μM AgNO_3 .

2.6. References

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CHAPTER-3

SHAPING GOLD NANOSTAR ELECTRIC FIELDS for SERS

ENHANCEMENT

Note: In this chapter, the synthesis of silica coating and etching of gold nanostars, and the application in field of SERS has been reproduced with the copyright permission from The Journal of Physical Chemistry C 2016. (Atta, S.; Tsoulos, T. V.; Fabris, L., The Journal of Physical Chemistry C 2016, 120 (37), 20749-20758.), and the mechanism of silica coating and etching of gold nanostars is currently being prepared for a following publication; Supriya Atta and Laura Fabris “Highly Tunable Growth and Etching of Silica Shells on Surfactant-free Gold Nanostars”.

Abstract

The application of gold nanostars in direct and indirect SERS sensing has significantly grown in the past few years, mainly because of the excellent field enhancement properties that these particles have demonstrated to possess. However, experimental demonstrations correlating SERS signal enhancements to specific morphology features of the nanostars are still scarce, primarily because of the complexity of the nanostar morphology itself. Herein, we report an efficient method to synthesize and etch silica shells of tunable thickness on gold nanostars. By inverting the order of the reagents of a traditional Stöber protocol and using CTAB to stabilize the surfactant-free nanostars, the silica shell thickness can be tuned in the range of 4-41 nm by simply varying the reaction time. For the lowest coating thicknesses, silica grows conformally around the nanostars; on the other hand, by first coating the nanostars completely with a spherical silica shell, and then etching it away at different degrees by using mild silica etching reagent, NaBH_4 , a novel nanostar coating is obtained, in which silica only covers the core, leaving the tips variably exposed. Compared to the traditional method employed to etch silica nanoparticles, NaBH_4 is advantageous as it affords high tunability and leaves the gold nanostructures unaltered. The resulting nanostars are interesting not only because they possess localized surface plasmon resonance bands of different intensity, which could be leveraged for near-field techniques but are also promising as testbeds for fundamental studies of catalytic events occurring primarily at the tips, such as those involving hot electrons. We have then functionalized the nanoparticles with a Raman active molecule, aminothiophenol (ATP), and compared the resulting SERS spectra with those obtained on surfactant-free stars functionalized with ATP. By comparing the experimental results with the electric field intensities and distributions calculated via finite element simulations, we have observed a strong correlation between the Raman signal enhancements obtained experimentally and the heat

losses calculated on 3D representations of the same nanostructures. We believe that our model could be used to predict the effectiveness of nanostars at enhancing SERS signals based on their overall morphology, even when thorough experimental characterization is lacking.

3.1. Introduction

In the last decade surface enhanced Raman spectroscopy (SERS) has grown to become one of the most important analytical techniques employed by the scientific community for highly sensitive, selective, and multiplexed detection of target molecules with minimal sample preparation, limited to no sensitivity to external conditions (e.g. photobleaching), and amenability to work in complex environments like living tissues.¹ By virtue of the SERS effect,² the intrinsically low Raman signals can be enhanced by over ten orders of magnitude when the analyte molecules are placed in close proximity to the surface of a plasmonic nanostructured material or located at so-called *hot spots*, i.e. locations such as edges, vertices, tips, or intermetallic junctions, where the local electric field is expected to be the highest.³ It has now been well established that two mechanisms are responsible for this enhancement, namely the electromagnetic and the chemical, even though the former plays a dominant role.⁴ When employing SERS for chemical analysis, the detection power of each SERS substrate is evaluated by calculating its enhancement factor (EF).⁵ EFs depend on the local and impinging electric field as described in **Equation 1**:

$$(1) \quad EF_{EM} = EF_{EM}(\omega_L)EF_{EM}(\omega_R) = \frac{E_{Loc}(\omega_L)^2 E_{Loc}(\omega_R)^2}{E_0(\omega_L)^2 E_0(\omega_R)^2}$$

Here, EF_{EM} indicates the enhancement factor originating from the electromagnetic mechanism, ω_L and ω_R are the frequencies of the excitation and the emission, and E_0 and E_{Loc} indicate the impinging field and the local field at the analyte position, respectively.

When ω_L and ω_R are very close to each other, Equation 1 can be re-written as **Equation 2**:

$$(2) \quad EF_{EM} = \frac{E_{Loc}(\omega_L)^4}{E_0(\omega_L)^4}$$

which brings us back to the well-known fourth-power relationship between EF and the electric field. Similarly, one can calculate the ratio between the SERS and the Raman signal intensities for a particular analyte, and correlate it to the local and impinging fields, as done in **Equation 3**, where any dependence on the polarizabilities is included within the proportionality factor:

$$(3) \quad \frac{I_{SERS}}{I_{Raman}} \propto \frac{E_{Loc}^2(\omega_L)}{E_0^2(\omega_L)}$$

SERS enhancements can be improved by modulating the morphology of the nanostructured substrates 1) to introduce *hot spots* and 2) to bring the localized surface plasmon resonance (LSPR) to be resonant with the wavelength used for SERS analysis. An additional way by which it is possible to increase the SERS response is by modulating the molecular packing of the analyte on the surface of the nanostructure so that higher signals can be achieved. For this reason, it is also important to obtain information on the surface properties of the nanostructure (e.g. its crystallography) and to understand how the affinity of specific functional groups for the metallic surface changes with the crystallographic properties, but this topic is beyond the scope of this work.

Among various types of plasmonic nanomaterials that can be used for SERS, gold and silver have been the most explored,^{6,7} even though alternative metals such as aluminum have started to gain importance in applied plasmonics research community.⁷ Gold, in particular, has been studied the most because of its stability and the possibility of manipulating it from the *bottom up* to obtain nanostructures of well-defined morphology that display extensive shelf life. One of the most interesting and perhaps most promising morphologies is the nanostar. Gold nanostars can be synthesized in solution employing both seed-mediated and seedless approaches,⁹ and their morphology can be tuned to

possess spikes of variable tip curvature protruding from the spherical core. Electric field enhancement in nanostars is due both to plasmonic contributions and to the lightning rod effect,¹⁰ and for this reason these nanoparticles display the highest enhancement factors both in direct and indirect detection approaches, as demonstrated by us and others.^{11,12} However, although gold nanostars are widely used in a broad range of SERS and other plasmonic applications, only little is known about their fundamental properties, especially when referring to the case of real nanoparticles in suspension,^{13,14} for which extreme LSPR band broadenings are observed.¹¹ For instance, the extinction coefficient of gold nanostars was only recently estimated and further information on their optical and physical properties is very scarce.¹⁵ For these reasons, we have focused our efforts on understanding, both experimentally and in simulation, what are the various contributors to LSPR position and broadening in nanostars and how their morphology and surface functionalization can affect their electric field enhancement properties and, as a consequence, their applicability in SERS experiments.

In this work we have synthesized surfactant free gold nanostars following a seed-mediated protocol, coated them with silica, and selectively etched the glassy shell away so as to expose only variable amounts of the spike's surface. The nanoparticles were then employed for direct SERS experiments employing a model analyte, aminothiophenol (ATP), from which we then estimated how the signal enhancements depend on tip exposure. Furthermore, we have carried out finite element electromagnetic field simulations employing the software COMSOL Multiphysics and studied the origin of the LSPR broadening and the localization of the electric near field in 3D models of nanostars built following the morphologies observed experimentally. Our results show a strong correlation between nanostar morphology, silica shell thickness, electric field intensity and

distribution, and SERS signal enhancements. We believe that our model could be useful to predict the effectiveness of a nanostar as field enhancer in SERS experiments even when its thorough characterization is lacking.

3.2. Results and discussion

3.2.1. Surfactant-free Gold Nanostars

Surfactant free gold nanostars were synthesized as previously reported in the literature.¹⁶ It is well known that seed-mediated approaches such as the one used herein can lead to nanoparticles with variable morphology due to the concerted effect of the chemical reagents used (citrate-capped seeds, ascorbic acid, HCl, HAuCl₄, AgNO₃), the reaction time and temperature, and the stirring speed. In our syntheses the two most common morphologies are the *asymmetric* and the *asymmetric branched* (see Figure 3.1 a and Figure 3.1b). Both nanostructures are expected to provide intense field enhancements, but their optical properties and field localizations differ due to these variations in morphology (*vide infra*). In Figure 3.2, the experimental optical spectra collected for the asymmetric and asymmetric branched nanoparticles are reported. As can be observed a blue shift of 16 nm (from 851 nm to 835 nm) of the LSPR occurs when going from the *asymmetric* to the *asymmetric branched* morphology. Moreover, a broadening of the LSPR band can be observed and correlated to the presence of the small side branches. For these data the absolute intensities cannot be correlated, as the samples were obtained from different syntheses.

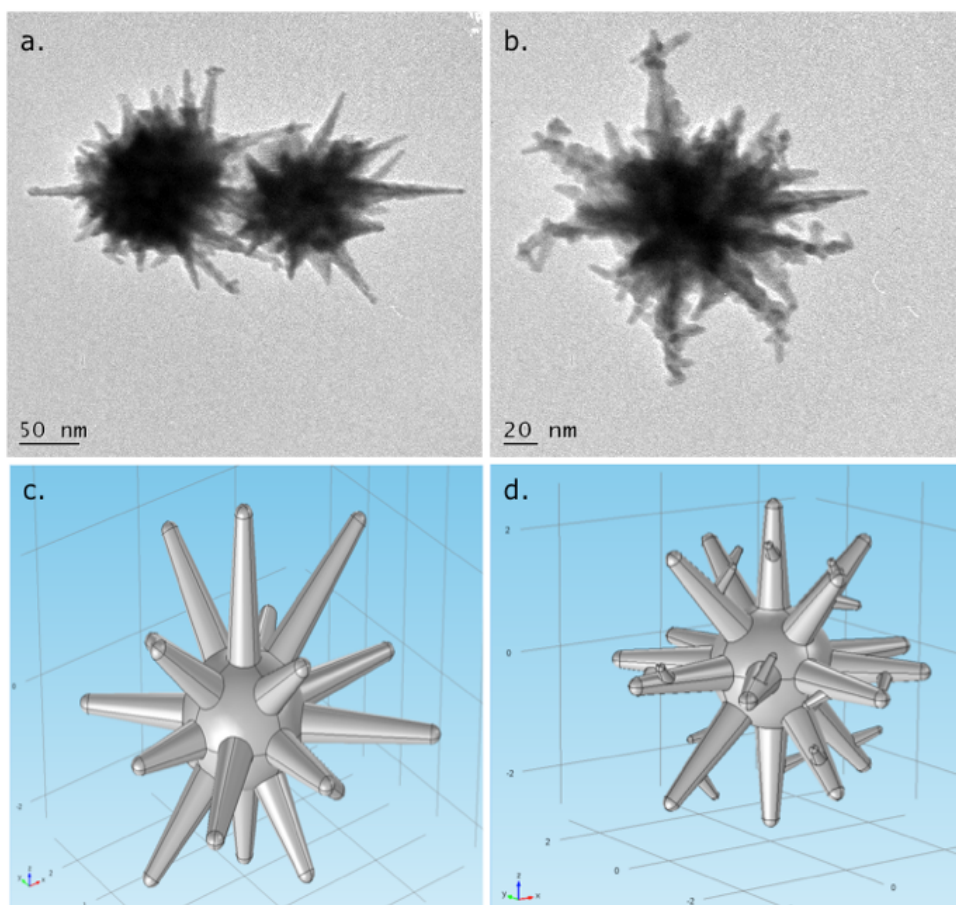


Figure 3.1. The morphology of gold nanostars can be extremely varied. TEM micrographs (a and b) of gold nanostars synthesized employing the same seed-mediated, surfactant-free, *bottom-up* protocol highlight that the morphology of the nanostars can go from asymmetric with sharp, non-branched spikes (a) to asymmetric highly-branched spikes (b). In order to simulate correctly the field enhancements in these nanostructures we have employed 3D geometrical topography models as close as possible to the non-branched (c) and branched (d) morphologies encountered in the synthesized nanoparticles. Number of spikes for the two 3D models $n=18$.

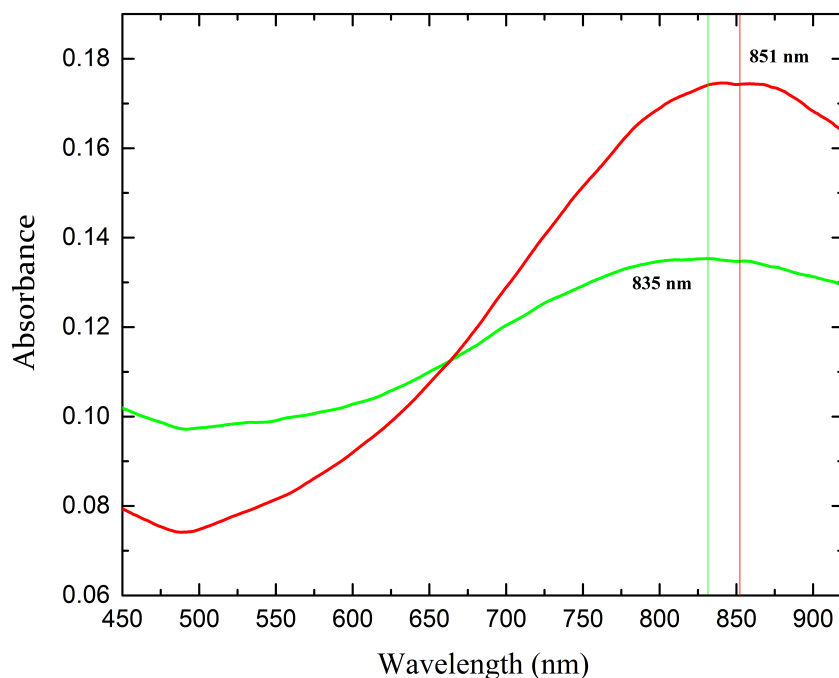


Figure 3.2. UV-Vis experimental results show a red shift and broadening of the LSPR going from the asymmetric (red) to the asymmetric branched (green) nanostar morphology. In the computed heat losses spectra reported in **Figure 3.3** it is possible to pinpoint a distinct broadening of the spectrum in the case of nanostars with asymmetric morphology compared to the symmetric counterpart, that further increases when branched spikes are simulated. The resonance peak is also blue-shifted, which is in agreement with the experimental results reported in Figure 3.2. What can be observed in the simulation is that the intensity of the blue-shifted peak is also higher than that of its non-branched counterpart. This result can be explained by considering that in both asymmetric cases (branched and not) the overall LSPR band becomes more heavily weighted by losses due to smaller features, which are known to absorb at higher energies,²⁴ and by an overall increase in volume, which is included in the calculation of the heat losses, as described in the Supporting Information. Moreover, when comparing the symmetric case (blue) to the asymmetric one (red), one can observe, for the latter, a tail at 700 nm due to the contribution

of the longer spikes and a blueshift of the maximum from 655 nm to 645 nm, as a consequence of the presence of the highly-absorbing short spikes, whose absorption convolutes with that of the average-length ones. The effect is even higher for the asymmetric branched case (green), in which the presence of 18 extra lateral branches with lengths between 3 and 6 nm shifts even more the absorption to the blue increasing its overall intensity when compared to the asymmetric case, as longer and pointier spikes are known to cause redshifts.²⁴ It should be noted that a direct comparison between experimental and computational results is not possible for the *symmetric* nanostar morphology, as this nanoparticle cannot be obtained synthetically. Moreover, as heat losses and absorption spectra do not represent the same physical phenomenon, but their interpretation can be correlated as reported in the Supporting Information, one should be aware of the fact that heat losses are useful to provide information on LSPR resonance positions and shift trends, but an overall intensity comparison cannot be done.

In the insets of Figure 3.3, one can also observe how the enhanced field in these nanostars is not located *exactly* at the tip of the spikes. This effect is due to two factors, 1) the spike length of the model nanostar and 2) the radius of curvature of the tip. A detailed explanation of these results will be the subject of a forthcoming publication. In all cases, the modes assignable to the spherical core do not appear to contribute significantly to these resonances, even though they need to be included in the plasmon hybridization model.²⁴ They do, however, contribute heavily to the resonant mode at 500 nm, as shown in **Figure 3. S1**.

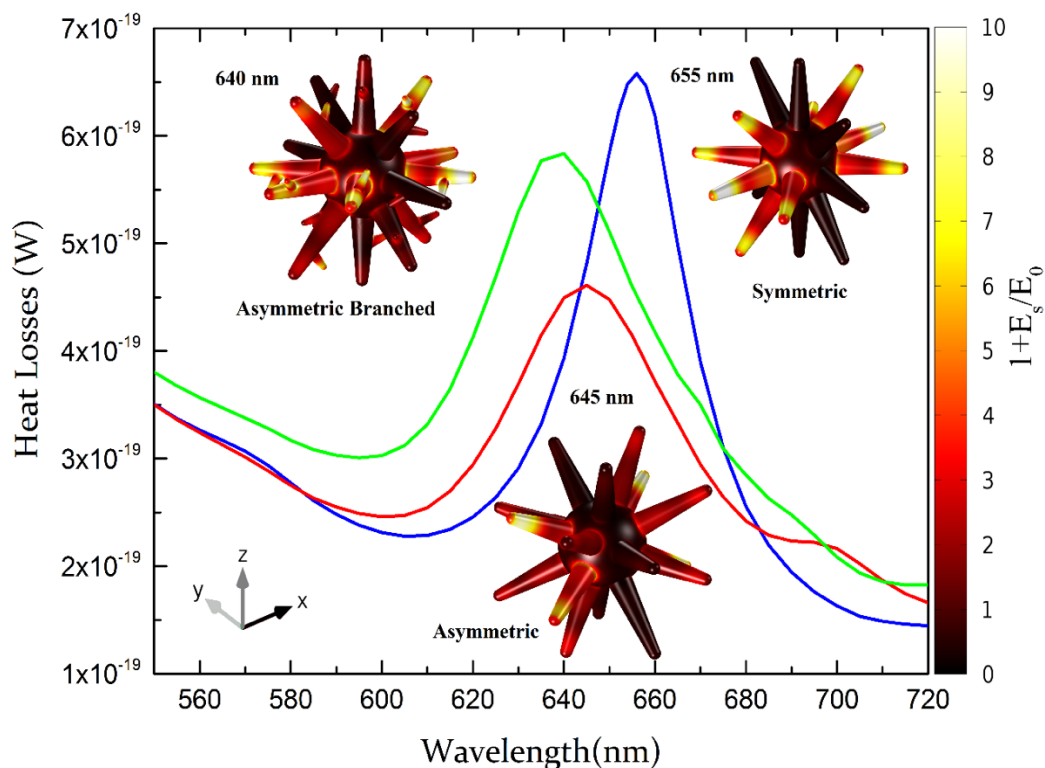


Figure 3.3. Heat losses and on resonance normalized electric field distributions for a symmetric (blue), an asymmetric (red), and an asymmetric branched (green) gold nanostar. From both spectra and E-field distributions it is possible to observe that the increase in asymmetry for the non-branched morphology (blue to green) leads to less intense LSPR bands, with the same locations on the nanostar providing reduced E-field enhancement. In addition, the increasing asymmetry factor leads to LSPRs that are blue-shifted, as a consequence of a weighted contribution to the losses from progressively smaller features, which absorb more at shorter wavelengths.

3.2.2. Silica coating of gold nanostars

We investigated an effective way to synthesize and etch silica shells on gold nanostars without changing the morphology of tips, very sensitive to ad-atom migration especially at

temperatures higher than 50°C. By tunably and isotropically etching the silica shell employing NaBH_4 we achieved unique and characteristic optical properties which depend on the thickness of the silica shell. Compared to NaOH , which is commonly used as a silica etching reagent, we observed that NaBH_4 etched the silica shell of silica-coated gold nanostars chemoselectively, leaving the gold nanostructure unaltered. In addition to the fundamental aspect of this silica etching process, this work also provides an effective route for the preparation of gold nanostructure having only the sharp protruding tips exposed, which can then be applied in fields such as catalysis, imaging, and drug delivery.

Protocols for silica coating of gold nanoparticles, especially gold nanorods and nanospheres, are well known and have been reported in the literature.¹⁹⁻²⁰ The silica shell synthesis is generally carried out in two steps. First, NH_4OH is added to the nanoparticle solution to render it alkaline. In the second step, the silica precursor tetraethyl orthosilicate (TEOS) is added to the nanoparticle suspension to initiate silica growth. However, silica coating of surfactant-free gold nanostars cannot be carried out because the gold nanostars are not stable in alkaline conditions; therefore, stabilization with a polymer or surfactant before coating is needed. Polyvinylpyrrolidone (PVP) is one of the most common polymers employed to stabilize gold nanostars.²¹ However, PVP forms a 5-10 nm coating on the gold nanostar's surface, which reduces the reactivity of the stars and hampers the coating process. To overcome this problem, we have employed cetyltrimethylammonium bromide (CTAB) instead of PVP, as CTAB forms a bilayer on the gold nanostars surface that can more readily be displaced. We have observed a blue shift of the LSPR band after NH_4OH addition which became even more pronounced after TEOS addition, which was indicative of spike reshaping during the coating process (Figure 3.4a). This hypothesis was confirmed by transmission electron microscopy (TEM), which proved that the spike length

was indeed reduced. We believe this effect to be due to the ability of NH_4OH to penetrate inside the CTAB micelle and etch gold at the tips (i.e., the most energetic gold facets). We hypothesized that TEOS could reduce this problem by replacing CTAB and binding strongly to the gold nanostar surface. Thus, reversing the order of addition of the reagents, compared to the traditional Stöber protocol,¹⁹⁻²⁰ allowed silica to polymerize without affecting the morphology of the stars, as observed in the TEM micrographs (Figure 3.4c), and confirmed by the consistent redshift of the LSPR band following the subsequent functionalization steps. We have determined by ^1H NMR that there was no characteristic proton peak of CTAB in NMR spectrum of silica-coated gold nanostars (Figure 3.S2).

