Breaking the symmetry of nanoparticles by anisotropic modification & fabrication of 3D sers platform for information storage application

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**BREAKING THE SYMMETRY OF NANOPARTICLES BY
ANISOTROPIC MODIFICATION & FABRICATION OF 3D
SERS PLATFORM FOR INFORMATION STORAGE
APPLICATION**

ZHANG QI

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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SERS PLATFORM FOR INFORMATION STORAGE
APPLICATION**

ZHANG QI

School of Physical and Mathematical Sciences

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Abstract

This thesis summarizes my 4 years of graduate research on tuning the plasmon resonance property of nanoparticles by anisotropic modification and fabrication of 3D SERS platform for further information storage applications. In detail, the anisotropic modification is first realized by introducing galvanic replacement at the nanoscale interface through micro-contact printing (Chapter 2). The kinetically controlled reaction leads to the deposition of Au dots on one facet of Ag cubes forming Janus nanostructures, which brings about unique plasmon resonance that can be detected by cathodoluminescence. Moreover, chemical etching is also applied to liquid-liquid interfacial assembled nanoparticles to break the symmetry of nanoparticles through the surface. This controlled etching process can lead to the formation of non-centrosymmetric nanoparticles such as Ag pyramids (Chapter 3). In another research direction, I apply the unique plasmon resonance properties of nanoparticles to the fabrication of efficient, surface-enhanced Raman scattering (SERS) substrates. By integrating two-photon polymerization and Langmuir-Blodgett techniques, I fabricate a 3D SERS substrate to systematically study the effect of tuning physical parameters on the resulting SERS signal intensity (Chapter 4). Based on the optimized parameters in the above study, a further application is developed as micro-barcode patterned SERS substrate is fabricated, which proves to be highly adept in information storage (Chapter 5).

Chapter 1

Introduction

ABSTRACT. In this chapter, we begin by reviewing some fabrication strategies of metal nanoparticles, followed by recent research in the plasmon resonance properties of these nanoparticles, such as physical parameter influence, plasmon coupling from assembly as well as applications of SERS, resulting from localized surface plasmon resonance (LSPR) of metal nanoparticles. Metallic nanoparticle fabrication strategies using both wet chemical synthesis methods and lithographic preparations are first discussed. Subsequently, the relationship between plasmon resonance properties and the physical parameters of metal nanoparticles, including size, shape, crystallinity, composition and symmetry will be discussed in detail. Since it has also been established that the inter-nanoparticle gaps can be engineered to maximize the efficiency of electro-magnetic field enhancement resulting from the strong plasmon coupling between individual metal nanoparticles, in this introduction, we also review the assembly methods of nanoparticles with focus on the bottom up strategies. Last but not least, we use SERS as an example to illustrate the significance of plasmon resonance of metal nanoparticles in application.

1.1 PLASMON RESONANCE PROPERTY OF METAL NANOPARTICLES

The discovery that certain materials exhibit different properties in the nanoscale than in bulk has sparked a widespread interest in nanotechnology research.¹ To date, a plethora of nanomaterials have been applied in fields of chemical catalysis, energy transfer, bio-diagnosis and so on. Certain nanomaterials, in particular noble metal nanoparticles, exhibit unique plasmon resonance properties. The application of these properties can be traced back to the medieval times, where embedded gold nanoparticles undergo plasmon light scattering to give rise to the brilliantly colored stained glass windows of Notre-Dame de Paris. However, this phenomenon remained largely unstudied until a century ago when German physicist Gustav Mie applied Maxwell's equations to illustrate the strong absorption of light by gold nanoparticles with subwavelength sizes for the first time. This discovery paved the way for scientists to study and understand the unique phenomenon of plasmon resonance.²

These days, plasmon resonance is defined as the oscillation of conductive band (free) electrons of the metal nanoparticle when excited by light. If the electrons are oscillating collectively in resonance to the wavelength of light on the surface of the nanoparticle, the surrounding electro-magnetic field will be greatly enhanced, giving rise to a phenomenon known as localized surface plasmon resonance (LSPR).^{3, 4} On the other hand, if a nanostructure were to be elongated in one dimension, such as in the nanowire or nanofilm, the electrons will propagate back and forth along the nanostructure, and this phenomenon is known as propagating surface plasmon resonance (PSPR). However, both modes of plasmon resonance demonstrate the amazing ability to manipulate light by either focusing or guiding it. Up to now, studies of plasmon resonance have been

expanded in various areas, including the tuning of optical properties,⁵ biological and chemical sensing,⁶ information storage⁷ and surface-enhanced Raman scattering (SERS).⁸ Here, in this introduction, I will focus on and discuss the applications of LSPR.

1.2 FABRICATION OF NANOPARTICLES

The unique plasmon resonance property of metal nanoparticles are predominantly determined and tuned by its physical parameters, such as size and shape.⁹ Therefore, fabrication strategies to obtain various nanoparticles with different physical parameters is the foundation for further study and application. In this section, two commonly used approaches: the bottom-up chemical synthesis as a simple, low cost method, and top down lithography to achieve precise engineering of nanoparticle shapes and sizes are mainly discussed.

1.2.1 CHEMICAL SYNTHESSES

For noble metal nanoparticle synthesis, the bottom-up wet chemical approach has been proven to be one of the most robust and versatile methods. Using this strategy, various shapes and dimensions of nanostructures such as spheres, cubes, bars and so on have been widely produced and reported (Figure 1). Therefore, in this part of introduction, three major strategies in accordance to the nucleation process would be discussed in detail, including direct reduction, seed-mediated and template-mediated method.

Figure 1. Examples of chemically synthesized nanoparticles, including (A) spheres, (B) cubes, (C) truncated cubes, (D) right bipyramids, (E) bars, (F) spheroids. Reprinted with permission from Ref [4]. Copyright © 2011 American Chemical Society.

1.2.1.1 DIRECT CHEMICAL REDUCTION

As one of the most important and widely used synthetic methods, direct reduction from a high valence precursor to obtain metal nanoparticles is straightforward. There are limited choices of a stable precursor salt due to the strong preference of metal in losing electrons. Taking Ag as an example, the most commonly used salt is AgNO_3 , and the use of other Ag precursors, such as CF_3COOAg are seldom reported.¹⁰ However, as compared to the limited choice of the metal salt, there are more candidates of suitable reducing agents which could potentially increase the variety of nanoparticles. Citrate is one commonly used reducing agent in the synthesis of noble metal nanoparticles.^{11, 12} In a typical process, the metal precursor is reduced in a heated colloid, where citrate is added as both reducing agent and stabilizer. Although such a strategy is conducted with relatively low cost and the reaction can be scaled up easily, mono-dispersed nanoparticles

are relatively hard to achieve using a citrate as a reducing agent.¹³ Therefore, this synthesis method is limited by the production of undesired shapes and sizes of nanoparticles, which is not ideal for precise scientific study.

Tollen's agent, famous for the silver mirror reaction, is another efficient compound for nanoparticle synthesis. Typically, Ag film is first coated on the wall of the reactor and subsequently sonicated into nanoscale particles.¹⁴ By using low cost reduction reagents such as sugar or aldehydes, this reaction is fast and easy to scale up even in the industry. However, though the size distribution of obtained nanoparticles is relatively narrow as compared to the citrate method, there is almost no efficient way to obtain shape-controlled nanoparticles from this synthesis process, which is likely due to the high reaction speed.¹⁵

In recent years, the use of polyols to reduce noble metal ions is popular and widely utilized. In this method, the Ag precursor is reduced in the presence of both polyol and surfactant, usually under high temperature, Polyol here acts as both solvent and reducing agent while the surfactant acts as a capping agent which influences the growth direction. Furthermore, as a mild reducing agent, the polyol is believed to be oxidized by oxygen in the air forming the aldehyde,¹⁶ which subsequently participates in the reduction of the noble metal ions. Due to the slow oxidation process of the polyol, the nucleation rate of the nanoparticle is believed to be decreased, allowing the reaction process to be more easily controlled. On the other hand, suitable surfactants have to be selected as they are essential to overcome the surface energy difference of face-centered cubic (fcc) lattice. Thus, by simply varying the reagent concentrations, especially the ratio of polyol and surfactant, it is possible to obtain kinetically controlled nanoparticle shapes such as cube,

octahedra,¹⁷ rod¹⁸ and wire¹⁹ in such a process.

Xia *et al.* and Yang *et al.* are the pioneers in the polyol synthesis processes, especially in the synthesis of mono-dispersed cubes, octahedra and their derivatives.^{20, 21} In a typical synthesis, silver nitrate and poly(vinylpyrrolidone) (PVP) were separately prepared as precursors before being added to the nearly refluxing pentanediol solvent. A trace amount of Cl⁻ was also added as it is believed to facilitate the growth of (111) facet. The periodic injection of the reagent guaranteed a continuous nucleation of the nanoparticles. By simply controlling the total amount of precursors, a series of shapes from cubes to octahedra were successfully obtained, where the intermediates were found to be truncated cubes, cuboctahedra and truncated octahedra.

Therefore, it is clear that polyol synthesis could be a robust and versatile way to provide mono-dispersed nanoparticles for further fundamental research and application. And in this thesis, this typical method is utilized as the basic reaction to obtain starting materials (nanoparticles) or substrates.

1.2.1.2 SEED-MEDIATED SYNTHESIS

As mentioned above, tuning the reaction rate is usually regarded as an efficient strategy to acquire shape-controlled nanoparticles. Thus, the seed-mediated procedure can benefit from the independent nucleation and growth process. In detail, if the metal precursor is isotropically deposited on the facets of as-prepared seeds, highly symmetric nanoparticles are expected, such as quasisphere,²² cubic structures,²³ and icosahedra.²⁴ In contrast, if the growth ratio of each facet is distinct from one another, anisotropic shapes could be achieved. For example, nanorods and nanowires are the most popular and widely

used applications derived from this method. Murphy *et al.* applied both negative and positive charged seeds with increasing sizes to control the aspect ratio of Au nanorods in solution phase.^{25, 26} The as-prepared seeds were expected to be the reaction site catalyzing the deposition of Au salt by ascorbic acid, where the tunable size of the seed was demonstrated to be the key factor of anisotropic growth.

It is important to note that the seed preparation and subsequent growth process are relatively independent. If a secondary element were to be introduced in the growth process, it is possible to build a more complex core shell structure through such a strategy. For example, Huang *et al.* grew a continuous layer of Ag onto Au rhombic dodecahedra to form a series of nanocrystals arranging from cubes to octahedra. These size-tunable, bimetallic nanostructures may boast interesting optical and catalytic properties.²⁷ In addition, the deposition of the second component anisotropically on the original seed further increases the complexity of the nanoparticles formed, which highlights the seed-mediated process as a versatile and efficient tool for the modification and optimization of morphology. Some examples of such complex nanoparticles include Janus nanoparticles, spiky shapes and other non-centrosymmetric structures which will be further discussed in the following sections.

1.2.1.3 TEMPLATE-MEDIATED SYNTHESIS

As the name suggests, nanoparticles are fabricated on pre-treated templates in template-mediated synthesis, where the morphology of the nanoparticles obtained can be controlled by selecting a suitable template. The predictable morphology and ease of control makes this method extremely attractive to pioneering nanochemists. Mirkin *et al.*

took advantage of an Anodic Aluminum Oxide (AAO) template to fabricate the as-designed nanorods.²⁸ Moreover, the simultaneous or alternating electro-chemical deposition of 2 or more metals inside the AAO could promote the formation of either alloys or segmented nanorods.^{29, 30} However, due to the periodically arranged pores of the AAO template, the morphologies that can be obtained are limited to one-dimensional nanostructures, such as rods or wires.

Experimentally, metal nanoparticles themselves are found to be good candidates as a template for complex structures. One typical example is the synthesis of Au nanocages from the Ag nanocube via galvanic replacement and the subsequent etching off of the residue. A more comprehensive discussion of this particular synthesis can be found under the bimetallic nanoparticles section.

1.2.2 LITHOGRAPHIC FABRICATION

Compared to chemical synthesis strategies, top-down lithographic fabrication could offer a precise control of both morphology and alignment on the substrate. A variety of methods, such as electron beam lithography (EBL),³¹ focused ion beam lithography (FIB)³² and two photon polymerization (2PP)³³ are now widely developed and applied. For example, Krenn *et al.* successfully fabricated arrays of dots, prisms and squares by EBL.³⁴ As shown, the periodically fabricated nanoparticles are well-defined with narrow size distributions (Figure 2A-C). Hence, lithographic techniques are advantageous over wet-chemical synthesis methods in attaining precise control over the fabrication of nanostructures. In another example, Yang *et al.* created a high resolution color print up to 100,000 dots per inch by tuning the size and gaps in nanodisk arrays.³⁵ Since the color of

whole arrays was largely dependent on the parameters of individual nanodisks, especially the precise interstitial spaces, the lithographic method emerges as the perfect candidate to satisfy such high precision requirements. Furthermore, significant progress has been made in the fabrication of three dimensional structures via lithography techniques. Using multi-photon lithography, Ag⁺ ions were instantly reduced and deposited under laser activation, forming 3D free standing metal nanomaterials (Figure 2E).³⁶ This procedure breaks the limitation of traditional lithography on a plane by demonstrating a unique strategy to obtain robust and versatile nanoparticles in three dimensions. However, to the best of our knowledge, there are almost no reported single-crystalline metal nanoparticles achieved by these lithographic fabrications. Besides, these approaches are almost always more expensive and time-consuming than chemical synthesis methods.

Figure 2. The nanoparticles are obtained from lithographic methods. (A) nanodots, (B) nanoprisms, (C) nanoplates, (D) vertical nanopillar, (E) 3D nanoarrays. (A-C) Reprinted with permission from Ref [34]. Copyright © 2007 Elsevier B.V. (D-E) Reprinted with permission from Ref [36] Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA,

Weinheim.

1.3 PARAMETER CONTROL OF INDIVIDUAL NANOPARTICLES

Up to now, great efforts have been made to study the relationship between the physical parameters of nanoparticles and their plasmon resonance properties. The variety of strategies mentioned above allow for systematic investigations on size, shape, crystallinity and composition of nanoparticles on the resulting optical properties. In this section, each parameter will be discussed accordingly and in detail.

1.3.1 SIZE

Ag and Au, two widely used noble metals to fabricate plasmon nanoparticles,^{37, 38} are found to exhibit size-tunable plasmon resonance properties. Zhong *et al.* observed that the solution color of colloidal gold nanospheres changed from dark red to light purple, corresponding to a shift in extinction peak from 519 nm to 569 nm, when nanoparticle size increases from 30 nm to 90 nm (Figure 3).³⁹ A plot of the maximum absorbance values against the diameter of nanoparticles demonstrated a linear relationship between the two parameters.

Moreover, other shapes with different sizes are have also been studied and reported, including symmetrical cubes²³ and anisotropic bars.⁴⁰ A similar red-shift of the UV spectra is observed when the sizes of the nanoparticles are increased. A possible explanation is that an increase in size indicates a longer plasmon resonance wavelength of the nanoparticle and hence a lower frequency of plasmon oscillation.

Figure 3. The size of nanoparticles shows strong influence on their plasmon resonance property. (A) The color images of solutions prepared with a diameter of 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm and 90 nm. And the TEM images are shown in (B-J) respectively. The according UV spectra are available in (K). Adapted with permission from Ref [39] Copyright © 2007, American Chemical Society.

1.3.2 SHAPE

Shape-controlled, especially geometrical nanoparticles are widely reported for plasmon resonance research as well.^{41,42} Due to the advancement in synthetic strategies, numerous types of regularly shaped nanoparticles with mono-distributed sizes have been synthesized, including spheres,⁴³ plates,⁴⁴ dodecahedral⁴⁵ and icosahedral,⁴⁶ of which the plasmon resonance properties are distinct from one another. For example, the well-established polyol method offered an approach to tune the shape of Ag cubes into truncated cubes, cuboctahedra, truncated octahedra and octahedra.²¹ The light scattering images showed an obvious color change from green to red, along with a marked difference in scattering spectra under the dark field microscope, indicating that shape is a crucial factor in determining the plasmon resonance properties of nanoparticles.

Irregularly shaped, complex nanostructures such as stars, spiky nanoparticles and branch-like structures,⁴⁷⁻⁴⁹ with tunable plasmon resonance properties have also been fabricated. In a previous work of our group, Goh *et al.* fabricated rough Ag nanowires via chemical etching for SERS detection.⁵⁰ The roughness enhancement of the nanowire resulted in an increase in the number of electromagnetic hot spots to effect strong Raman signals throughout the entire structure of a single nanowire. In comparison, the electromagnetic hot spots on a smooth Ag nanowire are usually localized at its ends. However, the fabrication of mono-dispersed, irregularly shaped nanostructures still remains a challenge today, as the homogeneity of irregularly shaped, complex nanoparticles are difficult to control in large scale. Hence, a study of an average of the nanoparticles is much preferred to single-particle studies when such irregularly shaped nanostructures are used.

The anisotropic modification of highly symmetrical, regularly shaped nanoparticles

appears to be a promising approach to fabricate irregularly shaped nanoparticles.⁵¹ Taking the anisotropic etching of Ag octahedra as an example, PVP is selectively bonded to the (111) facet and not the (100) and (110) facets due to surface energy differences. Hence, the rate of etching at the (100) and (110) facets is higher.⁵² As a result, octapod nanostructures and its derivatives can be obtained, leading to significant enhancement of Raman signals. In another example, Xia *et al.* anisotropically grew Ag onto just three out of six sides of nanocubes. The consequent final morphology demonstrated an interesting, non-centrosymmetric exotic shape, resulting in a unique change in plasmon resonance as characterised by UV spectra.

Figure 4. (A-D) The scanning electron micrographs of nanoparticles made by e-beam lithography. From left to right the shapes are, a rod, a disc, and two triangles with increasing size. (E-H) The dark-field colors are shown as blue, green, yellow and red, respectively. (I) The according dark-field spectra of the nanoparticles exhibit distinct peak shape and scattering wavelength. Reprinted with permission from Ref [42] Copyright ©

1.3.3 CRYSTALLINITY

The crystallinity of certain nanoparticles are found to affect their plasmon resonance properties. When the light scattering spectra of chemically prepared, single-crystalline Ag nanowires were compared against that of lithographically prepared, poly-crystalline Ag nanowires, it was found that the single-crystalline nanowires exhibited superior propagating plasmon resonance properties as compared to the poly-crystalline nanowires.⁵³ However, a systematic study of the relationship between crystallinity and plasmon resonance properties is an arduous process as it is technically difficult to account for crystalline defects within the nanostructures.

However, some studies have concluded that single-crystalline nanoparticles do exhibit superior localized plasmon resonance property. Tang and Ouyang inhibited the growth of multiply-twinned clusters by using chloride ions to achieve the comparable single-crystalline and poly-crystalline Ag nanoparticles in solution.⁵⁴ By exposing these nanoparticles to an ultrafast pump laser pulse, the multiply-twinned (poly-crystalline) nanoparticles exhibit a faster electron-phonon coupling, indicating an improved light transfer property. This again demonstrates that single-crystalline and poly-crystalline nanoparticles could potentially exhibit different plasmon resonance properties and hence more comparable target materials could be fabricated for further study in this area.

1.3.4 COMPOSITION

1.3.4.1 SURFACTANT MODIFICATION

In preparing different types of nanoparticles, in particular the ones fabricated by colloidal chemical synthesis, surfactants play a key role in controlling nucleation and growth of nanoparticles, by forming a layer on the surface of nanoparticles to stabilize the nanoparticles and prevent aggregation. The use of ligand exchange and ⁵⁵ oxygen plasma⁵⁶ to tune the ratio of surface components of nanoparticles can alter the chemical environment to favor the attachment of target molecules in sensing systems by means of physical adsorption or chemical bonding. The subsequent near-field excitation of the target molecules gives rise to the enhancement of Raman scattering. In addition, tuning the surface chemical composition of nanoparticles is also commonly used in self-assembly. For example, Xia *et al.* applied the micro-contact printing method to selectively modify the hydrophobicity on Ag cubes.⁵⁷ By selectively “printing” the hydrophobic ligands on one or more sides, the authors managed to control the assembly of the cubes into dimers, lines or even 3D superlattices, which strongly demonstrates that the properties and behavior of nanoparticles can be defined by the chemical composition on the surface of nanoparticles.

1.3.4.2 BIMETALLIC NANOSTRUCTURES

Bimetallic nanoparticles have been widely used in catalysis, magnetic application and bio-diagnostic tools for decades.^{58, 59} In this section, the relationship between the composition and the plasmon resonance property are highlighted.

Combining Au and Ag to form a single bimetallic nanoparticle usually boasts a hybrid of plasmon resonance properties from both metals. For instance, due to the small lattice mismatch of Au and Ag, it is possible to fabricate 5 nm size bimetallic

nanoparticles with increasing the Au percentage of 0%, 25%, 75% and 100%.⁶⁰ The absorbance peak of the nanoparticles were then observed to red-shift from 440 nm (pure Ag nanoparticle) to 530 nm (pure Au nanoparticle) accordingly.

