Synthesis and characterization of silver nanoprism-based nanostructures

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2012

Mohammad Mehdi Shahjamali. (2012). Synthesis and characterization of silver nanoprism-based nanostructures. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54727>

<https://doi.org/10.32657/10356/54727>

SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPRISM-BASED NANOSTRUCTURES

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A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2012

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ACKNOWLEDGEMENT

First and foremost, I would like to express my utmost gratitude and appreciation to both my supervisors, Assistant Professor Xue Can and Professor Freddy Boey for their insightful advice, constant encouragement and support throughout my graduate journey. I greatly appreciate both supervisors to give me the freedom in scientific thinking and attempt.

I also want to thank Associate Professor Zhang Hua, Professor Bo Liedberg, Professor Subbu Venkatraman, Assistant Professor Huang Yizhong, Assistant Professor Li Shuzhou and Dr. Huang Xiao for their valuable guidance and kind help during my graduate study. Special thanks to Dr. Tay Yee Yan and Dr. Stevin Snellius Pramana, Ms. Irene Heng and Ms. Guo Jun for their kind assistant and experience sharing in material characterizations. I also would like to thank Dr. Michel Bosman in the Institute of Materials Research and Engineering (IMRE) for his valuable help and advice in TEM characterizations.

Many thanks go out to all members of Professor Xue and Professor Zhang Hua's group that I have worked with during the past four years. I was fortunate to have this great opportunity to learn from many talented people in those groups. I am particularly grateful to those people who have provided invaluable support to my graduate research work. These include Ms. Wang Zheng, Ms. Yin Lisha, Dr. Cao Shaowen, Dr. Yin Zhen, Dr. Fang Jun, Mr. Cipto Liusman, Mr. Cao Xiehong and Dr. Ying Zongyou for their kind help and support during my graduate study.

I also thank Joyce Siew Phui Yee, Christina Lu Bee Lay and Chloe Chan Sze Hua for their kind assistance during my stay in school of Materials Science and Engineering.

Acknowledgement

Lastly and most importantly, I would like to thank my parents who gave me continuous love and support; I could not have this achievement without their encouragement. I owe them too much and cannot express enough my gratitude to both of them. This thesis is dedicated to my parents, Mr. Mohammad Hadi Shahjamali and Mrs. Rahmati Sajjadeh, for everything.

ABSTRACT

Noble metal nanostructures, ranging from a few atom clusters to micrometer-long nanocrystal, have attracted tremendous attention for more than half a century. They have shown the unique physical and chemical properties, which make them promising candidates in a wide range of applications, such as catalysis, electronics, optics, sensing, bioimaging and gene regulation. These properties can be tuned by controlling the structure size, shape and crystallinity, which have been considered as the ultimate goal in synthesis.

Metal nanoprisms are a novel class of anisotropic nanomaterials with exceptional optical properties dependent on their sizes, shapes, and compositions. Silver nanoprisms are of particular interest because their surface plasmon resonance bands are readily tunable in the visible and near-IR (NIR) region. The objectives of this thesis focus on synthesis of novel silver-nanoprisms-based nanostructure with better stability and functionality and to study their formation mechanism, optical properties, and their assembly strategies.

Therefore, it is desirable to develop novel strategies for the facile and efficient synthesis of silver-nanoprism-based nanostructures with controlled shape and size based on the knowledge of crystal growth mechanisms, and at the same time to explore new possibilities in obtaining structures with unusual properties. In order to achieve the mentioned goals, the following researches have been carried out.

First, a general wet chemical approach has been developed for the shape-controlled gold coating of silver nanoprisms. This method involves the controlled reduction of gold ions on the silver nanoprism (site-selective reduction) in a highly controlled reducing environment by slowly introducing chloroauric acid

and Hydroxylamine hydrochloride simultaneously into the Ag nanoprism solution with two separate tubes by using a mechanical syringe pump with specific concentration and infusion rate. By Engineering the total concentrations of HAuCl_4 using a seeding procedure and adjusting the process time, different gold coated silver nanoprisms with various morphologies have been obtained, including three unique structures, i.e. edge gold coated nanoprism ($\text{Ag}@$ Au-framed nanoprism), core-shell structure ($\text{Ag}@$ Au) and the triangular nanobox. All the aforementioned structures have better stability than bare Ag nanoprism due to the gold chemical inertness and have better localized surface plasmon resonance (LSPR) tunability. One of the main advantages of this protocol is that it can preserve the initial shape of the particles which is a key factor in preserving the optical properties for different applications.

The $\text{Ag}@$ Au structure has still single crystalline nature and can have sharp tips depend on the particle's initial morphology. The LSPR band of the $\text{Ag}@$ Au can be tune in a ~ 100 nm range with respect to its original LSPR which makes them good candidate in many application such as LSPR biosensing, bioimaging and energy conversion.

Second, the same gold coating protocol has also been applied to synthesize edge gold coated nanoprism ($\text{Ag}@$ Au-framed nanoprism) with ultrathin gold deposition on the edges of the nanoprism, upon etching of the silver template we achieved to synthesis surfactant-free high yield triangular gold nanoframe structure with sub-2 nm thickness. Despite previous reported ultrathin nanoframe structure which didn't show any specific LSPR band, this novel nanostructure show highly tunable dipole LSPR throughout visible or near-IR (NIR) region as a function of Au ridge thickness or interior pinhole diameter. The synthetic

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Lastly, the same gold coating protocol with some minor changes has also been applied to synthesize bimetallic nanobox with a proper integrity and uniformity, with preserving the initial triangular Ag nanoprism template. The challenge is to deposit gold atoms selectively on all facets of silver nanoprism to create a gold nanocage following by removing of silver part in the next stage and refilling the hole inside the created nanocage to make a perfect nanobox. The LSPR band of created core-shell nanoprism structures can be tuned in a wide range by controlling the Au shell thickness. On the other hand, the hollow cavity makes the encapsulation of materials of interest possible which candidates it for drug delivery, photothermal cancer therapy and other bioapplications.

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CHAPTER 1

INTRODUCTION

1.1 Background

Silver nanostructures such as Ag nanodots, nanocubes, nanorods, triangular prisms and nanowires have been receiving special attentions because of their unique physical and chemical properties. By tuning these properties through the control over their size, shape and crystallinity [1], Silver nanostructures have been explored in a wide range of applications, like electronics [2], optics [3], catalysis [4], sensing [5,6] and bioimaging [7].

Among those particles silver nanoprisms are more interesting nanoframe because of their interesting two-dimensional shape, high anisotropy and their unique and great LSPR sensitivity, but these nanoparticles suffer from instability and oxidation which limit their usage and applications.

During past decade, various methods have been investigated to prevent oxidation of silver nanoparticle by introducing a thin protective layer on outer surfaces of silver nanoparticles. Well-protected and very stable silver nanoparticles have been reported by Doty et al. by using poly(ethylene glycol) as capping ligand to produce spherical silver nanoparticles that can keep its stability even at high concentrated 1 M, NaCl solution. Since these capping ligands are uncharged and thus provide only steric stabilization, unfortunately this approach is not extendable to anisotropic structure or larger particles.

In another attempt Xue et al.[8] have introduced 16-mercaptohexadecanoic acid as a charged thiol for the stabilization of Ag nanoprisms against etching by amines during silica coating process. The SiO₂ shell can protect the Ag nanoprisms from etching, but the minimum thickness of silica coating needed for complete coating is ~10 nm and on the other hand the SiO₂ shell limits the usefulness of the nanoprisms because the silica shell will damp the nanoprisms' LSPR and as a result, the system becomes much less sensitive to change in the local environment which has drawbacks on the application of them.

Lee et al. [9] have shown that small spherical Ag nanoparticles can be protected against etching by chloride by utilizing oligonucleotides modified with three cyclic disulfide groups which can form a six thiol linkages in total to the silver surface. Unfortunately this approach isn't very practical as it is not easy and rather expensive to obtain significant quantities of such modified oligonucleotides. Besides, it has yet to be demonstrated that this approach can be extended to silver nanoprisms. For instance, there would be enhancement on electrostatic repulsion on flat surfaces between the negatively charged phosphate backbones of the oligonucleotides, thus this fact could cause some defect on surface coverage and leave some areas of the nanoparticle surface exposed to attack by chloride or any other etchants.

Coating of Ag nanoparticles with other noble metals such as Au, Pt, Pd has also been attempted.[10,11] Gold is an attractive and obvious choice because it is inert, thiol ligands bind strongly on it,[12] furthermore the small mismatch between Au and Ag (< 0.24% mismatch) plays an important role on conformational epitaxial growth of gold on silver.[13] However, coating silver nanoparticles with gold is not that straightforward due to galvanic replacement, a process whereby a metal is

deposited as a result of the reduction of relevant ions by another metal with a lower reduction potential. Galvanic replacement can easily happen for silver and gold ion due to their large electropotential difference. The standard reduction potential of the $\text{AuCl}_4^-/\text{Au}$ pair is 0.99 V versus the standard hydrogen electrode (SHE) whereas that of the Ag/Ag^+ pair is 0.80 V versus SHE.

For instance, hollow gold nanostructures such as nanoshells,[14-16] nanocages,[11,17-19] and nanorings, [20-24] can be produced by the consumption of sacrificial silver nanosphere, nanocube, and nanoprism templates by AuCl_4^- ions, respectively. There are many examples of coating of silver nanoparticles with a layer of gold for spherical nanoparticles [25-28] and for nanoprisms [29-31] although the few gold-coating reported for Ag nanoprisms are usually relatively thick or not uniform and can be quite rough and wavy.

One general strategy in the gold coating approaches for nanoprism is to engineer introduction of mild reducing agent to reduce the AuCl_4^- ion and thus avoid the oxidation of the silver. Here we carefully employ the Hydroxylamine hydrochloride-mediated approach to epitaxially and site-selectively deposit layer or layers of gold at Ag nanoprisms to make different nanostructures.

Taken together, due to the limitations of the previous reported synthetic routes, it is important to develop novel strategies for facile and efficient preparation of Ag-nanoprism-based nanoparticles with controlled shape and size (such as core-shell or nanoframe structure) based on the understanding of crystal evolution mechanisms, and at the same time to explore new possibilities to obtain structures with unusual physical and chemical properties.

1.2 Literature Review

1.2.1 Introduction to Ag Nanoprism

Ag nanoprism is nanometer scaled anisotropic particles with a triangular plate like morphology, where the two basal planes are commonly triangular in shape. From a geometric perspective, nanoprism is defined as flat, sharp triangular, truncated triangular, hexagonal, or even circular plates (disc) with large aspect ratios (Figure 1-1).[32] The Au or Ag nanoprism characteristically have edge lengths of 20 nm to 1 μm and thickness ranging from 5 to 50 nm. Nanoprism with edge lengths up to several micrometers have been reported, but they don't exhibit the chemical/optical properties similar to their smaller analogs.[33]

Silver nanoprism shows unique optical and chemical properties such as having of both sharp and tunable LSPR band (dipole and quadrupole peaks) which offers an interesting optical properties in the visible and infrared regions. On the other hand, the nanoprism's diverse and well-defined facets, creates an anisotropic chemical reactivity and catalytic properties. Combining these two physical and chemical properties made it a hot topic in many fields.

Fig.1-1. (A) Illustration of nanoprism dimensions, (B) A cartoon of nanoprism with indication of different faces on it (C) TEM image of nanoprism with a representative diffraction pattern for a single nanoprism (the [111] zone axis)

In principle, silver nanoprisms include three sharp tips (vertices) that play an important role in their chemical, optical and electronic properties.[34] The triangular shape facets of solution synthesized fresh nanoprisms are composed of atomically flat (111) crystal faces which makes them quite stable. Typically the edges of the nanoprisms are (110) or (100) facets, and high-resolution transmission electron microscopy (HRTEM) characterization proved that Ag nanoprisms have twin planes parallel to their flat (111) crystal facets.

The silver nanoprism have Surface Plasmon Resonance (SPR) that is tunable in both the visible and near Infrared (NIR) regions by adjusting nanoprism dimensions including edge length, thickness, or tips condition [35]. The Ag nanoprism solutions with varying edge length are shown in Figure 1-2b. The SPR is created by the coherent oscillation of conduction electrons at the surface of the nanoprism on all facets when the surfaces interact with the oscillating electric field of incident electromagnetic wave which is visible light in this case. The frequency of generated SPR depends on the density and effective mass of the elements' electrons, as well as the shape and size of the charge distribution.

Figure 1-2. UV Vis spectra (A) and corresponding solutions of nanoprisms (B) with different edge lengths. Nanoprism solutions which labeled with their irradiation wavelengths used to synthesized them.[36]

1.2.2 Why nanoprisms have this shape?

The triangular shape and two dimensional growths of Ag nanoprisms result from selective lateral growth of facets in the edges of the initial nucleus/seed. Due to the lamellar defect structure of Ag nanoprisms perpendicular to $\langle 111 \rangle$ direction, it is precisely at these edges where growth solution and ions interacts with the defects. Therefore the rearrangement of the crystal structure plays a critical role in two dimensional nature of nanoprism. During growth the hcp crystal layers (or in general any other regions with rich defects) at the edges of nanostructure must maintain high rate of silver atoms addition, in comparison to the other (111) or (100) facets existing in the structure. Since the hcp facets are not the natural facets for Ag nanostructure, it has less stability compared to fcc structure, so the edges containing hcp layer and exposed to the growth solution, have less stability in comparison to the (111) or (100) faces and this can cause the faster growth in two dimensional at the edges of Ag nanoprimis. The question remains to be explained is that why nanoprisms have triangular shape, and not hexagonal, as both fcc and hcp crystal nanostructures have a hexagonal symmetry.[37]

To answer the previous question we assume a flat, $\langle 110 \rangle$ oriented, fcc crystal as depicted in Figure 1-3A. It is proposed that a single fcc crystal can be cut in a way that opposite sides could have alternating (111) or (100) facets. That fcc crystal has six-fold symmetry perpendicular to the $\langle 111 \rangle$ axis, by this assumption the created hexagonal platelet could have the alternating faces as depicted in Figure 1-3B, now assume a more realistic hexagonal nanoplate (see Figure 1-3C) with different facets in each of its 6 edges which could be the consequences of the two dimensional growth from the initial seed.[37]

This implies that the defect-rich region (like hcp layer) sandwiched between two fcc regions (Figure 1-3C). The schematic is considered in such a way that the fcc regions on the sides of the central hcp region doesn't have same thickness, this thickness would define the facets type of the structure. It indicates that all the six edges of the nanoplate are not the same; three of them have a larger (100) facet area than the (111) face while the other three have a larger (111) facets than the (100) ones. [37]

Aherne et al. proposed that the three edges with the larger (111) faces will grow slower than the (111) facets, which is in consistent with the lack of growth on the big flat triangular shape (111) plane of the prisms.[37] On the other hand, the other three, with the larger and less stable (100) faces, will grow considerably faster, and create a triangular and not hexagonal shape nanoplate. Therefore, it can be proposed that the fcc thickness asymmetry on either side of the hcp layer defines triangular or hexagonal shape of the final crystal. [37]

After creation of a triangular shape, growth continues at the more stable edges with the smaller (111) faces, and as the result it opens up the preferred growth edges at the vertexes of the nanoprism for continual growth and since these preferred edges have faster growth, the final Ag nanoprism preserves the triangular shape, with both (111) and (110) growing in an aforementioned style.