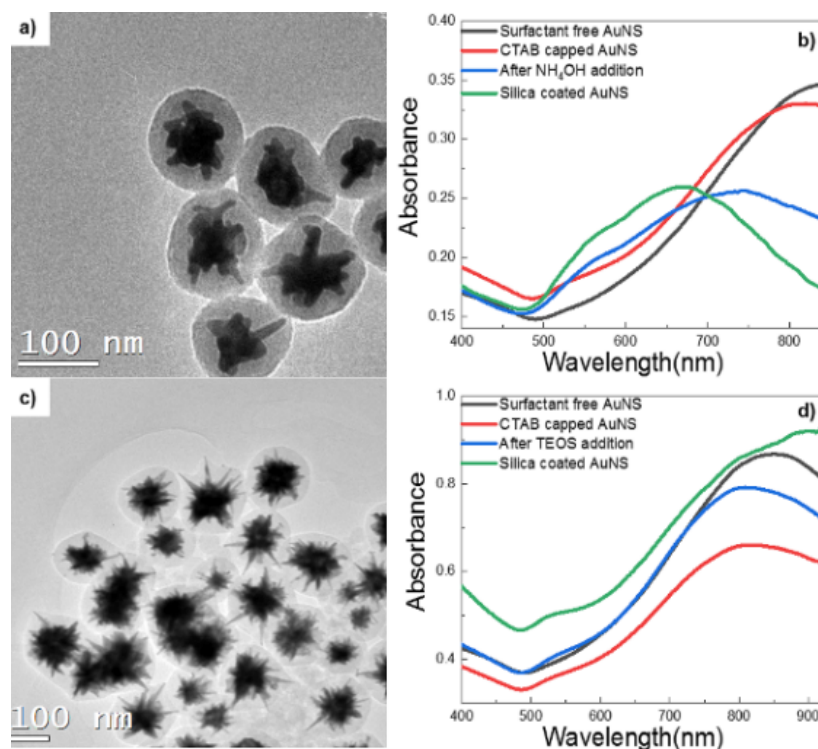


Figure 3.4. The inversion in the order of reagents allows to retain spike morphology compared to the traditional Stöber protocol. (a) TEM image of the silica-coated gold nanostars displays a decrease in spike length when NH_4OH was added before TEOS addition. (b) UV-Vis absorption spectra show a 200 nm blue shift for the reaction when

NH₄OH was added before TEOS indicating the decrease in spike length. (c) TEM image of the silica-coated gold nanostars shows that the morphology of the stars was retained when TEOS was added before NH₄OH addition. (d) a 300 nm red shift occurred when TEOS was added before NH₄OH addition.

Optimizing the concentration of TEOS is very important for achieving a uniform silica shell. We obtained a uniform silica shell at 5.3 mM TEOS concentration (Figure 3.5). The silica shell did not form well when the concentration of TEOS was kept below 5.3 mM, while silica nanoparticles were formed instead of silica-coated gold nanostars when the concentration of TEOS was higher than 5.3 mM. With our modified protocol, we achieved SiO₂ growth with high uniformity and were able to control the shell thickness by modifying reaction times, as confirmed by the TEM micrographs shown in Figure 3.5. TEM analysis reveals that a thin conformal silica shell was grown on gold nanostars after 15 min (Figure 3.5a), while the silica shell was grown isotropically to form spherical silica-coated gold nanostars after 1 hour (Figure 3.5d). The average silica shell thickness was 5 nm after 15 minutes which increased up to 40 nm after 45 min and reached a maximum of 70 nm after 1 hour. The silica growth was monitored by UV-Vis measurements. The initial UV-Vis spectrum of the gold nanostars suspension showed a broad LSPR band centered at 840 nm which red shifted by 125 nm and 185 nm after 15 min and 30 min from the addition of TEOS, respectively (Figure 3.5e). A further 228 nm redshift of the LSPR band was observed after 1-hour addition of TEOS (Figure 3.5e).

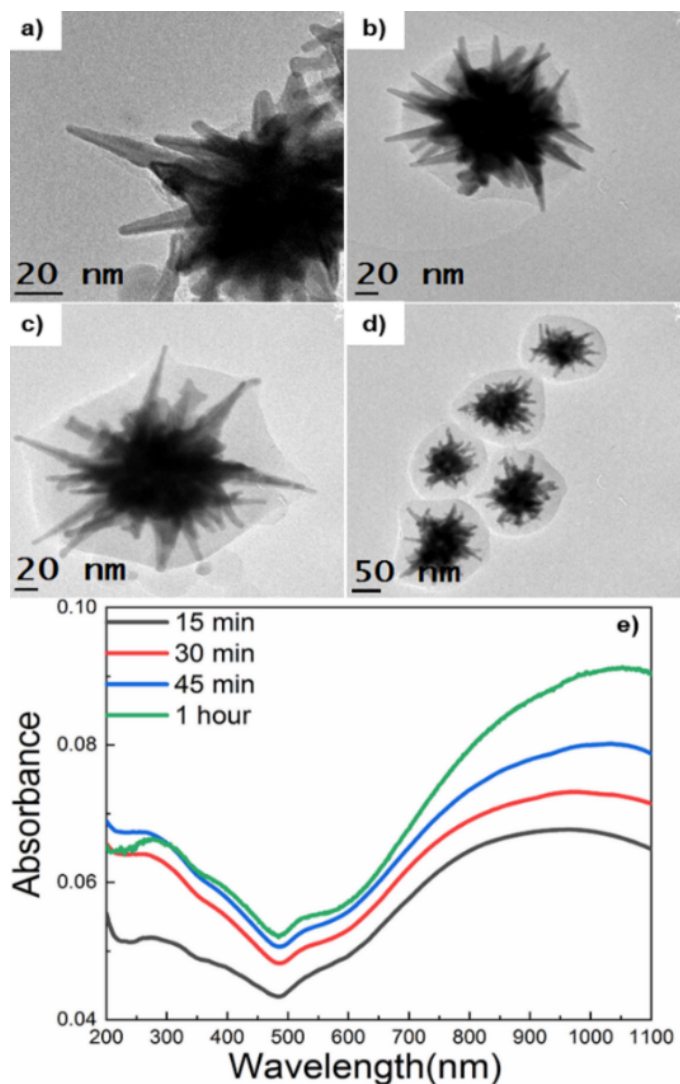
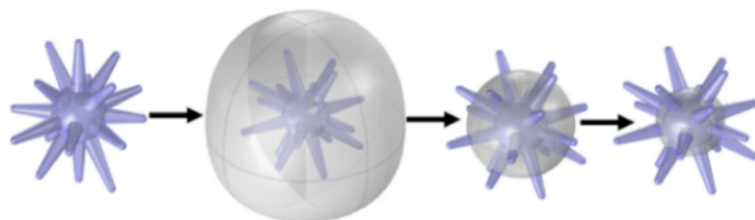


Figure 3.5. (a-d) TEM images of the silica-coated gold nanostars at a different time interval (15 min (a), 30 min (b), 45 min (c), and 1 hour (d) indicating that the thickness silica shell was increased with time. (e) UV-Vis absorbance spectrum shows a gradual red shift of LSPR of gold nanostars as the thickness of silica shell was increased with time.

3.2.3. Silica etching silica coated gold nanostars

By analyzing the growth patterns observed via TEM (i.e. silica initially grows conformally on the gold surface and then proceeds to grow isotropically to lead to a spherical shell), it was clear to us that to obtain a silica shell that could coat the core and leave the tips exposed (Scheme 3.1), it was necessary to first fully grow a spherical silica

shell and then proceed to partially etch it. To investigate the silica etching we first attempted with commonly used silica etching reagent NaOH.²²⁻²³ Despite being the most traditional silica etching reagent, we have observed that NaOH is not selective and leads to etching of both silica and gold (Figure 3. S3). Silica-coated gold nanostars exhibited significant changes in morphology due to random etching under alkaline conditions when NaOH was added to reach pH 11 (Figure 3. S3). Instead, by using NaBH₄ which is one of the mild silica etching reagents,²⁴⁻²⁵ silica etching proceeded slowly and tunably, allowing us to achieve intermediate SiO₂ thicknesses by varying the reaction times. Figure 3.6 shows the gradual decrease of the silica layer thickness, starting from an initial average thickness of 41 nm to reaching a thickness of 9 nm after 45 min. Sodium metaborate (NaBO₂) is also formed in this reaction, which further reacts with water and forms hydroxide ions (OH⁻) and HBO₂, establishing an alkaline environment (pH 11).²⁵ Then, OH⁻ slowly reacts with silica and dissolves silica to yield various silicate species. HBO₂ plays an important role in this reaction, binding strongly to the gold nanostar's surface and acting as a protecting agent against OH⁻, whose approach to the gold surface has become sterically hindered. Therefore, the effectiveness of NaBH₄ as etching reagent was the highest after 15 minutes (Figure 3.6f), then decreasing at later stages, probably due to the generation of HBO₂, which deposited on the silica shell upon *in situ* formation, thus preventing OH⁻ to enter in contact with the silica layer.



Scheme 3.1. Schematic illustration of the morphologies of silica coating and etching to expose only variable amounts of the spike's surface.

It is expected that the replacement of NaBH_4 with NaBO_2 can produce silica etched gold nanostars as NaBO_2 is an intermediate species generated from NaBH_4 and NaBO_2 can act as a strong base. To mimic the silica etching reaction, an equivalent concentration of NaBO_2 was added to silica-coated gold nanostars solution. After reacting with NaBO_2 for 15 minutes, the silica layer started to etch, with the reaction reaching minimum silica thickness after 45 min (Figure 3.7). As a control study, surfactant-free stars were added to a solution of NaBO_2 to prove that HBO_2 stabilizes the stars after complete etching, as the silica etching reagent is OH^- in both cases (Figure 3. S4). The morphology was indeed retained. After mixing with NaBO_2 , a red shift of the LSPR of gold nanostars was observed which can further confirm that HBO_2 was bound on the nanostars surface.

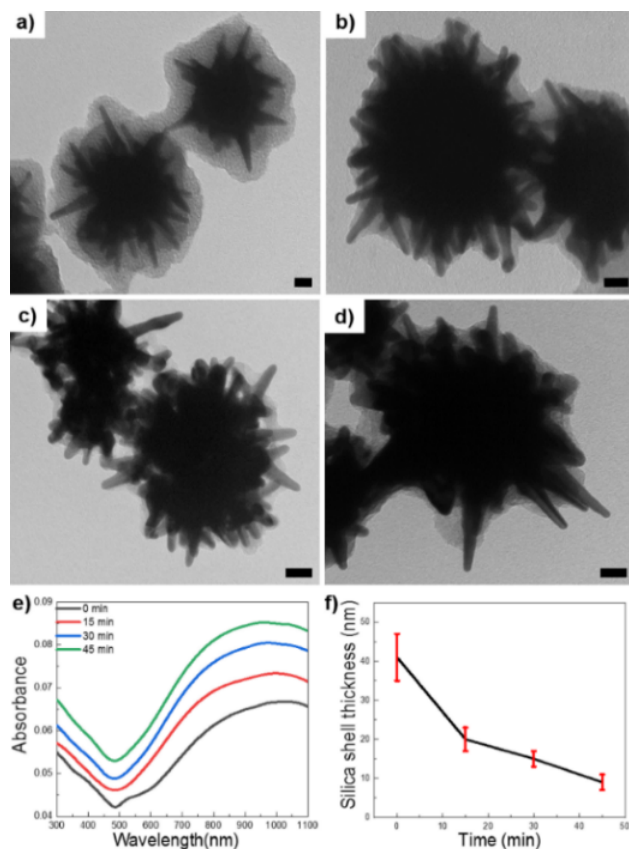


Figure 3.6. (a-d) Dependence of the time of silica-coated gold nanostars from fully coated with completely etched silica-coated gold nanostars. TEM images of silica etched gold

nanostars formed after reacting with NaBH_4 for 0 min (a), 15 min (b), 30 min (c), and 45 min (d). Scale bars are 20 nm. (e) UV-Vis spectrum of silica etched gold nanostars at different degree shows a gradual blue shift from 1068 nm to 964 nm as the silica thickness was decreased. (f) Evolution of the silica shell thickness with time shows that silica was etched in a faster rate up to 15 min.

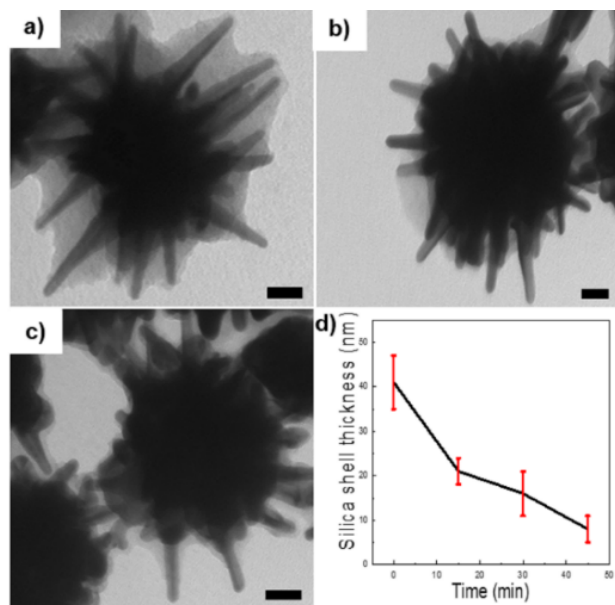


Figure 3.7. (a-d) TEM images of silica etched gold nanostars by NaBO_2 at different time interval- 15 min (a), 30 min (b), and 45 min (c) indicating that silica etching is also effective for NaBO_2 as NaBO_2 is an intermediate species generated from NaBH_4 . Scale bars are at 20 nm. (d) Evolution of the silica shell thickness with time shows a similar trend with NaBH_4 where silica shell thickness was decreased with time.

FTIR spectroscopy was used to characterize the silica-coated gold nanostars upon reaction with NaBH_4 . In Figure 3.8, the FTIR bands for silica-coated gold nanostars fall around 1225 cm^{-1} , 1088 cm^{-1} , and 965 cm^{-1} are attributed to the longitudinal-optical (LO) mode and transverse-optical (TO) mode of the Si-O-Si asymmetric bond stretching vibration, and the Si-OH stretching vibration, respectively.²⁴⁻²⁶ The Si-OH stretching

vibration band disappeared after exposing the silica-coated gold nanostars to the NaBH_4 solution at room temperature for 15 minutes. The TO mode of the Si-O-Si asymmetric stretching vibration band showed a $\sim 20 \text{ cm}^{-1}$ red shift from 1088 cm^{-1} to 1068 cm^{-1} and decreased in intensity during the silica etching process. Moreover, the band corresponding to the LO mode also showed a 10 cm^{-1} red shift from 1225 cm^{-1} to 1215 cm^{-1} and decreased in intensity, as the SiO_2 network became more open and the internal strain of the SiO_2 network was reduced, thus leading to the red shift of the Si-O-Si band.

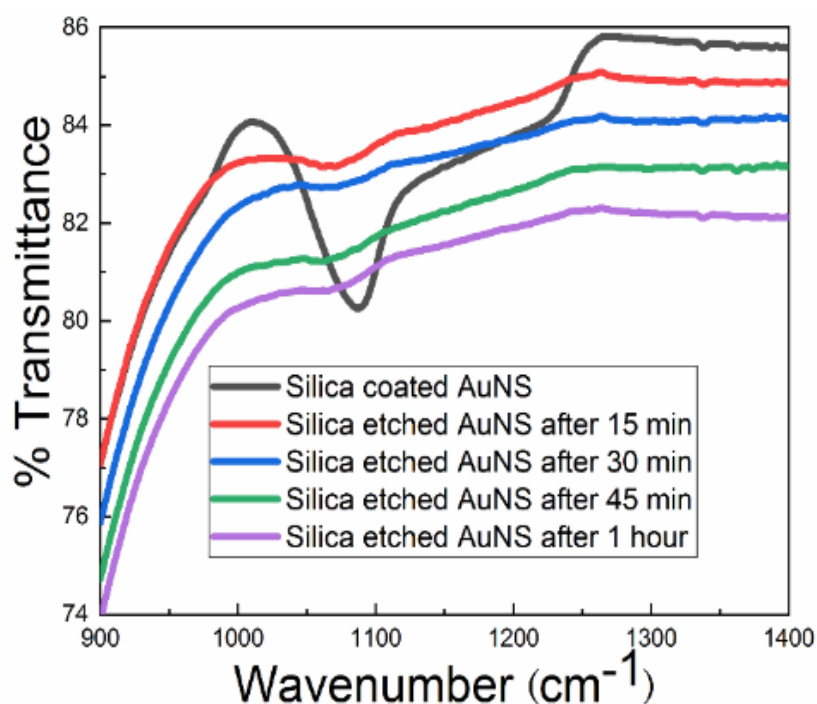


Figure 3.8. FTIR spectra of as-prepared CTAB capped gold nanostars (red), silica-coated gold nanostars (blue), and samples after reacting with 300 mg of NaBH_4 at room temperature for 15 min. (yellow), for 30 min. (green), and 1 hr. (violet).

3.2.4. Surface enhance Raman scattering (SERS)

With the increase in the number of applications in which gold nanostars have a fundamental role as near field enhancers,²⁷ we have become extremely interested in understanding how to rationally link their plasmonic properties to their morphology in

order to produce the most effective SERS platforms. In particular, we wanted to find the best way to computationally predict the enhancement and spatial distribution of the electromagnetic near fields for nanostars with morphologies observed experimentally in order to rationally design synthetic protocols producing nanostar morphologies yielding the highest enhancement factors. Furthermore, we wanted to prove experimentally that the nanostars computationally predicted to produce the highest scattered fields would indeed lead to the highest SERS signal enhancements. However, due to the morphological complexity of these nanostructures, selectively isolating locations on the metallic surface for Raman reporter binding can be experimentally problematic, if successful at all. Therefore, in order to simplify the issue, we have decided to approach it in a different way, that is, by selectively exposing only parts of the metallic surface at a time. In doing so, we wanted to be able to determine, by exclusion, the most effective combinations of nanostar morphology and surface functionalization, and to identify a working correlation linking the calculated E-field enhancements on specific nanostars to the SERS signal enhancement they produce.

Our approach to the problem has been to initially coat the nanostar with a thick silica layer and then etch it gradually away, thus enabling thiolated analytes to bind preferentially to the exposed gold surface. In this study however, we have chosen to use a Raman reporter molecule (ATP) capable of binding also to silica, so as to be able to measure SERS signal enhancements for the fully capped nanostars as well. Although we acknowledge that this may not be a fully comprehensive solution, it is a first step to correlating model and experiment even when a complete nanoparticle characterization is not available or not possible. In the following paragraphs, we will compare side by side the experimental and computational results in order to provide a comprehensive description of our strategy.