The first published synthesis of bimetallic nanostructure preparation could be traced back to 1857. Since then, a series of synthesis strategies, such as co-reduction, electrochemical deposition and biomimetic synthesis have been developed.⁶¹ Among which, the galvanic replacement reaction based on differences in redox potential is popular as a straightforward and fast method to fabricate alloy nanoparticles. Xia *et al.* contributed significantly in the fabrication of alloy nanocages and their derivatives based on as-prepared Ag nanocubes (Figure 5).^{62, 63} The Au^{3+} ion undergoes reduction to form Au atoms on the surface of Ag due to the higher standard reduction potential of Au^{3+}/Au (0.99 V vs standard hydrogen electrode, SHE) than that of Ag^+/Ag (0.80 V vs SHE). Subsequently, the free electrons of Ag diffuses outwards, to guarantee the continuous reduction of Au^{3+} on the surface. Meanwhile, the as-formed Ag^+ ions diffuse quickly into solution at a high temperature, which is a key factor to fabricate alloys with smooth surfaces. In addition, as 3 Ag atoms are needed to reduce 1 Au^{3+} , the increasing deficiency of Ag leads to a hollow interior. However, this hollow structure poses a problem; it is difficult to determine if the red-shifting of the extinction spectrum is due to chemical composition change or the variation in morphology of the nanoparticle. Therefore, Au salt of equal valence to Ag was also exploited for the galvanic replacement reaction to prevent a morphology change of nanoparticle.⁶⁴ Moreover, the galvanic reaction have also been extended to other noble metal systems, such as Pt and Pd.^{65, 66} Hence, by taking advantage of complementary metal redox pairs, galvanic replacement

demonstrates great potential for the fabrication of alloy nanoparticles.

Figure 5. (A) Scheme of the galvanic replacement reaction on Ag cubes. Reprinted with permission from Ref [66] Copyright © 2007, American Chemical Society (B-E) The SEM and relative TEM images of samples with different amount of Au precursor, 0 mL, 0.6 mL, 1.6 mL and 3.0 mL, respectively. (F) The UV spectra are listed accordingly, showing a strong red-shift with increasing Au concentration. (B-F) Adapted with permission from Ref [63] Copyright © 2006, American Chemical Society.

1.3.4.2 OTHER MATERIALS

To date, many other kinds of materials have been introduced into nanoscience, which contributes enormously to applications in various areas, including photocatalysis, nanomotors, drug delivery and so on.

With respect to plasmon resonance property, non-metallic nanoparticle systems are also known to demonstrate interesting phenomena. For example, Drezek *et al.* coated Au onto silica nanospheres, leading to a significant blue-shift of the UV extinction spectrum.⁶⁷ In another example, Han *et al.* coated a semiconductor photocatalyst, TiO₂ onto Au nanorods for the plasmon-induced photo-reduction of 4-nitrophenol.⁶⁸ Therefore, by simply changing the chemical composition, or tuning the order of coating, the plasmon resonance property of the nanostructure can be altered significantly.

1.3.5 SYMMETRY

The symmetry of nanoparticles is proven to be an essential factor which determines the resulting plasmon resonance property. In this section, we will use two specific structures, symmetric core-shell structure and anisotropic Janus nanoparticles, as examples to discuss the differences in plasmon resonance properties resulting from variation in symmetry.

1.3.5.1 SYMMETRIC CORE-SHELL STRUCTURE

The bimetallic core-shell structure is sometimes considered as a special type of alloy where each metal is separated by an interface. As expected, its plasmon resonance property differs from the conventional alloy and also shows great potential to be utilized

for further fabrication of complex nanoparticles, due to the unique independence of individual metal components.⁶⁹

To begin, the core-shell structure has been employed to tune the plasmon resonance property of the nanostructure. Nogami *et al.* introduced two approaches to either coat Ag shell around an Au core or *vice versa*, using the seed-mediated growth process.⁷⁰ In an Au@Ag core-shell structure, the UV extinction peak can be tuned from 520 nm to 400 nm with increasing thickness of Ag shell. More interestingly, a doublet peak could be easily observed which reflects the plasmon resonance peaks of both Au and Ag when the ratio of the two metals were carefully controlled. However, in the case of the Ag@Au core-shell structure, only one peak is observed, even though the UV extinction spectrum of Ag@Au could be tuned within a similar range, which highlights that the plasmon resonance property of bimetallic nanoparticles is dependent on the coating order of each component.

In addition, if geometry differences are introduced into the core-shell structure, a much greater range of LSPR is always expected. For example, when a layer of Ag was reduced by Ascorbic acid and deposited on the Au prism under basic condition,⁷¹ the UV-vis-NIR spectra red-shifted from 800 nm to 1250 nm, extending into the IR region as the amount of Ag precursor increased. So far, other diverse shape-controlled core-shell nanoparticles have also been fabricated, including rods,⁷² cubes,⁷³ octahedra⁷⁴ and so on, all of which absorb between the visible light to IR region on the electromagnetic spectrum.

Moreover, the core-shell structure inspired the fabrication of complex nanostructures by further modification. For example, the technique of galvanic replacement can be

applied to core-shell structures to obtain Russian Matryoshka like structures.⁷⁵ As discussed above, hollow structures are also obtained in such synthesis due to the insufficient replacement of metal ions, while at the same time maintaining the shape of the core. Xia *et al.* grew an Ag cube shell around an spherical Au core at the first step and subsequently conducted the galvanic replacement to etch off the Ag shell by Au.⁷⁶ Thus, Au-Ag hollow nanostructure containing Au nanocrystals within was created, which resulted in a red-shift of the extinction spectrum from 450 nm to 750 nm. Another widely used method to create a complex nanostructure is the layer by layer, continuous deposition of outer shell metal atoms. For instance, Yan *et al.* managed to obtain Pd@Au nanostructures, the further coated PdAu@Pd, and multiple Au and Pd layer coated Pd@Au nanocrystals.⁷⁷ Besides, due to the unique plasmon resonance properties of nanostructures, the extinction peaks could be observed to be red-shifted as the number of layers increased.

In summary, fabrication of core-shell structures is by itself, a constructive strategy to generate and tune the plasmon resonance property of metal nanoparticles. Besides that, it can also serve as a versatile platform from which various sophisticated morphologies can be fabricated and subsequently applied to plasmon resonance research.

1.3.5.2 ANISOTROPIC JANUS PARTICLES

Janus is the name of a god from ancient Rome. He is often portrayed as a god with two faces, where one face looks to the past and the other to the future. Similarly, a Janus nanoparticle can be described as containing two different and separate physical or chemical components within a single structure.^{78, 79} Unlike chemically symmetric alloy

nanoparticles, Janus refers to the non-uniform distribution of components, which is a good example of anisotropy in itself. It has been reported that breaking the symmetry of nanoparticles to fabricate chemically anisotropic Janus nanoparticles for instance, introduces potential applications that the chemically symmetric counterparts cannot fulfil. For instance, via electrochemical deposition in AAO membranes, Crespi *et al.* created nanomotors from Pt-Au bimetallic segmented nanorods and studied their movements in aqueous hydrogen peroxide solution.⁸⁰ However, when similar chemically symmetrical structures were used, such movement was challenging due to the balanced ratio of oxygen generation throughout the nanostructure. Janus nanoparticles can also exhibit tunable plasmon resonance. For example, when Ag was controlled to deposit anisotropically on only one, two, three, four, and five sides of a Pt cube instead of symmetrically on all six sides, the morphology of the cube could be tuned from a centric core-shell structure, non-centric core-shell structure to Janus nanoparticles.⁸¹ Such anisotropic growth subsequently leads to a dramatic red-shift in UV spectra, indicating the shifting of plasmon resonance.

Similarly, non-metallic materials have been utilized to further extend the applications of Janus nanoparticles. TiO₂ was anisotropically grown on as-prepared Au nanorods by controlling the precursor amount.⁶⁸ The simulation of near-field plasmon resonance demonstrates a significant electromagnetic field enhancement at the connecting region between the two components, which offers improved catalytic ability as compared to the centrosymmetric nanostructures.

With regards to the fabrication strategy, a variety of methods, including both physical and chemical processes, have been developed. Physical methods, such as

deposition, employ the changing physical states of materials to induce the nucleation and subsequent formation of particles. For instance, silica nanorods were vertically assembled under the influence of an electric field and was subsequently deposited with gold on the top surface to fabricate matchstick-like Janus nanoparticles for self-assembly.⁸² Chemical methods, including electro-chemical deposition,⁸³ cation exchange,⁸⁴ elemental affinity deposition⁸⁵ and epitaxial growth,⁸⁶ are used to adjust the chemical components of Janus nanoparticles. By circumspectly controlling the pH value of the reaction environment, Mirkin *et al.* used a plasmon-mediated, citrate reduction approach to heterometallically deposit Ag on one side of Au decahedral seed to form a Janus icosahedral nanoparticle.⁸⁷ In another example, Chen *et al* demonstrated the conversion of concentric Au-Ag core-shell structures into hybrid dimer structures by tuning the metal-metal interfacial energy using surface ligands.⁸⁸

Although great progress has been made in the fabrication of Janus nanoparticles, it is still challenging to synthesize bimetallic Janus nanoparticles in the five Platonic shapes (tetrahedron, octahedron, cube, icosahedron, and dodecahedron) due to their high symmetry. Hence, the synthesis of bimetallic Janus Platonic nanoparticles, which is believed to offer greater tunability of plasmon resonance properties, is seldom reported.

1.3.6 GAP EFFECT

Although the individual nanoparticle presents excellent opportunity to tune the plasmon resonance property through controlling the physical or chemical parameters, strong plasmon coupling between nanoparticles in close proximity is also found to be important to change the plasmon resonance.^{3, 89, 90} The effect of gaps from the simplest

dimers to the extensive 2D films and 3D arrays are discussed respectively in this section.

1.3.6.1 NANOPARTICLE PAIRS

Two Ag nanospheres with a gap of 10 nm can cause both a red-shift of the relatively strong absorbance arising from bonding plasmon mode and a blue-shift of the relatively weak absorbance from the anti-bonding mode.^{4, 91-93} Besides, the relatively stronger intensity of the bonding mode presents the elevated influence on concentrating and enhancing the electromagnetic field in the gap, producing a region of intense electromagnetic field known as “hot-spot”. If the gap decreases from 10 nm to 2 nm, further red-shift of the bonding mode and blue-shift of the anti-bonding mode occurs. Such sphere dimers are also found to exhibit polarity when light is induced along or perpendicular to the inter-particle axis. The scattering intensity evidently illustrates that only when the light propagates along the inter-particle axis, would a strong red-shifted coupling obtained from the gap be observed that represents the highest enhancement of the dimer (Figure 6).

To further investigate the findings from this pioneering research, Mulvaney *et al.* aligned two nanorods end-to-end, and side-to-side, to form T or L dimers.⁹⁴ The scattering spectra measured exhibited similar red- and blue-shifted plasmon resonances, however it was observed that the extent of red- or blue-shifting depended on the orientation of the nanorods, demonstrating the importance of orientation when using anisotropic nanoparticles.

Figure 6. (A) Energy level diagram illustrating the bonding and antibonding plasmon hybridization modes for the dipole plasmon of nanospheres with a 2 nm (blue dotted line) and 10 nm (red solid line). Reprinted with permission from Ref [4]. Copyright © 2011 American Chemical Society. (B, C) Two Ag dimers with different gap widths (left) and their corresponding scattering spectra (right). The dimers were excited with light polarized along the inter-particle axis (red) and perpendicular to it (green). Reprinted with permission from Ref [93]. Copyright © 2010 American Chemical Society.

1.3.6.2 TWO- AND THREE-DIMENSIONAL PERIODIC NANOPARTICLE ARRAYS

In 2D or 3D periodic arrays, it is similarly observed that the relative alignment of the

nanoparticles affects the coupling to a great extent. For instance, Zhang *et al.* elongated the dimers to chains containing 3, 4, 5 and 6 units, bringing about a simple shift of a single plasmon peak from 580 nm to 630 nm without observing any new peaks (Figure 7A-E).⁹⁵ In spite of this, according to the work of Kall *et al.*, if trimers were arranged as the points of a regular triangle plane instead of linearly, there will exist two different peaks in the extinction spectrum, which corroborates with the two major types of coupling mode, bonding and anti-bonding, that can be supported by finite-difference time-domain (FDTD) simulations (Figure 7F-I).⁹⁶ Thus, when extending the nanoparticles number to larger scale to form bulk 2D films or 3D super-clusters, it can be observed that plasmon coupling modes of the metal nanoparticles can appear much more complicated and hence the statistical significance of the different modes is usually taken into consideration.⁹⁷

Figure 7. (A-D) Typical SEM pictures of 1, 2, 3, and 4 particles in a line fabricated by standard e-beam lithography. (E) The according scattering spectra are shown with simply peak shift. Adapted with permission from Ref [94]. Copyright © 2004 American Chemical Society. (F) The SEM image of array contains 3 particles with a triangle arrangement. (G-H) The corresponding simulations exhibit two strong coupling mode with such alignment, which corroborate well with the scattering spectrum. Adapted with permission from Ref. [95]. Copyright © 2008 American Chemical Society.

1.4 ASSEMBLY OF NANOPARTICLES

As mentioned in the previous section, the plasmon coupling resulting from gaps significantly increases the electromagnetic field enhancement of nanoparticles. Therefore, strategies to engineer such gaps become emergent and essential in the study of nanoscience. Specifically, the fabrication of these gaps could be classified into intra-particle and inter-particles gaps. Intra-particle gaps can be found in hollow nanostructures, spiky shapes and other complicated morphologies of nanoparticles that have been mentioned in previous sections. Herein, we would like to focus on the generation of inter-particle gaps through arrangement of nanoparticles, including both top-down (lithography) and bottom-up (assembly) methods.

1.4.1 TOP-DOWN (LITHOGRAPHY) METHODS

As a typically applied physical strategy to fabricate nanoparticles in large array, lithographic arrangement of nanoparticles is also known as a top-down method. In general, such methods allows for the formation and precise control of particle positions to create

well-defined inter-particle gaps. For instance, Alivisatos *et al.* exploited double electron-beam lithography in combination with a double lift-off procedure to fabricate planar, gold and palladium nanoantennas of specific shapes.⁹⁸ The authors were able to precisely tune the inter-particle gaps from 10 nm to 90 nm to demonstrate the effect of inter-particle gap on resonance peak. However, as discussed in previous sections, such top-down methods would require complex preparations, highly specific equipment, and are both expensive and time consuming. Moreover, it is also technically challenging to obtain single-crystalline nanoparticles from lithography, which further limits their applications.

1.4.2 BOTTOM-UP (ASSEMBLY) METHODS

Assembling the as-prepared nanoparticles which are normally obtained by chemically synthesis is classified as a bottom-up approach. Single-crystallinity, complex morphologies and a relatively low cost are some advantages of using such an approach. Here we would like to discuss some strategies for the assembly of as-prepared nanoparticle for studies in plasmon resonance. In particular, we will focus on colloidal aggregation, interfacial assembly and template arrangement respectively.

1.4.2.1 COLLOIDAL AGGREGATION

Since the synthesis of nanoparticles in solution phase is widely developed, the colloidal aggregation method is considered one of the most straightforward strategies to directly assemble nanoparticles. In a colloid, the intermolecular forces at nanoscale include Van der Waals forces, electrostatic forces, magnetic interactions and hydrogen

bonding, all of which are proven to be robust yet versatile for assembly to occur.⁹⁹⁻¹⁰¹ By selectively modifying Au nanorods with DNA oligomers in a single direction, gold nanospheres were assembled via complementary base-pairing of the DNA oligomers. Subsequently, three types of clusters, including side-, end- and satellite- isomers were formed respectively with increasing number of modified Au nanorods used.¹⁰² The resulting Raman spectra of the 3 clusters also demonstrate an increasing number of hotspots with increasing shape complexity, which was further confirmed by the electrical field simulation.

Furthermore, 3D clusters with complex shapes could be accessible through colloidal aggregation, which are normally hard to achieve by other methods. For instance, Halas *et al.* assembled Ag nanospheres into well-defined 3D clusters containing 5, 10, 13-19 nanoparticles.¹⁰³ When dropped onto an ITO substrate, the 3D clusters were observed to be optically orientation dependent. Furthermore, Huang *et al.* took advantage of the evaporation method and surfactant diffusion method for the assembly of Au-Pd core-shell supercrystals, of which the size and shape could be tuned by carefully controlling the crystal concentration, temperature or surfactant.¹⁰⁴

1.4.2.2 INTERFACE ASSEMBLY

At the interface, the tendency to minimize the entire interfacial energy becomes the decisive driving force for the spontaneous assembly of nanoparticles.^{105, 106} A classic example is the Pickering emulsion phenomenon, where solid particles can be adsorbed and stabilized on the interface between two phases, leading to widespread applications in encapsulation, colloidosome formation and so on.

Langmuir-Blodgett technology is one typical interfacial assembly at the liquid-air interface.^{107, 108} A monolayer of nanoparticles is first dispersed on the interface, followed by slow compression of the particles. By applying either a horizontal or vertical lift-off, a monolayer of nanoparticles can be easily transferred onto platforms such as silicon wafer or glass. Yang *et al.* fabricated a monolayer using nanocrystals in a variety of shapes, such as nanorods, nanowires, nanocubes and so on, achieving tunable optical properties of nanoparticle films (Figure 8).^{109, 110} Langmuir-Schaefer assembly is another similar technology to obtain a monolayer of nanoparticles in large scale at liquid-air interface.¹¹¹ This technique was employed in our group to create a close packed 2D array of Au nano-prisms with sub-10 nm gaps, which functions as a SERS active platform with a high enhancement factor up to 10^4 .¹¹² All in all, such assembly technology at the liquid-air interface provides a versatile tool to assemble nanoparticles in large scale.

Figure 8. Close-packed Langmuir-Blodgett monolayers of nanocrystals and nanowires:

(A) spheres, (B) rods, (C) wires, (D) cubes, (E) truncated cubes and (F) octahedra.

Reprinted with permission from Ref. [109]. Copyright © 2008 American Chemical Society

In addition, self-assembly at the liquid-liquid interface has also been widely studied.¹¹³ The use of two liquids, instead of air, brings forth the potential to fabricate a SERS detection platform that can simultaneously detect compounds with different solubilities. Kim *et al.* demonstrated the assembly of vertical Au nanorods at the interface between Oleic acid and water.¹¹⁴ Due to the existence of both oil and water phases, such arrays allow for both hydrophilic and hydrophobic molecules to be detected by SERS simultaneously. Another advantage of the use of a liquid-liquid interface stems from the precise control over nanoparticle alignment. In our group, Lee *et al.* demonstrated that octahedral nanostructures can be made to self-assemble at the Decane-water interface on their vertices. Such unique orientations of nanoparticles offers a chance to achieve selective modification of nanoparticles, which will be discussed in this thesis.

1.4.2.3 TEMPLATE ASSEMBLY

It has been found that certain templates can function as a desirable platform for the alignment and assembly of nanoparticles. Generally, this strategy can be further classified into soft- template and hard- template assisted assembly based on the nature of the template.

DNA is a typical example of a soft template. The use of DNA to aid assembly has

also been extensively studied.¹¹⁵ The strong H-bond formed between complementary base-pairs allows for DNA to be both proficient in assembling particles in the nanoscale yet also efficient in engineering chiral clusters, where the interactions with light generate surprising optical properties that have not been observed in other naturally occurring materials.⁵

For hard templates, the rigidity of the structure offers tight control over the final clusters. Alvarez-Puebla *et al.* demonstrated the assembly of micro-size pyramidal arrays by stamping colloidal Ag nanospheres.¹¹⁶ Such an assembly technique benefits from both the colloidal driving forces at the nanoscale as well as the advantages of lithographic fabrication.

Likewise, micro-contact printing (μ CP) and its derivatives have drawn much attention these years. Precise control of micro-size pattern and possible contact forces on nanoscale makes the μ CP a robust and versatile method for template arrangement. For example, Paunov *et al.* applied the patterned Polydimethylsiloxane (PDMS) as a stamp to print polymer nanoparticles.¹¹⁷ Taking the height differences of the PDMS stamp into account, the contact surface with the substrate can be selective, hence successfully creating patterned assembly arrays (Figure 9).

Figure 9. Scheme of the template assembly μ CP. (A), (B) SEM images of a typical colloid

micropattern; (C) Optical microscopy image of positively charged colloids on negatively charged glass surface; (D) Fluorescence microscopy image of the deposited patterned polymer colloids microcontact printed on glass. Reprinted with permission from Ref. [117]. Copyright © Royal Society of Chemistry 2015.

Besides the direct printing of nanoparticles, μ CP is also widely used to fabricate the secondary template for self-assembly. Professor Whitesides is one of the pioneers in this field. First, a compound, $X(\text{CH}_2)_{15}\text{SH}$ (where “X” indicates an organic functional group) was chosen as the “ink” to selectively modify the surface of metal substrate, followed by soaking of the substrate in the crystallizing solution. Due to the preference of X-terminated molecules for itself, the crystals would form precisely at the positions of modified regions to produce patterned nanoparticle arrays. The highly flexible yet low-cost PDMS stamp has been reported to produce complex patterned and large-area nanoparticles arrays by means of μ CP, making this technique both a robust and versatile template assembly method.

1.5 PLASMON RESONANCE FOR SERS DETECTION

1.5.1 FROM RAMAN TO SERS

In this day and age, applications of plasmon resonance property are extensively established and studied, such as near-infrared optical microscopy,¹¹⁸ focusing and transferring of light¹¹⁹ and remote excitation of molecule.¹²⁰ For example, Nordlanders *et al.* created controllable plasmon nano-routers by routing plasmon of branched Ag nanowires onto different wire branches using polarized light, which contributed to the control and manipulation of light at the nanoscale.¹²¹ Among these, one of the most

flourishing applications of plasmon metal nanoparticles is in the detection of molecules through the use of SERS, which will be focused on in this thesis.