It is good to mention that in crystals which there are thickness symmetry for the fcc layers on both sides of the hcp layer, instead of triangular nanoplates, hexagonal ones are expected as there aren't any 3 preferential growth direction. In our photomediated approach the yield of triangular nanoplates are more than 98 percent which indicates that many of the nanoplate seeds are not symmetrical.

Figure 1-3. A) Schematic illustrating a (110) oriented segment of fcc crystal. The edges of a crystal cut in this manner have alternating pairs of (100) & (111) faces. B) Schematic of a nanoprism constructed from a single fcc crystal (no twin planes or defects). C) Schematic of a nanoprism with a defect-induced hcp layer sandwiched between two fcc layers of unequal thicknesses. D) An example of internal structure of nanoprism with a defect-induced hcp layer.[37]

1.2.3 Optical properties of Metal Nanoparticles

The optical properties of nanosized particles are significantly different to those of the bulk material. Adsorption band in the visible region are present in the UV-visible spectrum of silver, gold and copper nanoparticles, but these bands are absent when the spectrum of the bulk metal is recorded. These bands, which are known as surface plasmon resonance (SPR) bands, are the result of an interaction of the conduction electrons of the nanoparticles with an electromagnetic field.

When a spherical nanoparticle is irradiated by light, the oscillating electric field induces the coherent oscillation of the conduction electron and this, results in a displacement of the electron cloud relative to the nuclei. Because there is columbic force of attraction between the electron and nuclei, the electron could oscillate relative to nuclear framework. The frequency of this oscillation is determined by four factors; the density of electrons, the effective electron mass, and the size/shape of the charge distribution. The collective oscillation of valence electron is called the dipole plasmon resonance of the particle; this process is depicted schematically in Figure 1-4.[33]

Figure 1-4. Schematic of plasmon oscillation for a sphere, showing displacement the conduction electron could relative to the nuclei.

In 1908, Mie presented a solution to the Maxwell equation that describes the extinction spectra of spherical particles of arbitrary size. This theory is the only simple exact solution to Maxwell equation that is relevant to particles and remains of great interest till today. The extinction coefficient is taken as the sum overall electric and magnetic multipole oscillation contributing to the absorption and scattering of the interacting magnetic field. This is the simplest theoretical model and is given by the equation:

$$k = \frac{18\pi NV \varepsilon_m^{\frac{3}{2}}}{\lambda} \frac{\varepsilon_2}{[\varepsilon_1^2 + 2\varepsilon_m^2]^2 + \varepsilon_2^2}$$

where V is the volume of the nanoparticles, k is the extinction coefficient, N is the number of particles, λ is the wavelength of the absorbing radiation and ε_m is the dielectric constant of surrounding medium. The ε_1 And ε_2 represent the real and imaginary parts of the material dielectric function, respectively. As mentioned earlier surface plasma wave (SPW) or a surface plasmon-polariton is an electromagnetic wave which propagates along the boundary between a metal and a dielectric and behaves like quasi-free electron plasma as depicted in Figure 1-5. The surface plasma wave is a transverse-magnetic wave (magnetic vector is parallel to the plane of interface) and is characterized by the electromagnetic field distribution and propagation constant.[38] The propagation constant (β), can be formulated as:

$$\beta = \frac{\omega}{c} \sqrt{\frac{\varepsilon_M \varepsilon_D}{\varepsilon_M + \varepsilon_D}}$$

where c is the speed of light in vacuum, ω is the angular frequency, and both ε_M and ε_D are dielectric functions of the metal and dielectric, respectively. If the real part of ε_M is negative and its absolute value is smaller than ε_D , this equation can

depict of a SPW. In visible wavelengths, this condition is satisfied for several metals such as Cu, Au and Ag which are well-known in SPR systems. The real and imaginary parts of the propagation constant explain spatial periodicity and attenuation (in the direction of propagation) of an SPW, respectively. [38]

Figure 1-5. A Schematic of propagation direction of SPW at the interface. [38]

The SPR's electromagnetic field is confined at the metal–dielectric boundary and decreases exponentially into both metal and dielectric media (see Figure 1-6). For an SPW at the boundary between gold film and a dielectric with a refractive index of 1.32 the penetration depth into the dielectric is approximately between 100–500 nm. Penetration depth is the distance at which the amplitude of the field falls to $1/e$ of its value at the metal surface. [38]

Figure 1-6. Distribution of the magnetic field intensity at the gold-water interface in the direction perpendicular to the interface calculated at 630 and 850 nm wavelengths. The refractive index of water assumed as 1.32.[38]

1.2.4 Recent methods to synthesize Ag@Au

Recently preparation and characterization of colloids of bimetallic nanoparticles constituting various combinations of noble metals was the subject of numerous researches around the world. Nanoparticles composed of free-electron-like metals such as Ag and Au are known to provide strong resonance optical responses to irradiation, which result in amplification of light-induced processes undergone by molecules localized on their surfaces, such as Raman scattering, giving rise to Surface enhanced Raman scattering (SERS) [39]. Optical properties of bimetallic nanoparticles comprised of Ag and Au are thus the subject of considerable research and interest.

Bimetallic core shell Ag@Au, as defined, are nanoparticles which consist of an Ag nanoparticle core enclosed by a shell of Au. Various means of synthesizing such particles had been surveyed, via radiolytic [40,41], chemical reduction [42] or a combination of the both mentioned [43,44].

Strategies of AgAu nanoparticle preparation are based on reduction of the metal salts by radicals produced by pulse radiolysis as well as by chemical reductants. Since Ag and Au are miscible in all proportions, but differ in both redox potentials and surface energies, the results of a particular preparative strategy with respect to formation of either the alloyed or layered nanoparticle composition are not always readily predictable, and characterization of the composition of the resulting nanoparticles is thus of key importance[45].

Freeman et al [44] and Morriss and Collins [46] prepared nanostructures consisting of gold core and silver shell. Mulvaney et al.[40] deposited gold onto radiolytically prepared silver seeds by irradiation of KAu(CN)_2 solution, Treguer

et al prepared layered nanoparticles by radiolysis of mixed $\text{Au}_{(\text{III})}/\text{Ag}_{(\text{I})}$ solution. Silver colloid with gold reduced in the surface layer was prepared by Chen and Nickel by mixing a solution of HAuCl_4 with Ag colloid and addition of a phenylenediamine as reductant in the second step. A two-step wet radiolytic synthesis resulting in a size-dependent spontaneous alloying within Au-core and Ag-shell nanoparticles and a photochemical approach to Au-core Ag-shell nanoparticles preparation were recently reported.[47]

Particles with a silver core and alloyed shells had also been derived as a result of reduction processes conducted at a higher temperature (100°C).[47] Template based methods of using a sacrificial metal nanoparticles to generate hybrid and hollow structures exists as well, through the galvanic replacement reaction of Ag by a chloroaurate ions [20,48].

Very few methods have been developed for making core-shell anisotropic structures, especially silver nanoprism. Lately Sanederin et al have reported a protocol [29] for making a bimetal core-shell structure using silver nanoprism as core. In their method Ag nanoprism seeds were added to growth solution containing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, cetyltrimethylammonium bromide (CTAB), L-ascorbic acid and sodium hydroxide. As in the Sanederin protocol the rate of reaction and temperature and other parameters such as concentration of reagents and pH are not controlled or well optimized, the triangular shape of prism is not preserved and a large amount of truncation and large amount of pseudo-disc shape particles can be seen as it is depicted in Figure 1-7.

In this approach the role of CTAB is quite significant. Recently it has been proposed that the surfactant molecules potentially bind to specific crystal faces

and prevent etching of these surfaces by Au ions. After the whole surfaces such as (110) and (100) fully covered by gold atoms, the additional gold atoms can overcome the surfactant and first layers of gold film deposit on (111) faces, as in this stage the surface is not atomically flat like bare Ag nanoprism and growth of next layers of gold will be accelerated and makes core-shell structure.

Herein, in this PhD program we have used another mild reducing agent and controlled the key factors such as concentration of reagents, infusion rate, temperature and stirring rate to have a well-shaped triangular core-shell structure with a fully gold coated surface on silver nanoprism without using of surfactant and just by changing the aforementioned parameters. It is good to mention that even the small concentration of BSPP is removed by three times washing of nanoparticle with water and ethanol to be sure the final structure are surfactant free and can be freely use for any bioapplication.

Figure 1-7. TEM images of (A) triangular and (B) corrugated AgAu core-shell nanoparticles with $\text{Ag}^+/\text{Au}^{3+}$ ratio of 1:5 and 1:33, respectively. The inset is the respective magnified images. [9]

1.2.5 Introduction to gold Nanoframes (NFs)

Hollow nanostructures are an interesting promising category of materials which help us to better realize the structure-property relationship.[16,49-51] Although a considerable amount of work has already been done in developing synthetic approaches for hollow spherical particles, rods and cubes, [15,49,52] little work has been published for triangular nanoplates/nanoprisms.

Me'traux et al [20] have shown how one can chemically convert triangular nanoprisms into semi-triangular nanoframes in a face selective manner. They found that with galvanic replacement reaction of silver and gold triangular two-component nanostructures with filled or partially filled cores can be generated.

Figure 1-8 shows the schematic of formation of the nanoframes in two main steps. It is investigated that during the formation of these nanoframes the LSPR spectra of the particles randomly red-shifts and optical density decreases. The trend of UV-Vis spectrum of the nanoframe solution is outlined in figure 1-9a. Effects of variation of gold to silver ratio are also investigated in figure 1-9b-d.

Interestingly Me'traux et al found that after formation of nanoframes by introducing a mild reducing agent the silver and gold can be reduced back (refilled or back-filled) to the interior wall of the gold nanoframe and make nanoprism again although it is in low yield. The amount of the refilling process can be controlled which leads to form novel prisms with nanopores. This back-filling process is accompanied by regeneration and changes of the localized surface plasmon resonance (LSPR) bands in the UV-vis spectrum as depicted in figure 1-10. The back-filling can be used to tune the LSPR band of the nanoparticles and make it a good candidate for many applications.

Figure 1-8. In step A, HAuCl_4 etches silver nanoprisms, following by addition of L-ascorbic acid in step B, which causes gold and silver ions in solution to crystallize on the inner part of the nanoframes ridges and shrink the pore size. This steps A+B can be repeated to reduce the size of the central pore gradually.[20]

Figure 1-9. AuAg nanoframes. (A) UV-vis spectra of triangular nanoframes with varying Au/Ag ratios. I: Silver nanoprisms; II: Au/Ag=1:9; III: Au/Ag=1:5; IV: Au/Ag=1:3. (B-D) TEM images of gold-silver nanoframes. (B) Au/Ag=1:9;(C) Au/Ag= 1:5; (D) Au/Ag=1:3. Scale bars: (B, D) 100 nm;(C) 125 nm.

Figure 1-10. UV-Vis spectra and TEM images examining the refilling process of Au/Ag=1:9 nanoframes. (A,D) After the addition of L-ascorbic acid to triangular nanoframes. (B,E) After two cycles and (C,F) After three cycles of HAuCl₄/L-ascorbic acid. Scale bars: (D, F) 100 nm; (E) 125 nm.

1.2.6 Introduction to bimetallic Nanobox

Noble-metal nanocages and nanoboxes comprise a novel class of nanostructures possessing hollow interiors with porous and semi-porous walls, respectively. They can be prepared using a simple galvanic replacement reaction between solutions containing metal precursor salts and Ag nanostructures. The electrochemical potential difference between the two metal species drives the reaction, with the reduced metal depositing on the surface of the Ag seed. The most studied example, involving HAuCl_4 as the metal precursor, the resultant Au is epitaxially deposited on the surface of the Ag nanostructure, adopting their underlying shape form. Concurrent with this deposition, the interior Ag is oxidized or etched and removed, together with alloying and dealloying, to produce hollow and, eventually, porous or semi-porous structures that we commonly refer to as Au nanocages or nanoboxes. [53]

This approach is applicable for a wide range of morphologies available upon changing the shape of the initial Ag seed. Examples of such morphologies are mentioned in Figure 1-11 and 1-12 briefly. In addition to gold-based structures, switching the metal salt precursors to Na_2PdCl_4 and Na_2PtCl_4 allows for the preparation of Pd and Pt-containing hollow alloyed nanostructures, respectively. As mentioned earlier the galvanic replacement reaction represents a simple means of preparing bimetal or multimetal hollow nanostructures. The electrochemical potential difference between two metals drives the reaction, with one serving as the cathode and the other as the anode. The classic example is of a zinc strip in a solution containing Cu^{2+} ions. Because the Zn^{2+}/Zn reduction potential is more negative than the Cu^{2+}/Cu potential (-0.76 and 0.34 V vs the standard hydrogen electrode SHE, respectively), Zn is oxidized to Zn^{2+} while Cu^{2+} is reduced to Cu.