UV-Vis spectra of the bare and silica-coated stars were collected to provide evidence of 1) effective capping, 2) morphology retention, and 3) stability, and to establish a point of reference for the E-field simulations. In Figure 3.9 the experimental results (Figure 3.9a) have been compared to the heat loss spectra obtained computationally (Figure 3.9b). As expected, the resonance is red shifted in the presence of a full silica coating (blue) compared to the other three cases, as a consequence of the variation of the dielectric constant of the medium surrounding the nanoparticle (from 1.77 to 2.09). The red-shift is more pronounced for nanostars with a higher effective radius of silica, i.e. those presenting a silica overgrowth, with double exponential dependence of the red-shift vs. the effective radius, as reported in **Figure 3. S5**. The overall intensity decreases with the decrease in the amount of silica present, and the position of the LSPR is almost entirely regained in nanostars with close-to-fully etched silica coating (green). As seen before, the shoulder at ca. 695 nm is attributed to local morphology anisotropies in the individual nanostars. The intensities of the LSPR for the blue curves are higher than those for the red curves, as reported experimentally by Liz Marzan and coworkers for the case of gold nanospheres.³³

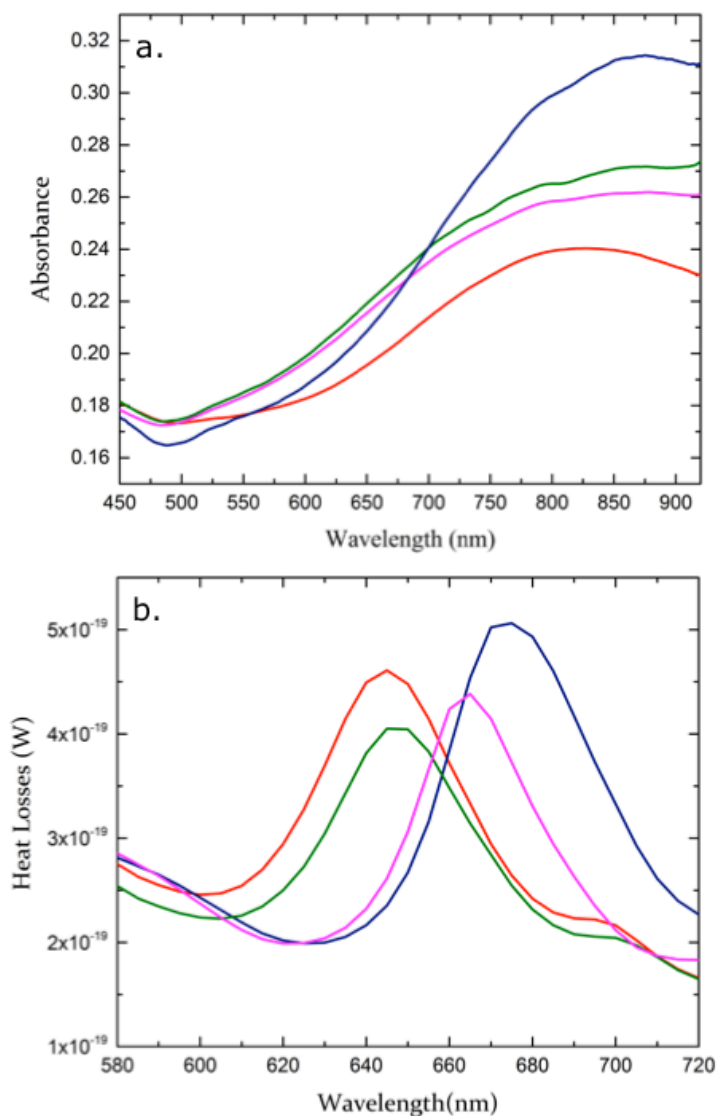


Figure 3.9. Experimental extinction spectra (a) can be explained using heat losses calculated from the simulation (b). In the simulation for asymmetric bare nanostars (red), asymmetric etched nanostars with 12.2 nm effective silica radius (green), asymmetric etched nanostars with 23.2 nm effective silica radius (magenta), and asymmetric coated nanostars with a 29 nm effective silica radius (blue), the intensity for the heat losses are higher in the presence of a full silica coating compared to the cases of bare and partially capped nanoparticles.

In **Figure 3.10** we report the computational simulation results describing the E-field localization on nanostars with a variable degree of SiO₂ coating. The 3D E-field maps were calculated for the four possible silica coating degrees that were described above in terms of effective silica *radii* from the center of the nanostar core to the silica-air interface. As previously observed, the most intense E-field for nanostars that are not fully coated by silica is not located exactly at the tips, but slightly away from it (Figure 3.10a-c). On the other hand, in the presence of a homogeneous silica coating, both the position and intensity of the most enhanced E-field change; the intensity increases, and its position is shifted to the tip of the spike (Figure 3.10d). The same behavior can be observed for the branched nanostars, as reported in **Figure 3. S6** of the Supporting Information.

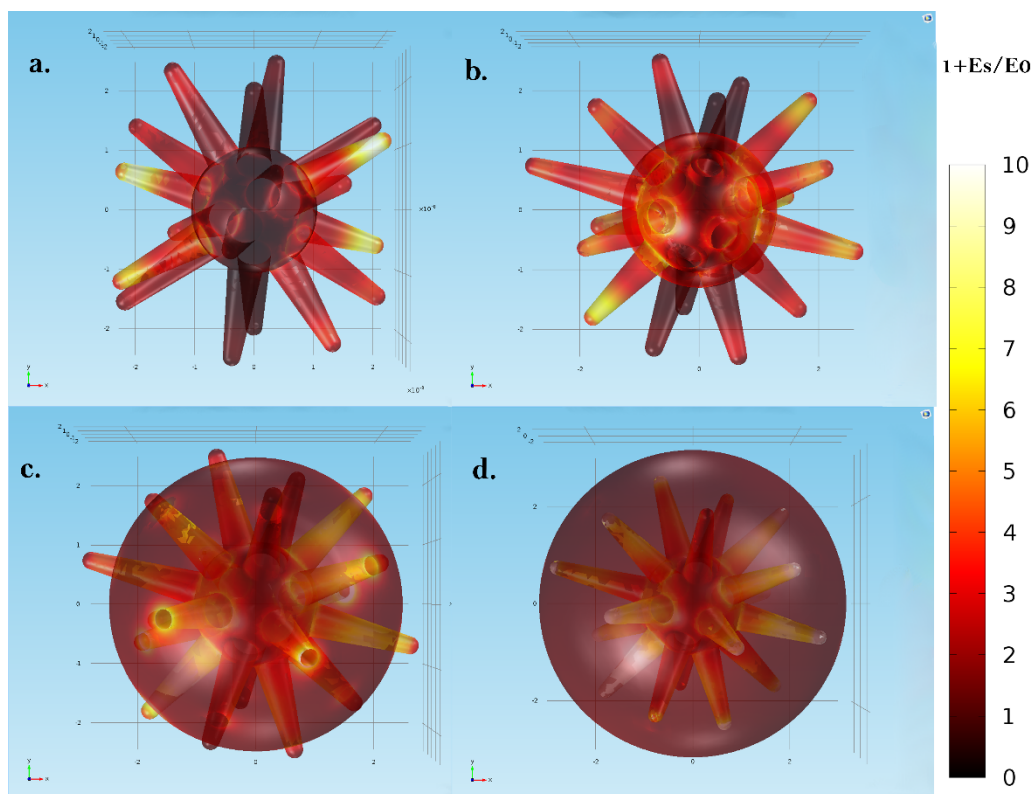


Figure 3.10. Finite element simulation of electric field distributions on uncoated, fully capped, and partially capped gold nanostars, carried out with the software COMSOL Multiphysics, show variable intensity and distribution of the field depending on the degree

of coating. Normalized electric field strength (xy face shown) representations of a bare asymmetric gold nanostar a), of gold nanostars with SiO₂ coating etched at varying degree (effective *radii* 12.2 and 23.2 nm respectively) (b and c), and of fully capped gold nanostar d) (effective *radius* 29 nm), all in water. Silica layers were drawn by hand to closely resemble those observed experimentally, which are not expected to be perfect spheres.

3.2.5. Evaluation of SERS Signal Enhancements

As a consequence of the results reported above, it is expected for the experimental SERS signals to be enhanced with respect to the corresponding Raman counterparts with a dependence from the electric field that varies with the morphology of the nanostructure and its effective silica coating layer, which not only changes locally the dielectric constant, but selectively exposes the tips. As the SERS signal enhancement depends quadratically on the impinging radiation as described in Equation 3 and considering that this second order dependence is the same extracted for the heat losses spectra (see Supporting Information) we sought to correlate both behaviors to the effective silica *radii* to identify analogies between the two.

In order to do so, we ran SERS experiments on surfactant free nanostars, fully coated silica nanostars with an effective silica radius of (54.2 ± 11.8) nm, and partially etched nanostars with an effective silica radii of (12.9 ± 3.0) nm, (20.8 ± 7.2) nm, (26.9 ± 4.1) nm, (40.0 ± 9.8) nm. The Raman reporter chosen was ATP, due to its ability to bind to both gold and silica, the former via the formation of Au-S bonds, and the latter through strong hydrogen bonds between the pendant amino moiety and the silanol groups on the surface of the silica shell.³⁴ The intensity of the peak at 1080 cm^{-1} (C-C + C-S stretching³⁵) was chosen to calculate signal enhancements for all cases ($I_{\text{SERS}}/I_{\text{Raman}}$). The experimental SERS spectra, collected for an ATP concentration of 1 μM , can be observed in **Figure 3.11** (a-f) while

the Raman spectrum for ATP in ethanol, at the same concentration, is reported in **Figure 3. S7**, along with all the individual spectra used to calculate the average data reported in Figure 3.11 (**Figure 3. S8**). The $I_{\text{SERS}}/I_{\text{Raman}}$ ratios vs. the effective silica *radii* trend obtained from the experimental results are plotted in **Figure 3.12**, along with the variation of the heat losses maxima vs. the effective silica *radii*. In both cases, it appears that a minimum in enhancement is achieved when a silica layer coats only partially the spikes, while it is maximum when silica cover completely the nanostars, but it is not so thick to completely quench the scattered near field before it can be experienced by the surface-bonded ATP molecules. The partial disagreement in level of enhancement observed for naked nanostructures (i.e. SiO₂ thickness of 0 nm) might be due to a possible preferential binding of ATP to selective facets on the tips, thus not enabling us to fully probe the enhanced field generated by the nanostars. Overall however, there is a very strong correlation between the two trends, indicating that our model could be used to accurately predict the effectiveness of a nanostar of specific morphology at enhancing SERS signals, and hence to potentially improve our ability to rule out some nanoparticle morphologies and prioritize others thus speeding up their use in applied SERS studies.

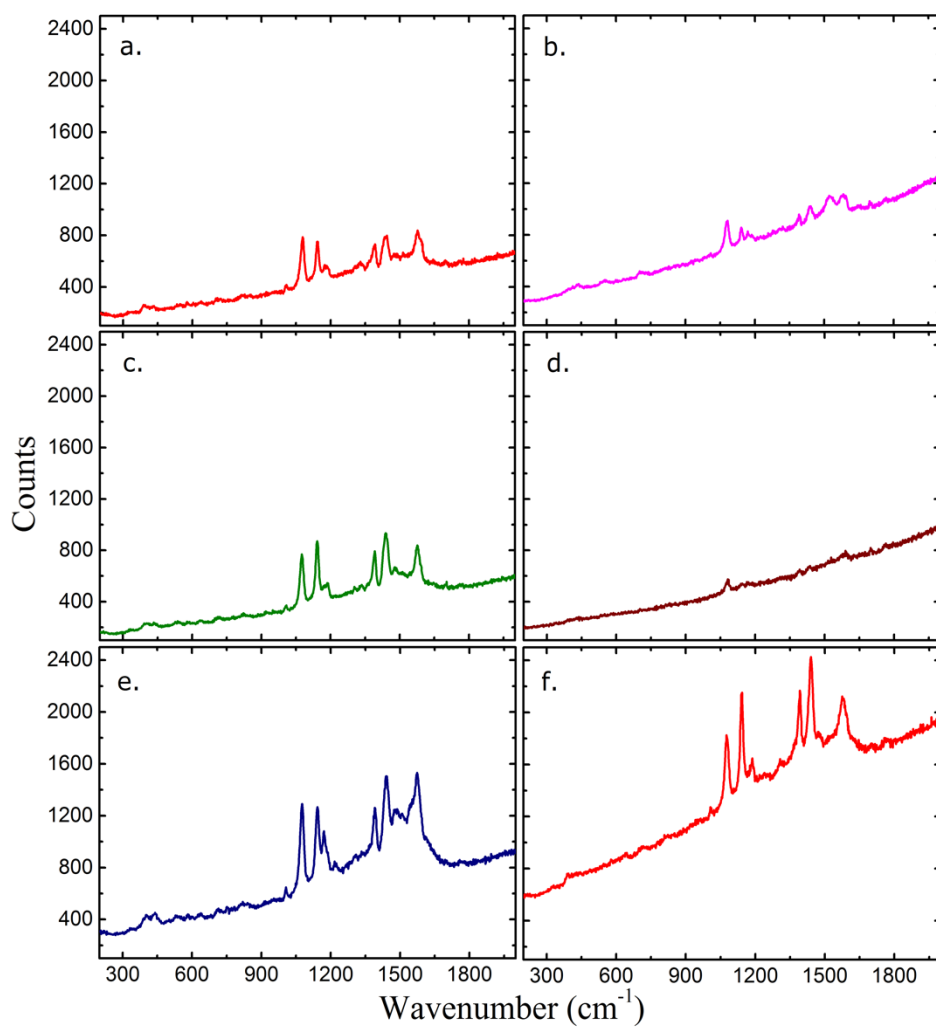


Figure 3.11. SERS spectra of aminothiophenol (ATP) on surfactant-free nanostars (a), partially silica coated nanostars (12.9 nm (b), 20.8 nm (c), 26.9 nm (d), 40.0 nm (e)), and fully coated nanostars (54.2 nm (f)). Acquisition parameters: 633 nm laser excitation wavelength, 1% laser power, 1 s acquisition time, one accumulation.

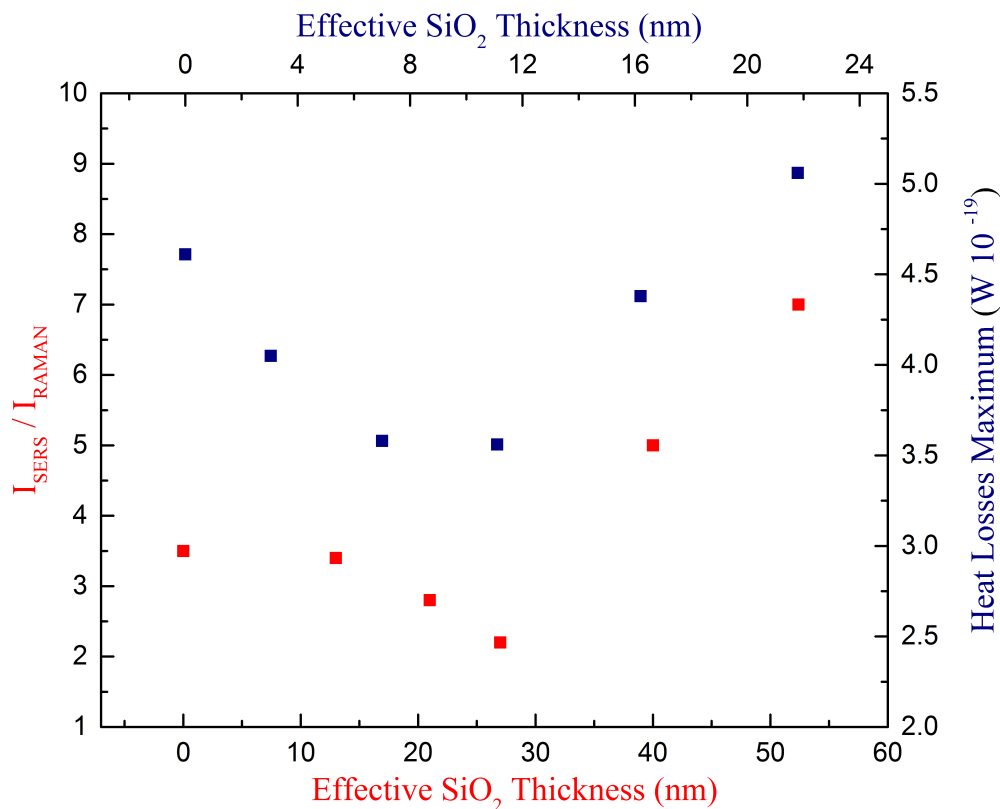


Figure 3.12. Comparison between experimental $I_{\text{SERS}}/I_{\text{Raman}}$ ratios (red) and computationally calculated heat losses maxima (blue) vs. Effective silica layer thickness trends. Both values depend on $|E|^2$ and their agreement is an indication of the validity of our approach. For the sample with no silica coating (i.e. naked nanostars) the partial disagreement may be due to selective ATP binding to preferential facets of the nanostar spikes that would thus reduce the intensity of the effective scattered field experienced by the molecule compared to what predicted by the simulation.

3.3. Conclusion

In summary, we have developed a facile route for silica coating of gold nanostars. The thickness of silica shell can be tailored from 4 nm to 41 nm by carefully regulating the reaction time. We have investigated silica etching of silica shell of silica-coated gold

nanostars by NaBH_4 and NaOH . We have observed that NaBH_4 acts as a chemoselective silica etching reagent. FTIR studies showed that the silica network of the silica etched samples was more open. The OH^- and BO_2^- ions generated from the gradual decomposition of NaBH_4 play crucial role for silica etching and stabilization of silica etched gold nanostars. Gold nanostars have demonstrated to be excellent SERS platforms and have been widely used in SERS-based imaging and sensing applications. However, fundamentally understanding how their morphology can impact their effectiveness as field enhancers is a complex task. In this work we have sought to understand how nanostar morphology can affect localization and intensity of the scattered electric fields and how these can in turn be linked to the measured SERS signal enhancements. By synthesizing silica-coated nanostars and selectively etching the silica layer away so as to expose increasing amounts of the tips, and by using these particles in model experiments where the Raman signal of aminothiophenol was enhanced in the presence of the nanostars, we were able to determine a strong correlation between the intensity of the nanostar morphology and its silica coating layer, the enhanced electric field, and the SERS signal enhancements. We believe that this model represents a very useful working platform to predict what factors mostly affect the effectiveness of nanostars as SERS substrates. We do recognize that these particles may be morphologically too complex to achieve an *exact* correspondence between model and experiment; for this reason, we are currently studying a much simplified nanostar model, for which experimental and computed morphology can be exactly matched. The results of this work will be reported shortly.

3.4. Experimental and theoretical methods

3.4.1. Materials

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), L(+)-ascorbic acid (AA), and trisodium

citrate dihydrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}\cdot 2\text{H}_2\text{O}$) were purchased from Acros Organics. Tetraethyl orthosilicate (TEOS), silver nitrate (AgNO_3 ; 99.995%), ammonium hydroxide (NH_4OH ; 28-30 % NH_3), sodium borohydride (NaBH_4), and aminothiophenol (ATP) were purchased from Sigma Aldrich. 12 N HCl was purchased from Fisher Chemical. Cetyltrimethylammonium bromide (CTAB) was purchased from GFS Chemicals. All of these chemicals were used without purification. Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used in all preparations. All glassware was aqua regia cleaned prior to each preparation.

3.4.2. Instrumentation

Absorption spectra were collected using a S.I. Photonics Fiber Optic CCD Array UV-Vis Spectrophotometer using a quartz cuvette with 1 cm path. Nanoparticle morphology was determined using a Topcon 002B transmission electron microscope depositing the nanoparticle suspension on Ted Pella Inc. PELCO TEM grids.

3.4.3. Synthesis of Gold Nanostars

Surfactant-free gold nanostars were synthesized following a modified seed-mediated method first developed by Vo-Dinh and coworkers.¹⁶ 12 nm citrate-capped seeds were prepared according to a modified Turkevich method and then concentrated 16 times via centrifugation prior to use, starting from a sample with 0.8 absorbance.^{17,18} Nanostars (10 mL) were synthesized by simultaneous addition under gentle stirring of 400 μL of 3 mM AgNO_3 and 200 μL of 0.1 M AA to a solution containing 10 mL of 1 mM HAuCl_4 , 20 μL of 1 N HCl, and 2.5 μL of the citrate capped gold seed solution. CTAB-capped gold nanostars were synthesized upon addition of 2 mL of 0.2 M CTAB to a 10 mL batch of freshly prepared surfactant-free gold nanostars under gentle stirring. The reaction was allowed to proceed for 30 min before purification of the suspension via centrifugation at

6500 g for 20 minutes.

3.4.4. Silica Coating of Gold Nanostars

A modified Stöber method was followed to re-cap the CTAB-functionalized gold nanostars with silica.^{19,20} Briefly, 50 μL of TEOS were mixed with 40 mL of 0.8 nM gold nanostars solution for 1 hour. Then, NH_4OH was added to the solution to *exactly* adjust the pH to a value of 8.6. The reaction mixture was allowed to stir for 24 hours. The particles were then purified by centrifugation at 6500 g for 30 min.

3.4.5. Silica Etching on Gold Nanostars

Silica etching of silica coated gold nanostars was carried out employing NaBH_4 . Briefly, 300 mg of NaBH_4 were mixed with 10 mL of 0.4 nM of silica-coated stars at pH 11.2 under gentle stirring for 56 hours at room temperature.²¹ Different degree of silica thickness can be achieved by stirring the reaction mixture at different time span from 8 hours to 56 hours.

3.4.6. Raman Measurements

Raman measurements were carried out with a Renishaw InVia Raman microscope equipped with a cooled CCD detector using a 633 nm laser excitation and a 50x short working distance objective with NA of 0.75. Gold nanostars (0.5 nM) were deposited on microscope glass slides by tethering them via aminopropyltriethoxy silane (APTES). The slides were then incubated in a 1 μM solution of the Raman reporter molecule, aminothiophenol (ATP). The substrates were then washed, air-dried, and used for Raman analysis. The spectra were collected between 200 and 2000 cm^{-1} using a grating with 1200 1/mm. Spectra for each sample were collected over six different locations and averaged for

statistical significance. No relevant variation in the peak pattern was observed within each individual sample.