To begin, Raman scattering is the inelastic scattering of photons by a molecule, where differences in energy between incident photons and scattered photons reflect the energy of various vibrational modes in the molecule. As different types of functional groups as well as chemical environments exhibit different vibrational energies, a Raman spectrum is unique to each molecule and can also be termed as a “molecular fingerprint”. Hence, Raman scattering is a highly useful technique for the identification of molecules. However, due to the relative small scattering cross section of most detection molecules, further utilizations of Raman scattering in academia and industry were quite limited until the 1970s, when researchers discovered that Raman scattering intensity can be significantly enhanced by roughened metal surfaces. A new term, surface-enhanced Raman scattering (SERS) was coined to describe this astonishing phenomenon, which introduces new possibilities for both detecting and identifying molecules with high efficiency and sensitivity.¹²²

In SERS, there are two widely accepted mechanisms to explain the significant enhancement in signal intensity; the chemical enhancement and electromagnetic enhancement mechanisms respectively. The chemical enhancement mechanism originates from interactions between the molecule and metal nanoparticles that contribute to an enhancement in signal intensity of approximately 10^3 .^{123, 124} On the other hand, the electromagnetic enhancement mechanism arises from the light-induced LSPR of metal nanoparticles, generating a “nanoantenna” that amplifies the local electric field around the nanoparticle. As a result, a molecule in close proximity to a “nanoantenna” as such is also

influenced by the enhanced electric field, leading to an electromagnetic enhancement of around 10^5 - 10^8 .^{125, 126} Hence, as the electromagnetic enhancement mechanism is shown to contribute greater to enhancement in Raman signal intensity, we will center our discussions on this enhancement mechanism from single particle SERS platform to the bulk 3D SERS platform.

1.5.2 SINGLE PARTICLE SERS PLATFORM

As discussed above, physical parameters, such as size, shape, crystallinity and so on, will critically influence the plasmon resonance of certain nanoparticles. This in turn directly influences the location and magnitude of enhancement of “hot spots” on the surface of the nanoparticle.¹²⁷ In particular, “hot spots” are found to be located at the sharp corners and edges of shape-controlled nanoparticles due to the higher free energy in these regions. In a recent work of our group, various morphologies of Ag nanoparticles, including nanosphere, nanocube and nanooctahedra, were combined with a graphene oxide monolayer for SERS sensing.¹²⁸ And among all, the octahedra was found to exhibit the largest enhancement factor. In addition, as discussed, the engineering of gaps for plasmon coupling is demonstrated to further enhance the electromagnetic field. Thus, it is important to create intra-particle gaps for SERS detection using a single-particle SERS platform. For example, Nam *et al.* modified Au nanospheres with DNA stripes and subsequently grew a second layer of Au shell with a sub nanometer gap, where the resulting plasmon coupling brought a intense SERS enhancement up to 1.5×10^9 , allowing for single molecule detection.¹²⁹ On the other hand, isotropic etching is proven to be another robust strategy. Yang *et al.* realized the selective etching of Ag

nanooctahedra based on the distinct surface energy difference between (111) and (110) (100).⁵² The obtained octapod structure was proven to offer a significantly enhanced SERS signal compared with octahedra, resulting from the gaps between the “arms”.

Besides the physical parameters of nanoparticle itself, the parameters of the incident light are also found to be crucial in influencing SERS signal intensity. A typical elongated nanostructure such as a nanorod or nanowire is found to exhibit two modes of plasmon resonance; a longitudinal low frequency oscillation and a transverse high frequency oscillation. Thus, laser excitation of nanoparticles along either the longitude or transverse mode will give rise to distinct SERS signals. For instance, Xia *et al.* and his co-workers changed the orientation of the incident laser with respect to static nanocubes functionalized with a Raman probe, 1,4-benzenethiol.¹³⁰ The intensity of 1,4-benzenethiol SERS peaks were observed to be critically dependent on the orientation of the laser; the SERS signal intensity was highest when the laser was polarized parallelly to the corner of the nanocube. Further explorations were extended to rod and even wires, where the split in plasmon resonance modes is more pronounced, leading to a larger difference in SERS signal intensity. In the work of our group, Cui *et al.* demonstrated that the SERS intensity of Ag wire along its longitudinal mode is significantly weaker than its transverse mode, owing to the momentum mismatch between the incident photon and the propagating plasmon.¹³¹

1.5.3 MULTI-DIMENSIONAL SERS PLATFORM

In both scientific and industry applications, single nanoparticle SERS platform is limited for large scale use. Thus multi-dimensional SERS platform is always needed,

which benefit from the increase of both hot-spots and the excited target molecules at large scale. Traditionally, fabrication of such SERS platform includes synthesis in colloidal solutions, interfacial sensing and solid phase films.¹³² For example, Au nanoparticles prepared from wet chemical methods were directly modified with thiolated DNA in solution for SERS detections.¹³³ Moreover, Au nanorods assembled at the oil-water interface proved to afford a much stronger signal SERS intensity compared to those prepared solution.¹¹⁴ However, be it in solution phase or at liquid-liquid interfaces, it is difficult for such platforms to produce stable signals over time due to the possible aggregation and movement in liquid. Therefore, in this thesis, solid state platforms are mainly reviewed and discussed.

One dimensional nanoparticle arrays have proven to be excellent candidates for SERS because incident photons can be confined between individual nanoparticles to result in an enhanced localized electromagnetic field. For example, Nogami *et al* successfully assembled Ag nanoparticles into dimers, trimeric and tetrameric chains, and observed that SERS signal intensity increases with the number of assembled Ag nanoparticles, with the tetrameric chains offering the highest SERS enhancement.¹³⁴ On the other hand, a 2D SERS platform can produce active hot spots spanning over 2 dimensions, which significantly increases the SERS capacity area. For instance, Lee *et al.* utilized the liquid-air interface to create a self-assembled monolayer of Au nanoprisms as a SERS platform. Due to the mirror effect of pre-coated Au film underneath the prisms, homogeneous enhanced SERS signals over a large area could be obtained.¹³⁵

In the past few years, 3D structure-based SERS substrates demonstrate a great advantage over others, as a result of the larger surface area of “hot spots” and for the

adsorption of target molecules. Tsukruk *et al.* reported a process to assemble Au particles onto a porous alumina membrane as a 3D SERS substrate with 2, 4-dinitrotoluene as a Raman probe, which produced a Raman signal intensity of about 10^5 times higher as compared to a 2D gold nanoparticle film.¹³⁶ Due to the large enhancement of signal, such 3D SERS substrates soon attracted much attention, of which two main strategies are commonly used, by stuffing particles or modifying surface. Using the first strategy, 3D SERS substrate can be constructed by the assembly or aggregation of composite nanoparticles themselves without the need for external supporting structures. Unfortunately, the efficiencies of both the “hot spots” and absorption of target molecules within the 3D construction are low because the buried nanoparticles cannot interact with incident light. As reported previously by our group, we successfully constructed a 3D woodpile-like structure layer by layer, generating “hot spots” between both parallel and vertically aligned Ag nanowire pairs.¹³⁷ However, we observed that the intensity of Raman signal reaches a maximum at 3 layers, due to the blocking of light by top layers. Therefore, such inefficiency limits the potential application of the 3D SERS substrate in z direction.

On the other hand, the surface modification strategy always maximizes the SERS capacity of “hot spots” with the aid of an external 3D support. Surface modifications can be introduced atop an external 3D support, via nanoparticle assembly,¹³⁸ direct deposition of nanocrystals¹³⁹ and wet chemical growth.¹⁴⁰ This ensures that most if not all of the nanoparticles are exposed to incident light, for maximum electromagnetic field enhancement. Moreover, the increasing roughness resulting from the external 3D support will help to produce a larger area of “hot spots”. For example, Fan et al. decorated Si/ZnO

arrays with Ag nanoparticles by photo-chemical deposition to fabricate a 3D SERS platform, which offers large signal enhancement due to geometry effect as compared to a 2D surface.¹⁴¹ Up to now, even though other strategies have been developed to build 3D SERS platforms, such as reactive ion etching, template metal deposition, electron beam lithography and direct chemical growth, there is a lack of study on morphology influences of the external support construction, which could offer varied designs for 3D SERS substrates.¹⁴² Therefore, by breaking the morphology and topography limitations of current fabrication technology, we hope to extend the potential applications of 3D SERS platforms in the near future through continuous and systematic research. Yet, to the best of our knowledge, it is still a great challenge to fabricate a 3D SERS substrate with well-defined and also tunable external support construction. Thus, the search for a robust and versatile way to fabricate a tunable 3D SERS structure remains an area of interest.

As mentioned above, due to the wavelength of incident light used, a hierarchical combination of microscale supporting structures decorated with nanoparticles is ideal for enhancement of Raman signals. Hence, finding a suitable method to introduce the nanoparticles onto the constructed 3D platform is also widely investigated. Recently, various strategies to deposit metal nanoparticles, such as physical vapor deposition, direct particle growth, and self-assembly of particles have been explored to enhance the Raman intensity. For example, Zhu *et al.* fabricated a 3D Ag-ZnO array via ion sputtering for trace SERS detection of biphenyls.¹⁴³ However, a methodological heterogeneity of decorated Ag particles on the array could be observed along the transverse cross-sectional axis of the substrate. The Raman heterogeneity arising from the deposited nanoparticles could be potentially reduced or avoided through pretreatment of the platform before

assembly.

1.5.4 PRACTICAL APPLICATIONS

To date, the practical applications of SERS have been widely studied and developed, including biological sensing and chemical tracing. For example, the antibody conjugated gold nanoparticle was applied *in vivo* for cancer targeting.¹⁴⁴ The SERS signal detected was mainly localized within tumor areas in the liver, indicating high potential for medical diagnosis. However, even though great progress has been achieved in such traditional fields, the unique property of SERS spurs people to pursue new applications. In our group, Cui *et al.* has also successfully applied the aforementioned, polarization dependent property of SERS in anti-counterfeiting and intensity-dependent multi-dimensional information transfer.^{145, 146} In all, new practical applications of SERS are constantly being sought after and explored as the human's imagination knows no bounds.

1.6 MOTIVATIONS AND OBJECTIVES

In this chapter, we focused on the discussion of the plasmon resonance of nanoparticles. At the very beginning, we reviewed the fabrication strategies of nanoparticles from both chemical synthesis and lithographic preparations. Subsequently, we also summarized the effect of physical and chemical characteristics, including size, shape, crystallinity, composition and symmetry on the plasmon resonance properties of nanoparticles, where symmetry control is determined to exert the greatest change in plasmon resonance. Following which, we examine how the isotropic and anisotropic modification of nanoparticles could potentially generate new plasmon resonance

properties, and conclude that the most unique plasmon resonance properties are obtained from asymmetrical, anisotropic nanoparticles. Finally, by highlighting SERS as the most promising plasmon resonance application of nanoparticles, we summarize some of the SERS platforms that have been fabricated thus far and discover that there is still a lack of studies in 3D SERS platform. Motivated by this, we try to create a hierarchical 3D SERS substrate by combining two photon lithography and LB assembly techniques, where systematic studies of physical parameters is discussed and further application of the substrate for information storage is demonstrated.

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Chapter 2

Bimetallic Platonic Janus Nanocrystal

ABSTRACT. We demonstrate the creation of Ag-based bimetallic Platonic Janus nanostructures by confining galvanic replacement reaction at a nanoscale interface on highly symmetrical nanostructures such as Ag nanocubes and nanooctahedra using reactive micro-contact printing (μ CP). The extent of galvanic replacement reaction can be controlled kinetically to derive Janus nanostructures with Au nanodots deposited on either one or multiple facets of Ag nanocubes. The selective deposition of Au dots on a single facet of Ag nanocubes breaks the cubic symmetry and brings about unique and anisotropic plasmon responses. High-resolution cathodoluminescence hyper-spectral imaging of single Janus nanocube demonstrates that surface plasmon resonances corresponding to Au and Ag can be excited at different spots on one Janus nanocube. In addition, we demonstrate the fabrication of alternating Janus/non-Janus segments on 2D Ag nanowires by using a line-patterned PDMS stamp for galvanic replacement. Aside from Au, Pt and Pd can also be selectively deposited onto Ag nanocubes. These Janus nanostructures may find important applications in the field of plasmon-enhanced catalysis.

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2.1 INTRODUCTION

Janus nanoparticles possess distinct surface patchiness and exhibit at least two physicochemical properties within a single nanoparticle.¹⁻⁴ The presence of anisotropic chemical composition and/or surface functionalities on a single nanoparticle imparts unique directionality and chemical ordering to these nanostructures, highlighting the potential of Janus nanoparticles as future advanced materials. Among the diverse Janus nanoparticles reported, noble metal-based Janus nanoparticles are emerging as attractive nanomaterials^{5, 6} due to the synergistic interactions of localized surface plasmon resonances arising from the noble metal nanoparticles with the other components present in the Janus system. Indeed, the inclusion of Au and/or Ag in Janus nanoparticles has produced multifunctional nanostructures with multi-modal imaging capabilities,⁷⁻¹⁰ enhanced catalysis,^{11, 12} unusual light scattering with selective excitation of magnetic or electric dipolar plasmon resonances.^{13, 14}

Currently, most of the plasmon Janus nanoparticle works are based on spherical systems, and there is a lack of research in shape-controlled metallic Janus nanoparticles,¹⁵⁻¹⁸ such as Platonic nanocrystals. Platonic nanocrystals of Au and Ag exhibit complex plasmon resonances, support multiple well-resolved higher-order plasmon modes, and importantly, create intense local electromagnetic fields around the sharp edges.^{19, 20} As such, there is an imperative for more structure-to-function investigation of anisotropic Janus bimetallic nanoparticles using Platonic nanocrystals. To date, there have been a few reports on the significance of structural and compositional anisotropy on the optical properties of the resulting non-spherical Janus metal nanomaterials.^{21, 22} For example, in the formation of eccentric Pd-Ag nanobars, new

plasmon resonances are observed, together with an increase in extinction intensities from the resulting Janus nanostructures.²³

One of the main challenges in the synthesis of shaped-controlled Platonic Janus nanoparticles is the selective chemical/structural modification on a specific facet on geometrically symmetrical Platonic metal nanoparticles. The surface energies of Platonic nanoparticles are asymmetrical compared to spherical nanoparticles due to their sharp vertices and edges.^{24, 25} The vertices of Platonic nanoparticles exhibit higher surface energies than their facets.^{26, 27} Hence it is challenging to selectively modify the surface patchiness of a Platonic nanocrystal, such as the deposition of a secondary metal on a specific facet, by solution-based approaches. Solution-based approaches will lead to secondary metal deposition on all the high-energy vertices followed by the facets.²⁸⁻³²

Here, we fabricate bimetallic Platonic Janus nanoparticles with controllable surface patchiness, and study their anisotropic plasmon resonance properties at the nanoscale. The aim is to break the compositional symmetry on Platonic nanoparticles to derive novel plasmon resonance properties. Our fabrication uses localized galvanic replacement reaction with the aid reactive micro-contact printing (μ CP) to achieve directional compositional modification of Ag nanocubes to Au, Pd and Pt at the nanoscaled interface of direct conformal contact. We will demonstrate the tuning of surface patchiness as well as hollowness of bimetallic cubic Janus nanoparticles by controlling the kinetics of galvanic replacement reaction. We also map the localized surface plasmon resonances of the Au-Ag Janus nanocubes using cathodoluminescence hyper-spectral imaging. The presence of Au on the bimetallic Janus nanoparticles gives rise to anisotropic plasmon responses compared to pure Ag nanocubes. In addition to nanocubes, we demonstrate the

use of reactive μ CP to achieve Janus nanooctahedra as well as segmented Janus nanowires by printing with topographically patterned PDMS.

2.2 RESULT AND DISCUSSION

Reactive μ CP localizes galvanic replacement to the nanoscale interface between an elastomeric stamp and Ag nanocubes, enabling bimetallic Janus Au-Ag nanocubes to be fabricated (Figure 1A).³³⁻³⁶ Our experimental design allows local chemical composition tuning of Platonic nanoparticles at the facets with direct conformal contact with PDMS stamp, creating directional surface chemical patchiness on these highly symmetrical nanocrystals that are otherwise challenging to synthesize using solution-based galvanic replacement approach. To begin, a flat oxygen-plasma treated hydrophilic PDMS stamp is immersed in a $\text{HAuCl}_4/\text{THF}$ solution to load Au precursors into the porous networks of the PDMS stamp.³⁷ This PDMS stamp is then blown dry and brought into conformal contact with a monolayer of Ag nanocubes pre-assembled using the Langmuir-Blodgett method. Conformal contact between the PDMS stamp and Ag cubes allows localized diffusion of Au precursors at the contact points, triggering galvanic replacement reaction to occur selectively on the top facet of the Ag nanocubes. Subsequently, the substrate is soaked into saturate NaCl solution for 30 min and dried for further characterization.

Figure 1. (A) Preparation procedure of bimetallic Janus particles. A PDMS stamp loaded with Au precursors is brought into conformal contact with a monolayer of Ag nanocubes. A concentration gradient of Au precursors across the area of conformal contact leads to diffusion of Au precursors from the PDMS stamp to the Ag nanocube surface, triggering galvanic replacement to occur selectively on the top facets. (B - M) Morphological evolution of Janus nanocubes with increasing concentrations of Au precursors is characterized using SEM. With low Au precursor concentrations of (B, C) 5 mM and (D, E) 25 mM, the galvanic replacement reaction is limited on the top surface of silver cubes. At moderate Au precursor concentrations of (F, G) 75 mM and (H, I) 100 mM, surface patchiness increases with more deposition of Au nanodots. The sizes of Au nanodots also increase in size. Deposition on the side walls of the nanocubes are observed in (G) and (I) at these concentrations.

No obvious macroscopic changes to the appearance of the Ag nanocube monolayer

films are detected visually at < 75 mM Au precursor concentrations after microcontact printing. When > 75 mM Au precursor is used, a distinct macroscopic color change of the nanocube monolayer film from silvery to golden brown is observed. This is due to the increase in Au compositional patchiness (from single facet to five facets) of the Platonic Janus Ag nanocubes (Figure 2).

Figure 2. Digital images of the various substrates before and after reactive μ CP. Image of the (A) as-prepared Ag nanocube monolayer film, (B) Ag nanocube film upon ECP with 5 mM Au precursors, and (C) Ag nanocube film upon μ CP with 75 mM Au precursors.

The density of Au particles deposited and surface patchiness of Au-Ag Janus nanocubes can be kinetically manipulated by tuning the concentrations of the Au precursors from 5 mM to 200 mM (Figure 1). At 5 mM Au precursor concentration, less than two Au nanodots with average diameters of approximately 7 nm are detectable on the top surface of the Ag nanocubes using scanning electron microscopy (SEM) (Figure 1B and C). Characterization of the Au nanodots, including XPS and EDS, are detailed later in Figure 3 and Figure 6, respectively. The number of visible Au nanodots on the nanocubes increases when the precursor concentration is increased 5-fold to 25 mM (Figure 1D and E), leading to an increase in surface patchiness and roughness on the top

facet of the Ag nanocubes. The formation of Au nanodots is a direct indication of galvanic replacement reaction happening via conformal contact at the interface between Ag nanocube and Au-precursor-loaded PDMS stamp at room temperature. At Au precursors ≤ 25 mM, the chemical reaction is limited to the top facet on Ag nanocubes that is in direct conformal contact with PDMS stamp. The side walls of the Ag nanocubes generally remain smooth and clean, with no Au dots observed (Figure 1C and E). These observations ascertain the selective compositional modification of a particular facet of the nanocubes using reactive μ CP.

Figure 3. The XPS data of the sample shows the information of Au and Ag. The Au 4f scan (Figure 2A) reveals a doublet at 87.2 and 83.5 eV separated by ~ 3.7 eV, which is in good agreement with the characteristic of the metallic Au doublet spaced at 3.65 eV. In Figure 2B, a doublet at 373.1 eV and 367.1 eV corresponding to Ag (0) is evident, matching well with the signature peaks of metallic Ag 3d_{3/2} and Ag 3d_{5/2}, with a 6 eV separation of the doublet and an intensity ratio of 2: 3.

The surface patchiness of Au nanodots on Ag nanocubes can be kinetically extended to multiple facets by further increasing the concentrations of Au precursors during the

printing process. More and much bigger Au dots with sizes of about 10 nm are obtained using 75 mM Au precursors (Figure 1F). In addition, several Au dots are observed to form on the nanocube side walls (Figure 1G), increasing the surface patchiness to five facets of the Janus nanocubes. This arises from the diffusion of Au precursors from the conformal contact area to the side walls during the reaction. The trend of increasing surface patchiness, Au dot's surface density and sizes with increasing Au precursor concentration continues at 100 mM (Figure 1H). The Au dots have grown to around 21 ± 4 nm at this precursor concentration and can also be easily seen on the side walls of some nanocubes (Figure 1I).

TEM characterization shows that there is slight hollowing of the nanocube interior near the edges as a consequence of the Kirkendall effect (Figure 4A).^{38, 39} Moreover, high-resolution TEM imaging indicates that the lattice fringes with a spacing of 2.2 Å observed from the Au dots can be indexed to the [100] plane of Au (Figure 4B).

Figure 4. The identity of the nanodots deposited onto Ag nanocubes at 100 mM Au precursor is characterized using HRTEM. (A) TEM and (B) HRTEM images of the nanodot. (A) TEM image of the nanostructure prepared with 100 mM Au precursor shows the partial hollowing of the cube interior. The lattice fringes observed in (B) can be indexed to the [100] plane of Au.

Topographical selectivity of the localized galvanic replacement on Ag nanocubes reaches its limit when the concentration of Au precursors used exceeds 100 mM. At 120 mM, the top surface and side walls of the Ag nanostructures are fully covered with Au dots (Figure 5A). Perforations to the nanocube corners can also be discerned after the reactive μ CP process (Figure 5B). The hollow interiors of the nanocubes are clearly observed at 130 mM of Au precursors due to the disintegration of some of the nanocube surfaces during galvanic replacement (Figure 5C and D). Nanoframes are formed at > 150 mM Au precursor concentrations (Figure 5E and F), with increasing precursor concentrations leading to nanoframes with thicker borders (Figure 3G and H).

Figure 5. (A, B) Nanoboxes structures are formed when the Au precursor concentration reaches 120 mM. (C, D) With 130 mM, nanoparticles with opening could be observed. (E, F) Above 150 mM, the morphology of nanoparticles is further tuned to frames. (G, H) Accordingly, the frames with thicker edges could be obtained when 200 mM Au precursor is used.