Figure 1-11. (A) SEM of Ag nanocubes; electron diffraction (inset) indicates that they are single crystals. (B) SEM of particles after 0.30 mL of 1 mM HAuCl_4 solution was added to a 5 mL 0.8 mM initial Ag nanocube solution; a pinhole (lower inset) is observed on the exposed face of ~ 1 in 6 nanocubes and TEM (upper inset) of a microtomed sample reveals early hollowing. (C) SEM of particles after 0.50 mL of HAuCl_4 solution was added; TEM (inset) of a sample shows the hollow interior of the nanobox. (D) SEM of particles after 2.2 mL of gold salt solution was added; porous nanocages were fabricated. (E) The scheme sums up the morphological changes, the coloration points out the conversion of a silver nanocube into a Au/Ag nanobox then a Au nanocage.[53]

This phenomenon is extendable to other systems; the metal strip can be replaced with metal nanostructures. Regarding the preparation of gold-based nanocages, the reduction potential of $\text{AuCl}_4^-/\text{Au}$ (0.99 V vs SHE) is more positive than that of AgCl/Ag (0.22 V vs SHE). Thus, Ag nanostructure can serve as a template for reaction, being oxidized by HAuCl_4 according to;

Figure 1-12. A-B) TEM images of edge-oriented triangular AuAg nanoboxes prepared without sufficient reducing agent to reduce the entire added HAuCl_4 different sample. C) A schematic image shows a side view of a typical growing AuAg nanobox which illustrates the manner of growth of triangular, hollow AuAg nanoboxes from Ag nanoprisms.

The produced Au is confined to the template shape, growing on it and adopting the template morphology, as interior Ag is oxidized to produce a hollow structure. In principle, this Ag template-engaged replacement reaction can be applied to any metal whose redox potential is more positive than the AgCl/Ag pair.

1.2.7 Objectives and Scope

Due to the great properties and huge application of Ag nanoprism and the limitations of current stabilization methods, this project aims to develop novel strategies for facile and efficient preparation of stable and shape-controlled silver-nanoprism-based nanostructures.

Silver-nanoprism-based nanostructures with controlled shape and size are synthesized based on the understanding of crystal evolution mechanisms, and at the same time we explored new possibilities to obtain structures with unusual physical and chemical properties.

In order to achieve the objectives mentioned above, the following works are carried out in this project: first, a novel wet chemical approach with controlled reducing power (by varying experimental conditions) is used to introduce gold on specific facets of Ag nanoprism; second, by discovering the mechanism of the process previous approach is used to make triangular nanobox structure; lastly, a facile method is developed to synthesize sub-2 nm Au nanoframe. The synthesized structures are characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) in order to analyze their morphologies, crystal structures and chemical compositions.

1.2.8 Short Summary

In this section, the properties and synthetic methods of anisotropic nanoprism based structures (Including core-shell, nanoframe and nanobox structures) have been briefly reviewed. Some of the current synthetic routes have shown limitations, such as low morphology control, multiple steps, long reaction time, and high reaction temperatures for the core-shell structure. Hence, facial and efficient methods with the good controllability over the shape and size of final structure are desirable and require continuous development. In addition, we further optimized the gold coating protocol in order to use the same setup and parameters to produce different nanostructures (e.g. triangular nanoframe structure

and triangular nanobox/nanocage) with different optical, catalytic and electronic properties.

Chapter 2

Experimental Details

2.1 Chemicals and Materials

Silver nitrate (99%), Tetrachloroauric acid (99.5%), sodium borohydride (99%), trisodium citrate dihydrate (99%), polyvinylpyrrolidone, hydrogen peroxide, 30 wt% (99.999%), Ammonium hydroxide solution (28% NH_3 in H_2O , $\geq 99.99\%$), Hydroxylamine hydrochloride (99%), Bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium (BSPP), sodium hydroxide ($>97\%$) were supplied by Sigma-Aldrich and were used without further purification. All glassware was washed with Aqua Regia, $\text{HCl} : \text{HNO}_3 = 3:1$ (v:v), and rinsed with ethanol and Milli-Q water (CAUTION: Aqua Regia is a very corrosive oxidizing agent which should be handled with great care). Ultrapure Milli-Q water (Milli-Q System, Millipore, Billerica, MA, USA) was used in all the experiments.

2.2 Silver nanoprism synthesis

2.2.1 Silver nanosphere synthesis

In our typical synthesis, Millipore water (190 mL), sodium citrate (2 mL, 25 mM) and AgNO_3 (1 mL, ~ 30 mM) were mixed in a 500-mL three-neck flask. The three-neck flask was immersed in an ice bath at 0°C for an hour, and the water was bubbled with nitrogen gas under vigorous stirring for 30 minutes. One milliliter of freshly prepared NaBH_4 (70 mM, prepared with ice-cold water) was quickly injected into the flask. In the next 30 min, 5-10 drops of the NaBH_4

solution were added every 2 min into the solution. In the next step 1 mL solution of BSPP solution (5 mM) plus 1 mL NaBH₄ solution were added dropwise into the reaction mixture in the flask. The mixed solution of Ag nanoparticles was stirred in slower rate for another 3 h in the ice bath container and then allowed to age overnight at about 4 °C at refrigerator in the dark.

2.2.2 Photomediated approach to synthesis Ag nanoprism

20 mL of Ag nanoparticle solution was irradiated with a 150 W halogen lamp coupled with an optical bandpass filter centered at 500 ± 20 , 600 ± 20 or 660 ± 20 nm. The irradiation was observed carefully by UV-vis spectroscopy in certain time period, and stopped when the major extinction band (dipole spectra) did not show any more obvious changes.

2.3 Wet chemical gold coating process

2.3.1 Preparation of setup

Setup was prepared as follows: a 100 ml glass vial placed on an ice bath basin under vigorous stirring. The entire basin is wrapped up by Aluminum foil and the experiment is done under low light intensity. The two tubes connected to a syringe pump are adjusted in a way that the droplet of each tube mixed inside the 100 ml glass vial.

2.3.2 Shape control gold coating of silver nanoprism

The as-prepared Ag nanoprism solution in section 2.2.2 (20 mL) was added into 20 mL of ultrapure water in a glass vial. The glass vial placed in an ice bath and the solution is under vigorous stirring. It was followed by infusion of up to 4 mL

solution of 5.7 mM HyA and up to 4 mL solution of 0.27 mM HAuCl_4 into the solution with two separate tubes. In order to have a good accuracy we used a programmable mechanical syringe pump. The infusion rate of the reagents was set as 1 or 3 ml per hour depends on the stage of the gold coating. Basic HyA solution (in the table below) is prepared by adding 200 μL NaOH (0.5 M) into 6 mL as-prepared HyA solution. The synthetic route has 4 different stages as summarized in table 2-1.

Stage name	Duration [Min]	Infusion Rate [ml/hr]	Reducing agent	[HAuCl_4] [μM]
1	0 to 30	1.0	Normal HyA	270
2	30 to 120		Basic HyA	
3	120 to 135	3.0	Normal HyA	810
4	135 to 190	1.0	3x Norma HyA	

Table 2-1. Different experiment stages of the gold-coating process.

2.4 Triangular nanoframe synthesis

2.4.1 Synthesis of Ag@Au-framed nanoprism

To 20 mL of Millipore water in a glass vial, 12.5 mL of Ag nanoprism solution were added. This was followed by infusion of 4 mM $\text{NH}_2\text{OH}\cdot\text{HCl}$ (HyA) and 0.27 mM HAuCl_4 by two separate tubes with mechanical syringe pump upon vigorous stirring of solution in the glass vial with 2 ml/hour of injection during process. After 5 min. basic HyA solution is used to enhance the reducing power and deposition rate for another 10 min. Basic HyA solution is made by mixing 6 ml of as produced HyA with 200 μL of 0.5 M Sodium hydroxide.

2.4.2 Gold/Silver alloy frame formation by $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$

To 6 mL of as-synthesized Ag@Au-framed nanoprism in a 20 ml glass vial with maximum stirring rate 0, 50, 100, 150, 300, 500 and 900 μL of mixture of $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ are introduced respectively in a dropwise manner. The concentration of H_2O_2 and NH_4OH are adjusted as 50 mM in an equal volume ratio. After reaching each of these 6 values the solution kept for 20 min to reach the stable condition and UV-Vis spectroscopy of the solution is done.

2.4.3 Gold/Silver alloy frame formation by gold salt etching

To 8 mL of as-synthesized Ag@Au-framed nanoprism in a 20 ml glass vial with maximum stirring rate 0, 50, 100, 150, 300, 500 and 900 μL of gold salt added dropwise. After reaching each of these 6 values the solution kept for 20 min to reach the stable condition and UV-Vis spectroscopy of the solution is done.

2.5 Triangular nanobox synthesis

2.5.1 Synthesis of Ag@Au-framed nanoprism

This process is exactly the same as part 2.4.1.

2.5.2 Gold/Silver alloy nanobox formation by gold salt etching

To 8 mL of as-synthesized Ag@Au-framed nanoprism with maximum stirring rate (at 80 min according to part 2.3.2) in a 20 ml glass vial, 10, 20, 30, and 40 μL of gold salt added dropwise in 10 min. After reaching each of these 4 values the solution washed 3 times with ethanol and acetone and redispersed in water, in next step the solution kept for 20 min to reach the stable condition and UV-Vis spectroscopy of the solution is done.

2.6 Self-assembly of the Nanoprism-Based Nanoparticles

2.6.1 Preparation of amine-terminated substrates

15x15 mm glass microscope slides or quartz slides were pretreated with Boiling Piranha solution ($\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4, 1:3, \text{v/v}$) for 2 hours and washed and then immersed in a 2-propanol solution of 1% 3-aminopropyltrimethoxysilane in the presence of 0.1% acetic acid for 1 h. The modified substrates were rinsed with pure ethanol three times prior to use. The substrate immersed in particles solution for 6-24 hours (depends on the required particles density on the substrate) and after it is carefully rinsed with pure water and ethanol three times prior to UV-Vis measurement and polymer blend coating.

2.7 Characterizations

2.7.1 Scanning Electron Microscopy (SEM)

Field Emission Scanning Electron Microscopy FE-SEM was done with a JEOL JSM-6700 field emission scanning electron micro-analyzer. All samples were deposited on Si/SiO_x substrates, dried naturally, and imaged with an accelerating voltage of 5 keV.

2.7.2 Transmission Electron Microscopy (TEM)

All samples were prepared by drop casting. Simply the solution containing the particles is used and a droplet of such nanoprism-based nanoparticles solution dried on a carbon-coated copper grid or a SiO₂-supported TEM grid (Ted Pella, Inc.). For flat-lying nanoprisms, the TEM grid was pretreated with ~0.05 wt% solution of polyethylenimine (PEI) prior to drying of the particles solution on the surface of the grid. For standing nanoprisms (vertical), the nanoprisms were

washed 3 times with acetone and ethanol and then re-suspended in ultrapure ethanol before deposition and drying on the TEM grid.

TEM measurements were performed on JEOL JEM-2010 or JEM-2100F TEM at an operation voltage of 200 kV for both. The HAADF-STEM imaging was carried out on a FEI Titan TEM with a Schottky electron source with an operation voltage of 200 kV. The electron probe diameter is measured as 0.2 nm approximately for the HAADF-STEM images. The EDX measurements were taken by using a probe with diameter of ~ 0.5 nm with acquisition time of 5 seconds for every spectrum.

2.7.3 X-Ray Photoelectron Spectroscopy (XPS)

For XPS, samples were transferred to an analysis chamber equipped with an X-ray photo-electron spectrometer (Thermo Fisher Scientific Theta Probe). Theta probe XPS sputtering rate (based on TaO_2) was 2.7 nm/min according to sputtering condition of 3 KeV, 1 μA and working area of 4 mm $\times$ 4 mm. An Al K_α (1486.5 eV) anode with a power of (15 kV) 100 W was used. XPS spectra were gathered using a hemispherical energy analyzer operated at pass energy of 20.0 eV for elemental analysis.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Gold coating of silver nanoprism

3.1.1 Introduction

Shape-controlled nanostructure synthesis of noble metals, such as silver and gold in particular, has attracted great attentions in recent years because of their unusual useful optical properties known as localized surface plasmon resonance (LSPR),[32,33,54,55] as well as their novel chemical,[56] electronic,[57] and catalytic properties.[58] Thereby a broad range of intriguing applications emerge in the field of photonics,[59] catalysis,[60] biological and chemical sensing,[56,61] surface-enhanced Raman scattering (SERS),[62,63] metal-enhanced fluorescence (MEF),[64-66] and energy conversion.[67,68]

The need to synthesis nanoparticles (NPs) with finely tuned LSPR has therefore led to vast research efforts on developing reliable routes to synthesize noble metal NPs with controllable shapes, sizes and compositions. In order to modify the NPs properties and improve their performance for different applications, researchers have developed many wet chemical methods for generating Ag and Au nanocrystals with a rich variety of isotropic on anisotropic shapes, including sphere,[69] rod,[70] wire,[71] prism,[35,72] cube,[73] octahedron,[74] decahedron,[75,76] icosahedron,[73,76] and bipyramid.[77]

Composite nanomaterials like core-shell structures (Ag@Au) are attractive, since it can provide significant plasmon tunability, hybrid chemical and surface modification properties and functionality, and also it provides an insight into the

growth of anisotropic nanostructures. These properties make them excellent testbed for both fundamental studies and technological advances in many fields.