3.4.7. Finite Element Simulations

In order to simulate the behavior of nanostars under optical fields, several models were developed using the RF Module of COMSOL Multiphysics 5.0. These models consist in solving **Equation 4**, a wave equation for a homogeneous dielectric, in four concentric geometry domains: 1) An outermost perfectly matched layer (PML), which functions as a spherical fully absorbing layer, 2) a spherical water layer which is assigned a relative permittivity of 1.77, 3) a capping layer which is assigned the SiO₂ dielectric constant value of 2.09, and 4) a core nanostar domain, characterized by the dielectric properties of bulk gold from the Lorentz-Drude model by Johnson and Christie.²² Layer 3) is only used in the case of SiO₂ coated/ etched nanostars and not for the purely metallic ones. The whole geometry is divided in finite tetrahedral 3D elements and the solution of equation (3) is calculated in each one of them. The density of these tetrahedra is increased in the vicinity of the nanostars and gradually decreased inside the outer layers. The final results are obtained by matching the solutions on the boundaries of the geometry domains defined above. In all simulations carried out in this work, there was no interest in characterizing the magnetic field behavior, thus the relative permeability was taken to be 1 in all geometry domains without loss of generality.

$$(4) \quad \nabla \times \frac{1}{\mu_r} (\nabla \times \mathbf{E}) - k_0^2 \left(\epsilon_r - \frac{j\sigma}{\omega\epsilon_0} \right) \mathbf{E} = \mathbf{0}$$

Tabulated values of the real and imaginary part of the dielectric constant (ϵ_r) are inserted in the COMSOL RF E/M Waves Frequency Domain module, where an interpolation is carried out. The conductivity (σ) is also obtained from the Johnson and Christie values.²² The angular frequency (ω) is calculated from the input wavelength values. An electromagnetic field of the form described in **Equation 5** is introduced with the electric field polarized in the x direction and the magnetic field polarized in the y direction, when the direction of propagation is the z direction.

$$\mathbf{E} = e^{-jk_0z} \hat{x} \quad (5)$$

Heat losses associated with the absorption of the impinging electric field described by (5), which can be correlated to the absorption spectra as described in the Supporting Information, are calculated along with the scattered electric field. It is also of great interest to calculate and report on the spatial localization of the local electric field, whose intensity is enhanced by the presence of the nanostars. This local scattered field is associated to the plasmonic resonances assignable to the spikes of the nanostars and can be correlated to SERS EFs as briefly described in the Introduction and extensively discussed later on in this work.

The cases of an ideal symmetric and a more realistic asymmetric 18-spike gold nanostar have been studied thoroughly, along with the SiO₂-coated and selectively etched versions of these. Nanostars with 18 spikes were chosen because they reproduce the morphology of highest possible complexity while maintaining a reasonable computing time. It should be noted however that, while herein with *asymmetric* we refer only to nanostars with spikes of randomly distributed lengths, in the real case nanostars are characterized by asymmetries of different nature, such as, for instance, different spike tip

curvature, spike orientation, or number of spikes, thus a perfect matching between the simulation and the experimental results was not achieved in this work. The SiO₂ layers in the coated and etched versions were hand designed in order to best match the shapes of the SiO₂ coatings observed via TEM. An 18-spike asymmetric branched gold nanostar model has also been developed and studied in order to match the experimental results, as seen in **Figure 3.1**.

3.5. Supporting information

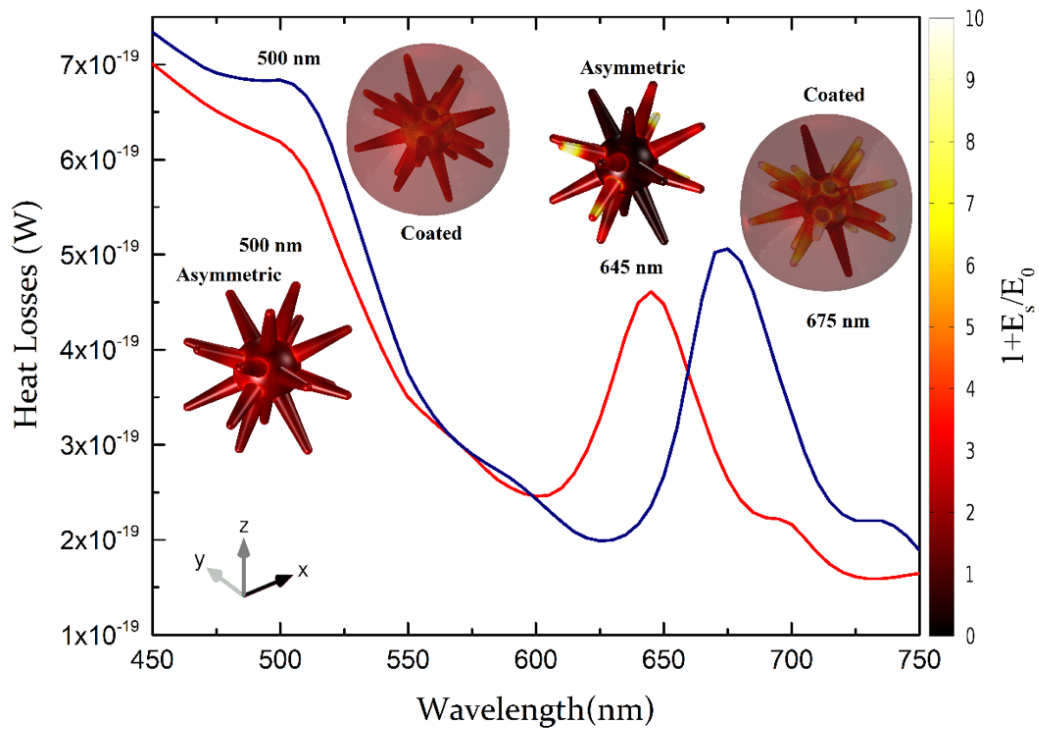


Figure 3. S1: Full heat losses spectra for bare (red curve) and silica coated (blue curve) nanostars show that the spherical core modes contribute more heavily to the 500 nm resonance.

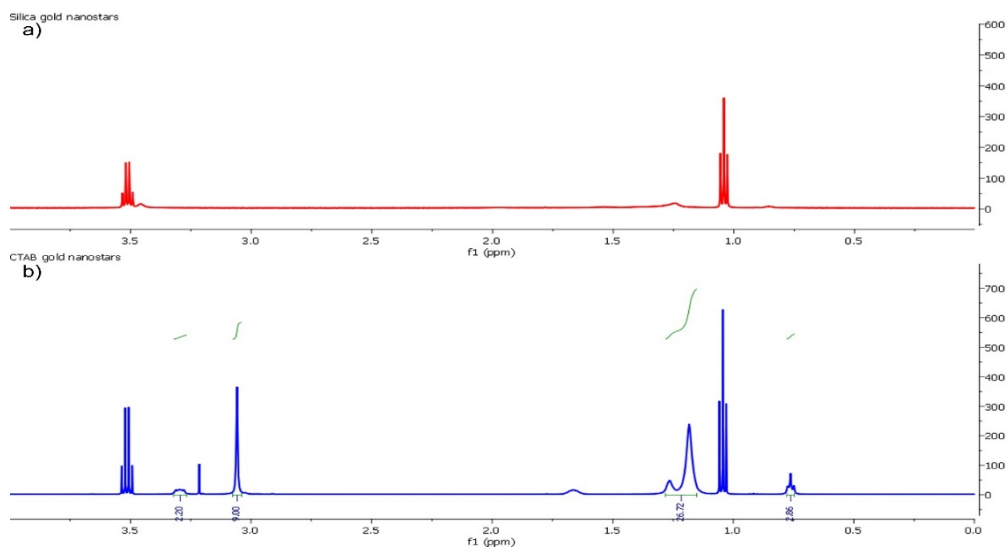


Figure 3. S2. ^1H NMR spectrum of silica coated gold nanostars (a), and CTAB capped gold nanostars (b) which reveals that there is no CTAB in silica coated gold nanostars. Deuterated water was the reference solvent.

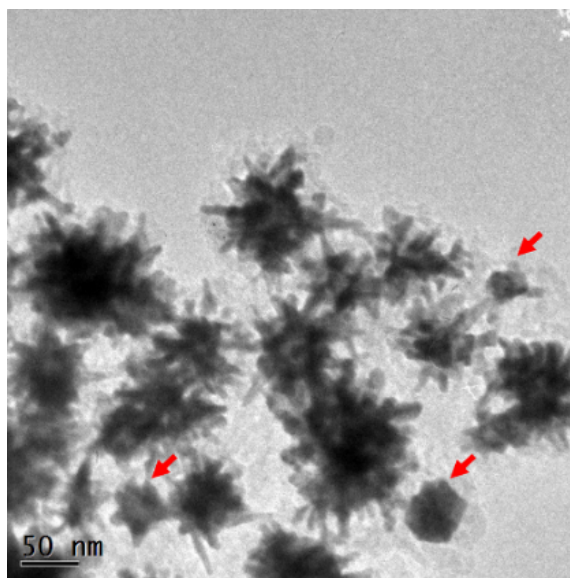


Figure 3. S3. TEM image of silica etched gold nanostars with NaOH reveals that OH^- randomly etched silica shell as well as gold nanostars. Red arrows indicate that OH^- dissolves the spikes of the stars.

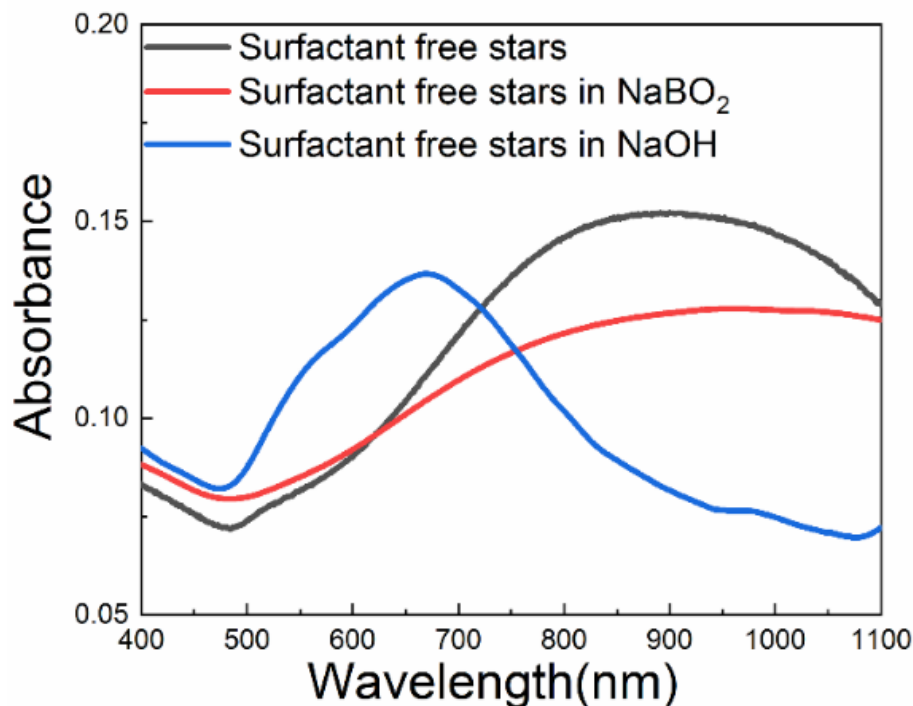


Figure 3. S4. UV-Vis absorption spectrum shows that there occurs a 120 nm red shift after NaBO₂ addition, and 230 nm blue shift after NaOH addition.

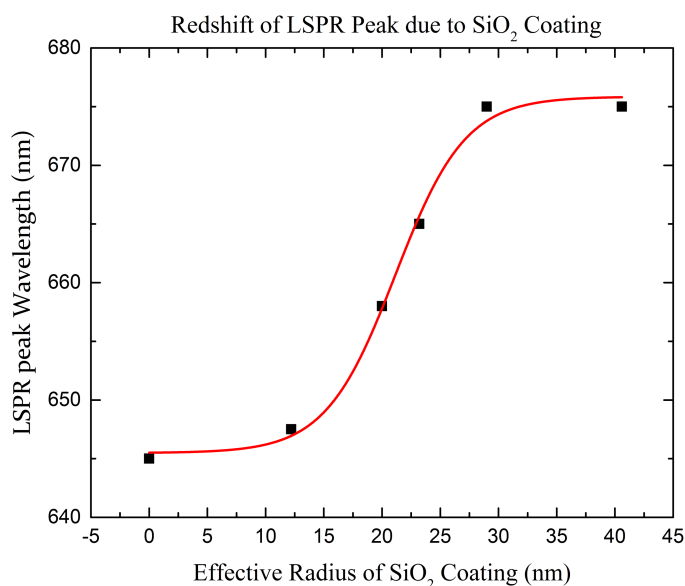


Figure 3. S5. The LSPR position can be calculated for nanostars with silica coating of variable thickness by calculating heat losses. The resonance of the maximum red-shifts with the increase in shell thickness, following a double exponential dependence.

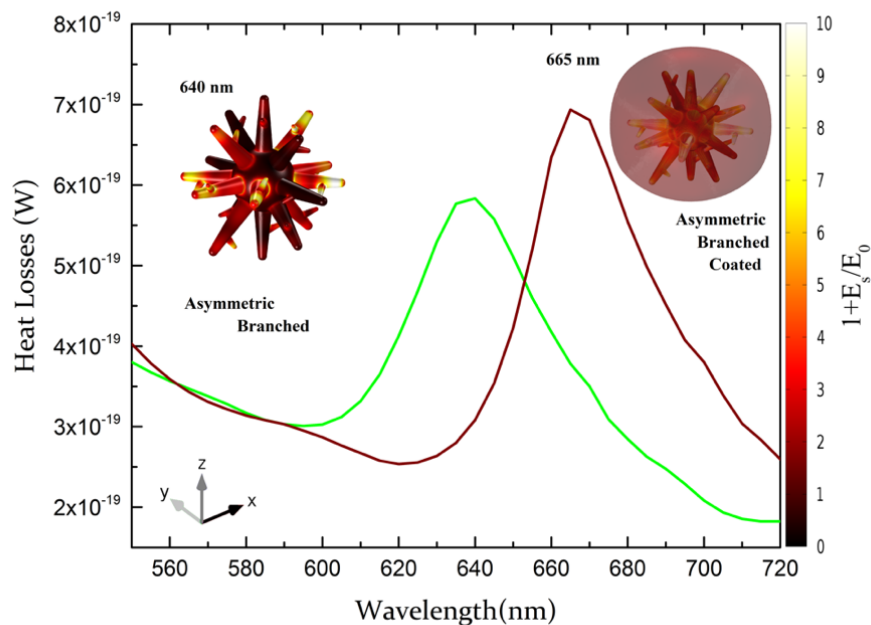


Figure 3. S6. A red-shift of the LSPR can be observed when a silica shell is made to surround an asymmetric branched gold nanostar, with a behavior resembling what observed for the non-branched counterparts.

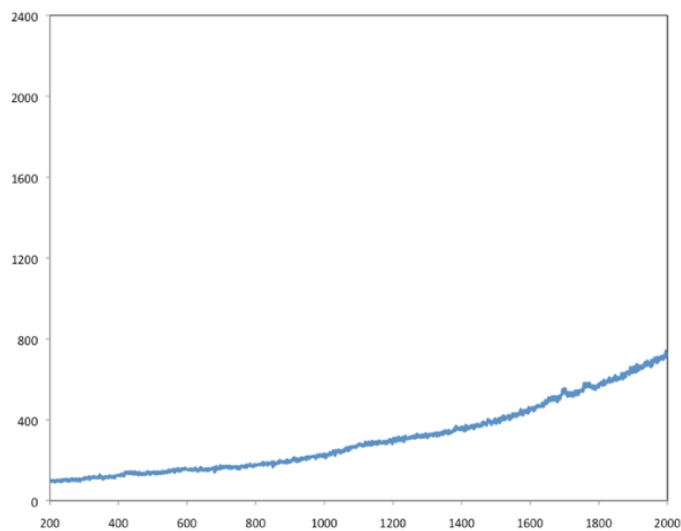


Figure 3. S7. Averaged Raman spectra of a 1 μM solution of ATP in ethanol used to calculate the $I_{\text{SERS}}/I_{\text{R}}$ ratios. Acquisition parameters: 633 nm laser excitation wavelength, 1% laser power, 1 s acquisition time, one accumulation.

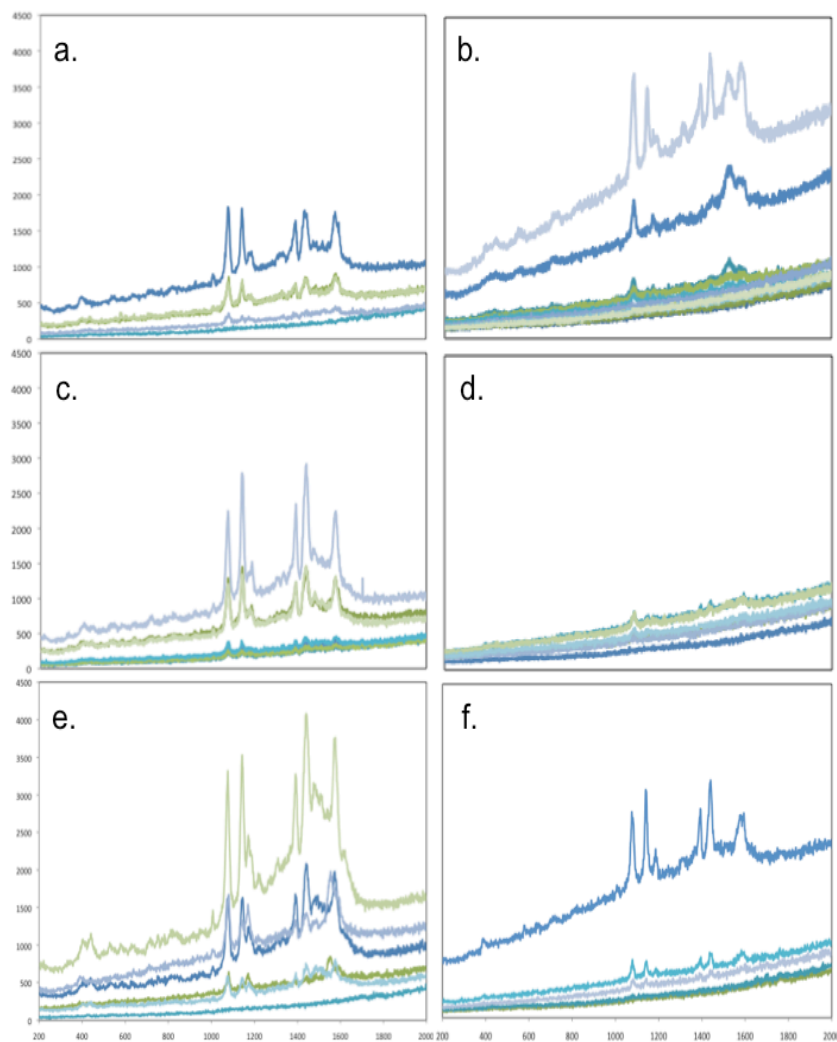


Figure 3. S8. Individual Raman spectra collected on each of the six samples and used to calculate the average spectra reported in Figure 7. Effective silica thicknesses: 0 nm (a), (12.9 ± 3.0) nm (b), (20.8 ± 7.2) nm (c), (26.9 ± 4.1) nm (d), (40.0 ± 9.8) nm (e), and (54.2 ± 11.8) nm (f). Acquisition parameters: 633 nm laser excitation wavelength, 1% laser power, 1 s acquisition time, one accumulation.

3.6. References

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CHAPTER-4
PHOTOCATALYTIC WATER REDUCTION in PRESENCE of TiO₂
on PLASMONIC GOLD NANOPARTICLES

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Abstract

Plasmonic nanostructure/semiconductor composites are receiving great interest as powerful photocatalytic platforms able to increase solar energy conversion efficiency compared to more traditional approaches. The possibility to grow a thin titania shell onto the gold nanoparticle, thus substantially increasing the metal-semiconductor area of contact, is expected to be ideal for photocatalytic water reduction, especially if the titania (TiO_2) coating displays limited thickness and high crystallinity. We argue however that the morphology of the underlying gold nanoparticle and the quality of the interface are the main drivers of photocatalytic performance. The growth of a conformal layer of crystalline TiO_2 on gold nanostars and nanorods was achieved by a simple hydrothermal route preserving the large aspect ratio of the protruding spikes of the nanostar and enabled the photocatalytic evolution of hydrogen under NIR illumination. The delicate structure of the underlying nanostars is otherwise extremely sensitive to atom migration. It has been revealed that the (101) crystal plane of anatase TiO_2 grows epitaxially on the surface of gold, and TiO_2 layer thickness and crystallinity can be controlled by varying synthesis conditions. TiO_2 -coated gold nanostars and nanorods displayed significantly enhanced photocatalytic activity under visible-NIR illumination compared to reported TiO_2 -coated gold nanoparticles and commercially available TiO_2 nanoparticles. The high photocatalytic activity is attributed to effective hot electron generation via absorption of radiation via localized surface plasmon resonance modes of the spikes and further injection to the conduction band of the TiO_2 shell across the gold nanoparticle- TiO_2 interface.

4.1. Introduction

Plasmonic noble metal nanoparticles such as gold nanospheres, nanorods, and nanostars have been recently proposed as promising additives to titanium dioxide (TiO_2) to increase the photocatalytic efficiency of the semiconductor under visible light.¹⁻² Owing to its stability in reaction conditions, relative abundance, low cost, and well-aligned valence and conduction bands, TiO_2 is a desirable semiconductor for use in multiple applications, in particular for the reduction and oxidation half-reactions of water splitting.³⁻⁴ The production of hydrogen from sustainable sources is one of the most actively investigated energy vectors due to the desire to convert solar energy to clean chemical energy.⁵ Numerous strategies for photocatalytic hydrogen production have been investigated over the years to enable the development of a visible-light active photocatalyst for hydrogen production.⁶ Unfortunately, conventional TiO_2 is characterized by a large band gap (3.20 eV and 3.03 eV for the anatase and rutile polymorphs, respectively),⁷⁻⁸ which limits its applicability primarily to ultraviolet (UV) irradiation conditions.