The yields of the bimetallic Janus nanoparticles can reach up to 70 % at lower concentrations of Au precursors, with the homogeneity of the Janus nanoparticles formed

spanning more than $100\ \mu\text{m}^2$ on the substrate. The surface chemical composition of all the nanoparticles are also characterized using electron dispersive spectroscopy (EDS). The mapping information is available in Figure 6A - H. And the amount of Au deposited increases with increasing Au precursor concentration used (Figure 6I). Janus nanoparticles prepared using 5 mM gold precursor results in a deposition of about 1.0 % of Au. The Au percentage gradually increases to $5.8 \pm 1.4\%$ for Janus nanocubes obtained using 100 mM Au precursors, and dramatically grow to $21.1 \pm 8.7\%$ and $94.6 \pm 3.4\%$ for the nanoboxes and nanoframes respectively.

Figure 6. (A - H) The EDS mapping image of nanoparticles obtained with Au precursor varying from 5 mM, 25 mM, 75 mM, 100 mM, 120 mM, 130 mM, 150 mM and 200 mM, respectively. (I) The amount of Au deposited onto the Ag nanocubes is quantified using EDS for every sample from 5 mM to 200 mM of Au precursor concentration.

Cathodoluminescence characterization of plasmon resonance

We then investigate the effect of anisotropic chemical surface patchiness on the plasmon resonance response of the bimetallic Platonic Janus nanoparticles.

High-resolution cathodoluminescence (CL) hyperspectral imaging is used to map the localized surface plasmon responses of Au-Ag bimetallic Janus nanocubes. Using an electron beam as the excitation source, the spatial and spectral variation of localized surface plasmon resonances on a single nanocube can be mapped down to a spatial resolution of ~ 10 nm. By raster scanning pure Ag nanocube as well as the bimetallic Janus nanocube prepared using 5 mM Au precursors (Figure 7), the radiative plasmon modes exhibiting higher CL emission intensities can be spatially resolved.

Figure 7. Respective SEM images of the (A) pure Ag cube and (B) bimetallic Janus nanoparticle are obtained from the cathodoluminescence microscopy.

CL maps for the pure Ag and bimetallic Janus nanocubes are presented in Figures 6A and B respectively. The cathodoluminescence intensities in the 430 nm and 580 nm energy windows are color-coded as green and red, respectively. The CL map of pure Ag nanocube presents a uniform green color throughout the entire cube, with the vertices being brighter than the center of the nanocube. The plasmon-induced emission at ~ 430 nm is clearly distinct at the four vertices (Figure 8A). By averaging the CL spectra collected from 1068 pixels that spans the entire nanocube, the averaged CL spectrum of pure Ag nanocube shows a resonance band centered at around 480 nm (Figure 8C - i). This peak can be further deconvoluted into two separate contributions, with a strong

resonance at 482 nm and a weaker resonance at around 430 nm. These two peaks arise from the dipole and quadrupole resonances of Ag nanocube, respectively.⁴⁰

Figure 8. Localized surface plasmon resonances of the pure Ag nanocube and bimetallic Janus nanocube are investigated using cathodoluminescence (CL) hyperspectral imaging. False-color CL maps of (A) pure Ag nanocube and (B) Janus nanocube prepared using 5 mM of Au precursors, respectively. The green and red colors correspond to 430 and 580 nm energy windows, respectively. (C) Averaged CL spectra of pure Ag nanocube, Janus nanocube, positions 1 and 2 on the bimetallic Janus nanocube.

On the other hand, the composite CL map of the bimetallic Janus nanocube shows both green and red in different parts of the nanocube, with the color-coded emission at ~ 580 nm localized at two spots on the top facet of bimetallic Janus nanocube (Figure 8B). The averaged CL spectrum of the bimetallic Janus nanocube shows a broader plasmon resonance with the central peak wavelength red-shifted to approximately 511 nm (Figure 8C - ii). This broad band can also be deconvoluted into a sum of three resonances corresponding to 437 nm, 511 nm and 580 nm. In general, the plasmon resonance is broadened as compared to pure Ag nanocube, and contributions from both Ag and Au are observable. At the green coded region of the Janus nanocube (position 1, Figure 8B), two plasmon resonances at 445 nm and 512 nm corresponding to the quadrupole and dipole resonances of Ag are observed. The change in dielectric in the presence of Au leads to a red-shift of the plasmon resonance in relation to pure Ag nanocube.⁴¹ In addition to the plasmon resonances of Ag, a new plasmon resonance at 580 nm arising predominantly from the dipole mode of Au can be observed towards the edges of the Janus nanocube at the position 2 in Figure 8B. This resonance band is considerably red-shifted relative to pure Au spherical particles of similar dimensions and is ascribed to the coupling of the dipole resonance of Au to the plasmon resonances of Ag.^{21, 41, 42} The exact nature of plasmon coupling leading to the observation of a new plasmon mode is beyond the scope of this work and is currently under investigation.

We do note that these observed trends are consistent, as shown by several other measurements performed on both pure and Janus nanocubes (Figure 9). These measurements highlight that selective deposition of Au nanodots on Ag nanocubes

produces anisotropic plasmon responses that are distinct from those of pure Ag nanocubes. Plasmon resonances of Au and Ag can be selectively excited at different regions on a single Janus nanocube, allowing the tailoring of the optical properties of Janus nanocubes on the nanoscale.

Figure 9. (A) False-color CL map with the corresponding SEM image and (B) averaged CL spectra of three pure Ag cubes. Green color corresponds to 430 nm. (C) False-color CL map with the corresponding SEM image and (D) averaged CL spectra of Janus nanocubes prepared using 5 mM of Au precursors. The green and red colors correspond to 430 nm and 570 nm respectively.

Extension method to other precursors and morphologies

In addition to the Au-Ag system, our reactive μ CP method can be extended to obtain Pd-Ag and Pt-Ag Janus nanoparticles using Na_2PdCl_4 and Na_2PtCl_4 as respective

precursors. The SEM images of the samples after reactive μ CP indicate the formation of bimetallic Janus Pd-Ag and Pt-Ag nanocubes upon metal exchange printing process (Figure 10). The presence of Pd and Pt is also verified using XPS (Figure 10C and F). These Janus nanoparticles decorated with catalytically important metals such as Pd and Pt may find important applications in plasmon-enhanced catalysis.

Figure 10. SEM micrographs of bimetallic Janus nanocubes of (A, B) Pd - Ag and (C, D) Pt - Ag. The XPS spectra of Pd and Pt are in (C) and (F), respectively.

Aside from Ag nanocubes, we use other Platonic nanostructures to demonstrate the versatility of our topographically selective metal exchange reaction. Similar observations can be made for Ag nanooctahedra after the printing process using 100 mM of Au precursor, with Au nanodots grown on the exposed facets of octahedra (Figure 11A). TEM characterization also indicates the selective surface roughening by Au dots formation on the octahedron facet in conformal contact with the PDMS stamp (Figure 11B).

Figure 11. Reactive μ CP used to fabricate Janus nanostructures of other morphologies. (A) SEM and (B) TEM image of bimetallic Janus nanooctahedra, obtained using 100 mM Au precursor. (C, D) The creation of alternating segments of Janus Ag nanowires is demonstrated using a line-patterned PDMS stamp (5 μ m lines at 15 μ m period with a height of 1 μ m) for reactive μ CP using 100 mM Au precursors.

Furthermore, we carry out spatially selective localized galvanic replacement reaction using topographically patterned PDMS stamp on Ag nanowires to produce compositionally segmented nanowires. Using a line-patterned PDMS stamp, spatially controlled galvanic replacement gives rise to Au nanodots at regular intervals, resulting in alternating segments of Ag nanowires deposited with Au nanodots and pure Ag nanowires (Figure 11C). The resulting line features of the PDMS stamp are clearly observable after reactive μ CP using 100 mM Au precursors. A close-up SEM image indicates that Ag nanowires are coated with Au nanodots only at the 5 μ m wide areas in conformal contact with the patterned PDMS stamp, whereas the areas without conformal contact remain

unchanged (Figure 11D). This gives rise to segmented Janus nanowires, demonstrating the versatility of our reactive μ CP as a topographically-selective compositional modification method. And the EDS mapping images of both octahedra and segmented nanowire are shown in Figure 12.

Figure 12. The EDS mapping images of bimetallic octahedra (A), segmented nanowires (B) and the corresponding zoom in image.

Discussion on the relationship between Au precursor concentrations and the resulting Janus nanoparticles

Three reaction regimes can be distinguished from the experiments based on the Au precursor concentrations used, i.e. the formation of Janus nanocubes, nanoboxes, and nanoframes. At low Au precursor concentrations (≤ 25 mM), galvanic replacement is localized to the top facets of Ag nanocubes, resulting in Janus nanocubes with a single facet patched with Au nanodots. The relatively small concentration gradient at the points of conformal contact confines galvanic replacement to the Ag nanocubes' top facets. At moderate Au precursor concentrations ($25 \text{ mM} \leq [\text{Au}^{3+}] \leq 100 \text{ mM}$), Janus Au-Ag nanocubes with higher surface patchiness and larger Au dots are obtained. The kinetics of

galvanic replacement increases due to steeper concentration gradients, with more Au dots formed on the surface of Ag nanocubes. The small Au nanoparticles formed on the surfaces of Ag nanocubes act as seeds for subsequent growth into larger Au nanodots. In addition, a secondary concentration gradient created between the top surface and the side walls of Ag nanocubes. Surface diffusion of Au precursors to the side walls of Ag nanocubes triggers galvanic replacement at the side walls as well. The solid Ag nanocubes becomes increasingly hollow at high Au precursor concentrations (≥ 100 mM), first forming nanoboxes and then nanoframes.⁴³ High Au precursor concentrations creates a steeper Au precursor concentration gradient at the points of conformal contact, leading to increased diffusion of Au precursors to the Ag nanocube surface, and hence an increased rate of localized galvanic replacement on the nanocube surface.

The formation of Au dots during the reactive μ CP process is in contrast with the commonly observed epitaxial growth of Au on Ag in solution-based galvanic replacement.^{44, 45} In our reactive μ CP process, galvanic replacement is carried out at room temperature. The lower diffusion rate of Ag and AgCl at lower reaction temperatures can lead to the non-epitaxial growth of Au dots.⁴⁶ This is similar to the rough surfaces with irregular dots deposited without selectivity on Ag nanocubes in solution-based galvanic replacement reactions carried out at low temperatures.⁴⁷ At the sites of galvanic replacement, multiple small pits are formed on the nanocube surfaces to enable outward diffusion of Ag and deposition of Au.⁴⁸ These small pits grow into larger holes and eventually close with progressive Au deposition, leading to the formation of Au-Ag nanoboxes.⁴⁹ When the Au precursor concentration is sufficiently high (> 150 mM), dealloying of the nanoboxes occurs, resulting in Au nanoframes.⁴³ Under such reaction

conditions, the nanoboxes and nanoframes obtained are similar to those derived from solution-phase galvanic replacement.

Scheme 1. The morphology change process of the bimetallic Janus particle via μ CP, comparing with the ones from solution phase preparation.

The reactive μ CP experiments conducted heretofore demonstrates the possibility of integrating galvanic replacement reaction with μ CP to create novel bimetallic Janus nanoparticles (Scheme 1). Galvanic replacement reaction becomes kinetically controlled, hence affording a range of different Janus nanoparticles by tuning Au precursor concentrations. This is in stark contrast with solution-based galvanic replacement, where thermodynamically stable structures with isotropic Au deposition on the vertices and/or facets of Ag nanostructures are formed.^{43, 47} The similarity in surface energies of all the nanocrystal vertices or facets does not permit the selective deposition of Au on a single vertex or facet in a thermodynamically stable system. Furthermore, the importance of controlled Au precursor diffusion provided by the PDMS stamps is shown by conducting galvanic replacement conducted on Ag nanocubes deposited on Si substrates without using PDMS stamps. This gives rise to random deposition of Au as well as immediate

formation of nanoframes (Figure 13).

Figure 13. The importance of using PDMS stamps for reactive ECP is demonstrated here. Control experiments performed without using PDMS stamps by drop-casting Au precursors (0.1 mM) directly onto the Ag nanocube monolayer leads to (A) homogeneous galvanic replacement. The formation of (B) nanoframes is also observed.

2.3 CONCLUSION

In conclusion, we have demonstrated the creation of Platonic Janus nanoparticles by integrating kinetically controlled galvanic replacement with reactive μ CP. Platonic Ag-based Janus nanoparticles, including nanocubes with one or multiple facets decorated with Au nanodots and octahedra can be formed using this fabrication method. Such Janus nanoparticles are structurally and optically distinct from Ag nanocrystals subjected to solution-based galvanic replacement. The selective decoration of Au nanodots on Ag nanocubes gives rise to unique and anisotropic plasmon responses from the bimetallic Janus nanocubes. By having different surface patchiness on a single nanocube, these Platonic Janus nanoparticles can potentially serve as building blocks to derive novel self-assembled structures with intriguing optoelectronic properties. In addition to Au, the formation of Janus nanocubes with Pt and Pd is demonstrated. These materials can also

have the potential to be utilized as a novel class of catalysts, where surface plasmon can be used to enhance the catalytic properties of Pt and Pd through plasmon-enhanced catalysis.

2.4 MATERIALS AND METHODS

Materials. Silver nitrate ($\geq 99\%$), gold (III) chloride trihydrate ($\geq 99.9\%$), anhydrous 1,5-pentanediol (PD, $\geq 97.0\%$), poly(vinyl pyrrolidone) (PVP, average $M_w = 55,000$), anhydrous ethylene glycol (EG, 99.8%) and 1H,1H,2H,2H-perfluorodecyltri-ethoxysilane ($\geq 98\%$) were purchased from Sigma Aldrich; sodium tetrachloroplatinate (II) hydrate (Pt $\geq 42.45\%$) and sodium tetrachloropalladate (II) trihydrate ($\geq 99\%$) were purchased from Strem Chemicals; copper(II) chloride ($\geq 98\%$) was purchased from Alfa Aesar; silicone elastomer curing agent and silicone elastomer base (Sylgard 184) were purchased from Dow Corning; NaCl (99.5%) was purchased from Goodrich Chemical Enterprise. All chemicals were used without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis & purification of Ag cubes. The preparation of Ag nanocubes was carried out following the methods described in literature.⁵⁰ In a typical synthesis, 10 mL of CuCl_2 (8 mg/mL), PVP (20 mg/mL) and AgNO_3 (20 mg/mL) were separately dissolved in PD. 35 μL CuCl_2 solution was added to the AgNO_3 solution. 20 mL PD was then heated to 190 °C for 10 min. 250 μL PVP precursor was added to flask dropwise every 30 s while 500 μL AgNO_3 precursor was injected into the flask every minute in one go. The reaction was allowed for approximately 20 min. Upon formation of Ag nanocubes, the Ag nanocube solution was re-dispersed in ethanol, and 100 mL PVP water solution (0.2 g/L).

This solution was then vacuum filtered multiple times using PVDF filter membranes (Durapore®) with pore sizes ranging from 5000 nm, 650 nm, 450 nm and 220 nm to remove impurities.

Synthesis of Ag octahedra nanoparticles. Ag nanocubes were used as the precursors for the preparation of Ag octahedra.⁵⁰ 10 mL of CuCl₂ (8 mg/mL), 30 mL of PVP (20 mg/mL) and AgNO₃ (40 mg/mL) were separately prepared in PD. After fully dissolving the AgNO₃ precursors, 120 µL CuCl₂ solution was added into the precursor solution. The nanocube solution in pentanediol above was heated to 190 °C and the PVP and Ag precursors were alternately injected into the flask following the same procedure as described in earlier. The reaction was allowed to proceed for 1.5 – 2 h.

Synthesis of Ag nanowires. 7 mg of NaCl was added to 10 mL of 0.45 M PVP in EG and the solution was heated at 160 °C. 5 mL of 0.12 M AgNO₃ in EG was added drop wise at a rate of 5 mL/h into the PVP solution by a syringe pump.⁵¹ The solution was kept at 160 °C for 30 min before cooling to room temperature. The reaction solution was then washed several times using acetone and ethanol until the supernatant became colorless, which helped to remove the small colloidal particles.

Preparation of monolayer of Ag nanoparticle film. 500 µL of purified Ag nanocrystal solution was dissolved into 750 µL chloroform and subsequently dispersed onto the water surface of Langmuir-Blodgett machine (KSV NIMA, KN1002). During the assembly of particles, the target surface pressure was set to 20 mN/m to ensure a densely placed monolayer of nanocrystals can be obtained.

Preparation of PDMS stamp. A Si wafer or Si mold (with 10 µm lines at 15 µm period with a height of 1 µm) was cleaned with oxygen plasma (Femto Science, CUTE-MP/R,

100 W, 0.1 torr) for 10 min and subsequently modified with 1H,1H,2H,2H-perfluorodecyltriethoxysilane in vacuum overnight. Two precursors, silicone elastomer curing agent and silicone elastomer, were carefully mixed in a 1: 10 volume ratio and evenly dispersed onto the Si substrate. The substrate was then heated in oven at 60°C overnight. The cured PDMS mold was peeled off from the Si substrate before use. PDMS stamp was pretreated with oxygen plasma (40 W, 0.1 torr) for 30 s. The hydrophilicity of the stamp was significantly increased, as observed through contact angle measurements, which changed from 116° to 49°.

Fabrication of Janus nanostructure. The cured PDMS stamp was cut into smaller pieces. These stamps were then soaked in x mM ($x = 5, 25, 75, 100, 120, 130, 150$ and 200) gold (III) chloride trihydrate in THF solution for 1 min.

The THF would serve as a nice solution to dissolve Au precursors compared other organic solvent with less polarity, such as toluene and hexane. However, water is not a good ink candidate to be absorbed by PDMS due to the surface tension. At the same time, Ethanol, a commonly used solvent, would quickly be transferred onto the substrate, which brings the difficulty to control the reaction kinetically.

For the preparation of Pd-Ag and Pt-Ag Janus nanoparticles, saturated $\text{Na}_2\text{PdCl}_4/\text{THF}$ and $\text{Na}_2\text{PtCl}_4/\text{THF}$ solutions (< 10 mM) are prepared due to the limited solubility of these metal salts in THF.

Cathodoluminescence sample preparation. To avoid the plasmon coupling between cubes, a much dilute substrate is prepared by decreasing the target pressure to 3 mN/m. Accordingly, 5 mM Au precursor is conducted to fabricate the Janus particles.

TEM sample preparation. Poly (methyl methacrylate) PMMA of 400 – 500 nm

thickness was coated on the Si substrate by using spin coating (SPS – Spin processor 150 mm) and subsequently modified with oxygen plasma for 1 min. Such substrate was used for Langmuir-Blodgett assembly of Ag nanoparticles. After the reactive micro-contact printing with x mM ($x = 5$ and 100) gold solution, the product was soaked in toluene to remove the PMMA and washed with saturated NaCl water solution once. The final sample was re-dissolved in water and drop casted on copper grid for TEM characterization.

Characterization. The samples after reactive micro-contact printing were directly characterized using scanning electron microscopy (SEM) (JEOL-JSM-7600F) at an accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopy (EDS) analysis (JEOL-JSM-7600F Oxford X-max 50 mm²) was performed using the same machine at a higher accelerating voltage of 30 kV. Transmission electron microscopy (TEM) (JEOL-JEM-1400) characterization was carried out at an accelerating voltage of 100 kV. High-resolution (HR) TEM images were acquired using a JEOL-2100 electron microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. Quantitative cathodoluminescence (CL) is carried out using an Attolight Rosa 4634 microscope, which tightly integrates a high-speed achromatic reflective lens (N.A. 0.72) within the objective lens of a field emission gun scanning electron microscope (FEG-SEM). The focal plane of the light lens matches the FEG-SEM optimum working distance. The cathodoluminescence collection efficiency is constant over a 300 μ m field of view so that cathodoluminescence emission can be compared quantitatively between two separate points. Cathodoluminescence is spectrally resolved

with a Czerny-Turner spectrometer (320 mm focal length, 150 grooves/ mm grating) and measured with an Andor Newton EM-CCD. Electron beam energies of 8 kV are used to excite the samples. The beam dwell time is set to 0.5 – 1 s and a resolution of 128×128 pixels is used for the mapping. The CL spectra are obtained by averaging around 1,000 points with high magnification shown in Figure 8 and around 200 points for the lower ones in Figure 9.

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Chapter 3

Fabrication of pyramid-like Ag nanoparticles by anisotropic etching on soft substrate

ABSTRACT. To date, interesting plasmon resonance properties can be obtained by simply breaking the symmetry of fabricated symmetrical nanostructures. However, due to the limitation in fabrication methods, such symmetry broken nanoparticles are still rarely reported. In this chapter, we succeed in preparing non-centrosymmetric Ag pyramids by selective etching of assembled octahedra. We examine the morphology of the resulting nanoparticles under SEM to confirm a significant decrease in symmetry from O_h point group to C_{4v} point group, which bring the optical property change measured by UV. Furthermore, by changing the orientation of assembled octahedra, our strategy is proven to be effective in fabricating other new morphologies with reduced symmetry. To better understand the etching mechanism, we also conduct experiments to examine the influence of the surface function and the effect of the soft substrate underneath. From those experiments, we find that the protect ligand on the surface of nanoparticles determines the etching pathway while the type of soft substrate used contributes to the control of final morphology after etching.

3.1 INTRODUCTION

The ancient Greeks recognized and believed that the beauty of nature lies in its symmetry; a belief which influenced the philosophy of science for over a thousand years.¹ However, as science and technology develop, people have found and demonstrated that it is symmetry breaking that really explain the origin of the universe.² The parity violation, as a classical example, explains the non-mirrored property of fundamental particles under weak interactions, where the weak isotopic symmetry of nuclear forces saves the universe from the quenching of matter and antimatter during the big bang.³ As a bridge between macroscopic cosmology and microscopic atom mechanics, research in nanoscience has also proven to exhibit this unique property when structural symmetry is broken.⁴ For example, the Fano resonance of nano-sized metamaterials resulting from its structural symmetry breaking gives rise to a dramatic decrease of the linewidth of LSPs via the coupling of metamaterial and free space.⁵ Such asymmetric line-shape scattering provides strong high quality factors with narrow transmission/ reflection pass and stop band, indicating an efficient plasmon performance.