Bimetallic AgAu nanocrystals are particularly attractive because they have broad range of plasmon tunability and adaptable surface functionalities as compared with the individual unit of Ag or Au nanocrystals. By combining Ag and Au nanocrystal into core-shell structures, their LSPR signatures can be controlled by not only varying the size and shape of the core but also the shell thickness and composition.[33,78] The close lattice match between Au and Ag ($< 0.3\%$ mismatch) plays a key role in achieving conformal epitaxial growth. For example, Au@Ag core-shell nanocrystals (Au-core Ag-shell) with various morphologies have been synthesized through an epitaxial growth process involving uniform Ag deposition on the surface of Au seeds.[79,80]

To date, Au@Ag core-shell nanocrystals with various morphologies have been synthesized and introduced using an epitaxial growth process that involves conformal deposition of Ag atoms on the surface of Au seeds, for instance, Xue et al. synthesized Au@Ag core-shell nanoprisms by using Au nanoprisms as templates with wet chemical [81] and also photoconversion process[79], Xia et al reported a facile approach for creation of Au@Ag core-shell nanocubes with controllable edge [82], Tsuji et al. and Wang et al. demonstrated the seed-dependent evolution of shape for Au@Ag core-shell structures with diverse morphologies [80,83], and Fan et al. synthesized Au@Ag nanocubes by using gold octahedra as template [84] but until now, the formation of triangular Ag@Au nanostructure from Ag nanoprism template has remained very elusive and there are just few case of non-uniform Ag@Au core-shell nanocrystals reported , this lack is due to difficulties and challenges of having a conformal shell on the Ag

nanoprism surface and also instability, catalytic oxidation and truncation of the silver metal structure and particularly Ag nanoprism during the coating process.

On the other hand, Ag@Au core-shell structures have complex optical features spanning the visible and near infrared regions; they show low toxicity and exhibit facile surface functionalization chemistry. It has been proved that co-operative and synergistic interactions between the metallic components could lead to an overall more helpful functionalities [26,85]. Therefore recently, extensive efforts have been devoted to the synthesis of more complex structures, such as core-shell or hollow NPs. Due to their increased surface areas, reduced densities, and their more functionality and tunable SPR features, these new class of nanostructures are expected to outperform their solid counterparts.

As discussed earlier, the formation of a structure with Ag core and Au shell remains challenging due to the significant etching of Ag cores by gold salt precursors, which is known as galvanic replacement and typically creates nanoframes,[20] or hollow nanoboxes,[86] or other irregular nanoparticles with random optical responses. The galvanic etching is quite serious when the seed is an ultrathin silver prism (<7 nm), and the tips are so vulnerable to oxidation and the flat (111) faces tend to be preferentially etched through the galvanic process. For example, by seeding with Ag nanoplates, Zou et al. produced bimetallic AgAu nanostructures with non-uniform gold coating or hollow structure.[31] Sanderin et al reported rounded-tip triangular Ag@Au core-shell structures with corrugated gold shells by using cetyltrimethylammonium bromide (CTAB) as the surfactant.[29] However, the presence of CTAB can't avoid severe tip truncation of Ag prism. More seriously, the strong passivation of gold shell surfaces by CTAB induces tremendous difficulties when further surface modification is

needed for application purposes. Although the vulnerability of these ultrathin nanostructures makes the shape-controlled gold-coating process really challenging, the targeting nanostructure with Ag nanoprism core and controllable Au shell thickness is very attractive since the SPR wavelength of Ag nanoprisms can be finely tuned in the entire visible spectrum and even part of near-IR range. The ideal gold coating provides much better stability and allows the full functionalities of gold surfaces that enable broad applications.

Herein we report a facile method of gold coating of silver nanoprisms while retaining the shape of triangular Ag nanoprism (Scheme 4-1). Electron microscopic analysis is used to confirm the formation of Au layers on all facets of Ag nanoprism seeds, which leads to a core-shell structure preserving optical features of Ag nanoprisms and offers better stability against oxidation and versatile functionalities as compared to bare Ag nanoprisms. We also systematically investigate how different parameters, such as pH, concentration and infusion rate, influence the gold coating process.

Scheme 3-1. Schematic illustration of gold-coating of silver nanoplates with triangular and hexagonal shapes.

3.1.2 Gold-Coating of Silver Nanoprisms

In the present work, our major goal is to utilize readily available reagents to coat Ag nanoprisms with a favorite thickness layer of gold with preserving prism triangular shape and minimizing the Ag prism etching by gold precursor ions (AuCl_4^- and AuCl_2^-). Here we use a simple but optimized seed-mediation approach that involves hydroxylamine (HyA) to reduce the gold salt.

The reaction is designed to be very mild to ensure epitaxial gold growth on Ag nanoprism and on the other hand to guarantee the reduction of gold salts only occurs on the surface of Ag nanoprism seeds while avoiding spontaneous nucleation of gold NPs in the solution. Besides, it is notable that HyA exhibits very little etching on silver and gold nanocrystals comparing with other mild reducing agents such as ascorbic acid which has been reported to demonstrate etching on silver and gold such as Ag nanoprisms,[87] and gold nanorods.[88]

In our method the gold coating process was carried out by slowly introducing HyA and HAuCl_4 simultaneously into the Ag nanoprism solution through two separate tubes with an accurate syringe pump. During the entire process, the solution was kept under vigorous magnetic stirring. The synthetic route has 4 different stages as summarized in Table 3-1. Since the reducing power of HyA is enhanced at higher pH,[31] in stage 2 we introduced certain amount of NaOH into hydroxylamine solution to increase pH in order to enhance the gold deposition rate and avoid etching. As the LSPR bands of gold and silver NPs are highly sensitive to the changes of their size and shape, we tracked and evaluated the structural changes during the coating process based on their extinction spectra with Ultraviolet–visible (UV-vis) spectroscopy.

Stage	Duration of stage[Min]	Rate [ml/hr]	Reducing agent	[HAuCl ₄] [mM]
1	0-30	1.00	Standard NH ₂ OH.HCl	0.27
2	30-120		Basic NH ₂ OH.HCl	
3	120-135	3.00	Standard NH ₂ OH.HCl	0.81
4	135-190	1.00	3x Standard NH ₂ OH.HCl	

Table 3-1. Different stages of the gold-coating process.**3.1.3 Explored factors for optimization of gold-coating process**

The main parameters used to achieve optimization of gold coating process. It consists of control over of etching damage, by delaying and also reducing its effects by different methods such as dilution of reagent and/or increasing the reducing power in the certain stages. Besides, to control the deposition reaction, increasing the reduction power of NH₂OH·HCl for better backfilling of etched cores can be effective (not mentioned here). Obviously the initial nanoprism condition can definitely affect the final product so using fresh prism with as less as possible amount of truncation is also considered to optimize the process.

3.1.3.1 Temperature

It is noticed in the experiments that samples which are tested in ice bath at ~0 °C have more uniform shape and the degree of etching is much less than experiments done in ambient temperature as it is illustrated in Figure 3-1. In addition in low temperature the reaction rate is slower so etching of (111) faces and also growth of the gold shell can be controlled more accurately in this way.

3.1.3.2 Rate of Injection

Our experiments showed that to have a uniform coating of gold on the surfaces of silver particles, it's required to control the amount of reagent's injection to the

Figure 3-1. TEM images of Ag@Au at 120 min (a) 0°C in ice bath and (b) at ambient temperature.

solution very precisely to control the kinetics of the process. Adding of reagent is done by pipette or burette initially. In both cases we found that we need a more precise instrument to control the quantity of both reagents separately and very accurately. Finally, using syringe pump with minimum infusion rate of 1.459 $\mu\text{L/h}$ and accuracy of $\pm 1\%$ helped us to control this factor. In our method we use two different rates of injection in different stages of synthesis (see table 3-1).

Another parameter which affects the experiment kinetics is the stirring rate of the solution. We have tried 500, 1000 and 1400 rpm and found that the highest stirring speed results in better homogeneity in morphology. This stirring rate is considered for all the gold coating experiments reported in this thesis.

3.1.3.3 AuCl_4^- Concentration

We observed that with a higher $[\text{AuCl}_4^-]$ used, a greater level of etching damage is observed on the Ag prism (111) faces. When $[\text{AuCl}_4^-]$ is further increased, the entire triangular plate structure may be even etched completely. This is the reason we carefully optimized the AuCl_4^- concentration in our seed growth process. So the etching of the Ag nanoprism was delayed by using diluted HAuCl_4 , as it can be seen in Figure 3-2b and c.

Figure 3-2. TEM images of silver nanoprism after 120 min injection of (A) 1 ml of HAuCl_4 without Hydroxylamine. (B) 2 ml of HAuCl_4 and Hydroxylamine according to a reported method.* (C) 2 ml of HAuCl_4 and Hydroxylamine according to our optimized concentration of reagents.**

* Literature $\text{NH}_2\text{OH}\cdot\text{HCl}$ and HAuCl_4 concentration used is 6.25 and 0.465 mM respectively.[27]

** Optimized $\text{NH}_2\text{OH}\cdot\text{HCl}$ and HAuCl_4 concentration used is 5.7 and 0.27 mM respectively.[89]

3.1.3.4 Concentration of Silver Nanoprism

It is observed that when the initial optical density of the Ag prisms is around 0.6, (quantified by the intensity of the extinction peak of the prisms used for coating), the drop in the in dipole Plasmon (LSPR) of the Ag nanoprisms is slower. Therefore by using high concentration of Ag nanoprism, etching effect is appeared to be delayed and reduced. The above trends suggest that both a lower AuCl_4^- concentration and an increased initial Ag nanoprism concentration lead to a better controlled etching. This may be result of the galvanic replacement reaction being intensified when the anodic species (Ag^0) is small compared to the cathodic species (AuCl_4^-). This effect is already seen in the epitaxial deposition of prisms studies where etching damage becomes apparent at a higher $\text{AuCl}_4^-/\text{Ag}$ ratio.

3.1.3.5 Increasing deposition rate by using basic HyA

The use of basic $\text{NH}_2\text{OH}\cdot\text{HCl}$ to accelerate of deposition reactions operates by driving the reaction equilibrium to the right in the presence of higher concentration of OH^- ions via an increase in pH.

Experimentation with the use of basic $\text{NH}_2\text{OH}\cdot\text{HCl}$ as the reducing agent during 30–120 min. of seed growth showed that the main extinction peak red shifted and dampen at a lower rate compared to a seed growth using the standard $\text{NH}_2\text{OH}\cdot\text{HCl}$ reducing agent as depicted in Figure 3-3, as illustrated in blue curve the increase in absorbance and blue-shift after the initial damping of the peak is also faster which indicate more change in morphology which is not favorite. In TEM analysis of Figure 3-4 it is noticed that by using basic HyA solution the etching problem can be minimized.

Figure 3-3. Effect of pH of HyA solution on the extinction band of the Ag colloid.

Figure 3-4. TEM images of gold coated silver nanoprism at 60 min (A) by using basic Hydroxylamine hydrochloride. B) By using normal Hydroxylamine hydrochloride. Reducing agent syringe changed to syringe prepared with 5ml of 5.34mM Hydroxylamine +250 μ l of 0.5M NaOH.

3.1.3.6 Quality-control of Ag nanoprisms

Use of prisms immediately after photoconversion; It is known that Ag nanoprisms are not stable on its own even in the dark, and is prone to truncation or rounding of the tips even at presence of BSPP, which also has a dual role as a capping agent and a silver solubilizer. Hence, to avoid the effects of truncation in the dark and to preserve the triangular shape morphology of the prisms, they are immediately used for coating experiments after photoconversion. Aged Photoconverted nanoprism is tending to truncation which it introduces other factors to the gold coating process and makes the process more complicated.

Use of dual staged photoconverted prisms; The Ag prisms synthesized via the dual staged irradiation process (yielded green colored prisms), are found to be exhibit longer edge length, mainly sharp tipped prisms with less truncated tips, as compared to single wavelength irradiated prisms. Furthermore diversity in size of this green prism is much less than single wavelength irradiated prism which is purple in color. The main reason for less diversity of green prism is that by using dual photo converting method which contains two steps of photo-irradiation at first a large number of triangles is produced and then with help of second irradiation step the growth of these triangles happens more uniformly and the final particles have less diversity due to controlled growth of the particles.

In correlation of these morphological changes, the use of dual stage irradiated prisms exhibited reduced severity and delayed in damage and truncation, compared to single wavelength irradiated prisms as illustrated in the following TEM images of Figure 3-5.

Figure 3-5. TEM images of (A₁) silver nanoprism after shining with 500 nm band pass filter [purple prism] (A₂) Ag@Au of A₁ after gold coating process. (B₁) Silver nanoprism after shining with dual photo converting method (500 nm and then 600 nm band pass filter) [green prism] (B₂) Ag@Au of B₁ after gold coating process.

To observe the gold coating process accurately, the particles solution was checked at a 5 to 15 min interval during the reaction for characterization by transmission electron microscopy and UV-Vis spectroscopy.

Figure 3-6 indicates in the first stage, the LSPR band red-shifts with increasing intensity, corresponding to the gold deposition on the Ag prism edges, which is observable with the darker contrast of the edges at TEM images (Figure 3-7B). It is due to the high surface energy of the (110) planes on Ag prism edges so that

gold atoms choose to place on those high energy spots. As the relative surface energies of facets of fcc crystal are in the order of $\gamma_{111} < \gamma_{100} < \gamma_{110}$, the Au atom deposition prefers to take place at the prism edges, leading to an edge-gold-coated structure referred as Ag@Au-framed nanoprism. The decrease in optical density and further red-shift of the spectra is related to the (111) Ag planes etching by HAuCl_4 . [87] Consistently, Figure 3-7C presents some small pinhole formation on the (111) facets of Ag nanoprism which exhibit low contrast. The mentioned etching or galvanic replacement takes place when HAuCl_4 concentration gets high. We propose that the etching makes the Ag nanoprisms thinner; this might be quite apparent in the center part of the triangular nanostructure and can cause the LSPR band to red-shift. When the structure is thin enough, pinholes will create but the gold nanoframes on the edges remain undamaged.

In Stage 3, a gradual blue-shift with increasing intensity of the LSPR band is recorded. TEM and EDX analysis reveals that the etched area on the (111) planes are refilled by AuAg alloy (Figure 3-7D) followed by pure Au deposition towards formation of a fully gold-coated nanostructure (Figure 3-7E and 3-7F). The detailed structure characterizations have been specified in next sections. In fact the backfilling process refills the pinholes and increases the thickness and result in blue-shift of the LSPR band.

In order to obtain more clear view on the LSPR band correlated with structure changes at different process time, the evolution of spectra during the whole gold-coating is illustrated in Figure 3-6B as “peak evolution curve” which is the connection of the peak point of the spectrum at each single reading of the solution by the UV vis spectrophotometer.