It has been proposed that the photocatalytic activity of TiO_2 , especially towards hydrogen generation, may be further extended in the visible-NIR range by taking advantage of plasmonic nanoparticles and their ability to generate hot electrons.^{2, 9-13} Jiang *et al.* conducted hydrogen evolution reactions from a 20% methanol/water solution and found that plasmonic silver nanoparticles supported on nitrogen-doped TiO_2 produced $200 \mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ after 30 minutes under visible illumination ($\lambda > 420 \text{ nm}$).¹⁴ Kou *et al.* reported $320 \mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ from a 50% methanol/water solution under visible illumination conditions ($\lambda > 400 \text{ nm}$) for gold nanorods coated with amorphous TiO_2 , while the rate increased to $1.9 \text{ mmol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ upon annealing in hydrogen.⁹

In our approach, plasmonically-generated hot electrons can be transferred across the Schottky barrier between the Fermi level of the metal (Au) and the conduction band of the semiconductor (TiO_2) and affect the photocatalytic activity of TiO_2 . This process can be favored via the formation of a defect- and strain-free gold nanoparticle- TiO_2 interface, which provides a channel for electron transfer from gold to TiO_2 . However, many of these heterocatalysts suffer from poor activity due to the lack of intimate contact between metal and semiconductor, which leads to inefficient electron transfer through the interface.¹⁵⁻¹⁶ In several examples reported in the literature, a surfactant is often used to allow adsorption of the gold nanostructures to the surface of the semiconductor. However, this surfactant creates a barrier between gold and TiO_2 that hinders electron transfer. Calcination at 500°C is commonly used to remove surfactants, but non-spherical gold nanoparticles, i.e. those that provide tunable, localized surface plasmon resonance (LSPR) bands and effective generation of hot electrons in close proximity to the metal-semiconductor interface, are temperature sensitive. High adatom mobility in regions of high curvature leads to nanoparticle reshaping and loss of LSPR modes in the NIR when thermal treatment at high temperature is carried out.

The most temperature-sensitive gold nanoparticles are nanostars. Nanostars are also the most promising particles for hot electron generation and consequently are ideally suited platforms for the synthesis of nanostructured photocatalysts. First, they are synthesized in the absence of any surfactant,¹⁷ allowing the TiO_2 shell to be grown directly onto the crystalline gold surface. Second, their morphology can be modified by design to alter spike number and dimensions allowing for predictable tunability of the LSPR bands from the visible to the NIR. This ability is particularly intriguing as it is not achievable with spheres and is hampered by the presence of a difficult to remove surfactant

(cetyltrimethylammonium bromide, CTAB) in nanorods. Third, gold nanostars can generate intense localized electromagnetic field enhancements around their spikes, which leads to a concentration of hot electrons right at the interface between metal and TiO_2 .² Hot electrons are electrons that have absorbed sufficient energy from the excited plasmons to be promoted above the Fermi level from the valence band of gold to the conduction band of TiO_2 across the interfacial Schottky barrier.^{2, 18} The ability to implement a synthetic method to grow crystalline titanium dioxide directly on the surface of gold nanoparticles has been a hurdle that has so far not been overcome. To address this issue, we have developed a new sol-gel method that hydrolyzes titanium precursors (titanium-(triethanolaminate) isopropoxide (TTEAIP) and titanium(IV) isopropoxide (TTIP)) into crystalline TiO_2 polymorphs at low temperature.

To verify the hypothesis that hot electrons can be generated at the tips of TiO_2 -coated gold nanostars and then be transferred across the metal-semiconductor interface to enable photoreduction reactions, light-induced dissociation of water with methanol as the sacrificial reagent in the presence of TiO_2 -coated gold nanostars (AuNS@TiO_2) was performed. The excitation wavelength proved to be essential to control photoreduction, indicating that the photocatalytic reduction is occurring through LSPR-mediated electron transfer from gold nanostars to TiO_2 . In addition, we have observed that the rate of hydrogen production increases with increasing TiO_2 crystallinity, further suggesting a hot electron-mediated photoreduction process, in which unobstructed electron motion through a crystalline lattice facilitates transfer across the interface. Also, the crystalline TiO_2 coated gold nanostars derived from TTIP showed higher activity when both the anatase and rutile polymorphs of TiO_2 were grown simultaneously on the nanostar, suggesting a synergistic effect between the band edges of the different crystalline polymorphs and the LSPR-

mediated electrons. These results show that intimate contact between TiO_2 and gold is necessary for plasmon-driven photocatalytic reactions.

Building from these observations, we further investigate the effect of each design parameter on the photocatalytic efficiency of Au nanorod/ TiO_2 systems in HER reactions. We focus in particular on 1) nanoparticle morphology, 2) LSPR tunability, 3) interface properties, and 4) TiO_2 shell quality, including uniformity, thickness, and crystallinity. We are interested in particular in dissecting how meeting (or not) one of the design constraints reported above improves (or not) the performance of the photocatalyst. We report on a new method to synthesize crystalline TiO_2 without initial addition of polymer, whose role is to stabilize the nanorods in organic solvent prior to exposure to the titanium precursor, but that drastically affects electron transfer at the interface, as it interferes with the epitaxial growth thus hindering electron pathways. Importantly, our low temperature protocol generates crystalline TiO_2 without modifying the morphology of the nanoparticle. We investigated the photocatalytic activity of TiO_2 coated gold nanorods toward HER under broad illumination conditions and compared it to that of nanostars with the same LSPR position, observing an initial higher performance of the nanostars. While this trend inverts after 20 minutes, possibly due to heating and reshaping of the nanostar tips, these results underscore once again the importance of the nanostar morphology as the main parameter affecting performance. Furthermore, because our nanorods, synthesized in the absence of any polymer overcoating as stabilizers, show identical performance to similar systems reported in the literature, characterized by a complete TiO_2 shell grown in the presence of polymer,⁹ we confirm our hypothesis that capping agents left at the interface hinder hot electron mobility and are deleterious to photocatalytic performance.

4.2. Results and Discussion

4.2.1. AuNS@TiO₂ Synthesis

The synthesis of AuNS@TiO₂ was carried out via a sol-gel protocol. Two methods, varying titanium precursor and annealing method, were explored (Table 4.1). In Method 1, TTEAIP is hydrolyzed in an acidic environment to grow the TiO₂ shell. An optimum concentration of TTEAIP (3.6 mM) is necessary for achieving a uniform TiO₂ shell. When the concentration of TTEAIP was below 3.6 mM the TiO₂ shell did not form, while when the concentration of TTEAIP was above 3.6 mM TiO₂ nanoparticles were formed instead (Figure 4. S1).

The time dependence of TiO₂ growth on gold nanostars was investigated at the optimal TTEAIP concentration. TEM micrographs of the surfactant-free gold nanostars and the TiO₂-coated gold nanostars at different time intervals are shown in Figure 4.1. The absorption spectrum of gold nanostars shows a broad LSPR band centered at 840 nm. At 1-hour reaction time an additional peak appears at 270 nm which can be assigned to the TiO₂ shell, whose thickness can be estimated via TEM micrographs to be of 2 nm (E:Am:2nm; Am = amorphous). Therefore, we employed the TiO₂ absorption band at 270 nm and the LSPR band of gold in the NIR (840 nm), which increased and decreased with time, respectively, as indicators of the progress of the reaction. Furthermore, the LSPR band of gold showed broadening and red-shift due to an overall increase in the refractive index of the dielectric environment surrounding the gold nanostars at increasing TiO₂ shell thickness.¹⁹ After 24 hours the TiO₂ thickness reached 40 nm (E:Am:40nm). TEM micrograph confirms the presence of a uniform TiO₂ coating in AuNS@TiO₂, which is however revealed to be of amorphous nature via HRTEM (Figure 4.1h).

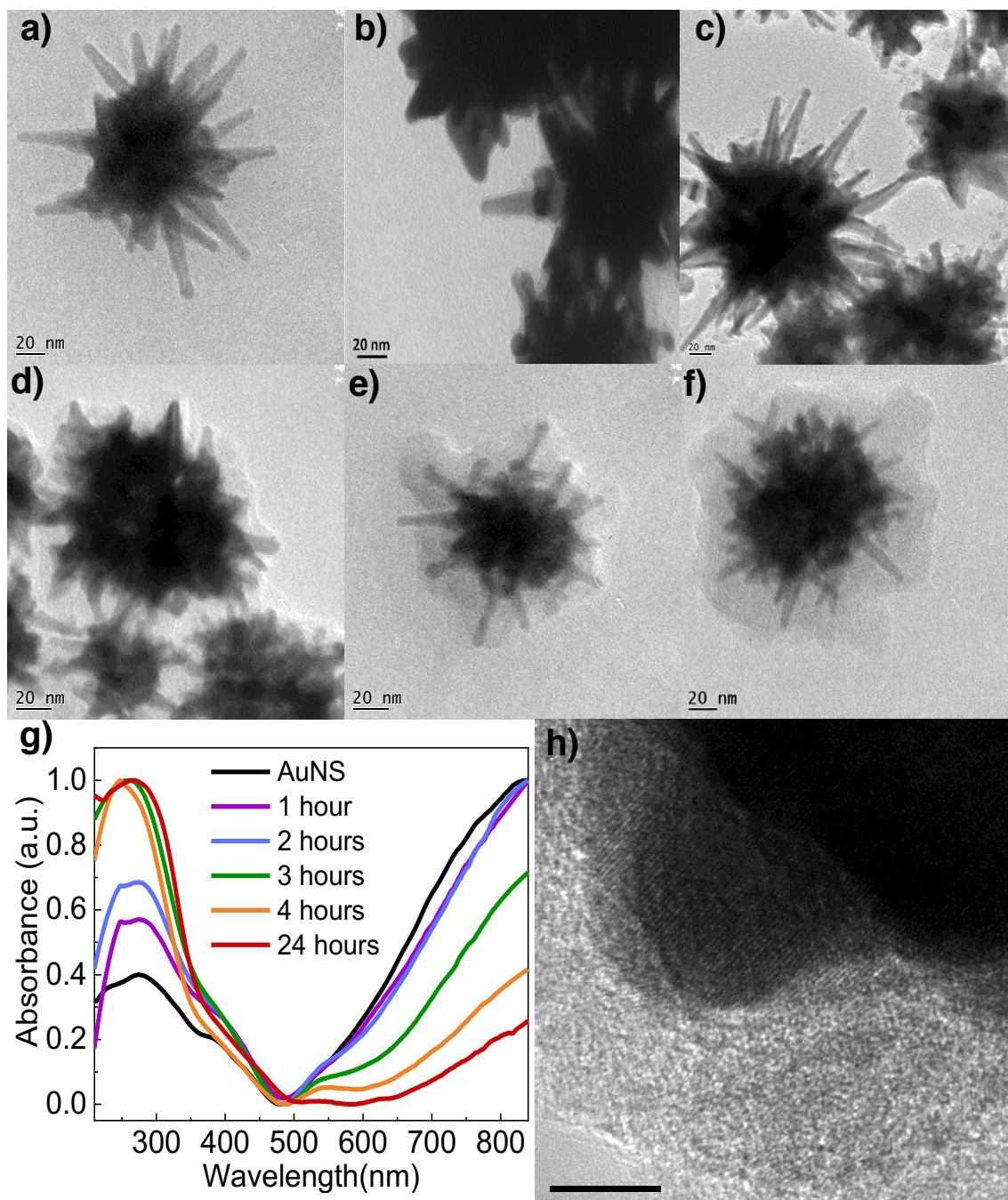


Figure 4.6. TEM micrographs and UV-Vis spectra of AuNS@TiO₂ as function of synthesis time. TiO₂ synthesis time-shell thickness of a) 0 h-0 nm, b) 1 h-2 nm, c) 2 h-5 nm, d) 3 h-15 nm, e) 4 h-20 nm, f) 24 h-40 nm. g) Increased UV-Vis absorption at 270 nm indicates the growth of the TiO₂ layer. h) HRTEM of AuNS@TiO₂ shows amorphous nature of TiO₂ after 24 h; only the crystalline (111) facet of gold can be observed.

Although the growth of a uniform TiO₂ coating on the nanostars increases their stability, its amorphous nature leads to an increased probability of exciton (electron/hole) recombination.²⁰ Additionally, the thickness of the TiO₂ shells produced with this protocol can be much larger than the bulk exciton transport distances in TiO₂ films (e.g. 5 nm for anatase and 2.5 nm for rutile⁷). Any hot electrons generated in the nanostars and transferred to the conduction band of TiO₂ will have a low probability of reaching the external surface of the TiO₂ shell before electron-hole recombination takes place, limiting their ability to participate in surface reactions.²⁰⁻²¹ To impart good photocatalytic activity, thinner shells made of crystalline TiO₂ are needed.²²⁻²³ Moreover, the photocatalytic ability of TiO₂ depends greatly on crystal polymorphs present. Anatase exhibits higher photocatalytic activity compared to rutile and amorphous TiO₂ due to more efficient exciton transport through the bulk and lower electron-hole recombination.^{20, 24-25} Many studies on TiO₂ nanoparticles have shown that mixed-polymorph TiO₂ exhibits increased photocatalytic activity relative to single-phase samples, which is attributed to the synergistic effect between the anatase and rutile band edges.²⁶⁻²⁸ Therefore, to increase the photocatalytic capabilities of AuNS@TiO₂, simple methods to grow crystalline layers of TiO₂ polymorphs on gold nanostructures were investigated.

The first approach used to increase the crystallinity of the TiO₂ shell was high-temperature annealing of powdered AuNS@TiO₂ at either 200°C (E:200:2h) or 400°C (E:400:2h) under ambient air in a calcination furnace. It is well known that annealing at higher temperature helps to crystallize amorphous TiO₂, and 400°C is well below the anatase to rutile transition temperature. HRTEM reveals that crystalline TiO₂ did indeed form (Figure 4.2c), but at the cost of shrinking of the gold nanostar spikes, as seen in TEM micrographs (Figure 4.2 a-b), as the motility of gold atoms at the tips of the spikes is highly

increased at the elevated temperatures necessary to crystallize TiO_2 . At sufficiently high temperatures gold atoms at the tips of the spikes will migrate toward the spherical core and coalesce, forming nanospheres. Burrows and coworkers have reported that surfactant-free stars cannot retain their morphology with well-defined spikes when they are synthesized at or above 40°C .²⁹ Despite this, the addition of the TiO_2 shell increased the temperature stability of the nanostars, as the sample annealed for 2 hours at 200°C retained some of its spikes, albeit shortened. The nanostars annealed for 2 hours at 400°C became spherical despite the TiO_2 coating.

The UV-Vis absorption spectra of E:400:2h and E:200:2h show a dramatic blue-shift of the LSPR band of gold nanostars after heat treatment (Figure 4.2d), from 840 nm to 670 nm for particles annealed at 200°C , and a substantial, 200 nm blue-shift to 645 nm shown by particles annealed at 400°C , both indicative of substantial nanoparticle reshaping.

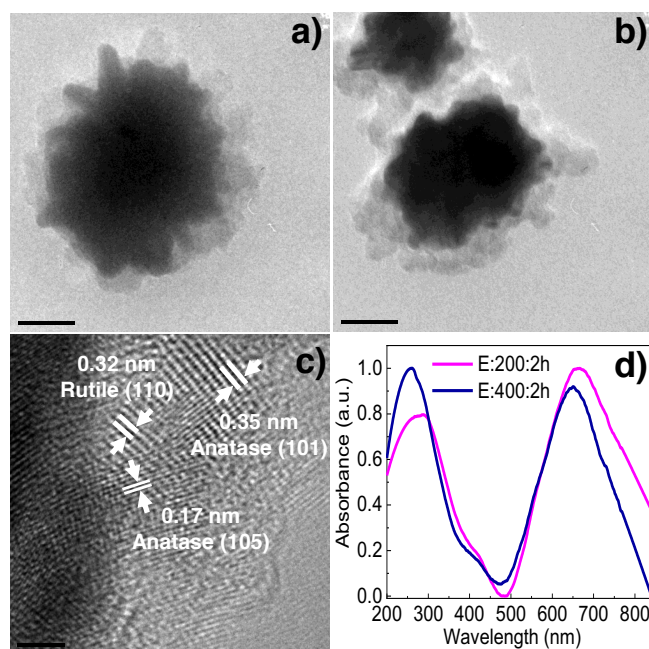


Figure 4.7. TEM micrographs and UV-Vis spectra of the AuNS@ TiO_2 heated to 200°C and 400°C . Heated at a) 200°C (E:200:2h) and b) 400°C (E:400:2h) for 2 hours displays

shortening of the nanostar spikes. c) HRTEM micrograph shows the crystalline nature of TiO_2 layer in E:400:2h. d) UV-Vis spectra of AuNS@TiO_2 suspended in aqueous media display a 200 nm blue shift in the plasmonic resonance of the gold nanostar from ~ 840 to 650 – 675 nm for AuNS@TiO_2 annealed to 400 – 200°C.

An amorphous AuNS@TiO_2 sample was annealed in an oven at mildly elevated temperature (58°C) for a longer time period (10 days) (E:58:10d). It was expected that the TiO_2 -encapsulated nanostars would preserve their morphology under mild heating, while the extended exposure to slightly elevated temperatures would allow for slow crystallization of the TiO_2 to occur. HRTEM (Figure 4.3d), UV-Vis (Figure 4.3c), and XRD results (Figure 4.3f) indicate that the morphology of nanostars was preserved, but the percentage of crystalline TiO_2 was still very low, and the shell was not uniform (Figure 4.3a). This feature indicated that 58°C might not have been sufficient to promote elevated levels of crystallization within the amorphous TiO_2 and that higher temperatures might be needed to improve the properties of the shell. To overcome these problems, the amorphous AuNS@TiO_2 was annealed in an oven at 75°C for 4 days (E:75:4d). The morphology after heat treatment is shown in Figure 4.3b, in which TEM characterization supports the hypothesis that the TiO_2 shell might effectively protect the gold nanostars from reshaping into nanospheres at high temperature. After annealing at a 75°C for 4 days, the TiO_2 shell thickness shrank from 40 nm to 10 nm, which rendered the TiO_2 more compact, possibly facilitating electron transfer during photocatalysis.³⁰⁻³¹ HRTEM shows clear anatase (101) lattice fringes, confirming its crystalline nature (Figure 4.3e), and XRD shows the presence of both crystalline anatase and rutile domains (Figure 4.3f). The higher temperature was accompanied by a reduction in spike length by around 5 nm for I:75:4d relative to E:58:10d, which is evidenced by the blue shift of the LSPR (Figure 4.3c).

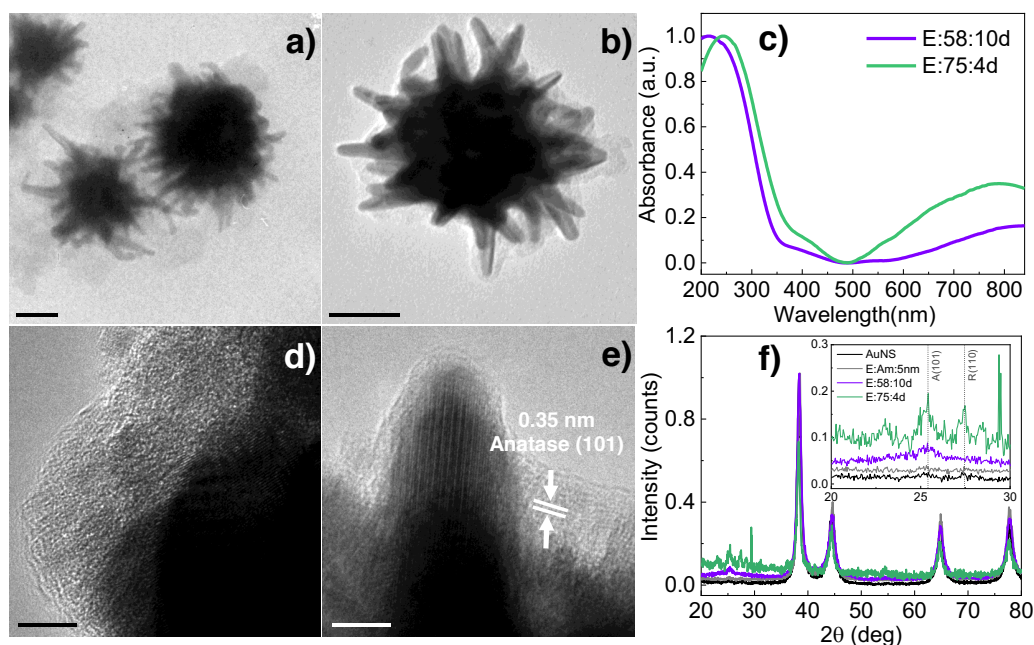


Figure 4.8. TEM micrographs, UV-visible absorbance, and XRD pattern of AuNS@TiO₂ heated to 75°C demonstrate that the thickness of the TiO₂ shell was reduced from 40 nm to 10 nm. TEM micrographs a) E:58:10d, and b) E:75:4d. c) UV-vis absorption spectra show blue shift of plasmon resonance upon spike shortening after heat treatment at 75°C. HRTEM and XRD confirm the amorphous nature of E:58:10d (d and f) and the presence of crystalline anatase and rutile TiO₂ in E:75:4d (e and f).