Thus, to further explore the unique properties of structural asymmetry in nanoscience, the synthesis and fabrication of such particles become emergent in recent studies.^{6, 7} These days, great effort has been made to realize the symmetry breaking in the solution phase, such as heterogeneous cation exchange,^{8, 9} ligand induced interfacial energy defect,¹⁰ and direct epitaxial growths in colloids.^{11, 12} For example, a non-centrosymmetric Au-TiO₂ hybrid was synthesized by tuning the ratio of precursors in solution, which exhibited better capacity in plasmon driven photocatalysis than a symmetric system.¹³ However, thermodynamics on the other hand favor highly symmetric

structures in solution,^{14, 15} of which shapes such as nanospheres,^{16, 17} nanocubes,^{18, 19} nanoicosahedra,²⁰ and so on are widely fabricated and studied.²¹ Due to such a preference, it is technically challenging to extend symmetry breaking strategies in solution phase to a wider variety of morphologies.

To break the limitation of solution phase synthesis strategies, we developed a symmetry breaking approach by combining micro-contacting printing technology and galvanic replacement reaction as in the previous work.²² This region-selective symmetry breaking strategy was proven to be versatile which could be applied to different target morphologies from nanooctahedra to nanowires. Cathodoluminescence measurements demonstrate that unique optical properties can be obtained from such anisotropic nanoparticles. However, by galvanic replacement, a secondary element is always introduced into those anisotropic product, which may introduce complications in distinguishing between plasmon resonance changes resulting from geometry and composition. Thus, the motivation to avoid the secondary element introduction spurs us to fabricate a pure symmetry broken nanostructure.

Here, we demonstrate a fabrication process of non-centrosymmetric pyramid like Ag nanoparticle with single component by breaking the symmetry of Platonic octahedra. The Ag octahedra are first assembled at the liquid-liquid interface, forming exposed pyramidal arrays aligned edge-to-edge. Using a slow-setting gel, the orientation of Ag octahedra is maintained and the arrays are subsequently transferred onto PDMS substrate. With the protection of such PDMS, a selective etching is introduced in the solution mixture which contains NH_3 and H_2O_2 (volume ratio of 1:1), leading to the anisotropic modification of the octahedra. By controlling the reaction time, it is possible to obtain the high yield of

etched-off portions of exposed nanoparticles. The remaining embedded portion within the PDMS, removed from the PDMS mold by sonication and then drop-casted onto Si, is confirmed to be the non-centrosymmetric Ag pyramid. Furthermore, the fabrication process is demonstrated to be easily extended to other non-centrosymmetric Ag nanoparticles by simply changing the orientation of the assembled nanoparticles. Last but not least, experiments on surface functionality, substrate material and etchant composition are studied to better understand the etching mechanism.

3.2 RESULT AND DISCUSSION

The fabrication of pyramid-like Ag nanoparticles begins with the interfacial assembly of Ag octahedra functionalized with 1-hexadecanethiol ($C_{16}SH$) at the oil/water interface (Figure 1A). The $C_{16}SH$ modified Ag octahedra gives rise to a square superlattice with the octahedra aligned edge-to edge at the oil/water interface, where the hydrophobicity of the ligand results in a larger proportion of each octahedral nanoparticle being submerged in the oil phase. The facet-selective etching of Ag octahedra to nanoparticles of lower symmetry is performed by first transferring the assembled octahedra onto a PDMS “soft substrate”. SEM images of the transferred assembled Ag nanooctahedra show a square superlattice with exposed pyramidal structures above the PDMS (Figure 1B). Following which, the PDMS substrate is in an ice bath cooled etchant solution containing H_2O_2 , NH_4OH and H_2O in the volume ratio of 1: 1: 10. The etching process is quenched at regular time intervals by removing the PDMS substrate from the etchant and immersing it in ethanol.

Figure 1. (A) The scheme describes the preparation of PDMS substrates with assembled Ag nanooctahedra and the subsequent etching process. (B- G) The SEM images of the assembled Ag octahedral are taken from both top view and at a tilted angle, to clearly illustrate the changes to the exposed pyramid structure above the PDMS as the etching duration increases from 0 min to 5 min. The AFM images of the assembled nanoparticles (H) before and (I) after etching show a clear morphology change from pyramids to flat

square structures on the PDMS substrate. (J) The AFM cross-sectional height profiles of the assembled nanoparticles before and after etching, where the significant decrease in height after etching confirms the removal of the exposed part above PDMS. (K) The etched square structure obtained at 4 min is considered to be the target morphology and its yield increases from $1 \pm 1\%$, $10 \pm 4\%$, $50 \pm 6\%$ to larger than $97 \pm 3\%$ before 4 min, however drops dramatically back to $0 \pm 0\%$ when etching duration increases to 5 min.

The morphology of the etched octahedra is dependent on the etching duration. After 1 min of etching, small irregular perforations and some pseudo-hexagonal pores are observed to have formed on the (111) facets of the exposed pyramid structures (Figure 1C). These pores are approximately 30 nm in diameter, and appear darker under SEM due to their hollow interior. Larger hexagonal pores approximately 100 nm in size are observed to form on the (111) facets after 2 min of etching, together with some square structures with the exposed (111) facets totally etched off (Figure 1D). The hexagonal pores can form on more than one (111) facet on the same octahedron, and these pores appear to merge after 3 min of etching to form partially etched octahedra nanostructures (Figure 1E). At the same time, some of the exposed pyramid structures appear to have been etched off completely, forming flat squares on the surface of the PDMS substrate. Upon 4 min of etching, however, more than 95 % of the exposed pyramid structures on the PDMS substrate over an area of $15 \mu\text{m}^2$ have been etched off completely to form flat squares (Figure 1F). After 5 min of etching, both the exposed and the embedded portions of Ag octahedral nanoparticles within the PDMS are completely etched off in their entirety, leaving behind the PDMS mold underneath (Figure 1G).

AFM measurements of substrate before (Figure 1H) and after (Figure 1I) etching exhibit a significant topographical change as the exposed pyramid structures arrays get etched off. The AFM cross-sectional height profile of the pyramid structures (in orange) and the flat square arrays (in blue) shows the height of the pre-etched pyramid structures to be 107 ± 16 nm whereas the height of the frame surrounding the flat squares post-etching is approximately 46 ± 12 nm (Figure 1J). The frame arises from the way the octahedra are embedded within the PDMS mold during the self-assembly process. Approximately 70 % of the hydrophobic octahedra are in contact with the oil phase, and this leads to 70 % of the octahedra embedded inside PDMS (Figure 2), which explain the formation of the frame at the base of the pyramid post-etching.

Figure 2. (A), (B) The SEM images of as prepared Ag octahedra, where the distance between vertices to center is calculated to be 254 nm (C). Combined with the AFM data which exhibits the height above PDMS, it is confirmed that 28 ± 5 % of the octahedra are embedded in substrate, leading to the un-etched frame.

In addition, while the yield of etched-off exposed pyramid structures on the

PDMS substrate to form flat squares gradually increases when the reaction time is lengthened from 0 to 4 min, this number decreased drastically when etching time is extended beyond 4 min (Figure 1K). To obtain a more accurate estimate of the yield, we examine a large area ($> 400 \mu\text{m}^2$) where three random areas are selected and measured to ensure homogeneity across the sample (Figure 3). The calculated yields of flat squares for different etching duration from 0 min to 5 min are $0 \pm 0\%$, $1 \pm 1\%$, $10 \pm 4\%$, $50 \pm 6\%$, $97 \pm 3\%$ and $0 \pm 0\%$, respectively.

Figure 3. The low magnification SEM images of sample obtained at 4 min, indicating a high yield of the square structure more than 95% within an area around $400 \mu\text{m}^2$.

We also examine how reduced symmetry changes the optical properties of the pyramid structure in comparison with the octahedra. The pyramid array of as-assembled Ag octahedra on the PDMS substrate is multi-color in appearance, whereas the flat squares post-etching exhibit a silver mirror-like reflective shine (Figure 4). These macroscopic visual observations corroborate well with the extinction spectra measured from the PDMS substrates. The Ag octahedra appear multi-color due to the broad peak

spanning from 410 to 610 nm and centered at 480 nm. On the other hand, the extinction spectrum of the post-etched octahedral is relatively featureless, but spanning across the entire visible light region, giving rise to a silver mirror-like reflective surface. In general, the Bragg reflection of the pyramid structures gives rise to the multi-color, but when etched off it becomes relatively flat, hence appearing as a silver mirror.

Figure 4. The UV-vis spectra of the PDMS substrates show multiple extinction peaks from 410 nm to 610 nm before etching (in black) while a broad and featureless peak after etching (in red). Accordingly, the photographs show the clear change from rainbow like multi-color to silver mirror like color. Subsequently, such particles are sonicated off from substrate for further characterizations.

SEM and TEM characterizations of the remaining portion of the post-etched octahedra embedded within PDMS, removed entirely from the PDMS mold (Figure 5A, B) show pyramidal particles of lowered symmetry (point group C_{4v}) as compared to the highly symmetrical Platonic octahedra (point group O_h). Side view characterizations show that these pyramid structures are surrounded by a frame (Figure 5C, D).

Figure 5. The morphology of individual nanoparticle is confirmed by SEM & TEM, also exhibiting a pyramid like nanostructure. The SEM image (A) and TEM image (B) of nanoparticle are taken with the orientation lying on the etched square facet. (C, D) In comparison, nanoparticles lying on the triangle facet of pyramid is seldom observed.

Moreover, XPS characterization also indicates that Ag remains in its metallic form after etching, with clear Ag peaks observed from high resolution Ag 3d scans (Figure 6). A doublet at 373.1 eV and 367.1 eV corresponding to Ag (0) is evident, matching well with the signature peaks of metallic Ag 3d_{3/2} and Ag 3d_{5/2}, with a 6 eV separation of the doublet and an intensity ratio of 2: 3.

Figure 6. The XPS spectra of Ag before (on top) and after etching (at bottom) indicates the same Ag (0) composition of octahedra and pyramid nanoparticle.

Extension of the etching process

To extend our etching process to include more morphologies, we assemble PVP functionalized Ag octahedra at the interface and subject them to ligand exchange with $C_{16}SH$ to maintain similar surface functionality, followed by etching. PVP functionalized Ag octahedra assemble to form a hexagonal close-packed superlattice. The hydrophilicity of PVP leads to the predominant submersion of the Ag octahedra in the aqueous phase to minimize contact surface area with the oil phase, resulting in the formation of a hexagonal close-packed superlattice. To maintain the same surface functionality for etching, this substrate is immersed into 10 mM $C_{16}SH$ ethanol solution for 7 hours for ligand exchange to take place. During the etching process, $C_{16}SH$ -octahedra is also observed to undergo a similar facet-etching process despite the change in superlattice structure (Figure 7A-D). After 1 min of etching, small pores less than 30 nm are observed on the (111) facet of the Ag octahedra (Figure 7A). Subsequently, an irregularly-shaped hexagonal hole with edge length around 120 nm is observed on the surface of (111) at 2 min of etching (Figure 7B). At 3 minutes of etching, the exposed portion of the assembled octahedral appear to have been etched off partially to form flat truncated triangular faces which differs from our previous observation (Figure 7C). As reaction time increases to 4 min, the exposed portions of the nanoparticles are further etched off to form flat hexagonal faces, corresponding to the body-center cross section of octahedra along (111) direction, on the surface of the PDMS (Figure 7D).

Figure 7. To extend the application of etching on soft substrate, octahedra with different orientation are applied to the etching with the same surface function. (A-D) The SEM and zoom in image are taken accordingly with equal time interval. (A) At 1 min of etching, there are similar small dots observed on the triangle (111) facet of octahedra. (B) The larger hole with edge of over 100 nm is observed on the particles under a further etching of 2 min. The dark contrast of SEM also indicates a deep depth of such hole. (C) Subsequently, etched off particle with exposed truncated triangular faces are observed after 3 min etching, where the morphology differs from previous observation. (D) At 4 min, similar hexagonal planes but with regular shape are finally obtained.

The optical properties of the substrate before and after etching are characterized by UV-Vis spectroscopy and visual observation (Figure 8). Though large morphology changes have been confirmed, we observe little color change, as both substrates appear grey. Accordingly, the featureless extinction spectra of both substrates span across the entire visible region which lead to the grey color surface.

Figure 8. The UV extinction spectra of the PDMS substrate show both featureless peaks before and after etching and accordingly the photographs corroborate well showing little change of grey colors.

The remaining portion of the post-etched octahedra embedded within PDMS, removed entirely from the PDMS mold show particles of lowered symmetry with point group of C_{3v} . From the SEM characterization, the particles with a smooth triangle surface are majorly found in the sample (Figure 9A, B). And the side view exhibits a tailored triangle facet with length of 210 nm, which is much shorter than the one of octahedra (Figure 9C, D).

Figure 9. The SEM images of single particle are taken from different orientations and

solution based extinction is measured before drop-casting on Si substrate. (A, B) The nanoparticle lies on the etched triangle facet and shows a smooth triangle facet. (C, D) The nanoparticle stands on one of the tailored facet and exhibit another tailored triangle plane with length of 210 nm, which is much shorter than the edge length of octahedra (360 nm).

Mechanism of etching

Aside from surface functionality, we find that the presence of ammonia is quintessential in driving the etching reaction (Figure 10). No large scale etching is observed in the absence of ammonia even under prolonged 15 min immersion within the etchant (Figure 10A, B). Only small perforations of less than 20 nm are obtained on partial vertices of the octahedra. In the presence of 0.1: 1 $\text{NH}_3\text{H}_2\text{O}$: H_2O_2 , square structures similar to Figure 1J, K are observed (Figure 10C, D). However, the frames surrounding the squares are almost 3-fold thicker, indicating an incomplete etching process. As suggested in the zoomed out image (Figure 10C), such thicker frames are randomly distributed over the substrate, where some particles show thicker frames at all four edges. The optimal ratio for achieving high-yields of square pyramids ranges from 1:1 to 5: 1 ($\text{NH}_3\text{H}_2\text{O}$: H_2O_2) (Figure 10E, F), showing square structures with homogeneous thin frames. Further increasing the H_2O_2 : $\text{NH}_3\text{H}_2\text{O}$ ratio to 10:1 gives rise to a rough surface post-etching (Figure 10G, H). It is worth mentioning that the reaction is complete in seconds, which contributes to the difficulty in fine-tuning the conditions to obtain a smooth surface.

Figure 10. The importance of ammonia in controlling the morphology of obtained particles is demonstrated by varying the ratio of $\text{NH}_3\text{H}_2\text{O}$ to H_2O_2 , of which is 0: 1, 0.1: 1, 5:1 and 10:1, respectively. (A, B) Without ammonia, there is only the occasional small perforation observed at the vertices of octahedra without other significant morphology change. (C, D) Increasing the ratio of $\text{NH}_3\text{H}_2\text{O}$: H_2O_2 to 0.1: 1, the etched particles with three times thicker frame is observed indicating an incomplete etching. (E, F) With a ratio optimized to be 1:5, the similar square structures are also achieved. (G, H) Further increasing ratio to 10: 1 gives rise to rough surface on the nanoparticles.

The role of PDMS is to serve as a protective mold to enable symmetry breaking of octahedra particles via wet chemical etching. Similar pyramid structures can also be obtained when PDMS is changed to another polymeric substrate, such as poly(methyl

methacrylate) (Figure 11A, B). However, a more isotropic etching is observed using particles on Si substrate with a pseudo-hexagonal lattice (Figure 11C-F). Such substrate is obtained by directly transferring of PVP coated octahedra at liquid/ oil interface onto Si instead of curing with PDMS and subsequently such substrate proceed with ligand exchange of $C_{16}SH$ for 7 hours to guarantee similar surface functionality. Hexagonal-etching of all the exposed (111) facets of the octahedra particles is observed, beginning with the formation of small pores which subsequently grow with increased etching time. While the high-order symmetry of the etched particles is preserved, the etched particles also exhibit a frame like structure arising from the facet-etching process. In addition, there is no other regular shape detected from etching.

Figure 11. The effect of substrate is detected by changing its material. (A, B) PMMA as another soft substrate is applied, from which similar square structure is obtained. However, when a hard substrate such as Si is used, pyramidal particles are not observed. (C, D) Similarly, small dots are first observed on the (111) facet as shown. (E, F) Subsequently, a larger hexagonal hole is formed on the same facet, forming a frame like structure.

The observed difference in etching pathways between C₁₆SH coated octahedra and PVP coated octahedra arises from surface functionality differences and not because of the superlattice structural dissimilarity. To prove this, hexagonal close-packed superlattice capped with PVP was directly etched with the same etchant (Figure 12). During this etching process, we do observe a much faster reaction rate of PVP coated substrate than the one with C₁₆SH. And we suppose that it is the ligand hydrophilicity of PVP that leads to the faster penetration of aqueous etchant solution. After 10 s of etching, the SEM images show the formation of small irregular perforations on the vertices of the octahedra particles (Figure 12A, B), resulting in a truncated triangle plane of (111) facet. These pores are approximately 40 nm in diameter, and appear darker under SEM due to their hollow interior. A higher density of perforation is observed to spread from the vertices to the edge of the PVP coated octahedra after 20 s of etching (Figure 12C, D). At 30 s of etching, partially etched PVP functionalized octahedra with a hexagonal morphology is observed instead of a truncated triangular plane as previous, but an incomplete etching leaves a hat-like structure on top of the octahedra (Figure 12E, F). By 40 s of etching, more than 70 % of the particles over a 20 μm^2 area on the PDMS substrate has achieved a

flat hexagonal morphology (Figure 12G, H). We notice that such regular hexagonal shape is similar to the previous substrate obtained from $C_{16}SH$ coated octahedra. Thus, we propose that although the etching pathway differs, the surface functionality is not the key factor to control the final morphology.

Figure 12. When the Ag octahedral are coated with PVP, the etching proceeds by a different pathway but giving a similar final morphology as when $C_{16}SH$ is used. (A) After etching for 10 s, the etching process is observed to begin from the vertices of octahedra instead of triangular (111) facet, indicating the etching pathway changes with different surface functionality in the beginning. (B) After 20 s etching, small dots are observed to form along the edges of triangle plane but the relative smooth (111) facet remains. (C) The partially etched off particle is still observed on the substrate as reaction time increases to 30 s. (D) Although the etching pathway is different, the same flat hexagonal facets are obtained after 40 s of etching.

Furthermore, we also investigate the etching processes of both $C_{16}SH$ (Figure 13A) and PVP (Figure 13E) coated octahedra in solution phase to further confirm the different etching pathways and the protective influence of the soft substrate. The extent of etching

of Ag octahedral functionalized with C₁₆SH is determined by introducing X μ L of as prepared etchant, where X equals to 250, 750 or 1250. Likewise, small perforations with diameter less than 20 nm are first observed on the (111) facet (Figure 13B). As the amount of etchant is increased to 750 μ L, both the quantity and sizes of irregularly-shaped and pseudo-hexagonal perforations observed on more than one facet increases (Figure 13C). When the volume of etchant is further increased to 1250 μ L, larger size hexagonal pores are observed, with a length of approximately 100 nm, indicating the same frame-like structure as that obtained on Si substrate, without soft substrate protection (Figure 13D). The etching selectivity on PVP coated octahedra has been reported under similar conditions where the morphology changes from concave octahedra to octapod structure indicating an etchant preference of the (100) and (110) facet.²³ We first prepare the PVP coated octahedra of an equal concentration with that of C₁₆SH coated octahedra. By adding the PVP-functionalized octahedral into 750 μ L etchant, we observe that the edges and corners of octahedra are etched, leaving gaps of approximately 20 nm (Figure 13F). When the amount of etchant is increased to 1250 μ L, an octapod structure with short “arms” less than 40 nm in length is observed (Figure 13G). Finally, when 1500 μ L of etchant is used, octapod structures with longer “arms” of 100 nm are observed (Figure 12H). By comparing the morphology changes of Ag octahedra functionalized with C₁₆SH and with PVP, it is clear that etching pathway of octahedra is highly dependent on the surface function.

Figure 13. The etching of both $C_{16}SH$ (A-D) coated and PVP (E-H) coated octahedra are conducted in solution phase and then dropped cast on Si substrate. Prior to etching, there is almost no difference between octahedra coated with $C_{16}SH$ (A) and with PVP (E). (B) By using a hydrophobic ligand $C_{16}SH$, the etching pathway appears to begin with small dots on the (111) facets when little etchant of 250 μL is added. As the amount increases by three or five times, bigger hexagonal holes on this facet (C) or the complete etching of the whole facet forming frame structure (D) is observed accordingly. On the other hand, the etching pathway differs with PVP. (F) If 750 μL of etchant is applied, the edge truncated octahedra is observed leaving gaps around 20 nm. (G) Adding 1.5 fold of etchant, it is clear that the (111) remains while the (100) and (110) are removed leading to an octapod structure obtained. (H) As etching goes further with 1500 μL etchant, the octapod structure with longer “arms” is obtained, which exhibit the lower etching degree on (111).