Figure 3-6. UV-Vis spectra during the gold-coating reaction. A) Spectra of formed nanostructures from 0 to 200 minutes. B) Peak evolution curve of part A (each point corresponds to $\lambda_{\max}$ of the solution at different time/stage). C) UV-Vis spectra during the process. Offset Y diagram spectra to better illustrate red and blue-shifts of the spectra during the synthesis process. D) 3D diagram of the extinction curves which illustrate the changes in optical density during the entire process.

Figure 3-7. Transmission electron microscopy (TEM) images of A) the initial used silver nanoprisms as the seeds; B) nanoprisms at 45 minutes with Au deposition on the prism edges; C) nanoprisms with some tiny pinholes at stage two; D) nanoprisms with partially refilled pinholes at 120 minutes in the third stage; E) nanoprisms with fully pure gold shells corresponding to stage 4 at 200 minutes; F) a typical gold-coated nanoprisms after ~200 min (inset is the cross-section view of the nanostructure with a scale bar of 20 nm).

In next attempt in order to simplify the gold coating protocol, single step process is introduced which make the process much easier due to using single growth solution for gold coating. TEM images of this protocol are shown in Figure 3-8. The modified gold-coating process was continued in a controlled reducing manner by slowly introducing HAuCl_4 and $\text{HyA}+\text{NaOH}$ into the Ag nanoprism solution simultaneously through two separate tubes with mechanical syringe pump at the rate of 1 mL/hour. The concentration of HAuCl_4 and HyA optimized at 0.27 and 11.4 mM to get the best controlled condition for gold deposition during the whole process which can take up to 4 hours depends on the desired gold shell thickness, the reaction bottle was maintained under vigorous stirring for the entire process.

Since in this modified protocol the infusion rate of the reagent is fixed at 1 mL/hour the entire process might take longer but instead the final coated particles are much smoother and more uniform. On the other hand the yield of fully gold coated nanoprism is enhanced to 90 percent in the modified version which is enhanced compared to the first protocol with ~70 percent yield. It is good to mention that in the modified protocol some small spherical particles is synthesized which can be easily separated by using either centrifugation or polymer filters as these spherical particles are much smaller than the gold coated particles. The formation of these spherical nanoparticles might be related to low rate of infusion. In this low infusion rate there is not sufficient HyA to reduce gold on the nanoprism surface and the gold can be reduced (by water or light) and make some tiny spherical nanoparticles. On the other hand these spherical nanoparticles might be the broken pieces of nanoprism which has been growth during the gold deposition.

Figure 3-8. TEM images of core-shell nanoparticles A) Initial deposition of gold on the edges of silver nanoprism and slight pinhole etching after 60 min. (In all X1 and X2 images corresponds to the cross section and flat-lying particles respectively). B) Formation of more Pinholes and their refilling after 150 min. C) Pinhole-Refilled particles with gold after 200 min. D) Not uniform shell of gold on the silver nanoprism template after 230 min. E) Thick and uniform shell of gold on the silver nanoprism at 265 min.

Scale bar for right (x1 or x2) and left (x) column is depicted at images E and E1.

3.1.4 Structure Analysis of Gold-Coated Silver Nanoprisms

In order to obtain convincing evidences on the structures morphology, precise microscopic examinations were done for the particles for all the four stages. The average edge length of nanoprism is characterized as 56 ± 9 nm and the thickness as 6 ± 1 nm. The contrast between gold and silver may not be distinguishable under normal bright field TEM images (see Figure 3-7B). at the early stage (when gold starts to deposit on Ag prism edges), hence we used the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), where the images signal is relative to atomic number. So the large difference of Z values of silver=47 and gold=79 allows clear differentiation between these two elements. In Figure 3-9A, the brighter edges of the prisms in dark-field mode indicate the gold coating just on the edges after 45 min passed for the reaction. The gold-coating tends to stretch into the center of the (111) facets when the time increases, for instance at 60-min (Figure 3-9B). EDX line scan examinations of the nanoparticles at the side view (Figure 3-10B and C) prove that the triangle surface consists of both Au and Ag elements.

Figure 3-9. A) A HAADF-STEM image, indicates clear deposition of Au layer on the edges of a Ag nanoprism at 45-min. B) A HAADF-STEM image, showing the deposition of Au on the prism edges at 60-min which stretched into the (111) plane at the center of nanocrystal as indicated by the arrow.

Results and Discussions

Figure 3-10. HAADF-STEM images and EDX profiles of Ag@Au nanoprisms at (A-C) at 60 minutes and (D) at 200 minutes.

On the other hand, the final nanostructure of gold-coated silver nanoprisms proved to be a fully gold-coated surface, as shown in the EDX profile at the edge (Figure 3-10D). The thickness of the nanoprisms can reach up to 17 nm (~ 3 times bigger than original silver seed) at the end of gold coating process while the initial thickness of the silver nanoprism is characterized as 6 ± 1 nm. (Figure 3-11).

Figure 3-11. A) AFM image and B) Height profile of Ag@Au core-shell nanoprisms showing thickness of ~ 16.9 nm. C) TEM image of the sample from the side view. The final thickness of Ag@Au is measured as 16 ± 1.5 nm which is $\sim 3\times$ of the thickness of initial silver nanoprisms.

As depicted in Figure 3-12, in the High-resolution TEM images (HRTEM), the final core-shell structure is still single crystal and the triangle face has close-packed hexagonal lattice. The X-ray photoelectron spectroscopy (XPS) were carried out to better prove and understand of the morphological features. As you can see in Figure 3-13, the core-shell nanocrystals are sputtered with Ar^+ ions. By study the gold and silver signals we found that the Au/Ag ratio firstly declines followed by an increase which is a good evidence for having a core-shell or sandwich morphology of the final structure. This graph emphasizes the results and having a full gold coating on the external layer of initial nanoprism. For XPS

characterizations, samples were transferred to an analysis chamber equipped with an X-ray photo-electron spectrometer (Thermo Fisher-Scientific Theta Probe). Theta probe XPS sputtering rate (based on TaO_2) was 2.7 nm/min according to sputtering condition of 3 KeV, 1 μA and working area of 4×4 mm. An Al K_{α} (1486.5 eV) anode with a power of (15 kV) 100W was used. XPS spectra were gathered using a hemispherical energy analyzer operated at pass energy of 20 eV for the elemental analysis.

Figure 3-12. A) TEM image of the Ag@Au nanoprism and B) HRTEM image of the same particle taken along a direction perpendicular to the flat top faces. The lattice spacing of 2.83 Å and interplane distance of 2.36 Å is measured corresponding to Au (111) plane. The FFT patterns show a 6-fold hexagonal symmetry at the inset.

3.1.5 Discussion on the growth stages

Based on the TEM, EDX and XPS analysis of the particles in many batches of samples taken during the gold-coating process, a common trend of morphological changes can be seen and proposed for the formation of Ag@Au core-shell nanoprisms. Herein we proposed a four-stage gold coating process as below;

i) Initial deposition of Au atoms on the prism edges: In the first few minutes of the process, HAuCl_4 concentration is too low to induce noticeable etching while

Figure 3-13. X-ray photoelectron spectroscopy (XPS) analysis of Ag@Au triangular nanoprism. A) High resolution scan related to Au 4f. B) High resolution scan related to Ag 3d. C) Plot of atomic ratio of Au/Ag versus sputtering time, the Au/Ag ratio on the nanocrystal surface decreases with sequential Ar⁺ sputtering (with sputtering rate of 2.7 nm/min) on top side of the core-shell structure and on the bottom side increase do to symmetry of structure in cross sectional view, consistent with the TEM observation in which the Au exists in the outmost layers of the Ag nanoprisms (top and bottom).

the deposition of Au atoms on the (110) and (100) facets of Ag nanoprism still going on as the high surface energy of these two facets enables effective activation of the reaction between HAuCl₄ and HyA. The initial Au deposition on the nanoprism edges is similar to the epitaxial Au growth reported by Aherne et al, where a Au layer along the Ag nanoprism edges was observed by using ascorbic

acid.[87] He has proposed that the initial Au film deposited on the Ag nanoprism edges can shield the prism edges against etching by Cl^- and AuCl_4^- . [87] The chemical reactions involved in the initial gold coating process are believed to occur as following;

ii) Etching of (111) facets: By increasing the HAuCl_4 amount, the (111) facets start to be oxidizing through the galvanic corrosion, but the edges of Ag nanoprism are inert as they are already covered by thin Au layers. This etching is due to the difference in the redox potentials between Ag^+/Ag (0.8 V vs. SHE) and $\text{AuCl}_4^-/\text{Au}$ (0.99 V vs. SHE), which can cause oxidation of Ag nanoprisms by gold ion/s.[90] In this stage if the silver etching rate is wildly fast, some random structures can be observed, including semi-hollow structures with lots of pinholes (Figure 3-14A), or small broken pieces of initial nanoprisms (Figure 3-14B). The template engaged replacement reactions can be described as below;

iii) Backfilling of the pinholes with AgAu alloy: The etched pinholes on (111) facets were backfilled by AgAu alloy in the third stage. The backfilled pinholes sites are often presented by a darker triangular frame structure having a core with varied contrast in the TEM image (Figure 3-7D). The primary reaction observed in the backfilling process is AgAu deposition on the inner edges of the pinholes with preserving the initial nanoprism thickness. Therefore the backfilling is

believed to be plane-selective. The inner edges of pinholes possess higher surface energy than the outer prism edges, which is why backfilling happens there, thus Au deposition occurs mostly at the inner edges or in fact pinholes in order to minimize surface energy of the system. Meanwhile, in the presence of mild reducing agent (HyA), the Ag nanoprism acts as “electron transfer mediator” to catalyze the reduction of gold ions and even silver ions from oxidatively etched Ag prisms to deposit on the prism surfaces. The gold-coating process is illustrated as the following reactions.[31] (Ag_x and Ag_xAu_y represent pure Ag nanoprisms and bimetallic nanocrystals, respectively.)

The reactions (7) represent a bimetallic growth towards fully gold-coated structure, while reactions (8) shows the possible co-reduction of silver ions that come from the etching of Ag nanoprism. The concurrence of these 2 reactions creates AgAu alloy deposition in the refilling process. In order to get a final fully gold-coated structure and not a bimetallic one, reactions (7) has to be leading which is achieved by appropriately increasing the reagents' pH and controlling the injection rate. It is proved that by successive formation of Ag_xAu_y shells on the Ag nanoprism surface with constantly increase of y/x ratio, eventually fully gold shell or in other words a pure gold shell on the external layer of nanoprism will be created and make Ag@Au core-shell nanoprisms.

Figure 3-14. TEM image of A) partially etched nanoprisms; B) widespread etched prisms with small pieces of gold/silver particles (indicated by arrows); C) nanoparticles with a wavy Au shell due to fast Au shell growth; D) nanoparticles with dendrite gold shells produced by more Au deposition on wavy nanoparticles in part C. E) Extinction spectra showing blue-shift with intensity increase by adding highly concentrated gold salt (0.81 mM) to the solution from 135 min to 200 min. It is corresponding to continuous gold deposition on the prism surface with no silver etching.

iv) *Further Au deposition on all facets to form fully gold-coated structure*: After complete backfilling of the pinholes, further Au deposition occurs on all nanoprism surfaces and facets including tips, edges and triangular faces. From the HAADF-STEM image (Figure 3-15), it is obvious that the brightness of the (111) triangular facets decreases due to increase in thickness of the structure and also from higher atomic number of gold than silver. The fully gold-coated nanoprisms are very stable and show excellent etching resistance (Figure 3-7f) to HAuCl_4 . In fact, the stability and morphology of the structure didn't change after a six-month period.

In our experiments we found if the Au deposition rate is uncontrollably fast in the last stage (stage 4), we could observe wavy or dendritic structures (Figure 3-14A and D), which are not favored and affects the optical properties.

A schematic morphological evolution chart of the growth model from the cross-sectional view is illustrated in scheme 3-2 in order to better illustrate the four stages of gold coating. It should be noted that the four growth stages are proposed just to better explain the gold coating process and the process duration can be considered as a reference and it may have overlap period between the stages, in particular at the end or beginning of each stages.

Figure 3-15. A HAADF-STEM image of a fully gold covered nanoprism after 200 min of gold-coating.

Scheme 3-2. Schematic morphological evolution chart of gold-coating from the side view. It shows a side view of a typical growing core-shell Ag@Au nanoprism and the trend of its growth. In first step, gold atoms are deposited at the edges of Ag nanoprisms (Stage 1). The Ag prism oxidation is indicated by small pinhole formation while most Ag prisms remain unchanged (Stage 2). In next stage (stage 3) more Au atoms are deposited on the nanoprism facets (along with co-reduction of silver ion to form an alloy AuAg shell but with increasingly larger Au to Ag ratio. Finally in last stage (Stage 4), the Ag@Au nanoprisms with full gold shells grow up with increment of both edge length and thickness due to gold deposition on all prism facets.

3.1.6 Short Summary

This section presents a facile surfactant-free gold-coating process of silver nanoprisms with systematic morphological study and formation mechanism and characterizations. The results presented in this chapter are significant as it is the first successful surfactant-free attempt to fabricate fully gold-coated triangular core-shell structures (from Ag nanoprism templates) with preserving the prism

triangular morphology and their tips. The pure gold shell of Ag@Au provides much better stabilities against etching and also provides a lot of functionalizations on the Au surfaces. TEM characterizations prove that the structure that we fabricated with this approach has a core-shell nature rather than being a nanobox or a nanocage. The LSPR spectra of final core-shell nanoprism structures could be tuned in a broad range from ~500 to ~1300 nm by controlling the edge length, composition and Au shell thickness. More importantly, these surfactant-free gold-coated nanoprisms have very clean surface, which endows easier and more flexible bio-functionalities for a large number of potential applications in medical and biological application especially in biosensing and bioimaging.