In Method 2, TiO₂ growth on gold nanostars was performed from TTIP as the precursor in a non-aqueous environment (isopropanol). The reaction was carried out in isopropanol to slow down the hydrolysis of the TiO₂ precursor. In water, rapid hydrolysis of TTIP led to the formation of a white and turbid solution. Acetic acid was added to the growth solution to control TiO₂ growth. It has been reported that by increasing acetic acid concentration during the synthesis of TiO₂ nanoparticles the overall size of the particles decreases and a small percentage of anatase nanocrystals is formed.³² Similarly, in our experiments we observed the formation of a thin layer of amorphous TiO₂ after addition of TTIP. Next, crystallization was accomplished via heat treatment of the AuNS@TiO₂

particles in isopropanol. Two different heating temperatures were used, 70°C (for 2 days, I:70:2d) and 62°C (for 2 days, I:62:2d, and 7 days, I:62:7d). TEM micrographs show that the morphology of the stars was retained after 2 days at either 62°C or 70°C (Figure 4.4a-b, d-e). However, the number of spikes and spike length were reduced when the stars were heated at 62°C for 7 days (Figure 4.4g-h). As a result, the LSPR band of the gold nanostars blue shifted to the greatest extent with heat treatment for 7 days (Figure 4.4j). HRTEM (Figure 4.4c, f, i) and XRD (Figure 4.4k) show that when the reaction temperature was kept at 62°C, the crystallization formed anatase, whereas at the higher temperature of 70°C, the crystalline TiO₂ shell consisted of both anatase and rutile polymorphs. The greater crystallinity of I:70:2d is evident from the stronger absorbance of UV light and the sharper and more intense XRD peaks relative to 62°C samples.

Most importantly, we have observed a well-defined interface between the crystalline gold core and the TiO₂ shells from both preparation methods. HRTEM micrographs of the TiO₂-coated gold nanostars obtained from AuNS@TiO₂ TTEAIP-prepared samples heated in air (E:75:4d), and TTIP-prepared samples heated in isopropanol (I:70:2d) are shown in Figure 4.5. The preferential growth of TiO₂ occurs at the metal-semiconductor interface with Au and TiO₂ lattices in intimate contact, which indicates strong interaction established between Au and TiO₂ during the annealing process.³³ The spacing between adjacent lattice fringes of gold is 0.23 nm and 0.35 nm for TiO₂. A clear relationship between the lattices of Au and TiO₂ was observed where (101) facets of anatase aligned to the (111) facets of gold, confirming that epitaxial growth of TiO₂ on Au is likely occurring, as it is reported to be thermodynamically favorable at these relative orientations.³³

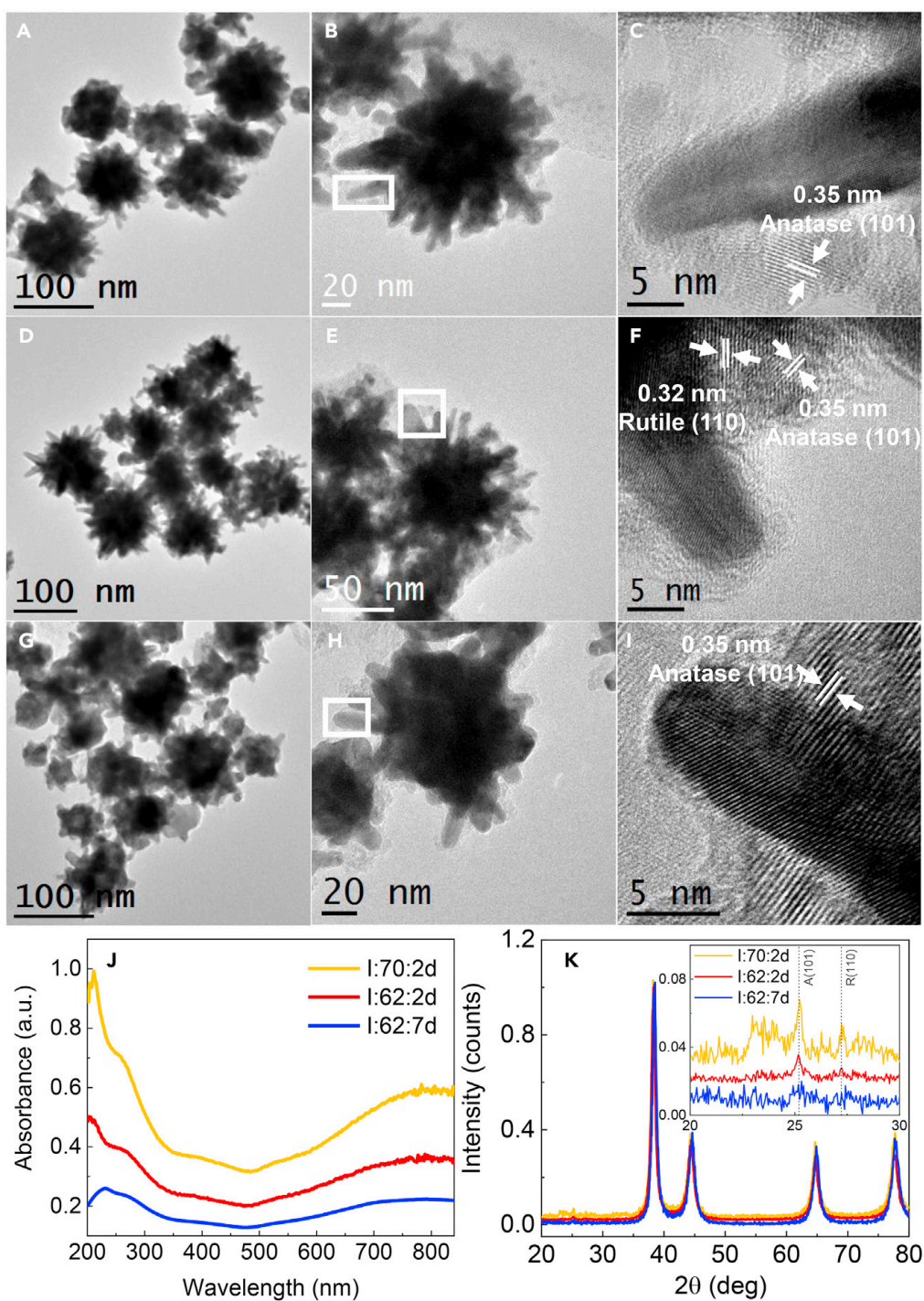


Figure 4.9. TEM and HRTEM micrographs, UV-visible absorbance, and XRD patterns of AuNS@TiO₂ with crystalline TiO₂ layers. a-b, d-e, g-h) TEM and c, g, i) HRTEM micrographs of a-c) I:62:2d, d-f) I:70:2d, and g-i) I:62:7d. HRTEM images and k) XRD

patterns show the formation of crystalline anatase and rutile. j) Stronger UV-visible absorption for I:70:2d indicates greater crystallinity of TiO₂ shell.

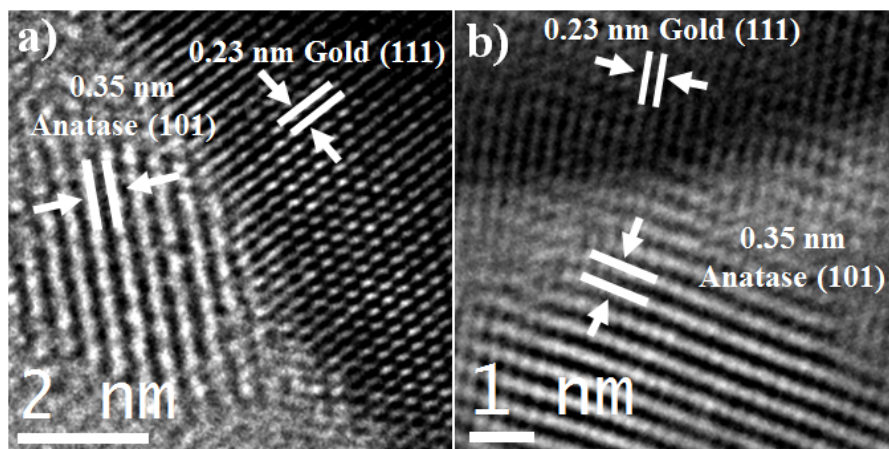


Figure 4.10. HRTEM micrographs of TiO₂-coated gold nanostars show intimate contact between TiO₂ and gold at the interface. a) E:75:4d, and b) I:62:2d.

Sample Code	TiO ₂ Precursor	Heat Treatment	Heat Treatment Temperature	Heat Treatment Time	TiO ₂ Shell Thickness
AuNS	--	None	--	--	0 nm
E:Am:2nm	TTEAIP	None	--	--	<2 nm
E:Am:5nm	TTEAIP	None	--	--	~5 nm
E:Am:40nm	TTEAIP	None	--	--	~40 nm
E:200:2h	TTEAIP	Oven Annealing	200°C	2 hr	~23 nm
E:400:2h	TTEAIP	Oven Annealing	400°C	2 hr	~16 nm
E:58:10d	TTEAIP	Oven Annealing	58°C	10 d	~22 nm
E:75:4d	TTEAIP	Oven Annealing	75°C	4 d	~10 nm
I:62:2d	TTIP	Hydrothermal	62°C	2 d	~5 nm
I:62:7d	TTIP	Hydrothermal	62°C	7 d	~5 nm
I:70:2d	TTIP	Hydrothermal	70°C	2 d	~5 nm

Table 4.1. Naming convention, precursor, heat treatment conditions, and TiO₂ shell thickness of AuNS@TiO₂ samples.

4.2.2. AuNR@TiO₂ Synthesis

The protocol for the synthesis of TiO₂ shells on gold nanorods has been reported in the literature,⁹ and is characterized by three steps. In the first step, gold nanorods are protected by a polymer (poly (sodium 4-styrenesulfonate), PSS) to prevent agglomeration in organic solvent, where the growth of the shell occurs. Then, the TiO₂ shell is grown on gold the nanorods, in the presence of the TiO₂ precursor TiCl₃. In the third step, amorphous TiO₂ is crystallized at 450 °C. The high temperature treatment, while substantially improving the crystallinity, leads to the generation of Ti³⁺ species and oxygen vacancies.²² However, the presence of the polymer layer creates a barrier for electron transfer from gold into the semiconductor, likely reducing the performance of the photocatalyst. We therefore propose here a new low temperature protocol for the synthesis of a crystalline TiO₂ shell on gold nanorods in the absence of polymer overcoating.

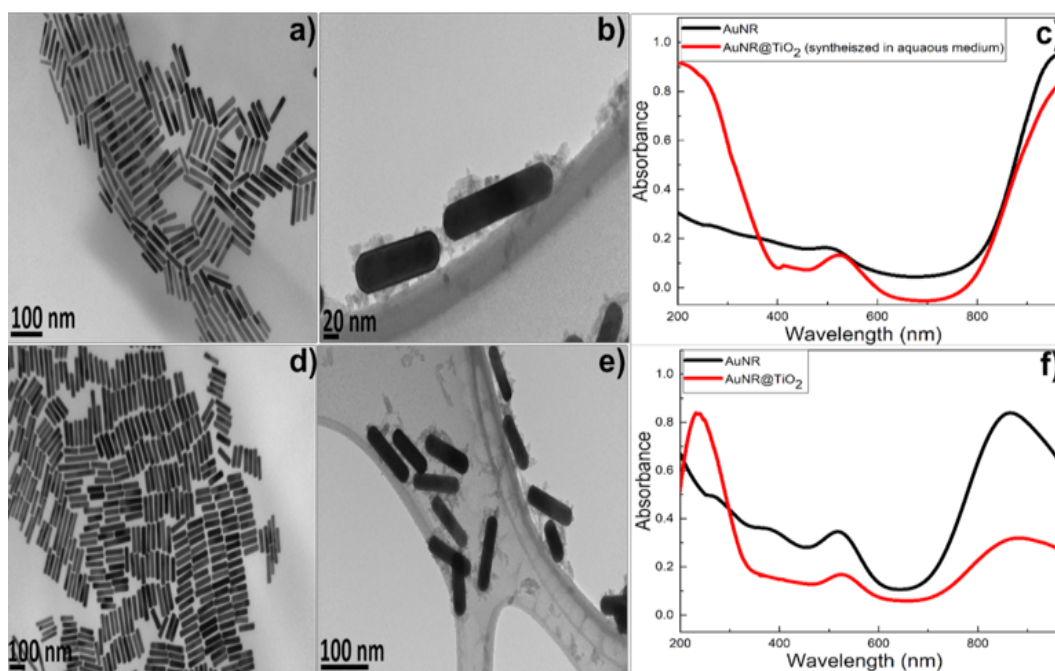


Figure 4.6. (a) TEM micrograph of CTAB-capped gold nanorods characterized by a LSPR at 940 nm. (b) TEM micrograph of the same nanorods after TiO₂ coating realized in aqueous medium, showing that the morphology of the nanorods is retained. (c) UV-Vis extinction spectra show that a 50 nm red shift occurs when TiO₂ coating is realized via

TTIP in aqueous medium. (d) TEM micrograph of CTAB-capped gold nanorods characterized by a LSPR at 840 nm. (e) TEM micrograph of the same nanorods after TiO_2 coating. As in the previous example, the coating appears not to be forming uniformly around the nanorods. (f) UV-Vis extinction spectra show that a 30 nm red shift occurs when TiO_2 coating is realized via TTIP in aqueous medium.

Traditional protocols cannot be carried out in these conditions as the nanorods precipitate and coalesce in organic solvents, even when mildly polar, such as isopropanol. Our water-based method relies on the use of titanium isopropoxide (TTIP) as the Ti precursor and is run at 70°C for two days. It is well known that the gold nanorod LSPR maximum should red-shift upon TiO_2 shell formation due to the increase in the dielectric function of the surrounding medium in going from water to TiO_2 . As we suspected, in the absence of polymer overcoating the LSPR of gold nanorods disappeared in isopropanol, consistent with nanorod aggregation and precipitation (Figure 4. S2). Transmission electron microscopy (TEM) micrographs show substantial aggregation of the gold nanorods (Figure 4. S2a), inconsistent with mere aggregation induced by water drying or the electron beam. We believe instead that the aggregation is entirely due to the increase in critical micelle concentration (CMC) for cetyltrimethylammonium bromide (CTAB), the surfactant employed for the synthesis and stabilization of the nanorods, in water/alcohol mixtures. Increase in CMC leads to the unzipping of the CTAB micelle and consequent nanorod aggregation. On the contrary, by running the reaction in water, we avoided nanorod aggregation and were able to grow a, albeit not complete, TiO_2 shell on the nanorods. TEM characterization shows that while the TiO_2 shell results not uniform, the nanorod morphology is retained (Figure 4.6 a-e). The presence of the TiO_2 shell is further confirmed by the redshift and reduction in intensity of the LSPR band (Figure 4.6 c, f), as we observed

with gold nanostars. Importantly, while the growth of the shell was not possible in pure water, the addition of acetic acid, aimed at reducing the rate of hydrolysis of TTIP, led to its formation. Following our previously reported protocol for crystallization of the TiO_2 shell on gold nanostars, we heated the reaction mixture to 70°C and maintained it at this temperature for 2 days. High resolution TEM characterization (HRTEM) shows crystallization of TiO_2 with formation of anatase, although amorphous TiO_2 is still present (Figure 4.7 b).

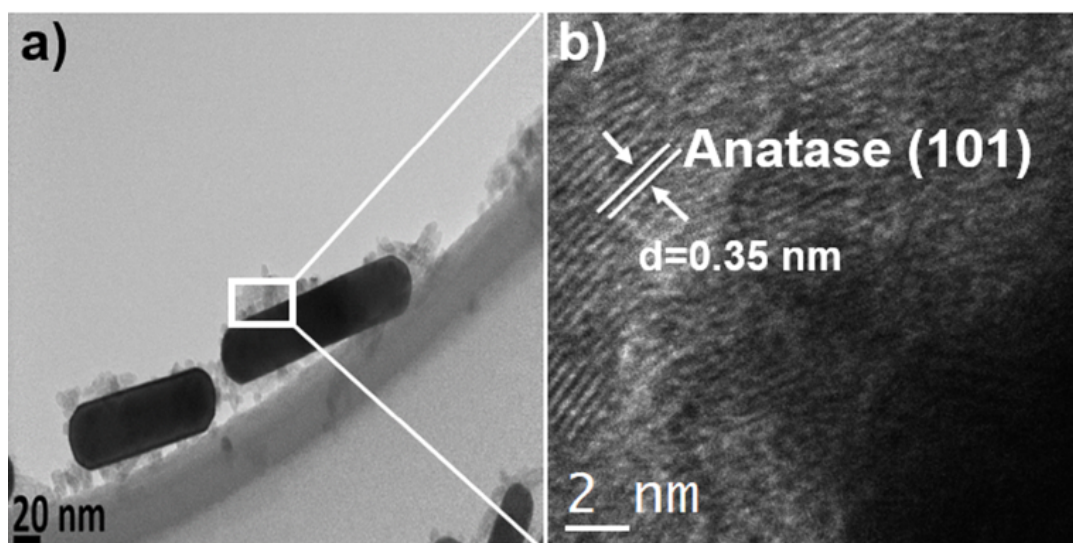


Figure 4.7. HRTEM micrographs of TiO_2 -coated gold nanorods. In a) the morphology of the rod is retained upon coating with TiO_2 , even though the shell is not complete. In b) the high magnification micrograph provides evidence of crystallization into anatase TiO_2 (d space 0.35 nm) even though the presence of amorphous region is still evident.

Gold nanorods of increasing aspect ratio, and therefore with redshifted LSPR maxima (870 nm, 910 nm, and 980 nm), were synthesized to understand the effect of resonant position on photocatalytic efficiency. An LSPR maximum at shorter wavelength should generate a larger population of highly energetic electrons (proportional to integrated plasmon absorbance scaled for solar flux at each wavelength³⁴) available for transfer into the

semiconductor and subsequent photocatalytic reduction. As we have observed before,¹⁷ red-shifted LSPR bands are more intense and are correlated to increased electric near fields; in our study however, nanorods with 910 nm LSPR show substantially broadened and less intense resonances, which will be interesting to correlate integrated plasmon absorptivity to hot electron generation and photocatalytic efficiency.

TiO₂-coated gold nanostars were also synthesized to compare our nanorod-based platform to a system that we have previously proven to be an excellent photocatalyst for HER. Gold nanostars were synthesized to possess an LSPR maximum at 980 nm after TiO₂ coating, to study how the morphology of the nanoparticles and the quality of the coating affect the photocatalytic performance at equal absorption maximum (**Figure 4.8**). In Figure 4.8c we can observe a TEM micrograph of the Au nanostars upon coating with TiO₂, in which the presence of a rather uniform shell can be observed. On the other hand, Figure 4.8c also shows the presence of isolated TiO₂ particles that were difficult to remove and may impact the activity of the photocatalyst. Interestingly, when comparing the UV-Vis extinction spectra of the TiO₂-coated nanorods and nanostars with coinciding LSPR maxima at 980 nm, one can observe how the extinction spectrum for the nanostars shows a more intense TiO₂ band compared to the case of the nanorods, consistent with the presence of the isolated TiO₂ nanoparticles. More importantly, the LSPR band for gold nanostars is substantially broadened compared to the nanorod counterpart. This broadening, and reduced intensity, may result detrimental with respect to the photocatalyst performance, considering the correlation between the electric field intensity and the number of hot electrons generated, as explained above.

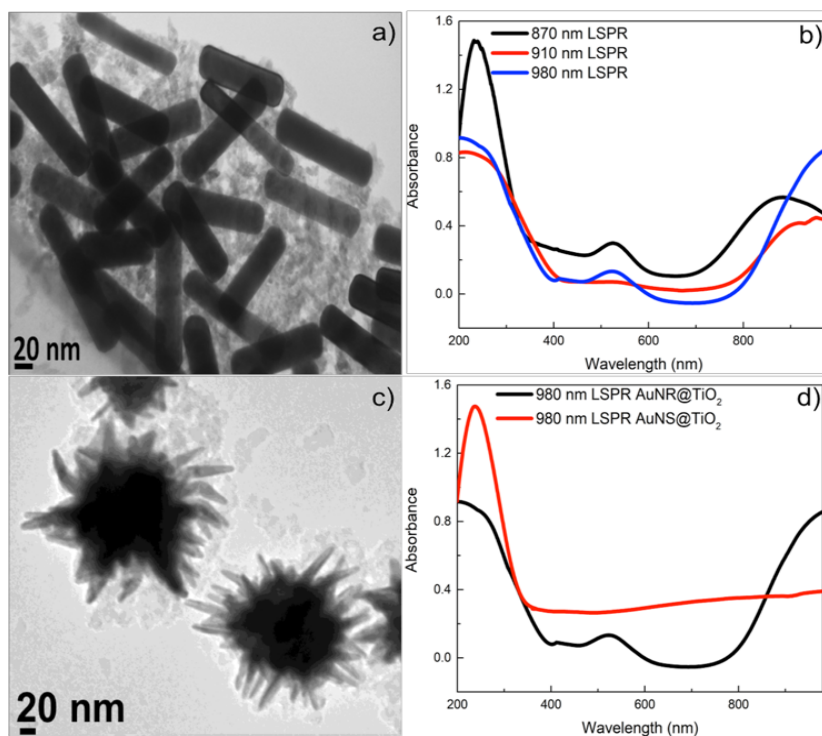


Figure 4.8. (a) TEM image of CTAB capped gold nanorods where the plasmon resonance comes at around 910 nm which is a mixture of 870 and 980 nm LSPR gold nanorods. (b) UV-Vis absorption spectra of three different gold nanorods sample. (c) TEM image of TiO₂ coated gold nanostars. (d) UV-Vis absorption spectra of TiO₂ coated gold nanostars and nanorods where the plasmon resonance comes at 980 nm.