Based on the previous studies of surface functionality and substrate influence, a possible mechanism is proposed up in Scheme 1. Since (111) facet has a lower surface energy than (100) and (110), we assume that the hydrophobic ligand of $C_{16}SH$ prefers to bond with the more reactive facet. Thus, it is harder for ammonia which is the key factor for etching to contact with such facets. Hence, there are always small pores observed on the (111) facet in the beginning and subsequently when the reaction proceeds further (Figure 1, 7, 11 and 13). In case of PVP, which is much more hydrophilic ligand, the etchant prefers to etch the more reactive facets of (100) and (110). Thus, the opposite selectivity is expected which matches well with the observations from Figure 12 and Figure 13. But as demonstrated, such selectivity of the etching direction only changes the etching pathway rather than the final morphology obtained. As illustrated in Scheme 1, all intermediate morphologies during the course of the etching process have a large exposed surface area to the etchant phase. Their instability is also evident from the random distribution of the different intermediate morphologies at the beginning of the etching process. On the other hand, the flat morphologies which are parallel to the substrate has the smallest surface area in contact with the etchant, making it possible to kinetically control the etching reaction. Therefore, we propose that the etching pathway is dependent on the surface functionality while the final morphology is controlled by the presence of the soft substrate.

Scheme 1. The proposed etching mechanism. The (111) facet is treated as a relatively low surface energy facet which is preferred by the ammonia, leading to a sped-up etching ratio on this facet. However, all such intermediates are unstable due to a large exposed surface to the etchant phase. In contrast, the etched off particle with flat surface would experience a much reduced surface area in contact with the etchant, which explains the increasing yield of the etched off nanoparticles on substrate. This proposed mechanism has also been further confirmed when octahedral is assembled with different orientation.

3.3 Conclusion

The symmetry breaking of nanoparticles can be realized by the selective etching in the presence of a protective soft substrate, which leads to unique optical properties. Here,

we demonstrate a unique strategy by using nanooctahedra to fabricate non-centrosymmetric Ag pyramids. By changing the orientation of assembled octahedra, such a process is easy to be extended for the generation of new morphologies. To confirm the importance of surface functionality on controlling etching pathway, octahedra coated with C₁₆SH or PVP is etched under identical conditions on both substrate and in solution phase. However, based on evidences that the final morphologies obtained from Ag nanooctahedra with different surface functionalities are similar, we propose that it is the protection of the soft substrate that contributes to the control of final morphology.

3.4 MATERIALS AND METHODS

Materials. Silver nitrate ($\geq 99\%$), 1,5-pentanediol (PD, $\geq 97.0\%$), poly(vinyl pyrrolidone) (PVP, average $M_w = 55,000$), n-decane, 1-hexanethiol (HDT, $\geq 95\%$) were purchased from Sigma Aldrich; copper(II) chloride ($\geq 98\%$) was purchased from Alfa Aesar; silicone elastomer curing agent and silicone elastomer base (Sylgard 184) were purchased from Dow Corning. Gellan Gum (KELKOGEL®) was kindly sponsored by CP Kelco (USA). All chemicals were used without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis & purification of Ag octahedra. Ag cubes were synthesized via polyol synthesis method as reported in literature.^{24, 25} Briefly, 35 μL of 8 mg/mL CuCl₂ were mixed with 10 mL of 20 mg/mL AgNO₃ PD to form the Ag precursor solution. 10 mL of 20 mg/mL PVP PD solution was also prepared, which functioned as the capping agent. To a 100 mL flask, 20 mL of PD was added and heated at 190 °C for 10 min. Following which, 250 μL of PVP solution was injected dropwise twice while 500 μL of AgNO₃

precursor was injected once per minute. This injection circle was continued for 20 min, until the greenish color of the reaction mixture fades and turns reddish.

The synthesis of cuboctahedra and octahedra were based on the obtained cubes. 40 mg/mL AgNO₃ PD solution was prepared as Ag precursor. The as prepared nanocubes were heated at 190 °C, and the same injection circle was performed for 20 min to obtain cuboctahedra and another 40 min to obtain octahedra.

After the synthesis process, the Ag PD solutions were washed by acetone and re-dispersed in 100 mL PVP water solution (0.2 g/L). According to the size of Ag nanoparticles, PVDF filter membranes (Durapore®) including pore size of 5 000 nm, 650 nm and 450 nm were used for the purification of octahedra while 220 nm pore size filter membranes were used for cubes.

Ligand exchange reactions. The purified Ag octahedra dispersion was generally allowed to sediment overnight. 0.5 μL of the sediment was dispersed in ethanol and centrifuged once more before dispersing in 1.5 mL of ethanol/isopropyl alcohol (1:1). 100 μL of 10 mM C₁₆SH was then added dropwise to this dispersion under stirring. Ligand exchange was allowed to take place for 4 hrs, followed by 2 rounds of centrifugation, re-dispersal in 1.5 mL of ethanol/isopropyl alcohol (1:1), and addition of fresh thiol solution under stirring. This step was allowed to continue for another 3 hrs, followed by 3 rounds of centrifugation and washing with isopropyl alcohol/water (1:1). Subjecting Ag octahedra to 2 rounds of ligand exchange removed the replaced PVP and facilitate subsequent ligand exchange.

Similar ligand exchange process was applied to the nanoparticles on substrate after assembly. 10 mM C₁₆SH was prepared with stirring, and the substrate was submerged in

the ligand solution for 7 hours.

Gel-trapping self-assembly experiments. 2 wt% aqueous gellan gum solution was used as the water phase and n-decane was used as the oil phase. The gellan gum solution was first heated to approximately 80°C in an oil bath to ensure that the gel was fully hydrated. Subsequently, pre-heated n-decane was added to the top of the gellan gum solution to create the oil phase. Either C₁₆SH or PVP coated Ag octahedra were then added to the oil/water interface and the entire mixture was left at 80°C for approximately 15 min before being allowed to cool slowly to room temperature. This ensured that the nanoparticles had sufficient time to spread and achieve thermodynamic equilibrium at the oil/water interface. Once the gel had set in the aqueous phase, the oil phase was then decanted gently. In place of n-decane, a layer of premixed PDMS precursor mixture (5:1 elastomer: curing agent) was poured over the nanoparticle monolayer and the container was left at room temperature for the PDMS to cure. After the PDMS had hardened, it was lifted off from the gel and washed in hot water. Gellan gum was shown to have no effect on the oil/water interfacial tension, hence it does not have any impact on the type of assembled structures.

Etching process on PDMS substrates. In a vial with ice bath, hydrogen peroxide, ammonia and water were mixed with a volume ratio of 1: 1: 10 as the etchant solution. Subsequently, the as prepared PDMS substrates was directly submerged into this etchant. To avoid the inhomogeneity resulting from the bubbles arising from the decomposition of hydrogen peroxide, the substrate was removed after 30 s and immediately soaked in pure ethanol to quench the reaction. After drying in air, the etching and quenching process was repeated, for approximately 4 min until a silverish color appeared.

Etching process in solution phase. One batch of functionalized C₁₆SH-octahedra sediment was re-dispersed in 500 μ L water with stirring. Subsequently, X μ L of the as prepared etchant (X = 250, 750 or 1250) was added in one quick injection. A vigorous effervescent reaction spanning over a few minutes was observed. After half an hour, the solution mixture was directly drop-cast onto Si for characterization. This process was repeated with PVP coated octahedra in solution.

Lifting etched particles off from PDMS. The etched PDMS substrates were immersed in chloroform for 30 min, followed by sonicating for 10 min in chloroform, until the PDMS substrate turned colorless and the solution turned into a liquid suspension. The liquid was decanted into a centrifuge tube and centrifuged at 6000 rpm for 4.5 min. The sediment of aggregated nanoparticles was re-dispersed in ethanol for UV measurements and subsequently SEM /TEM characterization, respectively.

Characterization. Scanning electron microscopy (SEM) (JEOL-JSM-7600F) was performed at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) (JEOL-JEM-1400) characterization was carried out at an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. Atomic force microscopy (AFM) from Bruker Dimension ICON® with NanoScope V controller was used to investigate the morphology of the self-assembled Ag octahedra monolayers. The morphology before and after the etching process on the PDMS molds was acquired by Tapping mode (non-contact mode) using silicon probes (model Tap300Al-G) from BudgetSensor®. Data analysis was done by using freeware WSxM Scanning Probe Microscopy Software from Nanotec Electrónica S.L..

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Chapter 4

Hierarchical 3D SERS Substrates Fabricated by Integrating Photolithographic Microstructures and Self-Assembly of Silver Nanoparticles

ABSTRACT. Most of the surface-enhanced Raman scattering (SERS) substrates are 2D planar systems, which limits the SERS active area to a single Cartesian plane. Here, we fabricate 3D SERS substrates with the aim to break the traditional 2D SERS activate area limitation, and to extend the SERS hotspots into the third dimension along the z-axis. Our 3D SERS substrate is tailored with increased SERS hotspots in the z-direction from tens of nanometers to tens of micrometers, increasing the hotspot density in the z-direction by at least an order of magnitude larger than the confocal volume ($\sim 1 \text{ m}$) of most Raman spectrometers. This offers the possibility of increasing the accessibility of such 3D SERS substrates for on-site measurements by untrained personnel, where instrumental configurations are not always comparable to those used in the laboratory. Various hierarchical 3D SERS-active microstructures are fabricated by combining 3D laser photolithography with Langmuir-Blodgett nanoparticle assembly. 3D laser photolithography creates microstructured platforms required to extend the SERS-active area into 3D, and the self-assembly of Ag nanoparticles ensures homogeneous coating of SERS-active Ag nanoparticles over the entire microstructured platforms. Large-area 3D Raman imaging demonstrates that homogeneous signals can be collected throughout the

entire 3D SERS substrates. We vary the morphology, height, and inclination angles of the 3D microstructures, where the inclination angle is found to exhibit strong influence on the SERS signals.

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4.1 INTRODUCTION

One of the main challenges in surface-enhanced Raman scattering (SERS) is the capability to produce a SERS-active substrate with large number of hotspots that can give rise to high enhancement factors.^{1, 2} SERS substrates utilize the collective plasmon resonances arising from the interactions of the localized surface plasmon resonances (LSPRs) of noble metal nanostructures and/or nanoparticles, especially those of Ag and Au.³ The LSPRs of metallic nanoparticles/nanostructures are capable of confining light into sub-wavelength volumes, generating intense local electromagnetic fields in their proximities, giving rise to strong SERS enhancement. While 2D arrays of metallic nanostructures and/or nanoparticles have been widely studied and can potentially achieve high SERS enhancement factors,^{4, 5} the maximum number of SERS hotspots that can be achieved for such substrates are limited to a single Cartesian plane. On the other hand, the laser confocal volume used for SERS measurements is a 3D space, indicating that the 2D SERS substrates are under-utilizing the active confocal volume even though large-area hotspots are presented within the x-y plane. This also implies that the incident excitation source needs to be tightly focused on the correct plane in order to achieve optimal SERS enhancement, which reduces the versatility of such substrates, especially for on-site applications.

To address these issues, 3D SERS-active substrates with considerable extension in the third dimension are actively pursued to increase the versatility of a 3D SERS platform,⁶⁻⁹ by increasing the number and utility of SERS hotspots in all three dimensions such that SERS-active regions are not limited to a single Cartesian plane. In addition, the extension of a SERS substrate from 2D to 3D brings about a larger overall surface area

which in turn enables more target molecules to be adsorbed and detected in the third dimension, especially along the z-axis.^{10, 11} Moreover, higher tolerance in focus misalignment along the z-direction can also be achieved.¹²

Many fabrication strategies have been put forward to build 3D SERS substrates, such as reactive ion etching,¹³ template metal deposition,^{14, 15} electron beam lithography¹⁶ and direct chemical growth.¹⁷ While majority of the structures investigated mainly revolves around pillars, cylinders or columnar architectures,¹⁸⁻²¹ they may not be the most efficient design for SERS. For instance, in the trace sensing of biphenyls using 3D ZnO cone-shaped arrays ion sputtered with Ag nanoparticles,²² the unidirectional sputtering of Ag leads to inhomogeneous nanoparticle deposition and results in variations in SERS signals, especially along the z-axis.

On the other hand, self-assembly of noble metal nanoparticles into defined supercrystals has also been demonstrated to be an alternative approach to generate 3D SERS substrates.²³⁻²⁵ Even though the use of supercrystals enables the construction of diverse 3D SERS architectures, only the nanoparticles in the outermost layers are SERS-active.²⁶ In particular, the nanoparticles near regions of high asperities are shown to contribute most significantly to the SERS signals detected.²⁷⁻²⁹ Our group constructed a layer-by-layer assembly of Ag nanowire woodpile structure for 3D SERS application,¹² which demonstrates that the SERS signals become saturated beyond three layers of Ag nanowires assembled due to limited skin depth and laser penetration issues. This implies that an ideal 3D SERS substrate does not need to be constructed with multiple layers of nanoparticles. No doubt that the extension of a substrate from 2D to 3D has provided the capability to generate higher hotspot densities per unit volume and enriched research on

SERS, the most efficient 3D architecture as well as the optimal fabrication route remains to be uncovered. Moreover, an impartial comparison between structural variations along the z-axis on the SERS activities of a 3D SERS substrate has yet to be fully investigated.

Herein, we create hierarchical 3D SERS-active substrates by integrating 3D laser photolithographically fabricated microstructures with the self-assembly of single-crystalline Ag nanocubes. The aim is to design an optimal 3D architecture possessing high hotspot density in all x-, y-, and z-dimensions. Particular emphasis is on structural variations in the z-direction to increase the SERS hotspots from nanometer to micrometer length scale. The versatility of 3D laser photolithography enables a variety of 3D microstructures to be easily fabricated. This allows a systematic investigation on the various structural parameters which might affect the SERS efficiencies of a substrate in three dimensions, including structural morphology, height, and the inclination angle in relation to the x-y plane. Following the fabrication of 3D microstructures, they are metalized via thermal evaporation and a monolayer of Ag nanocubes is then deposited on the microstructures to generate a 3D monolayer-over-mirror configuration. 3D SERS imaging is used to highlight the signal homogeneity of our 3D SERS substrates over a large detection area.

4.2 RESULT AND DISCUSSION

The fabrication process of the hierarchical 3D SERS substrates is realized by combining 3D laser photolithography³⁰ and Langmuir-Blodgett assembly³¹ of nanoparticles (Scheme 1). 3D laser photolithography is first used to construct a variety of 3D microstructures with various morphologies through the two-photon polymerization of

the photoresist. The microstructures are fabricated by using an XYZ piezo stage to precisely control the laser focal positions, and this consequently enables accurate control over the positions at which the photoresist polymerizes to form the microstructures. After developing, the microstructures are thermally evaporated with a 50 nm-thick Ag film to create a 3D metallic mirror and these microstructures are subsequently referred to as metallized microstructures. A monolayer of 4-methylbenzenethiol (4-MBT) is then assembled on the metallized 3D microstructures. 4-MBT is used as the probe molecule for the SERS experiments because it is known to form a well-defined self-assembled monolayer on the silver surface with a characteristic molecular fingerprint in the Raman spectra.³² The construction of the hierarchical 3D SERS substrate is completed by using Langmuir-Blodgett assembly to deposit a uniform monolayer of Ag nanocubes over the metallized microstructures and create a 3D monolayer-over-mirror substrate.

Scheme 1. The fabrication process of hierarchical 3D SERS-active substrates begins with 3D laser lithography to fabricate various 3D microstructures. The microstructures are then metallized with a 50-nm thick Ag film via thermal evaporation and then assembled with a

monolayer of 4-methylbenzenethiol probe molecules. Langmuir-Blodgett technique is used to deposit a monolayer of Ag nanocubes over the substrate to create a SERS-active 3D monolayer-over-mirror configuration.

We begin the study with a pyramidal structure. A typical scanning electron micrograph (SEM) of a square pyramid after Ag metallization is as shown in Figure 1A (additional SEM images are available in Figure 2A). The base of the pyramid is 10 μm by 10 μm , with a height of 5 μm and an inclination angle of 45° relative to the x-y plane. The fabricated microstructure is well-defined in the three orthogonal directions. It is also noted that the walls of the pyramid are not topologically smooth due to the layer-by-layer polymerization of the photoresist in the z-direction during the writing process. The feasibility of using Langmuir-Blodgett technique to assemble Ag nanocubes on the fabricated microstructures is demonstrated in Figure 1B (additional SEM images are available in Figure 2B-D). Near close-packed monolayers of Ag nanocubes are assembled on the metallized pyramid and on the rest of the substrate. By integrating lithographically fabricated microstructures with the assembly of Ag nanocubes, a hierarchical 3-dimensional SERS-active substrate is created.

Figure 1. (A) SEM images of the 3D SERS substrates before and (B) after Langmuir-Blodgett assembly of Ag nanocubes. The height of the pyramid construction is $5\ \mu\text{m}$ with a ground inclination is 45° relative to the x-y plane. The yellow lines in A and B correspond to the positions at which the x-z SERS maps are measured and shown in (C) and (D) respectively. (E) 3D SERS maps of the hierarchical 3D SERS substrate and (F) corresponding SERS spectra of 20 randomly selected points from the image in (E).

A 1.4-fold increase in SERS-active surface area in three dimensions can be achieved from the four side facets of the pyramidal microstructures as compared to a planar unpatterned surface of identical dimensions as the square base ($10\ \mu\text{m} \times 10\ \mu\text{m}$). Below is the detail of calculation and Figure 3 includes the condition where the inclination is set at 45° .

Comparison of excited areas between 3D microstructure and flat 2D plane

3D microstructure

$$S = 4 \times S_{\text{triangle}} = 4 \times \frac{1}{2} \times h \times d = 4 \times \frac{1}{2} \times 7 \times 10 = 140 \mu\text{m}^2$$

2D plane

$$S = 10 \times 10 = 100 \mu\text{m}^2$$

$$\text{Increase in excited area} = 140/100 = 1.4$$

Typical SERS spectra of 4-MBT are presented in Figure 1F. Two main characteristic peaks at 1080 cm^{-1} and 1578 cm^{-1} are observed, with the 1080 cm^{-1} peak corresponding to a combination of phenyl ring breathing, C-H in plane bending and C-S stretching and the 1578 cm^{-1} vibration arising from phenyl ring stretching.³³ The vibrational mode at 1080 cm^{-1} is used for subsequent Raman mapping and analyses to minimize potential interference that may arise from the PVP used to stabilize the Ag nanocubes.³⁴

The creation of a monolayer-over-mirror in three dimensions generates a high density of SERS hotspots on the SERS substrates. By comparing the x-z SERS maps of the substrates before and after Ag nanocube deposition (Figures 1C and D, respectively), it is clearly evident that the hierarchical Ag nanocube-decorated microstructure (Figure 1D) exhibits a much higher SERS signal than the metallized microstructure (Figure 1C). The outline of the pyramid's cross section can be distinctly observed in the SERS map of the Ag nanocube-decorated pyramid. The 3D SERS map of the entire pyramid substrate decorated with Ag nanocubes in Figure 1E also highlights the 3D SERS activities across the entire substrate. The homogeneity of the SERS signals on the hierarchical

SERS-active microstructure is demonstrated in Figure 1F, where the Raman spectra of 20 randomly selected points from Figure 1E are shown in the same plot. Uniform SERS signals of 310 ± 38 counts are collected throughout the substrate (Figure 1F), along the side walls of the pyramid from the tip to the base. The SERS enhancement factors of the hierarchical 3D substrate is calculated to be $(2.6 \pm 0.3) \times 10^6$ by comparing with a 1 M standard ethanol solution of 4-MBT.

In contrast, the metallized pyramid without Ag nanocubes shows significantly weaker and inconsistent SERS signals with the SERS enhancement factor estimated to be $(1.1 \pm 4.7) \times 10^4$ (Figure 2A - i) and the pyramidal structure can hardly be discerned (Figure 1C). Since the numbers of probe molecules are identical on both substrates, the two orders of magnitudes enhancement in the SERS signals observed is directly correlated with the difference in SERS enhancement brought about by the Ag nanocube monolayer (Figure 2C).

Figure 2. (A) Schematic of four different substrates used to determine the ideal

configuration for 3D SERS. In (i), 4-MBT is directly self-assembled on Ag film; (ii) 4-MBT ligand is assembled onto the Ag film before deposition of Ag nanocube monolayer; (iii) Ag nanocubes are subjected to a second round of ligand exchange after Langmuir-Blodgett assembly; (iv) Ag nanocubes ligand exchanged with 4-MBT deposited on glass. (B) Average SERS spectra of the respective substrates. (C) SERS enhancement factor of each substrate calculated using the 1080 cm^{-1} peak of 4-MBT, of which the enhancement factors of substrate (i) is $(1.1 \pm 4.7) \times 10^4$, substrate (ii) is $(2.8 \pm 0.2) \times 10^6$, substrate (iii) is $(1.2 \pm 0.1) \times 10^6$ and substrate (iv) is $(1.6 \pm 0.4) \times 10^5$.

The advantage of monolayer-over-mirror configuration (Figure 2A - ii) is highlighted by comparing with 4-MBT decorated Ag film (Figure 2A - i), monolayer-over-mirror configuration that is subjected to a second round of ligand exchange of 4-MBT molecules (Figure 2A - iii), and 4-MBT coated Ag nanocubes onto un-metallized glass substrates (Figure 2A - iv). The respective SERS spectra are presented in Figure 2B and their corresponding enhancement factors are calculated to be $(1.1 \pm 4.7) \times 10^4$, $(1.2 \pm 0.1) \times 10^6$ and $(1.6 \pm 0.4) \times 10^5$, respectively (Figure 2C). The importance of the Ag mirror is demonstrated by comparing with structure that is not coated with Ag film (Figure 2A - iv), where the latter gives rise to enhancement factor of $(1.6 \pm 0.4) \times 10^5$, 16-fold lower than the monolayer-over-mirror configuration, despite having 5.5-fold more probe molecules per unit area. For monolayer-over-mirror configuration that is introduced with second round of ligand exchange with 4-MBT molecules (Figure 2A - iii), approximately 5.5-fold increase in total number of target molecules are chemisorbed onto the Ag nanocubes. While this results in higher SERS signals of (680 ± 31) counts, the SERS enhancement

factor is calculated to be $(1.2 \pm 0.1) \times 10^6$, which is still more than two-fold lower than our monolayer-over-mirror substrate. Based on these control experiments, we deem the monolayer-over-mirror to be the optimal configuration for our subsequent 3D SERS experiments.