3.2 Sub-2nm Ultrathin Triangular Gold Nanoframe

3.2.1 Introduction

Hollow metal nanostructures have attracted growing research interests owing to their tunable optical properties, large surface area, surface permeability, low density and lower cost.[16,20,50,91,92] These characteristics allow for extensive potential applications in many fields such as optical sensing,[24,93] catalysis,[94-96] bio-imaging,[97-99] drug delivery,[100,101] and photothermal cancer treatment (PTT).[53,102] In general hollow nanostructures can form according to different strategies including galvanic replacement,[16,103] chemical etching,[104,105] Kirkendall effect,[106] and nanoparticle assembly,[107] to create anisotropic nanobox,[86,105,108] nanocage,[18,98,99,108] and nanoframe structure [6,20,22-24,105,109-114] with various sizes and shapes.

Among these synthetic routes, galvanic replacement which has been pioneered by Xia group,[91] has been commonly used to create various hollow nanostructures of noble metals through templated strategies,[115] for instance, through the reaction of Ag nanocrystals (as sacrificial template) with different salt precursors of Pd, Pt and Au.[16-18] Nevertheless the galvanic replacement has very low and limited capability to achieve ultrathin nanostructures with precise control over the size and uniformity because it involves oxidative etching of the template structures and the atom deposition onto the templates at the same time, this redundant pairing between core etching and deposition makes it difficult to fine-tune the process and have ultrathin structure. The interest in ultrathin nanostructures has been highlighted by latest progresses in frame structures [22,109] and ultrathin gold nanowires.[116-118] Their synthetic methods were

mainly based on surfactant-mediated growth[117] or template-assisted synthesis.[119,120] Herein we demonstrate a novel templating approach to synthesize triangular nanoframes composed of three ultrathin gold nanowires through selective gold deposition on the edges of triangular silver nanoprisms and subsequent chemical etching (instead of galvanic replacement) with mild wet etchants. These gold nanoframes are surfactant-free with tailorable ridge thickness down to 1.8 nm and interestingly they still exhibit tunable surface plasmon resonance (SPR) bands in the visible and near-IR region.

Silver nanoprism is used as the template because of its unique anisotropic structure, well-defined facets, narrow size distribution and their sharp SPR. Each individual Ag nanoprism contains two main (111) facets on the triangular planes and three (110) facets on the edges as illustrated in Scheme 3-3.

The gold coating process on the Ag nanoprism edges was carried out by slowly introducing HAuCl_4 and hydroxylamine (HyA) simultaneously into Ag nanoprism solution with certain controlled reducing conditions (pH, infusion rate) through our reported protocol with some modifications.[89] As the relative surface energies of different facets of Ag are in the order of $\gamma_{111} < \gamma_{100} < \gamma_{110}$, the Au atom deposition prefers to take place at the prism edges, leading to an edge-gold-coated structure referred as Ag@Au-framed nanoprism. The chemical reactions in the gold coating are listed as reaction (9) and (10). Here HyA acts as the reducing agent to reduce AuCl_4^- .

Scheme 3-3. Schematic illustration for the structure evolution based on the silver nanoprism template towards various nanoframe structures. Reaction A: selective gold deposition on prism edges; Reaction B: removal of silver atoms by $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ forming ultrathin gold nanoframes; Reaction C, etching of silver atoms by Au^{3+} leading to thin Ag-Au alloy nanoframes.

The selective gold-coating on prism edges is confirmed by transmission electron microscopy (TEM) characterization. As shown in Figure 3-16A, darker contrast is observed at the prism edges.[89] Consistently, accompanying with the gold deposition, the SPR band exhibits a red-shift trend with increasing intensity (Figure 4-10B), which correlates to the increase of the prism edge-length due to gold deposition.

As depicted in Figure 3-17 the increase in optical density and red-shifting happens for nanoprisms with different initial edge-length. The subsequent chemical etching of silver atoms from the Ag@Au-framed nanoprisms was

Figure 3-16. A) TEM image of the Ag nanoprism with gold coated on the edges referred as Ag@Au-nanoframe. B) Evolution of extinction peak wavelength and optical density the nanoprism solution with respect to the reaction time during the gold-coating process.

carried out through the treatment with a mixture solution of hydrogen peroxide and ammonium hydroxide (referred as wet etchant). In literatures, silver etching has been achieved by various etchants such as $\text{Fe}(\text{NO}_3)_3$, [105] H_2O_2 , [22] NH_4OH , [121] and $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$. [111] We found that the combination of H_2O_2 and NH_4OH performs effective and fast etching of Ag or Ag_2O without introduction of new ions such as Fe^{3+} into the structure as other etchants do which can make the final structure not biocompatible.

Herein, in our intentionally basic medium experimental procedure (pH 10), H_2O_2 plays a role demonstrated in reaction No. 11 with standard redox potential of 0.878 V, So the silver part of the gold-coated nanoprism etches away according to reaction No. 12 with a mild difference standard redox potential (~ 0.08 V) which control the rate of dissolving in a reasonable manner to have a very smooth and well-defined nanoframe structure;

Figure 3-17. UV-vis-NIR spectra during 15-min deposition of gold on the (110) edges of nanoprism A) size A (37 ± 9 nm) nanoprism and B) size B nanoprism (58 ± 10 nm). Surface plasmon resonance band and optical density evolution during the 15-min initial gold deposition C) for size A nanoprism and D) For Size B nanoprism. A continuous red-shift pattern with increase in intensity is observed by increasing Au/Ag ratio up to 17 % for the both sizes of A and B.

And for the aqueous ammonia reaction with Ag_2O we have;

By this method the nanoframes were obtained in situ by oxidative etching by $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ at room temperature. As shown in Figure 3-18, most of the resulting nanoframes still preserve the triangular shape with the ridge thickness around 1.8 nm which is quite close to the boundary of metal to superatom transition for gold.[122] Further analysis by Energy-X-ray spectroscopy reveals that the nanoframes are composed of 95 wt% gold (Figure 4-13). The minor residue silver signal might come from the Ag atoms embedded in the nanoframe due to the inter-atomic diffusion.[22,23] The high-resolution TEM image (Figure 2c) taken from [111] zone axis shows a fringe spacing of 0.25 nm corresponding to the forbidden $1/3(422)$ reflection. This result indicates that the nanoframe structure is single-crystalline with growth direction along [101]. Note that due to the ultrathin ridges, these Au nanoframes are highly susceptible to high-energy electron beam and over exposure under TEM will lead to partially melting and distortion of the structure (Figure 3-20) although they are quite stable in normal condition due to inertness of gold metal. In addition, the gold-coating and silver etching processes did not alter the edge height of the structure as tested by Atomic Force Microscope (AFM) in Figure 3-21.

The extinction spectra were monitored during the silver etching process to track the structure evolution as the SPR bands of the prism-based nanostructure are very sensitive to the structure evolution. Figure 3-22 shows that as we introduce more and more wet etchant solution (50 mM $\text{H}_2\text{O}_2 + 50$ mM NH_4OH), the dipole plasmon peak continues red-shifting with decreased intensity, which is corresponding to the gradually enlarged void area in the interior of Ag@Au-framed nanoprisms.

Figure 3-18. TEM images of A) ultrathin gold nanoframes in large area view; B) a representative ultrathin gold nanoframe showing the ridge thickness of ~ 1.8 nm; the inset is the electron diffraction pattern of this nanoframe. C) HRTEM image of the ultrathin gold nanoframe indicating 0.25 nm lattice distance corresponding to forbidden $1/3(422)$ reflection and growth direction along 101.

A)			B)		
Element	Weight %	Atomic %	Element	Weight %	Atomic %
Au _M	95.27	91.7	Au _M	77.99	66.0
Ag _L	4.73	8.3	Ag _L	21.01	34.0
Total	100.0	100.0	Total	100.0	100.0

Figure 3-19. Energy dispersive X-ray Spectroscopy of gold nanoframe with 10% Ag/Au ratio which silver nanoprism dissolved with A) $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$. B) Gold salt. The table below each diagram corresponds to the EDX integrated peak areas of Au_M and Ag_L. Cu peaks is related to the copper supporting grid. C) STEM image of a single nanoframe. D) Energy dispersive X-ray mapping of part C correlate to Au_M peaks in green color shows a frame structure. E) Energy dispersive X-ray mapping correlate to Ag_L peaks in red color.

Figure 3-20. A-B) TEM image of 3 nm gold nanowire after 150 and 250 seconds exposure to TEM electron beam. C-D) TEM image of ~4 nm gold nanoframe after 120 and 300 seconds exposure to TEM electron beam. In all the above cases partial melting and changes in morphology such as necking and bulging noticed although these nanoframes are quite stable in normal condition due to inertness of gold metal.

Figure 3-21. A) AFM image of nanoframes on SiO_2 substrate shows the thickness of 6 ± 1 nm which proves the equal height for nanoframe structure, Ag@Au-framed nanoprism and nanoprism. B) TEM image of a single Ag@Au-framed nanoprism from cross sectional view. C-D) Height profile of some nanoframe on SiO_2 substrate. E-F) AFM image and height profile of Ag@Au-framed, all these results are consistent with each other and show Height of 6 ± 1 nm.

Figure 3-22. UV-vis spectra evolution of Ag@Au-framed nanoprism solution during dropwise addition of A) the wet etchant solution (50 mM H_2O_2 + 50 mM NH_4OH); B) HAuCl_4 solution.

Figure 3-23. Normalized UV-vis-NIR spectra of A) Au Nanoframe synthesized by H_2O_2 + NH_4OH etching (a1) the original triangular gold coated nanoprism with LSPR band at 755 nm. (a2-a7) Au nanoframes in different H_2O_2 + NH_4OH amounts which is 50, 100, 150, 300, 500, 900 μl into 6 ml gold coated solution corresponding to a2-a6, respectively. B) Au Nanoframe synthesized by gold salt etching (b1) the original triangular gold coated nanoprism with LSPR band at 742 nm. (b2-b7) Au nanoframes in different HAuCl_4 amounts which is 50, 100, 150, 200, 220, 240 μl in 8 ml gold coated nanoprism solution corresponding to b2-b6, respectively.

Figure 3-24. A-C) Nanoframes with different ridge thickness corresponding to different gold deposition time. The ridge thicknesses are 1.8, 3.2 and 5.7 nm for image A to C respectively.

The final gold nanoframes exhibit extinction peak at 1074 nm (Figure 3-23), indicating a red-shift of ~400 nm after etching in comparison to the SPR band of initial Ag@Au-framed prisms. By this method the ridge thickness of the gold nanoframes can be tailored from 1.8 to 6 nm as depicted on Figure 4-18 through adjusting the initial gold coating process ($\text{Au}/\text{Ag}=3$ to 17%) on the edges of silver nanoprism nanoparticles.

Note that dissolution of silver from Ag@Au-framed nanoprism with less than 2% gold lead to many small pieces of gold nanorods with different length which states that at low ratio the nanoframe cannot preserve their structural integrity. With progressive increases in the amount of gold it is experienced that gold will increase the ridge thickness of gold frames on the edges of the nanoprism, when the ratio of Au/Ag is 3% ultrathin and uniform nanoframes with reasonable rigidity and ridge thickness of ~1.8 nm, with high yield of ~95% can be achieved. The deposition of up to 17% Au/Ag under the optimized conditions resulted in smooth, uniform structures with excellent preservation of the original triangular

morphology, as confirmed by TEM. At this ratio the thickness of the ridges is around 6 nm and still have high yield. Higher Au/Ag ratio (c.a. 23%) was resulted in formation of interior branches (Figure 4-20A) which will have drawback on optical properties.

In order to show the differences between the chemical etching and galvanic replacement reaction, nanoframe with gold salt etching is synthesized as well. Indeed, due to large difference in reduction potentials between Ag^+/Ag (0.8 V vs. SHE) and $\text{AuCl}_4^-/\text{Au}$ pairs (0.99 V vs. SHE), we can oxidize the silver portion of the structure inside the gold frame (Figure S7b) by using excessive gold salts to accomplish the Ag etching process as indicated in reactions (14), but at the same time reaction 7 would happen and avoid ultrafine structure;

Figure 3-25. A) TEM image of the thin alloy nanoframes generated from etching of nanoprism by HAuCl_4 . B) A representative Ag-Au nanoframe showing the ridge thickness of ~ 10 nm.

For this etching process the spectra evolution (Figure 3-22A) is almost similar to that of etching by the wet etchant, while the major extinction peak shows relatively smaller (~ 200 nm) red-shift to 884 nm. The small shoulder at 650 nm rose from the irregular Ag/Au nanoparticles that are generated from the broken pieces dislodged from original nanoprisms (Figure 3-26B). Figure 3-25 indicates that the etching by gold salt results in final nanoframe structures with the ridge thickness of 12 nm. We refer this structure as "thin nanoframe" to differentiate it with the "ultrathin nanoframe" with sub 6-nm ridge thickness. EDX analysis reveals that these nanoframes contain 22 wt% silver which is relatively higher than ultrathin nanoframe (Figure 3-19). This higher Ag content is attributed to the simultaneous occurrence of Ag oxidation and Au deposition throughout the whole process which leads to high chance of Ag-Au alloy formation and enveloping of Ag inside the frame ridges.

Figure 3-26. A) Formation of gold branches by exceeding the Au/Ag ratio more than 20%, creation of these branches will affect the optical properties and make it unpredictable, in our process we tried to stop the process before reaching this point. B) The arrows illustrate the broken particles or spherical particles which show a peak at ~ 520 nm. C) Nanoframe from previous step reacted with higher amount of gold salt which leads to dendrite gold structure on the Au-Ag alloy nanoframe.

Interestingly if we continue deposit Au onto the gold nanoframes through simultaneously introducing HAuCl_4 and HyA, some dendrite nanostructures are formed with many branches connecting with the three ridges of the nanoframe (Figure 3-26C). In this case the extinction peak red-shifted unpredictably and became broad with good potential application as active SERS substrate.[123]

In order to distinguish the unique characteristics of the ultrathin gold nanoframes, we carried out the catalytic reduction of 4-nitrophenol (4-NP) with the nanoframes. As shown in Figure 3-27, the ultrathin gold nanoframes with ~ 2 nm ridge thicknesses exhibit a reduction rate of $2 \mu\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ while the thin nanoframes with ~ 10 nm ridge thickness show much lower partial efficiency of ($0.83 \mu\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$). This indicates that the presented ultrathin ridges in the gold nanoframes have significant contribution to high catalytic activities and therefore enable great potential applications as highly active catalyst.