4.2.3. Photocatalytic Water Reduction

To test the photocatalytic activity of the AuNS@TiO₂ particles, water reduction with methanol as a sacrificial agent was carried out under dark, UV, visible, and broad-spectrum illumination using 1.5 mg of AuNS@TiO₂. Photocatalytic results over heat-treated samples with crystalline shells E:75:4d, I:62:2d, I:62:7d, and I:70:2d are given in Figure 4.9, and results over amorphous-shelled samples E:Am:2nm and E:Am:40nm are given in Figure 4. S3.

All heat-treated samples plus amorphous sample E:Am:40nm showed minor activity in the dark, which is explained by potential ambient illumination of samples prior

to reaction. Photo-generated electrons and holes can persist in TiO_2 for days, and the small amount of hydrogen formed in the dark was likely due to trapped excitons in the samples.

Owing to their large band gap energies, both anatase and rutile do not absorb much visible light, and consequently hydrogen formation under visible illumination conditions were not expected to be significant. Control experiments with anatase and rutile (without gold, discussed below) showed no activity under visible illumination. The visible light range for these experiments cuts off wavelengths below 630 nm, so the majority of the LSPR band excitation energies were absent. The absorption spectra for hydrothermally treated samples (Figure 4.4j) do show non-negligible visible light absorption between 420 nm and 630 nm, especially for I:70:2d, which was probably responsible for the visible light activity observed for these samples. The oven-treated E:75:4d by contrast shows very weak visible light absorption in Figure 4.3c, and consequently activity in visible light was significantly reduced compared to hydrothermal samples. E:75:4d containing both anatase and rutile showed roughly double the productivity compared to the anatase-only hydrothermal samples, which showed roughly doubled activity compared to the oven-treated sample containing both anatase and rutile. E:Am:40nm showed some absorption in the visible range, most likely due to band overlap from a multitude of valence and conduction band energies depending on local geometry in the amorphous sample. This led to hydrogen evolution comparable to I:62:2d and I:62:7d despite the very thick metal oxide layer. By contrast, the thin oxide layer E:Am:2nm was completely inactive under visible illumination.

The samples were similarly or slightly more active under UV illumination compared to visible light (420– 630nm). Even when irradiated with wavelengths capable of photoexcitation in the TiO_2 shells, the lack of significant improvement over visible light

suggests that photoexcitation alone is unable to impart high activity to the samples. It is possible that the primary sources of activity under the two illumination conditions are completely separate mechanisms, given that the plasmonic effects leading to activity enhancement in the visible are unavailable under UV illumination. Among the crystalline samples, the order of the sample activities was the same as under visible light: I:70:2d > I:62:7d $\approx$ I:62:2d $\gg$ E:75:4d.

Illuminating the catalysts with broad-spectrum radiation (200 nm – 1500+ nm, i.e. unfiltered sunlight-emulating from the 150 W Xe arc lamp) revealed the true benefits of growing crystalline TiO₂ domains on gold nanostars. All samples lacking either gold (anatase and P25) or crystalline anatase and/or rutile (E:Am:2nm and E:Am:40nm) showed no difference in activity between UV and broad spectrum irradiation. For these samples, the broad spectrum only provided the same usable UV light that was available under UV-illumination only, and no hydrogen evolution enhancement was possible.

The hydrogen productivity of crystalline AuNS@TiO₂ increased significantly compared to all other samples. I:70:2d was able to produce >2.5 mmol H₂ g⁻¹ of catalyst in 20 minutes. I:62:7d and I:62:2d, samples containing only anatase, roughly doubled their hydrogen output. Samples containing both anatase and rutile, I:70:2d and E:75:4d, experienced a seven-fold increase in hydrogen productivity. This last result is remarkable, since the absolute values of the two samples' rates were quite different from one another under all illumination conditions. Yet both samples responded the same way to switching from visible light to UV light (no change) and experienced the same proportional increase in productivity upon exposure to NIR wavelengths in the broad-spectrum experiments, pointing to a shared mechanism of action. Since both UV and visible light produced the same amount of hydrogen for crystalline samples, adding the two wavelengths would be

expected to at most double the hydrogen yield when no other mechanisms are available. This is what was observed for I:62:7d and I:62:2d. The additional enhancement in I:70:2d and E:75:4d must therefore be derived from a new mechanism only available when illuminating the multi-phase TiO₂ samples with NIR light resonant with the LSPR band of the underlying nanostars.

The evidence suggests that, under broad spectrum illumination, light absorption via the gold nanostar LSPR band at ~800 nm is able to generate hot electrons and inject them into the conduction band of the crystalline TiO₂ shell. As these two samples were characterized by thin TiO₂ layers, the electrons could migrate from the metal-semiconductor interface to the solid-liquid interface where they then catalyzed proton reduction and hydrogen evolution. This mechanism is illustrated in Scheme 4.1. The additional requirement for effective transfer of electrons across the Schottky barrier at the metal-semiconductor interface appears to be the presence of both rutile and anatase phases, as only mixed-polymorph samples experienced the 7x enhancement effect. This is likely due to band-bending synergistic effects between the conduction bands of the two semiconductors with the metal, lowering the apparent electron transfer barrier at the interface. The enhancement effect seems to be universal, despite the wide disparity between the activities of the two samples. The thinner shell in I:70:2d is probably responsible for the majority of the difference between it and E:75:4d, where exciton recombination probability is lower in a thinner TiO₂ film.

Control reactions under all illumination conditions were run with no catalyst and bare gold nanostars without any TiO₂. Both the control reactions showed no hydrogen evolution, which is expected since a semiconductor with appropriately positioned valence and conduction bands is required for the reduction of water to generate hydrogen gas.

Additional control experiments (Figure 4. S3) were run on TiO₂ nanoparticles in the absence of gold nanostars in order to discriminate between the influence of the plasmonic hot electrons from the gold nanostars and the photoexcitation of electrons from the TiO₂ valence band upon UV illumination. As the AuNS@TiO₂ were roughly 35% TiO₂ by mass, the control reactions with anatase and P25 were conducted with 0.5 mg of catalyst and compared to reactions over 1.5 mg of AuNS@TiO₂ samples. Neither anatase nor P25 showed any activity under dark or visible illumination conditions, and while P25 was three times as active as anatase, both samples showed little difference between results under UV and broad-spectrum illumination. Alone, TiO₂ is unable to use visible irradiation, given that there was no reaction, and is unable to use NIR irradiation since no rate enhancement from broad spectrum illumination was observed. The activity of both TiO₂ samples was significantly lower than that of the AuNS@TiO₂ with crystalline TiO₂ shells under broad spectrum illumination, further indicating that the gold nanostars enhance the rate of hydrogen illumination via hot electron injection into the conduction band of TiO₂ through plasmonic excitation at NIR wavelengths. Under both UV and broad-spectrum illumination, P25 was more active than anatase. P25 is a 3:1 mixture of anatase and rutile TiO₂, and the rate enhancement observed in P25 further suggests that synergism between anatase and rutile phases assists in hydrogen evolution from water, as was seen in I:70:2d. Compared to other reported Au@TiO₂ photocatalysts, I:70:2d exhibits a substantially improved photocatalytic activity (2,632 $\mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ in 20 minutes). For instance, Qian *et al.* showed that small Au nanoparticles (4.4 ± 1.7 nm) deposited on P25 TiO₂ led to an increase in catalytic activity for H₂ production to yield $1376 \pm 60 \mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ in 2 h.¹¹ Wu *et al.* achieved a catalytic activity of $11.6 \mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ in 1 h with AuNR/TiO₂ nano-dumbbells,¹³ while Kou *et al.* obtained a H₂ generation rate of $1912 \mu\text{mol}_{\text{H}_2} \text{g}_{\text{cat}}^{-1}$ in 1 h

with Au@H-TiO₂ (gold nanorods encapsulated by hydrogenated TiO₂) catalyst.⁹ While these published results underscore the impact of plasmonic nanoparticles on the photocatalytic activity of TiO₂ for hydrogen evolution reactions, the hydrogen production over I:70:2d provides strong evidence that non-trivial improvements in photocatalytic activity can be achieved by concerted optimization of nanoparticle morphology, plasmonic properties, quality of the metal-semiconductor interface, and relative amounts of crystalline TiO₂ polymorphs.

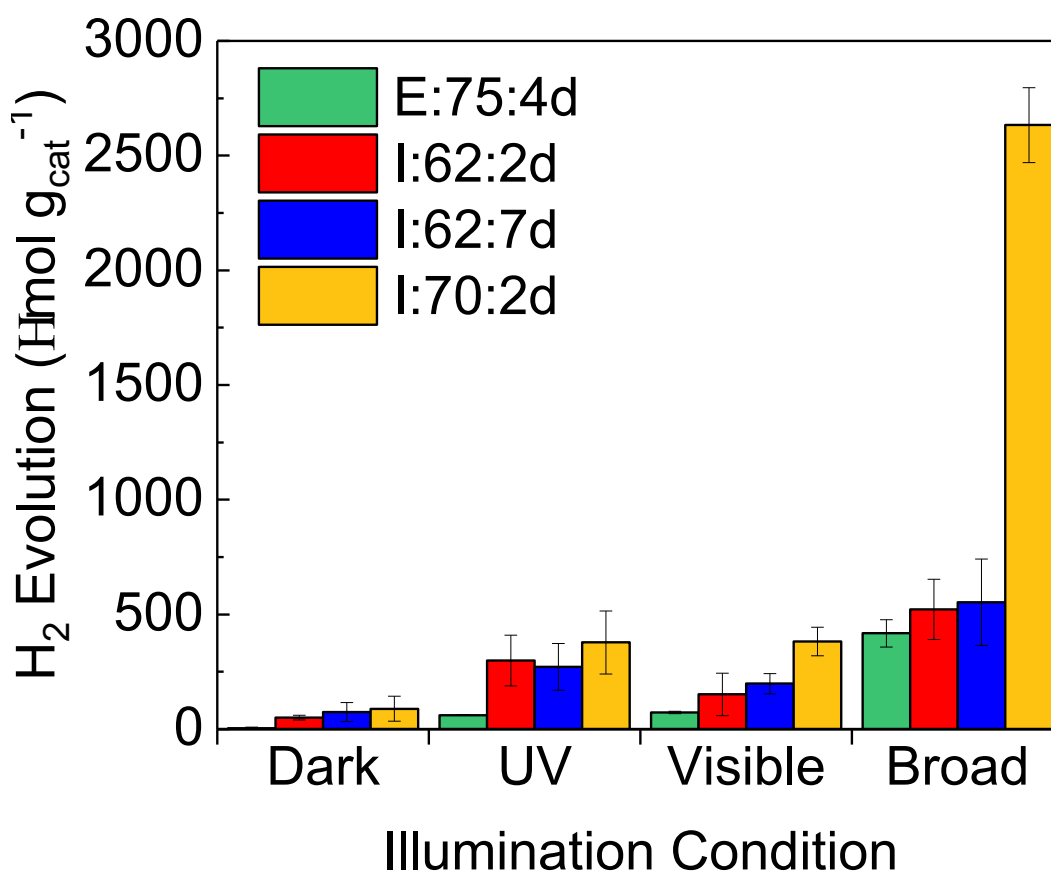
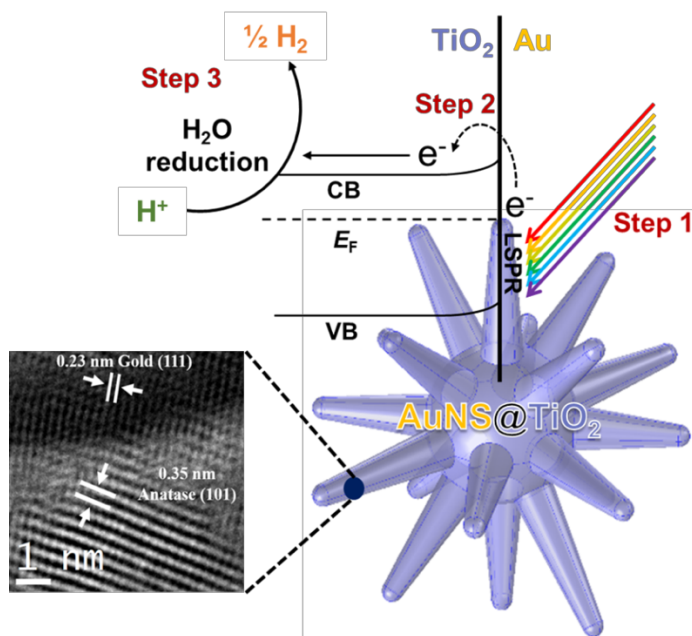


Figure 4.9. Hydrogen generation after 20 minutes from water reduction at specific illumination conditions over E:75:4d, I:62:2d, I:62:7d, and I:70:2d. UV illumination was 280 nm – 400 nm, visible illumination was 420 nm – 630 nm, and broad spectrum was 200 nm – 1500+ nm. Reaction vessel maintained at 40 °C with an oil bath.



Scheme 4.1. Illustration of the proposed photocatalytic enhancement in the AuNS@TiO₂ system. Broad spectrum light illuminates the TiO₂-coated gold nanostar (Step 1). While shorter wavelengths interact with the TiO₂ band gap and the gold transverse LSPR band, longer wavelengths (~800 nm) excite the longitudinal LSPR band of gold nanostars. The hot electrons at the nanostar tips overcome the Schottky barrier at the clean interface between the two materials and transfer into the conduction band of the TiO₂ semiconductor (Step 2). Conduction band electrons then reduce protons and evolve hydrogen (Step 3). By running hydrogen evolution reactions via broad spectrum illumination, we observed that the hydrogen productivity of crystalline TiO₂-coated gold nanorods increased with increasing plasmon resonance wavelength from 870 to 980 nm (**Figure 4.10**). By illuminating gold nanorods with 870 nm LSPR, 0.37 mmol H₂ per gram of catalyst were produced in 1 hour, whereas by illuminating the nanorods with 980 nm LSPR, 0.7 mmol H₂ g⁻¹ were instead produced, with an almost doubled yield. This result appears to correlate nicely with the integrated plasmon absorptivity for the two nanorod batches, even though they are counterintuitive if one simply looks at the position of the LSPR band. We then

monitored the activity of the gold nanorod batch with 910 nm LSPR, composed by a polydispersed mixture of particles. Interestingly, the hydrogen productivity of mixed TiO₂ coated gold nanorods was higher than the 870 nm and 980 nm LSPR samples, possibly due to a panchromatic effect, as shown by Mubeen *et al.*,³⁴ who demonstrated that the photocatalytic efficiency of a mixture of AuNR-TiO₂-Pt Janus nanorods increased compared to the efficiency of the individual rods, possibly due to the ability of the mixture to absorb a broader range of solar radiation.³⁴ Our results compare fairly well with what reported by Kou *et al.*,⁹ who showed ca. 320 $\mu\text{mol g}^{-1} \text{h}^{-1}$ of H₂ produced by their Au nanorod- TiO₂ system, in which a full titania shell was grown onto the nanorods but in the presence of polymer overcoating. This result suggests that the presence of a complete semiconductor layer around the nanorod is drastically affected by the lack of epitaxial interface, which will likely not grow because of the interference of the polymer. One therefore should not only pay attention to the completeness of the shell but also that no interfering molecules are trapped between metal and semiconductor, thus affecting electron mobility.

Photocatalytic water reduction studies were carried out under broad-spectrum illumination conditions also to compare the performance of gold nanostars and gold nanorods, using 1.5 mg of TiO₂ coated gold nanoparticles in each study, where methanol was again used as the sacrificial agent for hole capture and oxygen generation (Figure 4.10 b). The photocatalytic activity of TiO₂ coated gold nanostars and nanorods was roughly comparable at 20 minutes (with nanostars behaving only slightly better), with the nanorods performing instead better at longer times. This shift in performance could be due to localized heating occurring at the tips of the nanostars under illumination, which may cause increased Au atom mobility at the tips and local reshaping, rendering therefore the electric field intensity at these

positions lower over time, and decreasing the overall generation of hot electrons and injection into TiO_2 . This evidence suggests that, under broad spectrum illumination, and in the absence of heat-induced reshaping, light absorption via the gold nanostar generates more hot electrons than nanorods, primarily because each gold nanostar possesses an average of 100 spikes, as shown by us and others, where the enhanced electric field concentrates.¹⁷ What emerges from the results at 20 minutes correlates the extinction spectra of the gold nanostars (Figure 4.10d) to their performance. In fact, if one were only to advocate for the plasmon absorptivity to be the main determining factor in the photocatalytic performance, the conversion rates observed for the (non-optimized) nanostars reported here would not support this hypothesis. On the contrary it appears to be indeed the presence of the spikes to be the important morphology feature affecting the performance of TiO_2 -coated Au nanostars as photocatalysts in HER. While it could be argued that the nanorods do not possess a complete semiconductor shell compared to the nanostars, the results reported above, comparing different nanorod systems, should further strengthen the role of the spiked morphology as the relevant parameter with respect to hot electron generation and photocatalytic performance.

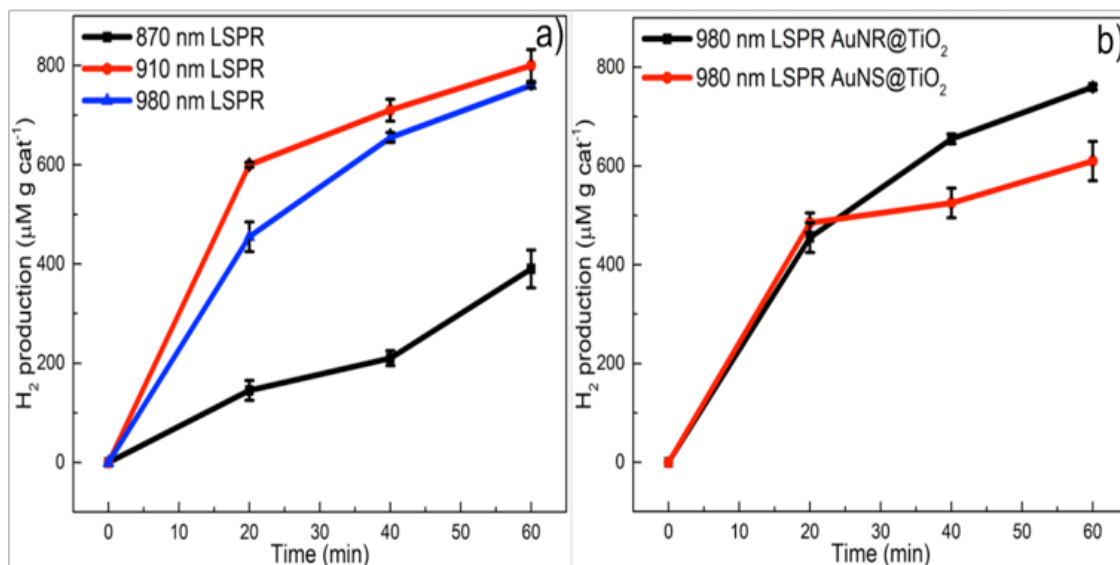


Figure 4.10. (a) Hydrogen generation at different time intervals (0, 20, 40, and 60 minutes) from water reduction at broad spectrum over three different TiO₂ coated gold nanorods having LSPR maxima at 870 nm (black), 980 nm (blue), and 910 nm (red). (b) Hydrogen evolution comparison for TiO₂ coated gold nanorods, and nanostars having LSPR maxima at 980 nm.

Taken all together, these results confirm our hypothesis that various materials design parameters need to be taken into account to synthesize effective photocatalysts for hot electron-induced chemical conversions. While we have herein focused on hydrogen evolution reactions, these considerations should be generalizable to a large extent. The main features that we have analyzed in this work include 1) the morphology of the nanoparticles, 2) the position and integrated absorptivity of the LSPR, 3) the quality of the metal semiconductor interface, and 4) the uniformity of the TiO₂ shell and 5) its crystallinity. While nanorods and nanostars can be synthesized to possess the same LSPR, it is the presence of the spikes on the nanostars that drastically affects the performance of the photocatalyst, similarly to what we observed before with respect to the magnitude of the extinction coefficient.³⁴ The integrated absorptivity appears to be the second most

important parameter, with higher absorptivity values correlating to higher yields of hot electrons and therefore to improved performance. The quality of the interface should also be kept high, ideally free of intermediate coating layers (e.g. polymers) that can hinder electron mobility. While we have not studied the role of the semiconductor shell thickness and its crystallinity in this work (all our samples showed a mix of anatase and amorphous titania), we have determined that the presence of a full semiconductor shell onto the plasmonic nanomaterial is not a fundamental driver of performance.