Calculation of enhancement factor (EF)

$$EF = \frac{I_{\text{surface}}}{I_{\text{solution}}} \times \frac{N_{\text{solution}}}{N_{\text{surface}}}$$

$$I_{\text{surface}} = 340 / 10$$

$$I_{\text{solution}} = 26 / 1200$$

(The 340 is the measured intensity of Raman from the substrate and 10 is the acquisition time of the measurement, according. Relatively, 26 is the measured intensity of Raman from 1 M solution and 1200 is the acquisition time of the measurement.)

In solution

$$N_{\text{solution}} = V_{\text{solution}} \times C_{\text{molecules}} \times \text{Avogadro's number} = \pi \times x/2 \times y/2 \times z \times c \times$$

Avogadro's number

$$x = 910 \text{ nm}$$

$$y = 680 \text{ nm}$$

$$z = 4320 \text{ nm}$$

$$c = 1000 \text{ mol/m}^3$$

$$N_{\text{solution}} = 1.26 \times 10^9$$

(In solution, the x, y, z are the physical dimensions of excited volume by laser, which are deconvoluted to the refraction of both solution and cover glass.)

In solid

$$x = 520 \text{ nm}$$

$$y = 380 \text{ nm}$$

$$z = 810 \text{ nm}$$

$$N_{\text{surface}} = S_{\text{Laser spot}} \times n_{\text{molecule}}$$

$$S_{\text{Laser spot}} = \pi \times x/2 \times y/2 = 1.55 \times 10^{-13} \text{ m}^2$$

$$n_{\text{molecule}} = 4.50 \times 10^{18} \text{ molecules/m}^2$$

$$N_{\text{surface}} = 6.98 \times 10^5$$

(In solid, the x, y, z are the physical dimensions of confocal volume of laser spot, which are obtained according to the parameter of Nanophoton machine.)

$$EF = (310 / 10) / (26 / 1200) \times (1.26 \times 10^9) / (6.98 \times 10^5) = 2.6 \times 10^6$$

When considering the error bar, the enhancement factor is $(2.6 \pm 0.3) \times 10^6$

In addition to the pyramid microstructure, we systematically investigate the effects of microstructure morphology on the SERS efficiencies of the hierarchical 3D SERS substrates. A right prism, truncated cone and square block (Figure 3A-C) are chosen for this study as they are sufficiently different in shape and possesses different sloping facets for the investigation of the effect of structural variation in the z-axis on the SERS intensity measured. The architecture of the microstructures can be easily engineered using two-photon lithography. While the height of all the microstructures are fixed at 5 μm , the right prism has sides of 5 $\mu\text{m} \times 10 \mu\text{m}$ with an inclination of 45° (Figure 3A); the truncated cone has a lower diameter of 10 μm and an upper diameter of 5 μm with an inclination around 60° (Figure 3B); and the square block has dimensions of 10 $\mu\text{m} \times 10 \mu\text{m}$ (Figure 3C). The structures are well-defined and near close-packed monolayer of Ag

nanocubes are deposited across the surfaces of the 3D microstructures (3A-C). Some small empty patches without Ag nanocubes are observed in the square block and right prism. This likely arises from the water contact line pinning to the 3D microstructures during the Langmuir-Blodgett assembly, leading to slightly uneven deposition of the Ag nanocube monolayers.

The orientation of the sloping facets in the various microstructures in relation to the plane of excitation and signal collection gives rise to very different signal intensities measured at different points. Cross-sectional SERS maps taken in the x-z direction from the middle of the three microstructures with Ag nanocube monolayers shows that all the 3D microstructures exhibit different SERS response along the x-z plane (Figure 3D - F). In the case of the right prism, the sloping 45° facet lights up brightly in the x-z SERS map while the facet normal to the x-y plane becomes almost completely dark (Figure 3D). The SERS enhancement factors are estimated to be $(2.5 \pm 0.4) \times 10^6$ (Figure 3G – ii and iii) and $(7.8 \pm 1.6) \times 10^5$ (Figure 3G - iv) for the sloping facet and the dark facet, respectively. As for the truncated cone, the top facet is also lit up with an average SERS enhancement factor of $(2.9 \pm 0.5) \times 10^6$ (Figure 3H - iii). However, the SERS enhancement factor drops to $(1.6 \pm 0.2) \times 10^6$ along the sloping facets (Figure 3H - ii and iv), nearly twice weaker than the top facet. The top facet of the square block is brightly lit, with enhancement factor reaching $(2.8 \pm 0.2) \times 10^6$, shown in Figure 6I - iii. In contrast, the SERS signals along the side walls are almost four-fold weaker, with average enhancement factor of $(7.6 \pm 0.1) \times 10^5$ (Figure 3I - ii and iv). The SERS enhancement factors for the various facets across the different microstructures can be broadly summarized as: $EF_{\text{top facet}} > EF_{\text{facet at inclined angle}} > EF_{\text{facet normal to x-y plane}}$. These experiments highlight the importance of the

morphology of microstructures in determining the SERS activities of the hierarchical 3D SERS substrate.

Figure 3. (A-C) SEM images of the hierarchical 3D SERS substrates of different morphologies, including (A) right prism, (B) truncated cone, and (C) square block. All the microstructures are standardized to identical heights of 5 μm . (D-F) Corresponding x-z SERS maps of the respective microstructures. (G-I) Corresponding averaged SERS enhancement factors obtained from five different points as shown in (D)-(F), respectively.

Among the four different microstructures fabricated thus far, the pyramidal microstructure is evidently the most efficient structure with all four sloping facets lit up brightly upon excitation by an incident laser beam. The remaining three microstructures all suffer from issues of non-uniform SERS signals at different regions of the same structure as a consequence of unfavorable orientation of the sloping facets in relation to the plane of excitation and signal collection (*vide infra*). Structural variations, particularly

in the z-direction, can lead to drastic differences in the SERS intensities collected from the 3D microstructures. As such, the pyramidal microstructure is used as the model architecture for the subsequent structural studies.

In the following section, the heights of the pyramids are varied to determine the maximum SERS active 3D volumes achievable from our substrates. This is in a quest to develop more robust 3D SERS-active substrates with high density SERS hotspots in the three orthogonal directions. In addition, this will also allow us to investigate the limit at which the microstructures will begin to produce inhomogeneous SERS intensities. The heights of the pyramids are fabricated at 2.5 μm , 5.0 μm , 7.5 μm , and 10 μm . The SEM images of pyramid structures with heights of 2.5 μm , 7.5 μm and 10 μm deposited with Ag nanocube monolayers are presented in 4A-C respectively. To keep the inclination angle of the side walls consistent at 45°, the base of the pyramid is increased from 5 μm to 15 μm and 20 μm respectively. This increase in the base dimensions of the pyramid microstructures with increasing heights is necessary to maintain identical aspect ratios for all microstructures. The triangular outlines of the pyramidal microstructures with Ag nanocubes deposited can be clearly distinguished from the corresponding x-z SERS maps for all heights investigated (Figures 4D - F). The averaged Raman spectra of all substrates are comparable in Raman intensity (Figure 4G). Further analysis indicates that the average SERS enhancement factors are $(2.6 \pm 0.5) \times 10^6$, $(2.8 \pm 0.3) \times 10^6$, $(2.7 \pm 0.6) \times 10^6$ and $(2.8 \pm 0.6) \times 10^6$, respectively, for various pyramidal microstructures with heights of 2.5 μm , 5.0 μm , 7.5 μm , and 10 μm (Figure 4H). This set of experiments demonstrates that homogeneous SERS signals can be obtained by varying the height of our 3D SERS substrates, even at heights up to 10 μm . Strong SERS enhancement factors are

consistently maintained at 2.7×10^6 despite the change in the height of the microstructure. This indicates that the SERS hotspots can be dramatically extended in the z-direction, with much larger SERS-active 3D volumes that are accessible as compared to a 2D substrate.

Figure 4. Pyramids of various sizes are fabricated to increase hotspot densities in 3-dimensions. The height varies from (A) 2.5 μm, (B) 7.5 μm to (C) 10 μm. The corresponding x-z SERS maps are shown in (D - F) respectively. (G) Averaged spectra of Raman shift versus enhancement factor from 20 randomly selected points on the slope of each substrate. (H) Corresponding plot of SERS enhancement factor with pyramid height.

The effect of microstructure inclination angle with respect to the x-y plane on the SERS responses of the hierarchical 3D SERS substrates is further examined by

fabricating pyramidal microstructures with various inclination angles, including 30°, 60° and 75°. The dimensions of the pyramidal base decrease from 17.3 μm to 5.8 μm and 2.7 μm with increasing inclination angles such that the heights can be standardized at 5 μm for all the microstructures. The SEM images indicate that all the pyramidal microstructures are well-defined and uniformly decorated with a monolayer of Ag nanocubes (5A-C). The corresponding x-z SERS maps taken from the center of the hierarchical 3D microstructures for inclination angles of 30°, 60° and 75°, are shown in Figures 5D - F. From these images, the importance of the structural inclination angles is evident, with increasing steepness leading to weaker SERS signals measured along the sloping facets. The averaged Raman spectra and the variation in SERS enhancement at different inclination angles are plotted in Figure 5G and 5H, respectively. SERS spectra from the basal plane, as well as from inclination angles of 45° and 90° discussed earlier are also included for discussion. The SERS enhancement factor first increases from $(2.8 \pm 0.2) \times 10^6$ to $(3.4 \pm 0.3) \times 10^6$ as the inclination increases from 0° to 30°. The highest enhancement is recorded at a sloping angle of 30°. As the steepness of the slope increases relative to the x-y plane, the SERS enhancement factors decrease to $(2.6 \pm 0.3) \times 10^6$ at 45°, $(1.9 \pm 0.5) \times 10^6$ at 60°, $(1.3 \pm 0.2) \times 10^6$ at 75°, and finally $(0.8 \pm 0.2) \times 10^6$ at 90° (Figure 5H, black columns).

Figure 5. (A-C) Pyramidal microstructures with various inclination angles with respect to the x-y plane are fabricated. Their dimensions are varied in order to fix the height at 5 μm . SEM images of the pyramids with different ground inclinations, ranging from (A) 30° , (B) 60° and (C) 75° . The corresponding x-z SERS maps are shown in (D)-(F) respectively. The averaged graph of Raman shift versus enhancement factor of 20 randomly selected points from the slope of each substrate together with 0° , 45° and 90° are shown in (G). (H) Graphs of SERS intensity changes with inclination under ideal (orange) and actual (black) experimental conditions using the 1080 cm^{-1} .

This experimentally observed trend is in contrast from the ideal trend (Figure 5H, orange columns) calculated using idealized Ag nanocube densities within the laser excitation confocal volume. This difference in SERS intensities observed at various inclination angles are influenced by the density of Ag nanocube monolayer as well as the

effective excitation area within the laser confocal volume. The laser spot is taken to be an ellipsoid for the determination of effective laser confocal volume (Figure 6).

Figure 6. (A, B) Scheme of confocal laser spot on both flat plane and the plane with an inclination of α . (C) Graph of excited area versus inclination angle. The areas of every angle studied are $1.55 \times 10^{-1} \mu\text{m}^2$, $1.68 \times 10^{-1} \mu\text{m}^2$, $1.85 \times 10^{-1} \mu\text{m}^2$, $2.07 \times 10^{-1} \mu\text{m}^2$, $2.31 \times 10^{-1} \mu\text{m}^2$ and $2.42 \times 10^{-1} \mu\text{m}^2$, for $\alpha = 0^\circ$, 30° , 45° , 60° , 75° and 90° respectively.

As the slope inclination increases, the excited area inside the laser spot will vary accordingly. Assuming the inclination angle with respect to the x-y plane is α , the excited area would be $\pi abc (1 + \tan^2 \alpha) / \sqrt{(c^2 + a^2 \tan^2 \alpha)}$, where a, b, and c refer to the intersection of the ellipsoid with the three orthogonal axes. Therefore, the real excited area within laser spot should be $0.155 \mu\text{m}^2$, $0.168 \mu\text{m}^2$, $0.185 \mu\text{m}^2$, $0.207 \mu\text{m}^2$, $0.231 \mu\text{m}^2$ and $0.242 \mu\text{m}^2$ for 0° , 30° , 45° , 60° , 75° , 90° respectively (Figure 6). The calculations are based on a $100 \times$ objective with a numerical aperture of 0.9, where the confocal laser spot is

estimated to be 520 μm , 380 μm and 810 μm along the x, y, z axes respectively. In addition, the ideal density of the Ag nanocube monolayer is also calculated similarly, by using the nanocube density at 0° as a reference point and by taking the ratio of the area of the sloping facet with that of the basal plane. The density of the nanocube monolayer at 0° is determined by visually counting the number of nanocubes within a surface area of 800 μm^2 . The ideal Ag nanocube density is thus estimated to be 62 μm^{-2} , 72 μm^{-2} , 88 μm^{-2} , 124 μm^{-2} and 239 μm^{-2} (orange line Figure 7).

Figure 7. Variation of Ag nanocube density with inclination angles under ideal (orange) and actual experimental (black) conditions within the confocal volume.

Calculation of excited area with certain inclination (α)

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$$

$$a = 260 \text{ nm } b = 190 \text{ nm } c = 405 \text{ nm}$$

As the y axis is in the plane

The coordinate of the apogee is (x, 0, z)

$$z = \tan \alpha \ x$$

$$\text{the axis of ellipse is } ac\sqrt{(1 + \tan^2 \alpha)} / \sqrt{c^2 + a^2 \tan^2 \alpha}$$

$$\text{therefore, the excited area is } S(\alpha) = \pi abc\sqrt{(1 + \tan^2 \alpha)} / \sqrt{c^2 + a^2 \tan^2 \alpha}$$

when $\alpha = 0^\circ$, $\tan^2\alpha = 0$, $S(0) = 1.55 \times 10^5 \text{ nm}^2$

when $\alpha = 30^\circ$, $\tan^2\alpha = 1/3$, $S(30) = 1.68 \times 10^5 \text{ nm}^2$

when $\alpha = 45^\circ$, $\tan^2\alpha = 1$, $S(45) = 1.85 \times 10^5 \text{ nm}^2$

when $\alpha = 60^\circ$, $\tan^2\alpha = 3$, $S(60) = 2.07 \times 10^5 \text{ nm}^2$

when $\alpha = 75^\circ$, $\tan^2\alpha = 13.9$, $S(75) = 2.31 \times 10^5 \text{ nm}^2$

when $\alpha = 90^\circ$, $\tan^2\alpha \rightarrow \infty$, $\lim S(90) \rightarrow 2.42 \times 10^5 \text{ nm}^2$

In our experiments however, the nanocube density decreases steadily from $62 \mu\text{m}^{-2}$, $58 \mu\text{m}^{-2}$, $51 \mu\text{m}^{-2}$, $47 \mu\text{m}^{-2}$ and $31 \mu\text{m}^{-2}$ as the inclination angle increases from 0° to 75° (Figure 8). Taking the inclination angle into account, the actual Ag nanocubes density excited within the laser confocal volume is estimated to be $62 \mu\text{m}^{-2}$, $67 \mu\text{m}^{-2}$, $72 \mu\text{m}^{-2}$, $94 \mu\text{m}^{-2}$ and $116 \mu\text{m}^{-2}$ (Figure 7, black line) for the same inclination angles. When compared against the ideal Ag nanocube density, a similar trend of increasing number of nanocubes (and SERS hotspots) with increasing inclination is observed. The difference between the ideal Ag nanocube density and that of the experimental one arises from the water contact line pinning during the Langmuir-Blodgett assembly to the 3D microstructures, which subsequently leads to disparities in the number density of Ag nanocubes deposited on various 3D microstructures.

Figure 8. (A-E) SEM images of the SERS substrates with different inclination angles, including 0°, 30°, 45°, 60° and 75° respectively. The numbers of Ag nanocubes on each slope are 5 550, 2 900, 1 800, 1 350 and 800 respectively. (F) Graph of changes in Ag nanocube density at various inclination angles; the densities of the Ag nanocubes are 62 μm⁻², 58 μm⁻², 51 μm⁻², 47 μm⁻² and 31 μm⁻² for inclination angles of 0°, 30°, 45°, 60° and 75° respectively.

On the other hand, the product of the SERS intensity and the real excited areas derived for various inclination angles will give an ideal SERS intensity from the substrate at various inclination angles based on the SERS intensity measured at 0° inclination (Figure 5H, orange column). The trend shows a monotonic gradual increase in SERS intensities with increasing inclination. Correlating this with the increase in ideal Ag nanocube density (Figure 7, orange line), the increase in SERS intensities is ascribed to the increase in number of Ag nanocubes within the confocal volume. However, the ideal situation is contrary to the experimentally observed phenomenon. The experimental SERS intensities observed increases slightly from 0° to 30°, and then decrease monotonically with increasing inclination angle thereafter even though the nanocube densities increase

monotonically, albeit at a lower rate of increase due to experimental limitations. This indicates that the differences observed in the SERS intensities measured experimentally are not solely determined by the density of Ag nanocubes (or hotspots), especially at various inclination angles. Rather, the ‘scattering efficiency’ of the inclined plane in relation to the objective also needs to be considered. Taking the comparison between 0° and 75° inclination angles as an example, the SERS intensity decreased by 2.1-fold despite a 1.9-fold increase in Ag nanocube density excited.

Table 1. The density of cubes on every slopes in both ideal and actual experimental conditions within the confocal volume

Inclination (°)	0	30	45	60	75
Ideal density (μm^{-2})	62	67	72	94	116
Actual density (μm^{-2})	62	72	88	124	239

At this point, it is important to note that the experimental SERS intensities measured at various inclination angles implies that 30° is the optimal inclination angle with respect to the x-y plane, where an increase in nanocube density within the confocal volume can give rise to a corresponding increase in SERS signals. Beyond 30°, the efficiency of the SERS signal collected decreases. This is especially evident in the case of 90°, where weak

SERS signals are consistently measured as seen in the case of the square block and right prism. At this inclination angle, the SERS signals cannot be collected efficiently. These findings highlight the importance of the inclination angle with respect to the incident laser beam in controlling the intensities of SERS signals measured. It also implies that the commonly reported 3D SERS substrates employing cylindrical or columnar structures such as alumina templates,³⁵ carbon nanotubes³⁶ and semiconductor supporting structures³⁷ may not be the optimal architecture for an efficient 3D SERS substrate.

4.3 CONCLUSION

We have demonstrated the fabrication of efficient 3D SERS hierarchical substrates by integrating 3D laser photolithography with the Langmuir-Blodgett assembly of Ag nanocubes. SERS hotspot densities are extended along the z-axis in our 3D SERS substrates, increasing the hotspots in the three orthogonal directions from tens of nanometers to tens of micrometers scale. Homogeneous and strong SERS intensities can be achieved with microstructures up to 10 μm tall using our hierarchical monolayer-over-mirror configuration. Among the various structural variations in the z-direction investigated, the inclination angle of the microstructures in relation to the x-y plane is shown to be more important than microstructure morphology or height.

4.4 EXPERIMENTAL SECTION

Chemicals. Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97.0\%$), poly(vinyl pyrrolidone) (PVP, average $M_w = 55\,000$), propylene glycol monomethyl ether acetate (PGMEA, $\geq 99.5\%$), 4-methylbenzenethiol (4-MBT, $\geq 98\%$) were

purchased from Sigma Aldrich; copper(II) chloride ($\geq 98\%$) was purchased from Alfa Aesar; iso-propyl alcohol (IPA, $\geq 99.96\%$) was purchased from Fisher Scientific; IP-L 780 was purchased from Nanoscribe GmbH. All chemicals were used without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system.

Synthesis and purification of Ag nanocubes. Ag nanocubes were prepared following the method described in the literature.^{38, 39} In a typical synthesis process, PVP (20 mg/mL) were dissolved in PD and 35 μL CuCl_2 (8 mg/mL) PD solution was added to the AgNO_3 (20 mg/mL) PD solution as precursors. 20 mL of PD was then heated and stabilized at 190 °C for 10 min. 250 μL PVP precursor was injected dropwise twice while 500 μL AgNO_3 precursor was added in one go once every minute. The reaction was allowed to continue for approximately 20 min. After synthesis, the Ag nanocube solution was washed by acetone and re-dispersed in 100 mL PVP water solution (0.2 g/L). Utilizing PVDF filter membranes (Durapore®) with different pore sizes, including 5 000 nm, 650 nm, 450 nm and 220 nm, the above solution was vacuum filtered and concentrated into 15 ml of ethanol.

Preparation of 3D laser lithography substrates. The 3D structures were designed in the 3ds Max (Autodesk 2012, 32 bit) before importing into the two-photon lithography system (Nanoscribe GmbH). IP-L (780)[®] was used as the liquid and sol-gel negative-tone photoresist with a laser power of 8 mW and the scan speed of 40 $\mu\text{m/s}$. The substrates were post-treated in propylene glycol methyl ether acetate (PGMEA) for 5 min and subsequently in iso-propyl alcohol (IPA) for 15 min.

Metallization of substrated. Ag film was deposited on the substrates using a home-built

thermal evaporator deposition system. The deposition rate Ag was 0.5 Å/s, which was monitored in-situ by a quartz crystal microbalance. Ag target with 99.99% purity was purchased from Advent Research Materials, UK.

Preparation of 3D SERS substrate. The metallized substrates were self-assembled with 20 mM 4-MBT for 6 hours. After rinsing with pure ethanol for 7 times, the substrates were kept in nitrogen environment for drying and storage. 600 µL of purified Ag nanocubes in ethanol was mixed with 900 µL chloroform. Then, the mixture was dispersed dropwise onto the air/water interface of Langmuir-Blodgett trough (KSV NIMA, KN1002). To ensure a dense packed monolayer of nanocubes, the target surface pressure was settled at 10 – 13 mN/m.