Figure 3-27. Plot of relative absorbance (A/A_0) at 400 nm of 4-NP solution versus the reaction time in the presence of ultrathin gold nanoframes (red line) and thin gold nanoframes (green line). The catalytic reduction of 4-NP by NaBH_4 completed in the presence of ultrathin nanoframe within 50 minutes, while only half completed in case of thin nanoframe, which demonstrates that the ultrathin structure is critical to have high catalytic activity.

We have selected the reduction of 4-nitrophenol (4-NP) by NaBH_4 to 4-aminophenol (4-AP) as a model reaction to test the catalytic activity of the Au nanoframe which can be used in water treatment of polluted water polluted by phenol and phenolic compounds.

Aqueous solutions of 4-NP and NaBH_4 were added to deionized water in quartz cuvette under stirring. After adding (20 μL) of Au nanoframe as catalyst, the bright yellow solution gradually fades as the reaction progresses. The final concentration of NaBH_4 became 7.2 mM, and 4-NP became 0.1 mM. After adding Au nanoframe solution to the cuvette kinetics of 4-NP reduction in presence of these Au nanoframe particles was studied in every 10 min interval in the range of 250-500 nm by UV-vis spectroscopy.

Figure 3-28 shows the UV-vis spectra for the reduction of 4-NP measured at a different time during the reaction. In a typical measurement, a successive decrease at peak intensity at 400 nm (attributed to 4-nitrophenolate ions) with time is noticed.

Aqueous solution of 4-NP has an absorption maxima at 317 nm (Fig. 3-28a). After the addition of freshly prepared NaBH_4 solution to the system the peak shifted to 400 nm, indicating the formation of 4-nitrophenolate ions. This peak remains unaltered with time, which suggests that the reduction does not proceed in absence of a catalyst as reported by other literatures. After the addition of R-Au particles, it was found that the peak height at 400 nm gradually decreases with time. With the gradual decrease in peak height at 400 nm, a new peak appeared at 298 nm, indicating the formation of 4-AP. This indicates that in the catalytic reduction the conversion of 4-NP gives only one product, 4-AP.

Results and Discussions

Figure 3-28. A) UV-vis spectra showing the 4-nitrophenol before and after adding NaBH_4 in green and red spectra respectively. The inset a to c shows 4-NP before and after adding NaBH_4 and final completely reduced solution. B) UV-vis spectra showing the gradual reduction of 4-NP with thin nanoframe (~10 nm ridge thickness) C) Plot of the absorbance versus time for the reduction of 4-NP of nanoframe in part b. D) UV-vis spectra confirms the creation of 4-aminophenol (4-AP) and reduction of 4-NP. E) Zoomed graph of part D on 4-AP creation at 295 nm. F) Plot of the absorbance versus time for the reduction of 4-NP of Au nanoframe which shows a linear relation.

Since in our experiment the NaBH_4 concentration largely exceeds the 4-NP concentration, the reduction rate of 4-NP can be assumed to be independent of borohydride concentration. The plot of Absorbance versus time for the reduction of 4-NP is shown in Figure 3-28d, The conversion process of 4-NP to 4-AP can be directly related to the ratio of the respective absorbance A_t/A_0 versus time with a linear readout ($R^2 = 0.90$). This linear dependence offers a simple method for reading out the concentration of 4-NP.

The process of etching of silver from Ag@Au-framed nanoparticles are depicted in Figure 3.29 as below.

Figure 3-29. A-D) Etching of Ag parts by adding 100, 300, 500 and 900 μL $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ into the solution. Images A to D also correspond to a3, a5, a6 and a7 spectra in Figure 4-17.

Results and Discussions

It seems that in many of the nanoparticles etchings starts in the middle part of the triangular facets and penetrates to the tips of the nanoparticles and make a hollow nanoframes at the end of the etching process.

In our experiments we noticed that for the ultrathin nanoframe if after the etching process the particles exerted by any external forces, they can change their ring structure shape and make irregular/regular shapes which can be interesting to investigate. In Figure 3.30, the TEM images show the nanoframe after applying mild gravitational forced by centrifugation or strong oxidation forces which can make irregular ring structure or small pieces of gold nanorods with random aspect ratio.

Figure 3-30. A-B) Triangular Nanoframe after centrifugation process. Plastic deformation can occur for ultrathin ridges less than 4 nm. C-D) Nanoframes can be broken under strong external forces and make short nanowires/nanorods.

In order to confirm that the nanoparticles used for making nanoframe structures are surfactant free we used X-ray photoelectron spectroscopy (XPS). Only BSPP is used as surfactant in the nanoprism synthesis. The XPS results didn't show any clue of phosphorus (which exist in BSPP) in the sample. P2p and P2s peaks has binding energy at 134 and 195 eV respectively, our XPS result didn't show any trace of both for the Ag@Au-frames nanoparticles which means that the nanoparticles we used to synthesis gold nanoframe are BSPP free.

Figure 3-31. X-ray photoelectron spectroscopy analysis of an Ag@Au-framed nanoparticles at A) 10 min gold-coating and C) 25 min gold-coating. B and D) High resolution scan related to Ag3d and Au4f of A and C, respectively.

3.2.2 Short Summary

In summary, we have developed a straightforward method to achieve high-yield synthesis of ultrathin triangular gold nanoframes through gold-coating on silver nanoprisms edges with subsequent silver etching. These ultrathin nanoframe structures have the ridge thickness tailorable from 1.8 to 6 nm and exhibit distinct SPR band in the visible and near-IR region. Importantly, the ultrathin ridges in the nanoframe structures are surfactant-free and allow superior catalytic activities and endow great potential applications for catalysis. Further, the synthetic strategy presented here can be generally extended to the fabrication of other new ultrathin frame-structures based on different anisotropic templates and open up new avenues for the buildup of novel complex ultrathin structures with more versatile functionalities.

3.3 Synthesis of bimetallic triangular nanoboxes

3.3.1 Introduction

Hollow noble metal nanostructures have attracted huge research interests owing to their tunable optical properties, larger surface area, surface permeability, lower density and cost.[16,20,50,91,92] These unique characteristics allow for extensive potential applications in many fields such as optical sensing,[24,93] catalysis,[94-96] bioimaging,[97-99] drug delivery,[100,101] and photothermal cancer treatment[53,102] due to the unique optical properties of these structures, such as the localized surface plasmon resonance (LSPR) and large surface areas. The LSPR peak is controlled by nanoparticle size, composition, shape, and aspect ratio, but in hollow nanostructure, the LSPR peak can be controlled by wall thickness without modification of nanoparticle size, shape and composition or aspect ratio. [49,55]

In general, galvanic replacement has been employed to fabricate core-shell or bimetallic hollow nanostructures with varieties of shapes, morphologies and compositions. Bimetallic hollow nanostructures have been synthesized by reacting Ag nanoparticles (as templates) with a salt precursor containing a less reactive metal such as Pt, Pd and in particular Au. The difference in redox potential of those metals drives the etching/oxidation of the template material by the metal salt precursor and resulting in a hollow nanostructure.

The most general example is the creation of hollow AuAg nanocrystals by epitaxial deposition of gold on the facets of a silver nanoparticle as template,[71,124,125] following by reduction of AuCl_4^- , alloying of the deposited

Ag with Au, and complete or partial oxidation of the Ag template, leaving fully or partially hollow nanostructures or even nanoframes.[16,20,22,24]

Other less reactive noble metals such as Pt and Pd containing hollow nanostructures can also be prepared by mentioned method.[10,11] A whole range of AuAg bimetallic nanostructures such as spherical nanoshells,[126] cubic nanoboxes and nanocages,[90] cylindrical nanotubes, [16] and multi-walled hollow nanostructures,[127] are reported in recent years with the same approach.

The galvanic replacement conditions can be controlled so that deposition of gold occurs only on the edges and corners of the anisotropic nanoparticle due to surface energy differences of their facets. After etching of the template nanoparticle, frame-like structure will be left behind. This approach can be easily apply to nanocubic structure although using Ag nanoprism is more sensitive due to their vulnerability and their ultrathin (5-7 nm) edge thickness. Aherne et al used galvanic replacement reaction to produce a AuAg rounded triangular nanobox from a silver nanoprism seed.[86] We tried to optimize the previous reported process to better control the morphology and conserve the triangular shapes of the template as the tips of nanoparticles play an important key role on optical properties and their usages in different applications.

Our major goal in this work is to establish and optimize a facile approach to create a tunable nanobox with a proper integrity and uniformity, with preserving the initial triangular Ag nanoprism template. The challenge is to deposit gold atoms selectively on all facets of nanoprism to form a gold nanocage following by removing of silver part in the next stage and refilling the hole inside the created nanocage to make a perfect nanobox with triangular shape.

Herein we show the synthesis of triangular nanoboxes and provide electron microscopy images and EDX data than proves their hollow and alloyed nature of the structures. We used our previous protocol of gold coating (part 3.1.2) till 100 min, in this stage a nanocages structure of gold is formed on the silver nanoprism but all the triangular facets are not fully covered by gold, this followed by addition of high concentrated gold salt (0.81 mM) to make a fast etching of silver template, after this stage normal gold coating (stage 1) is repeated for 15 min to get the final triangular nanoboxes. As the infusion rates of chemicals and the time of each stage is optimized we could achieve well-defined triangular nanoboxes with almost sharp tips with better optimization than Aherne et al reported work.

3.3.2 Structure Analysis of bimetallic triangular nanoboxes

Detailed microscopic analyses were done for the nanoboxes in order to obtain convincing evidences to confirm the morphology. The average edge length and thickness of the Ag nanoprisms used were measured as 61 nm and 7 nm, respectively. Under normal bright field TEM (Figure 3-32), the difference between core-shell and hollow nanostructure may not be clearly distinguishable therefore high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), is used for better characterization. The EDX line scan of the prisms from the side view in this mode reveal that the triangle surface consists of both Ag and Au elements, suggesting an alloy surface. As shown in Figure 3-33, the silver and gold have the same trend over the particles line scan which is not similar to core-shell structure that we've reported in chapter 3.1.4. After the process finished, the nanoboxes thickness (external thickness) can increase up to 18 nm while the initial thickness was just 7 nm.

Figure 3-32. TEM images of AuAg nanobox.

Figure 3-33. A) HAADF-STEM image and B) Cross-sectional EDX line profile of a nanobox structure etched by gold. Compositional profile clearly confirms a cavity inside the nanobox.

Figure 3-34. TEM images of A) Bare Silver nanoprism B) A nanobox structure with a 5-7 nm gold/silver shell thickness. HAADF-STEM images of C-D) Cross-sectional view of triangular nanoboxes.

Figure 3-35. Peak evolution curve of during nanobox formation.

Extinction spectra during the experiments indicate that in the first stage the LSPR band shows red-shift with increasing in optical density. Further red-shift of the LSPR band with dampening intensity is attributed to (111) face etching of Ag prisms by HAuCl_4 . These two stages show the same pattern exactly similar to core-shell structure synthesis. By introducing high concentrated gold salt a huge red-shift of the peak is observed which corresponds to formation of nanocages. In last step (stage 4) by refilling of nanocages' shell pinhole and making nanoboxes, a slight blue-shift occurred. The peak evolution curve is illustrated in Figure 3.35.

3.3.3 Discussion on the growth stages

Based upon the TEM, EDX characterizations of the particles taken during the formation of nanoboxes, a general trend of morphological changes can be observed which includes four main growth stages.

i) Initial deposition of Au atoms on the silver nanoprism edges: As mentioned earlier in core-shell synthesis at the very beginning, the HAuCl_4 concentration is too low to induce noticeable etching while the deposition of Au atoms on the Ag nanoprism (110) and (100) facets still proceeds as the high surface energy of these facets enables effective activation of the reaction between HyA and HAuCl_4 .

ii) Partial etching of nanoprism's (111) facets: As the HAuCl_4 concentration slowly increases, the (111) facets start to be partially etched through the galvanic corrosion, while the Ag nanoprism edges are protected by the initially deposited Au layers. Interestingly some partial gold deposition is also noticed on the (111) facets as HyA reduces the gold ions on this facets. Both etching and deposition reactions are mentioned in reactions 16 and 17 respectively.

iii) *Fast etching of silver core:* The partially etched (111) facets of Ag prisms were oxidized very fast by introducing high concentration gold salt in a short period (~5 min) at this stage. It is good to emphasize that in this stage no HyA introduced to prevent more deposition or spherical Au particle formation. After washing the particles to remove extra gold and silver ions, the hole in the nanocage in this stage is fulfilled by mild deposition of gold salt and HyA to make a perfect nanobox in the next (iv) stage.

iv) *Refilling and gold deposition of the nanocages to make nanoboxes:* in this stage the holes will be completely backfilled on the nanocages but the structure still remains hollow, further gold deposition takes place on all nanocages surfaces (the gold shell) and eventually makes a nanobox structure. The reason that the hollow space won't be refilled is that the orientation of crystal growth is in a way that it refilled the pinholes first and this directly avoids entering the ions in the hollow space and limit the growth inside this space. From the HAADF-STEM image (Figure 3.34C), we can observe that the nanoboxes have different wall thickness and this can be tuned by different gold deposition time.

In order to better illustrate these 4 stages of gold coating, a schematic of the formation mechanism from the cross-sectional view is depicted in scheme 2. It should be noted that these four growth stages may overlap together, particularly at the end of each stage.

Scheme 3-4. Triangular Nanoboxes Formation from silver nanoprisms. The scheme shows a side view of growing nanoboxes, illustrating the manner of growth. In the beginning gold ions reduced and deposited as Au at the edges of nanoprism particles (Stage 1). Some oxidation of the Ag is indicated by formation of the pin-holes, but most of the Ag remains (Stage 2). In next stage (Stage 3) the silver core is totally removed by introducing silver etchant to the solution. Finally, in (stage 4) complete nanoboxes grow increasingly thicker due to deposition of more and more Au atoms in all facets.