4.3. Conclusion

In summary, we have synthesized TiO₂-coated gold nanostars in which the relative amounts of crystalline TiO₂ polymorphs could be tuned via a simple, low temperature, sol-gel approach. The photocatalytic activities of the AuNS@TiO₂ systems were evaluated following hydrogen evolution from water reduction under UV, visible, and broad-spectrum irradiation. As hypothesized, the gold nanostars enhanced the photocatalytic activity for hydrogen evolution of TiO₂ under visible-NIR light irradiation, while increasing the crystallinity of the TiO₂ coating increased the photocatalytic activity of the AuNS@TiO₂ samples. Unique activity $>2.5 \text{ mmol H}_2 \text{ g}^{-1}$ of catalyst in 20 minutes was found for the AuNS@TiO₂ sample hydrothermally treated at 70°C for 2 days, owing to the synergistic effects between the two TiO₂ polymorphs present in the crystalline TiO₂ coating. Our results confirm the hypothesis that in TiO₂-coated gold nanostars hot electrons can be generated in close proximity to the tips and readily transferred across the metal-semiconductor interface to be promoted from the valence band of the metal to the conduction band of the semiconductor. By epitaxially growing a crystalline TiO₂ shell conformally onto the gold nanoparticle, unstrained pathways for electron transfer are

generated, so that effective electron injection across the Schottky barrier into the semiconductor is achieved. Only the successful synthesis of mixed polymorph crystalline layers permitted this effect to be observed under NIR illumination. Interestingly, we have observed that the photocatalytic reaction under broad spectrum illumination leads to higher H_2 production even when the plasmon resonance of the gold nanorods is shifted closer to 1000 nm, as long as the integrated absorptivity of the LSPR band is high. We have also confirmed the results of Moskovits and coworkers,³⁴ who showed that a panchromatic device, in which gold nanorods of various aspect ratios are mixed together, yields to higher H_2 production if the nanorods are tuned to absorb a broader spectrum of solar radiation. The catalytic activity of TiO_2 -coated gold nanostars was found higher than that of TiO_2 -coated gold nanorods within the first 20 minutes of reaction, with a trend reversing at longer times, probably due to local heating at the spike tip and atomic restructuring. These results promise to enable the implementation of the reported nanomaterials in innovative photocatalytic applications and to provide nanostructured platforms for the fundamental understanding of metal-semiconductor interfaces. Finally, the application of gold nanostar systems to drive other chemical reactions with infrared illumination should be explored, importantly to understand their suitability not only to increase conversion rates but also selectivity.

4.4. Experimental Procedures

4.4.1. Materials

Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), silver nitrate ($AgNO_3$; 99.995%), L(+)-ascorbic acid (AA), titanium-(triethanolaminate) isopropoxide ($N((CH_2)_2O)_3TiOCH(CH_3)_2$, TTEAIP) in isopropanol (80%), titanium(IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP), glacial acetic acid, isopropanol, and methanol were purchased

from Sigma-Aldrich. 12 N HCl was purchased from Fisher Chemical. Anatase was purchased from Acros Organics and P25 was supplied by Evonik. All of these materials were used without further purification. Ultrapure MilliQ water (18.2 M Ω ·cm) was used in all syntheses. All glassware was cleaned with aqua regia before each synthesis.

4.4.2. Instrumentation

Absorption spectra were collected using an S.I. Photonics Fiber Optic CCD Array UV-Vis Spectrophotometer using a quartz cuvette with 1 cm path. The nanoparticle morphology was determined using a Topcon 002B transmission electron microscope depositing the nanoparticle suspension on Ted Pella Inc. PELCO TEM grids. HRTEM analysis was performed on a JEOL 2010 F high-resolution transmission electron microscope. The spike length and thickness of the TiO₂ shell of the nanostars were measured by ImageJ software. Particle morphology was analyzed using Gatan DigitalMicrograph (TM) 3.11.1 for GMS 1.6.1. The values of average *d* spacing were obtained from Fourier transform analysis of high-magnification images. X-ray powder diffraction patterns were collected using a PANalytical Philips X'Pert X-ray diffractometer and analyzed to determine crystallinity and phase composition. The XRD measurements were carried using a Cu-K α source at 40 kV and 40 mA and angular incidence 2θ between 20° and 80°. The composition of samples was analyzed using a Pearson-VII profile shape function using PDF# 01-071-1169 and PDF# 01-076-1941 for anatase and rutile, respectively.

4.4.3. Synthesis of Surfactant-Free Gold Nanostars

Surfactant-free gold nanostars were synthesized following a previously reported method.¹⁷ 12 nm citrate-capped seeds were prepared according to the modified Turkevich method.^{35,36} The absorbance of the as-synthesized citrate-capped seeds was 0.6. The solution was concentrated eight times via centrifugation before use. Nanostars were

synthesized by simultaneous addition of 2 ml of 3 mM AgNO₃ and 1 ml of 0.1 M ascorbic acid to a solution containing 2 ml of 0.025 M HAuCl₄, 48 ml milliQ water, 40 µL of the citrate-capped gold seed solution, and 200 µL of 1 N HCl solution. An immediate, intense bluish-green color appeared after simultaneous addition of AgNO₃ and ascorbic acid. The solution was stirred for 7 minutes.

4.4.4. Synthesis of AuNS@TiO₂ from TTEAIP precursor

AuNS@TiO₂ was synthesized by following a modified method for TiO₂ coated gold nanorod synthesis according to the literature procedure.¹⁹ 40 µL of TTEAIP in isopropanol (80%) solution was added to 50 ml gold nanostar suspension and the mixture was stirred for 24 hours. The suspension was then washed with 1:1 MilliQ water and ethanol mixture twice, re-dispersed in 10 mL of acetone, and dried to produce a powder.

4.4.5. Synthesis of AuNS@TiO₂ from TTIP precursor

AuNS@TiO₂ was synthesized following an acetic acid-induced sol-gel TiO₂ nanoparticle synthesis method.^{32,37} 300 ml of gold nanostars were centrifuged at 5000 g for 15 minutes and dispersed in 60 ml of isopropanol. 6 ml acetic acid and 250 µL of TTIP were added to the solution and stirred for 30 minutes, followed by addition of 250 µL of MilliQ water. The resulting solution was stirred for 12 hours at room temperature and then heated at either 62°C or 70°C to crystallize the TiO₂ shell. The solution was washed with 1:1 MilliQ water and ethanol mixture twice and then dried to produce a powder.

4.4.6. Synthesis of Seeds

Gold seeds were prepared following a reported procedure.³⁸ Briefly, 5 mL of a freshly prepared 0.01 M sodium borohydride solution were dissolved in 5 mL of a freshly prepared 0.01 M solution of sodium hydroxide. 460 µL of the sodium borohydride aqueous solution

were added to 10 mL of a 0.1 M CTAB solution containing 0.5 mM HAuCl_4 under rapid stirring. The color of the solution changed from yellowish to light brown.

4.4.7. Synthesis of Nanorods

10 mL of a 0.5 mM solution of HAuCl_4 were added to the 0.1 M CTAB solution. 70 μL of 0.1 M AgNO_3 solution were added to the mixture, followed by addition of 500 μL of a 0.1 M hydroquinone aqueous solution. The resulting mixture was stirred for a minute. Then, 160 μL of seed solution were added to the growth solution. The growth solution was aged overnight. Gold nanorods were purified by centrifugation at 10,000 rpm and redispersed in 5 mL of milli-Q water.

4.4.8. Synthesis of TiO_2 coated Gold Nanorods

TiO_2 coated gold nanorods were synthesized using TTIP as the precursor in aqueous environment. Briefly, 300 mL of gold nanorods were synthesized and then centrifuged at 10000 g for 1 hour. It was dispersed with 100 nm Milli-Q water. 27 mL acetic acid and 250 μL of TTIP were added to the solution and stirred for 12 hours at room temperature. The resulting solution was then heated at 70°C to crystallize the TiO_2 shell. The solution was washed with Milli-Q water twice before use.

4.4.9. Photocatalytic Water Reduction

Photocatalytic activity of the samples was tested via batch phase water reduction with methanol as a sacrificial agent, similar to the procedure reported by Wu et al.¹³ The reaction was carried out in a 25 mL glass reactor filled with 10 mL of 20% methanol in MilliQ water. 1.5 mg of fresh AuNS@TiO_2 catalyst was dispersed in 10 mL of reaction solution via sonication for 5 minutes. For control experiments using anatase and P25, 0.5 mg of TiO_2 , or roughly the same mass of TiO_2 alone in the AuNS@TiO_2 samples, was used. The reactor was illuminated by a 150W Xenon Ozone-free Arc Lamp (Newport) with an approximate

flux of 3000 and brightness of 150 cd mm^{-2} using 20 V and 7.5 A of power. Four illumination conditions were investigated: dark (no illumination), UV illumination (280 nm – 400 nm), visible illumination (420 nm – 630 nm), and broad spectrum illumination (200 nm – 1500+ nm). UV and visible cutoffs were achieved via dichroic mirror beamturner assembly and glass bandpass filter. To ensure that illumination did not affect the reaction temperature, the reactor was kept at 40°C with a heated oil bath under all illumination conditions. Magnetic stirring was employed to ensure that the AuNS@TiO₂ remained suspended in the reaction media. The hydrogen production rate was monitored at 20 minutes for each condition via injecting a 300 μL aliquot of the reactor headspace gas into the TCD of a GC (Agilent 7890B). Hydrogen production is reported per gram of catalyst for all samples.

4.5. Supplemental Information

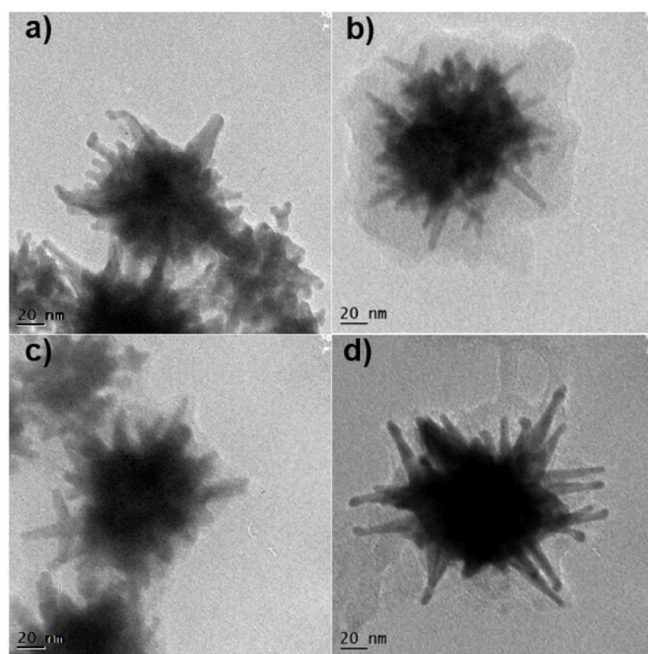


Figure 4. S1. TEM micrographs of gold nanostars following TiO₂ coating synthesis at different concentrations of TTEAIP. a) 1.8 mM with no TiO₂ growth, b) 3.6 mM (optimum

concentration), c) 5.4 mM, and d) 9 mM with TiO₂ nanoparticles growing without association to gold particles.

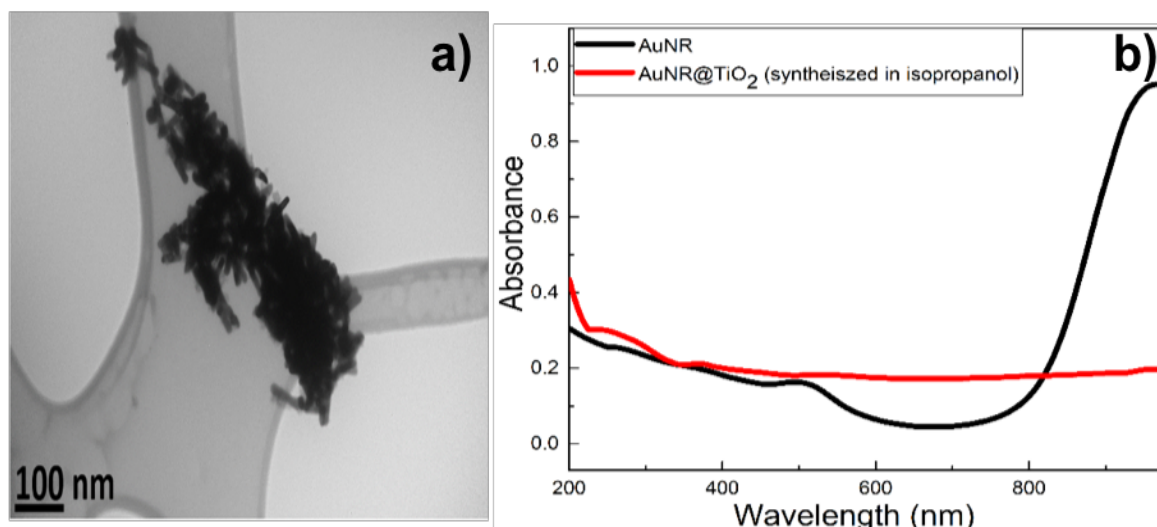


Figure 4. S2. a) TEM image of TiO₂ coated gold nanorods synthesized in isopropanol medium where the gold nanorods were aggregated. b) UV-Vis spectrum shows that the longitudinal plasmon band of gold nanorods at around 980 nm was disappeared when the reaction was carried out in isopropanol medium.

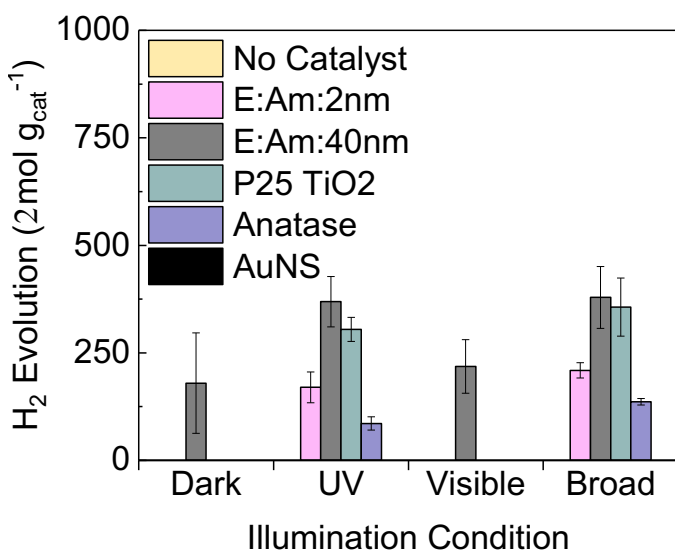


Figure 4. S3. Hydrogen generation after 20 minutes from water reduction at specific illumination conditions without catalyst, over gold nanostars without TiO₂ shells, and over AuNS@TiO₂ with amorphous shells, E:Am:2nm, E:Am:40nm. Results are compared to

P25 and anatase TiO₂. UV illumination was 280 nm – 400 nm, visible illumination was 420 nm – 630 nm, and broad spectrum was 200 nm – 1500+ nm. Reaction vessel maintained at 40°C with an oil bath.

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CHAPTER 5

CONCLUSIONS and FUTURE DIRECTIONS

5.1. Conclusion

The results of this thesis project are divided into two parts, focusing respectively on the synthesis and potential applications of gold nanostars. A cohesive study of both parts revealed the potential of seed-mediated synthesis for nanoparticle morphology tuning by design to meet the needs of their intended application.

In Chapter 2, we focused on the synthesis and growth mechanism of 6-branched gold nanostars and corresponding characterization of their crystal structures and optical properties. 6-branched gold nanostars were synthesized in high yield and high monodispersity for the first time. The major shape development stage in the growth of gold nanostars was shown to be dominated by the seed morphology, which showed five-fold twinning for 6-branched nanostars and multiple twinning for multibranched nanostars. Structure characterization of the nanostars showed that the growth of the spike proceeds along the twin axis, with a predominant role of AgNO_3 as both shape-inducing and stabilizing agent. These nanostars are promising for biological applications due to their tunable LSPR in the NIR spectral range.

In Chapter 3, we focused on investigating how the thickness of silica shells grown conformally on gold nanostars affects their surface enhanced response. In this project, we first focused on the silica coating and selective etching of silica on the gold nanostars, and then correlated the calculated scattered electric field enhancement generated in these structures to the experimental SERS signal enhancements, which showed that the effective enhancement results from two counteracting effects, namely the amount of higher dielectric function silica, and the amount of metal exposed. This work contributed to better understand the dependence of the SERS enhancement on the morphology of silica-coated gold nanostars.

Nowadays it is necessary to produce and store energy in a clean, efficient, and reliable way. Chapter 4 describes our efforts to develop a plasmon-assisted water splitting system under broad spectrum irradiation using gold nanostars coated with crystalline TiO_2 as a contribution to addressing our current energy needs. The influence of temperature, crystallinity, and nanostar morphology was studied with respect to H_2 evolution. Photocatalytic H_2 evolution results indicated that plasmonic hot electron injection occurred at the interface between gold and TiO_2 . By analyzing H_2 production, the water splitting yields were found to be substantially higher compared to the reported literature values. In conclusion, in this dissertation, wet chemistry approaches were developed to synthesize highly monodispersed and reproducible gold nanostars for the first time. The growth was initiated by inducing changes in the morphology of the single crystalline seed to produce a five-fold twinned seed. Through the modification of the reaction parameters, and/or by changing capping agents or precursors, other shapes of the gold nanostructure can be expected through this seed mediated synthesis method. It has been demonstrated in this thesis that a metal-semiconductor nanostructured material can be successfully synthesized to utilize the full solar spectrum in photocatalytic processes, and open new possibilities for efficient and stable water splitting catalytic systems for clean fuel generation and more sustainable production of clean energy.

5.2. Future Perspectives

The future of gold nanostars looks very promising especially for research in plasmonics. In recent years, scientists have been trying to push boundaries to understand the growth mechanism of these anisotropic nanoparticles, in particular by trapping reaction intermediates and using modern analytical tools to understand the dependence among

reaction parameters and monodispersity and then tailoring the surface properties to target specific applications in medicine, spectroscopy, and catalysis.

In this dissertation, we have taken an important step to understand the morphology of the reaction intermediates during the growth of gold nanostars, and investigate how their morphology affects our ability to synthesize highly monodispersed 6-branched gold nanostars. While we have established a good understanding of the growth mechanism and overall shape evolution, a more detailed study of the dependence of all reaction parameters will be needed to truly master the rational synthesis of these particles. For instance, we have seen that the morphology of the nanoparticles changes with increasing concentrations of ascorbic acid, Triton-X, and seeds. Multiply twinned nanoparticles formed when both Triton X and ascorbic acid concentration were lower than the ideal concentrations needed to obtain 6-branched nanostars. However, a mechanistic understanding of the origin of these multiply twinned nanoparticles is still lacking. This study can give some insight into branch formation, important when studying branched nanostructures other than 6-branched nanostars. For example, a mechanistic investigation is required for complex hyperbranched nanoparticles that form when the concentrations of both Triton X and ascorbic acid are higher than the ideal concentrations to obtain 6-branched nanostars; on the other hand, multibranched hollow gold nanoparticles form at very high concentration of Triton X and ascorbic acid. We have studied the effect of AgNO_3 on the surface reconstruction of the kinetically controlled growth of 6-branched gold nanostars. However, it is important to also study the effect of ascorbic acid and Triton-X on surface reconstruction.

In Chapter 3, we have developed a synthetic protocol to obtain silica-coated gold nanostars with variable silica thickness ranging from 4 nm to 41 nm, and to selectively etch away the silica to only leave the sharp spikes to protrude. Then, we have investigated the surface

enhanced Raman scattering (SERS) enhancement of the silica etched stars. Although it is out of the scope of this study, it is very important to investigate the growth mechanism of silica coating and etching of 6-branched gold nanostars as they have a narrow spectral broadening which is highly sensitive towards change in the dielectric medium surrounding the tips of the stars. Additional applications of this special type of partially silica-coated gold nanostars can be foreseen in-vivo and in-vitro, owing to the enhanced biocompatibility and stability of the particles.

In Chapter 4, we have developed a low temperature synthesis of gold nanostars coated by crystalline TiO_2 , which have shown considerably high photocatalytic activity than reported photocatalysts under broad spectrum illumination. However, it is important to investigate the photocatalytic water reduction for extended time frames, when keeping an eye toward industrial and practical applications. Moreover, this experiment will reveal the stability and reusability of the photocatalysts in the reaction medium. The kinetics and complete catalytic cycle of water splitting reactions mediated by TiO_2 coated gold nanostars have still not been investigated. A better understanding of the catalytic reaction and kinetics is of course very useful with the goal of designing improved photocatalysts. It is important to investigate other photocatalytic reactions as well- for instance, CO_2 reduction into useful products such as methanol and formic acid, and ammonia production from nitrogen gas. Herein, we have successfully demonstrated the syntheses of gold nanostars and their use in plasmonics and catalysis. However, the performances of these syntheses and applications are still limited to the benchtop, and thus still far away from optimization and large-scale production. For the purpose of optimization and large-scale application, several aspects should be considered in the future.