3.3.4 Short Summary

We present a facile way to synthesis bimetallic triangular nanoboxes with preserving the initial templates morphology. The results presented here are significant as they demonstrate a facile method to fabricate triangular nanoboxes with sharp tips and with a good yield. TEM analyses prove that the structure has morphology of nanobox or nanocage rather than core-shell nanoprism. The LSPR band of resultant core-shell prism structures could be tuned in a wide range by controlling the Au shell thickness. More importantly, the existence of the hollow

cavity raises the possibility of encapsulation and transport of materials of interest which make this structure a good candidate for drug delivery and other bio-applications.

3.4 Self-Assembly of Ag nanoprism based nanoparticles

3.4.1 Introduction

Films created from monolayer noble metal nanostructures especially Au and Ag are of considerable current interest in many fields due to their exceptional optical properties introduced by localized surface plasmon resonance (LSPR).[68,128] The excitation of LSPRs, which arises from the coherent oscillation of the free conduction band electrons in resonance with an incident electromagnetic field such as incident light, leads to enormous optical local field enhancement, remarkable photon scattering and localization at the nanoscale.[129-131]

Recently huge interest has been focused on the methods of controlling and usage of the LSPR properties of the metallic coatings and films, such as their optical density and the resonant peaks wavelength, transmission pass-bands, and enhancement of optical field's scale, which all are highly depend on the shape, size, composition and arrangement of the metallic nanostructure as well as the refractive indices of the surrounding dielectrics.[132-134] These metallic films with this exceptional tunable optical features have many potential applications in sensing (Bio and Chemical sensing) and Bio-imaging,[135-137] Organic photovoltaics, (OPVs) and energy conversion,[68,138] and optical processes.[139,140]

The main potential usage of the biochemical sensing by using metallic nanostructures films are in LSPR biosensing or surface-enhanced Raman scattering (SERS). Investigations proved that the SERS enhancement of

anisotropic nanoparticles such as nanoprisms, nanorods or aggregation of nanoparticles or their clusters show much higher sensitivity compare to spherical metallic nanoparticles or in general the non-aggregated isotropic metallic nanoparticles. Since the electromagnetic field at the sharp edges of the anisotropic metal nanoparticles or in the gap between each individuals can be increased up to several orders of magnitude and produce “hot spots” (which doesn’t exist in isolated spherical nanoparticles), such enhancement in SERS signal can be generated.[129,141,142] So the nanostructures with more sharp tips/edges are more interesting for such investigation and application.

Real-time change in the LSPR wavelength and/or its magnitude (due to local refractive index changes) is the main basis of LSPR sensing. The main concern in the practical application of LSPR sensors is the synthesis and improvement of proper nanostructured substrates with tunable LSPR wavelengths to accomplish better sensitivity with different refractive indices.[132]

The other new application of metallic monolayer substrates is to improve the light trapping for organic photovoltaics (OPVs). Metallic nanostructure on the surface of a photovoltaic cell can improve the output due to near-field enhancement or plasmonic scattering that efficiently trap incident light and couples that into the active absorption layer of photovoltaic cell. In this way, a significant improvement of solar energy efficiency can be achieved. Recent investigations have proposed that the light trapping performance of plasmonic scattering layers can be considerably improved by applying non-spherical or anisotropic metallic nanostructures with sharp tips and edges (e.g., nanoprism, nanorods).[68,123] Therefore, it is essential to fabricate large scale but cheap

metallic nanostructure films with widely tunable LSPR and excellent scattering/absorption enhancement to maximize light trapping.

Existing approaches for nanostructural metallic films fabrication include electron beam lithography (EBL), which has high control over shape, size, arrangement and consequently LSPR spectra of the nanostructure, but this method is unfortunately too expensive in practical usages.[143,144] Other reported methods such as sintering [145] or annealing[123] are cheap and also large-scale techniques but have modest to low control on the final shape of nanoparticles. Nanoimprintation [146,147] and Mask-assisted deposition[148] are also useful in the fabrication of regular nanostructure arrays using nanospheres or metallic strips, although it is not easy to produce elemental components with a controlled gap distance due to aggregation in this technique. A completely dissimilar mask-less cheap method consists of the self-assembly of colloidal particles to produce metallic films in large scale involving shaped metallic nanoparticles. Colloidal self-assembly approach has great interest in practical applications in sensing and photovoltaics as it's a facile, fast and low cost. However, presently metallic films (with self-assembly) are usually fabricated in an organic medium [149] or by using surface-modified substrates after complex modification processes.[150,151] It is quite challenging to assemble colloidal particles in large scale on substrate such as glass, or directly on organic substrates, especially in aqueous solution. Taken together, undoubtedly the main challenge in fabrication of large area nanostructural plasmonic films is the development of methods which simple, less substrate-selective, large scale and LSPR tunable.

Herein we illustrate a facile self-assembly technique using silver nanoprism-based nanoparticle to fabricate large scale thin films on various materials substrate. We found that, compared to current self-assembled metallic nanoparticles, metallic films fabricated with size-controlled nanoparticles shows a much broader frequency-selective response in both the visible and near infrared (NIR) wavelengths and has a broader control over preventing aggregation in large scale.

3.4.2 Result and discussion

We synthesized different sizes of colloidal silver nanoprism according to previously reported chemical synthetic methods in previous chapters. Silver nanoprism and Silver nanoprism-based nanoparticles are chosen because previous investigation have proved that the scattering enhancement and the LSPR tunability of such nanoparticles are much sharper and more sensitive than that of spherical nanoparticles which is due to their anisotropic geometry.[37,152] besides, compared with silver nanorods, which show multipole LSPR peaks,[142] silver nanoprism are better nominee for the development of metallic films with tunable LSPR response because they show almost single spectra related to the longitudinal resonance (dipole) for silver nanoprisms.[37]

Silver nanoprisms or Silver nanoprism-based nanoparticles were first centrifuged and then redispersed in 0.3 mM trisodium citrate. The cleaned glass/ITP substrate functionalized with 3-aminopropyltrimethoxysilane (APTMS) for 1 hour and then immersed in Silver nanoprisms or Silver nanoprism-based nanoparticles solution for several hours depends on the particle-density required on the substrate.

In this experiment, APTMS concentration and functionalization time has been proved to be an important factor for the self-assembly production of large-scale silver films in aqueous solution because it can effectively and significantly modify the surface activity of nanoprisms. High concentrated APTMS has etched the particles while the low concentrated one, will cause low particles density on the substrate, the same trend has been found for the time parameter. Therefore, both these key factors are optimized in our experiments.

Figure 3-36C and D shows a comparison of scanning electron micrographs of typical colloidal dispersions with and without APTMS modification on glass substrate. As it can be seen the substrate without modification cannot prevent nanoprism aggregation which can have negative effect on optical properties and application of the final films. As depicted in Figure 3-37 by controlling the particles density the final density of film can be easily controlled and packed, this parameter can be tuned by APTMS concentration, incubation time and nanoprism solution concentration.

The optical changes for these films that accompany wetting and drying (Figure 3-29A and B) can be attributed to the difference in refractive indices for air and water and the high sensitivity of the dipole resonance for silver nanoprisms or silver nanoprism-based nanoparticles to the dielectric medium.

This simple but precise system can provides a variety of substrates with tunable optical changes that can be observed by the naked eye and leads to a class of sensors based upon structures which can differentiate various analytes via visible colorimetric changes.

This facile rapid method for making large-area substrates coated with specific types of nanoprisms with excellent control over optical properties of such structures can be used for many applications such as Biosensing and SERS.

Figure 3-36. A-B) photographs of two 15 × 15 mm glass slides coated with dense monolayer films of edge gold-coated nanoprism (GSNP) with different edge length. C-D) Scanning electron micrograph of GSNPs particles with and without modifies substrate respectively.

Figure 3-37. Scanning electron micrograph of GSNPs particles after self assembly on silanized glass slide which shows high packed particle densities. Note that the rod shape particles are standing nanoprisms.

3.4.3 Short Summary

Herein we reported a robust self-assembly approach to fabricate large-scale metallic monolayer films on the surface of a variety of pretreated substrates. This technique is simpler, faster, and cheaper as it can be carried out in aqueous solution at room temperature without solvent evaporation or sample heating or any post treatment which offers a lot of advantages in comparison to the previously reported self-assembly methods. Because Ag nanoprism-based nanoparticles have anisotropic structure, the LSPR peak position of the fabricated

monolayer films is finely adjustable over a broad range in the visible to NIR region, this tunability is the main advantages of our presented films. The other advantage of using such system is that in general the Ag nanoprism-based nanoparticles are stable which makes the fabricated film quite robust and reliable. The anisotropic shape and the sharp corners and edges of the nanoprisms or nanoprism-based nanoparticles feature stronger near field enhancement effects and larger scattering to absorption ratios compared to spherical nanoparticles and, hence, are expected to provide larger absorption enhancements with tunable LSPR. The light trapping and scattering properties of such films can be obtained by simply changing the sizes, orientation and the gap distances between the nanoprisms.

All these unique combination of properties implies that the nanostructural metallic films can have great potential utility in many fields as diverse as color filtering, optical displays, biosensing and optical processing.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

In this thesis, optimized simple methods have been developed to realize the shape and size controlled synthesis of different novel silver-nanoprism-based nanostructures. Anisotropic nanoparticles with unusual properties have been fabricated by using this templated technique. The following conclusions have been drawn from these works:

A wet chemical approach has been developed for the shape-controlled synthesis of different nanoparticles by using silver nanoprism as the initial template. This method involves the infusion of basic $\text{HONH}_2\cdot\text{HCl}$ and HAuCl_4 by two separate tubes with a mechanical syringe pump to silver nanoprism solution (seed mediated protocol), nanostructures with different morphologies can be obtained, including two unique structures, i.e. the triangular core-shell structure (Ag@Au) and triangular ultrathin nanoframe. The Ag@Au maintains its single crystalline nature at the end of the process and proves the fact that Au atoms are epitaxially deposited on the Ag seed. Importantly, it is also demonstrated that in such a wet chemical synthesis, the thickness of the Au shell can be controlled precisely in the process which provides the tunability for these core-shell nanostructures.

For the first time, ultrathin gold nanoframes have been synthesized on the edges of silver nanoprism. The resulting nanoframes, with a side length of 30-80 nm, height of ~5nm and ridge thickness of 1.8 to 6 nm exhibit new properties, *i.e* these

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nanoframe have much better catalytic properties due to their high surface and ultrathin nature of the nanostructure. Interestingly, the LSPR of these nanoframes can be tuned in a very broad range depends on the void size inside the nanostructure which can be used as a precise sensor system.

The wet chemical method has also been applied to synthesize bimetallic triangular nanobox structure with preserving the initial templates morphology. The LSPR band of resultant core-shell prism structures could be tuned in a wide range by controlling the Au shell thickness. More importantly, the existence of the hollow cavity raises the exciting possibility of encapsulation and transport of molecules and materials of interest which make this structure a good candidate for drug delivery.

4.2 Recommendations for Future Work

The present work has realized the shape controlled synthesis of silver–nanoprism-based nanoparticles by using the wet chemical method, and the formation of novel anisotropic nanostructure through the template assisted approach. These methods can be further optimized and extended to synthesize other types of nanostructure with different materials such as Pd, Pt, Cu or alloys of those or different shapes such as hexagonal, disk shape or even cubic. Hence the following future works are recommended:

First, although the current photochemical method is able to produce different nanostructure with triangular shape, there are many other types of shapes which have not been synthesized in our approach, e.g. as hexagonal, disk shape or even cubic. In order to make the wet chemical method a robust synthetic route, it is recommended that other factors, such as temperatures and the simultaneous

Conclusions and Recommendations

addition of metal precursor for creation of alloy structure, to be further investigated. For example, since silver and palladium can be reduced together within the introduced wet chemical approach, alloy structure with triangular shape is expected which could have interesting optical and catalytic properties.

Second, the Au nanoframes prepared from the current method can be characterized more by using calculation and simulation method to further study their optical properties as this is the first time such structure with tunable uniform ridge thickness is introduced. More investigations on the nanoframe usage for catalytic properties should be done due to its high surface area and also having pure Au. In addition, because our wet chemical method is rapid and easy to carry out, it can be extended to synthesize nanoframes made of other noble metals such as Pd, Pt or Cu.

Third, all the three nanostructures presented here have many potential application in many fields such as catalysis, chemical and biosensing, biomedical and medical application and energy conversion. Recently the nanoprism is reported as highly sensitive plasmon resonance sensor by Charles et al[153] and bare nanoprism showed high sensitivity upto 1096 nm.RIU^{-1} (at λ_{max} 1093 nm) which is due to ultrathin edges and three sharp corners of each nanoprism. Since the Ag@Au-framed and Ag@Au nanoprism are much more stable[87,154] than the bare silver nanoprism and have exactly the same shape and size in case of Ag@Au-framed and the same shape for Ag@Au nanoprism, further investigation on their usage in plasmon resonance sensing is recommended. Many researches are focused on the application of nanoprism for SPR biosensing.[155-158]

Conclusions and Recommendations

In addition to the usage of nanoprism as SPR biosensor, it can be used for bioimaging as well. Recently biocompatible silver nanoplates are introduced by Homan et al[159] as a new photoacoustic contrast agent that can be easily functionalized for in vivo molecular photoacoustic imaging. Ag@Au-framed and Ag@Au nanoprism also can be used for such application since both of them have high amount of gold which makes them chemically inert and more biocompatible in comparison to bare Ag nanoprism.

Besides, more investigation should be made in order to systemically test the toxicity of the silver nanoprism and silver nanoprism-based nanoparticles on the living cells before introducing more applications for such nanoparticles for medical and biomedical applications.

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List of Publications

Visible-Light-Driven Hydrogen Evolution. *International Journal of Hydrogen Energy*, Accepted.

LIST OF PATENTS

US Provisional Patent Application

1- Core-shell nanoplate and method of making same

Inventors: Mohammad Mehdi SHAHJAMALI; XUE Can, BOEY Yin Chiang
Freddy
NTU Ref: PAT/010/12/12/USPRV
Application No: 61/734,139

2- Ultrathin Metal Triangular Nanoframes and Method of Making Same

Inventors: Mohammad Mehdi SHAHJAMALI; XUE Can, BOEY Yin Chiang
Freddy
NTU Ref: PAT/011/12/12/USPRV
Application No: 61/734,155

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