Characterization. Using scanning electron microscopy (SEM) (JEOL-JSM-7600F) at an accelerating voltage of 5 kV, the samples after Ag cubes deposition were characterized directly. Raman mapping was obtained by the Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan). The wavelength and power of excitation laser was set at 532 nm and 0.0022 mW, respectively. Besides, the excitation laser light was focused into a line on the sample through a cylindrical lens and an air objective lens (LU Plan Fluor 100 ×, NA 0.9). For each line, the samples were measured with an exposure time of 10 s. The x-y-z SERS map is constructed by using an image processing software which combines multiple x-y SERS maps at intervals of 0.5 µm into a single image.

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Chapter 5

Prismatic Hierarchical 3D SERS Substrates for Information Storage/Tagging as Barcodes

ABSTRACT. Nowadays, there are great demand and market to develop the new generation of information storage. Based on the findings in last chapter, prismatic hierarchical 3D SERS substrates are designed and fabricated by combining two-photon polymerization and LB self-assembly, which exhibits a great potential for information storage/ tagging. Taking advantage of the SERS detection height, different information is able to encode into barcodes in one single structure. Furthermore, tuning the parameters of the microstructure such as height, inclination and shapes, we succeed in changing both position and numbers of the barcodes, where the information storage capacity is improved. To further extend the tagging ability, woodpile structure is designed and studies to convert the two-dimensional binary matrix

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5.1 INTRODUCTOIN

Since early age of human civilization, people have realized the significance of information transition with safety and efficiency. Caesar Cipher, as the name suggested, has been established and applied for thousand years, especially in military and commerce.¹ To date, due to the booming of science and technology, the traditional information security is challenged by forgery in both the developing and developed countries, leading to serious counterfeiting crimes in many fields, such as passports, certificates and banknotes.² This issue brings a loss of trillion dollars every year and encourages emergent development of new materials and methods to solve it.³ And fortunately, there are already important progress of information storage and tagging in organic fluorescent dyes,^{4, 5} up-conversion nanocrystals,^{6, 7} photonic polymers⁸⁻¹⁰ and magnetic materials.^{11, 12}

In addition, noble metal nanomaterials have been widely detected as one reliable candidate due to the unique plasmon resonance property.¹³ Especially with the strong potential in optics, periodic nanostructures trap and convert light waves through oscillation of surface free electron, making them suitable for color information application, such as holograms,¹⁴ full color filters¹⁵⁻¹⁷ and polarizers.^{18, 19} For example, tuning the dimensional parameters of metal nanodisk, the bright-field color printing was achieved with resolution even up to optical diffraction limit.²⁰ Around 100,000 obtained dots per inch exhibit the great information storage capacity and the high requirement of precise control during lithography makes it hard to be copied by the counterfeiters. However, though the plasmon resonance of metal nanomaterials shows great potential as the next generation of information storage, the relative work is still limited in the

application of the optical properties, enhancing the possibility to be understood and subsequently duplicated.

In the recent work of our group, we successfully combined the molecule sensing of Raman with the plasmon resonance property of nanostructures, which is known as SERS, to increase the complexity of information tagging.^{3, 21, 22} Likewise, taking advantage of plasmon polarization of Ag wires, information encryption was realized by the selective Raman imaging.²¹ Moreover, introducing the multiplex of probe molecule even enabled us to extend the information storage ability to 2D multi-digit application, which contributes the difficulty of counterfeiting.³

Here, based on the previous research in hierarchical 3D SERS platform, we demonstrate a potential application of such substrates in the field of information storage/tagging as barcodes with prismatic structures. High intensity of Raman signal guarantee the efficiency and reproducibility of the barcode mapping images. And taking advantage of the extension of z-dimension from the microstructure, different information is converted by controlling the focusing position. Thus, using simple structures of prisms, we are able to create various layers of barcodes within a single architecture by simply changing the confocal plane of the excitation source. Furthermore, two-dimension binary matrix is proved to be encrypted by the woodpile structure as well.

5.2 RESULTS AND DISCUSSION

Based on the findings that 3-dimensional structural parameters on the SERS contributes to our hierarchical 3D SERS substrates, we extend the architecture of the microstructures to larger dimensions to further increase the SERS active regions in all

3-dimensions. Multiple triangular prisms forming grating-like structures are fabricated and the SEM image of the fabricated structures decorated with Ag nanocubes is shown in Figures 1A and C. The prism structures are 80 μm long, with heights of 5 μm and slope inclination of 45° relative to the x-y plane. The gaps between individual prisms are fixed at 10 μm . The x-z SERS maps of the prism structures are shown in Figures 2A while the x-y-z 3D SERS maps are shown in Figures 1B. The entire imaged area in the x-y-z map is lit up, indicating that the whole area is SERS-active. The validity of this estimation is justified by the x-z SERS map shown in Figure 2A, where the outline of the prisms is clearly delineated by the bright hotspots.

Figure 1. (A) SEM and (B) 3D SERS imaging of four prisms structures with height of 5 μm and the ground inclinations are 45° . (C) SEM and (D) 3D SERS imaging of four structurally varied prisms. The two prism structures on the left have 45° inclination angle with height = 5 μm and 7.5 μm , respectively. The third and fourth structures are a right prism and a prism with an inclination angle of 30° , both structures are 5 μm tall.

When the SERS maps collected in the x-y planes at various heights are further examined, a unique phenomenon is observed from these regularly spaced prisms. The x-y plane SERS maps taken at $z = 5 \mu\text{m}$ and $2.5 \mu\text{m}$ from the basal x-y plane are shown in Figures 2B and C respectively where lit up lines are observed. At the tip ($z = 5 \mu\text{m}$) of the prisms, four bright lines spaced $20 \mu\text{m}$ apart are observed (Figure 2B). However, in the middle of the prisms at $z = 2.5 \mu\text{m}$, the number of bright lines observed doubles to eight (Figure 2C) and the gaps between the lines alternate between $5 \mu\text{m}$ and $10 \mu\text{m}$. These bright and dark lines can be converted to correspond to two different sets of binary codes. In this case, the binary codes are defined by intervals of $2.5 \mu\text{m}$, where the dark area is regarded as 0 (in black) and the lit up area is 1 (in green). As such, the four lines in Figure 2B can be represented as a binary code of 010000000100000000100000001000000010. And a scheme of such encoding is shown in Figure 3. Similarly, the eight lines in Figure 2C can be coded as a binary number 101000001010000001010000010100000101. The difference in both the number and relative position of bright lines observed at different z-values stems from the different sections of the prisms that are excited by the incident laser beam, demonstrating the potential to encrypt two distinct binary codes into one individual structure.

Figure 2. Large prisms structures are also fabricated as hierarchical 3D SERS substrates.

For the first group, the heights of four prisms are equal to $5\ \mu\text{m}$ and the ground inclinations are 45° . The x-z SERS map of the prism structures are shown in (A). The x-y direction Raman mapping images obtained at different height, respectively $5\ \mu\text{m}$ (B) and $2.5\ \mu\text{m}$ (C). The numbers in green are the ones which can be read out as “1” from the binary sequence and others in dark are treated as “0”. Another group of four different prism structures are used to demonstrate the capability to generate barcodes with different features. From left to right, the heights of the first and second prisms are $5\ \mu\text{m}$ and $7.5\ \mu\text{m}$ with an inclination angle 45° ; the third microstructure is a right prism with an inclination of 45° ; the fourth microstructure is $5\ \mu\text{m}$ tall with an inclination angle of 30° . The corresponding x-z plane SERS map is shown in (D). The SERS maps obtained at $z = 7.5\ \mu\text{m}$ and $5\ \mu\text{m}$ is shown in (E) and (F), respectively.

The regularity of the bright lines observed as well as the capability to observe

distinct information sets at various heights within the same structure has not been reported for such a simplistic 3D design hitherto. These bright lines are reminiscent of the security barcodes that are used to identify and tag consumer products or personal identities. This potential application for binary code has certainly not been achieved among the various 3D SERS substrates before and is definitely only achievable with a well-designed hierarchical 3D SERS substrate with homogeneous SERS response over a large surface area.

Figure 3. Scheme illustrating the binary code assignment in the design of binary barcodes. Each line is coded 0 from the very beginning as shown in (A) and are 2.5 μm wide. The lit up lines in Figure 5D is also shown in (B) here as an example, which makes the corresponding code changes to 1.

As a proof-of-concept that the hierarchical 3D SERS substrates can be potentially used as micro-barcodes of the future with the capability to encode other binary code sets within a single set of structures, a set of different prism structures is fabricated. This set of 3D microstructures comprises four prisms (Figure 2D) with two prisms structures having 45° inclination angle with heights = 5 μm and 7.5 μm , respectively. The third and fourth structures are a right prism and a prism with an inclination angle of 30° , both structures

are 5 μm tall. The corresponding x-y-z 3D SERS map is presented in Figure 1D and the x-z SERS maps is included in Figure 2D. Both the x-y-z and x-z SERS maps demonstrate large SERS active areas and volumes despite combining structures of various dimensions. Similarly, the x-y maps measured at both the top ($z = 7.5 \mu\text{m}$) in Figure 2E and at middle ($z = 5 \mu\text{m}$) in Figure 2F clearly illustrate that the barcode information with distinct line spacings can be obtained easily by tuning the morphology of the 3D microstructures. At $z = 7.5 \mu\text{m}$, a single line is obtained with a corresponding binary code of 0000000000100000000000000000. At $z = 5 \mu\text{m}$, five lines with different widths arising from the change in height, shape and inclination of the prisms are observed with a binary code of 010000000101000001000011000. In addition to the ability to tune the line numbers and positions, the thickness of the lines can also be controlled by varying the structural parameters of the 3D microstructures, as exemplified by the last prism. A thicker line is observed due to the larger exposed area per unit volume at lower inclination angles within the same confocal volume. Consequently, this presents a possibility to derive two continuous read out numbers in the sequence. This set of experiments indicates the possibility of miniaturizing barcodes to the micro-scale by integrating lithographic approaches with self-assembly to create hierarchical 3D microstructures and using SERS as a readout technique.

We prove the possibility to extent the binary coding to two dimensions as well. Above the identical prisms (length = 80 μm , height = 5 μm and slope inclination = 45°), another layer with the same parameters is repeated with 90° orientation, forming a woodpile structure. After assembly, a homogenous decoration of nanoparticles is observe in SEM (Figure 4A). The x-y-z SERS mapping image of the entire woodpile and the x-z

SERS map at the center of woodpile are shown in Figure 4B and C, respectively. The x-y SERS mapping is taken at $z = 5 \mu\text{m}$ from the basal x-y plane, where is the contact junction of two layer of prism in Figure 4D. At vertical direction, four lit up lines with same interval of $15 \mu\text{m}$ are observed from the vertices of bottom layer, encoding a binary number of 010000000010000000001000000010. Likewise, eight lines with the alternate gaps between $5 \mu\text{m}$ and $10 \mu\text{m}$ present a number of 010010001001000100100010010 at horizontal direction. Thus, two dimension matrix of binary number is encrypted from as fabricated woodpile structure.

Figure 4. (A) The SEM image of the woodpile structure shows the homogeneity of nanoparticle decoration after self-assembly. (B) The x-y-z SERS mapping of the structure exhibit the clear outline of prism from both top layer and bottom layer. (C) The x-z map of SERS signal was taken at the center of the woodpile. (D) As taken at $5 \mu\text{m}$ from the

base, where is the structural junction of two layers, the cross arrays of lines prove the capacity to convert two dimension matrix of binary number into the woodpile system.

5.3 CONCLUSION

In the work of this chapter, the hierarchical 3D SERS platform is proved to encode binary number in barcodes as prismatic structures are applied. By simply tuning the scan plane of confocal laser, different information is able to be encoded and decoded, making the transition safe and efficient. Moreover, by changing the structural parameter of the prisms, the variety of barcodes is realized from their numbers and positions. The woodpile structure is further fabricated to demonstrate the possibility for binary number matrix encryption, which extent the barcodes application within a single architecture

5.4 MATERIALS AND METHODS

Materials. Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97.0\%$), poly(vinyl pyrrolidone) (PVP, average $M_w = 55\ 000$), proylene glycol monomethyl ether acetate (PGMEA, $\geq 99.5\%$), 4-methylbenzenethiol (4-MBT, $\geq 98\%$) were purchased from Sigma Aldrich; copper(II) chloride ($\geq 98\%$) was purchased from Alfa Aesar; iso-propyl alcohol (IPA, $\geq 99.96\%$) was purchased from Fisher Scientific; IP-L 780 was purchased from Nanoscribe GmbH. All chemicals were used without further purification. Milli-Q water ($> 18.0\ M\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system. Ag target with 99.99% purity was purchased from Advent Research Materials, UK.

Synthesis and purification of Ag nanocubes. Ag nanocubes synthesis was followed as

the reported method.^{23, 24} Typically, 20 mg/mL PVP solution in PD were prepared and 35 μ L of 8 mg/mL CuCl_2 solution in PD was added to the 20 mg/mL AgNO_3 solution in PD as precursors. Then, 20 mL of PD was pre-heated and stabilized at 190 °C in a 100 mL round bottom flask with stirring. 250 μ L PVP precursor was injected dropwise twice while 500 μ L AgNO_3 precursor was added in one fast injection once every minute. For approximately 20 min, the reaction was stopped as a pinkish color was observed. Cooling till room temperature, the Ag nanocube solution was washed by 1 time of acetone and 3 times of ethanol. Re-dispersed in 100 mL of 0.2 g/L PVP water solution, the nanocubes were filtered by PVDF membranes (Durapore®) with distinct pore sizes, following the order of 5 000 nm, 650 nm, 450 nm and 220 nm, accordingly. The purified Ag nanocubes dispersion was allowed to sediment overnight for further use.

Preparation of 3D laser lithography substrates. The 3D structures of prisms and woodpile were pre-designed in the 3ds Max (Autodesk 2012, 32 bit) and followed by importing into the two-photon lithography system (Nanoscribe GmbH). The liquid IP-L (780)[®] was dropped onto a thin glass slid as the sol-gel negative-tone photoresist. To introducing the polymerization, a pulse laser was applied with the power of 8 mW and the scan speed of 40 μ m/s. Subsequently, the substrate with polymerized 3D structures was firstly post-treated in propylene glycol methyl ether acetate (PGMEA) for 5 min and in iso-propyl alcohol (IPA) for 15 min.

Metallization of substrate. The as-prepared substrates with 3D structures were coated with Ag film using a home-built thermal evaporator deposition system. Monitored by in-situ quartz crystal microbalance, the deposition rate of Ag was controlled at 0.5 Å/s, where the homogenous layer of Ag was realized.

Preparation of 3D SERS substrate. Likewise, the metallized substrates were self-assembled with probe molecule of 4-MBT in a 20 mM solution for 6 hours. Followed by rinsing with pure ethanol and drying in nitrogen, the substrates were prepared for further application. Meanwhile, 0.5 μ L of purified Ag nanocubes sediment was dissolved in 1.5 mL mixture of ethanol and chloroform with volume ratio 2: 3. This mixture was then dispersed dropwise onto the air/water interface of Langmuir-Blodgett trough (KSV NIMA, KN1002) with the target surface pressure of 10 – 13 mN/m.

Characterization. Scanning electron microscopy (SEM) (JEOL-JSM-7600F) was applied to characterize the 3D SERS substrate directly at an accelerating voltage of 5 kV. Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan) was conducted to obtain the Raman mapping images with laser power of 0.0022 mW and wavelength of 532 nm. Noted that a cylindrical lens and an air objective lens (LU Plan Fluor 100 $\times$, NA 0.9) was designed in the system, the excitation laser light was focused into a line on the SERS substrates. Besides, the exposure time of each line was set at 10 s.

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Chapter 6

Summary and Outlook

6.1 SUMMARY

Breaking the symmetry of nanoparticles is of great importance to manipulate the plasmon resonance property. Therefore, in Chapter 2 and 3, we introduce two different strategies to anisotropically modify the morphologies of nanoparticles. In the first strategy, galvanic replacement reaction is kinetically controlled on one facet of nanocubes by microcontact printing. We optimize the precursor concentration to limit the deposition degree and apply our method to other platonic nanostructures, demonstrating a versatile and robust fabrication of a serial of Janus nanoparticles. By using high-resolution cathodoluminescence hyper-spectral imaging, we detect distinct surface plasmon resonances from both Au and Ag components on the individual Janus nanocubes. In this case, our Janus nanoparticles comprising two elemental components exhibit unique optical property. However, it is difficult to distinguish the effect of symmetry breaking and introducing secondary element on the optical properties. In order to investigate how the plasmon resonances can be tuned by breaking the symmetry in morphology, we subsequently develop a strategy reducing the symmetry of Ag nanoparticles by etching. In details, the anisotropic etching is achieved by using two steps. In the first step, nanooctahedra are assembled on the soft substrate such as PDMS. In the second etching step, the soft substrate protects the underneath part of nanooctahedra from etching while the uncovered part is etched. The morphological characterizations confirms the significant symmetry breaking of Ag nanooctahedra both on the substrate and in solution. In addition,

series of systematic study on mechanism is designed and conducted to achieve the better understanding of etching process.

In the second part of this thesis, an efficient 3D SERS substrate is developed for future anti-counterfeiting and data storage applications. Compared with the conventional 2D platforms, we extend the hotspots into the third dimension and to maximize the SERS efficiency of the substrate in three dimensions by investigating the laser confocal volume. Meanwhile, a sandwich hierarchical structure of monolayer decoration on Ag film is achieved by Langmuir-Blodgett assembly of Ag nanocubes providing much stronger hotspots due to a mirror effect. Besides, by optimizing morphology, height and inclination angles of the microstructures, more efficient design is achieved to tune the intensity of Raman signal. Based on that discovery, we succeed to utilize such 3D SERS substrate for barcode encryption, where simply changing the laser focus plane will provide distinct binary information. This phenomenon is proved to be able to tag the complex binary matrix message as well.

6.2 OUTLOOK

The work on fabricating the Janus nanoparticles demonstrates the versatility and robustness of our strategy to construct bimetallic nanostructures with distinct morphology and composition. As such, a further application on catalytic study will be conducted in the future based on those advantages.

As widely reported, the Au-Ag bimetallic nanoparticles exhibit a strong catalytic property for CO oxidation.^{1, 2} To be specific, Au and Ag parts assist in adsorbing CO molecules and O₂ respectively, enabling the synergistic interaction at the interface of

these two components and thus improving the catalytic performance. However, these catalytic studies are mostly conducted by using alloy and there lacks studies on shape-controlled nanoparticles. In addition, the Janus nanoparticles are reported to exhibit a stronger catalytic property than the centrosymmetric ones. Therefore, by using our Platonic Janus nanoparticles, we are able to accomplish systematic study on morphology effect and to achieve stronger catalytic ability in the future.

Moreover, by using our fabrication method, it is easy to change the secondary element to another well-known catalytic metals, such as Pt and Pd. Therefore, more catalytic reactions can be studied easily. For example, Monnier *et al.* increase the activity of the hydrogenation of 3,4-epoxy-1-butene by using Pt-Ag bimetallic nanoparticles.³ Moreover, Meng *et al.* reported that the Pd-Ag bimetallic dendrites possess higher catalytic ability to reduce 4-nitrophenol compared with the pure Pd or Ag nanoparticles.⁴ However, no studies on morphological control of these bimetallic nanoparticles are shown in these works since it is challenging to control the morphologies. In the future, we can accomplish series of these studies by fabricating the bimetallic Janus nanoparticles using our strategy.

Regarding to the pyramid nanostructures, further single-particle SERS study will be conducted. Etching of nanoparticles always results in morphologies with more SERS hot spots densities than the mother morphologies, leading to higher SERS enhancement. For example, Yang *et al.* conducted a heterogeneous etching of Ag octahedra in solution phase and the resulting octopod structure was reported to offer the highest enhancement of single-particle SERS.⁵ As such, it is necessary to investigate the SERS performance of our pyramid in order to study how the symmetry breaking affects the optical properties of

metallic nanoparticles. Moreover, Xia *et al.* reported the polarization-dependent SERS intensities on nanocubes.⁶ The pyramid with less symmetry is expected to exhibit stronger polarization-dependent properties. Thus, a study on polarity dependent SERS excitation is to be conducted to emphasize the importance of symmetry breaking.

Moreover, we only focus on etching of octahedra in this thesis. To extend to more applications by using our etching strategy, more work is to be done by etching other morphologies, such as spheres and cubes. All those Ag nanoparticles are nowadays widely developed and will bring distinct symmetry breaking. For the nanospheres, the hemispheres are always expected after etching due to the holosymmetry, which has seldom been reported as single-crystalline nanoparticles so far. For nanocubes, however, by tuning the assembly direction, cuboid, triangular prism and even tetrahedron might be obtained using our method (Scheme 1). It is challenging to fabricate these morphologies with single crystallinity. The potential optical properties of these nanostructures to be studied are essential for an overall understanding of the plasmon resonances of anisotropic metallic nanoparticles. Hence, there are bright future of anisotropic etching in the fabrication of different morphologies.

Scheme 1. The possible assembled orientation of nanocubes on PDMS, and the reasonable nanoparticles obtained accordingly from our etching method.

As to our 3D SERS platform, the stimuli-responsive materials are proposed to extend the variety of microstructure due to the ability of adapting to surrounding. Up to now, a wide range of such stimuli-responsive materials have been developed with distinct reaction-to-environment change which is sensitive to stimuli such as PH, temperature and light.⁷ Exploiting such adapting property, the intensities of Raman signals are reported to be tunable. For instance, Nie *et al.* applied the PH responsive polymer onto the surface of Au nanoparticle, realizing the switch on and off SERS detection.⁸ In this thesis, we have developed a platform to encrypt tunable information within the inflexible microstructures by changing laser focus plane. Here, we propose an information encryption platform with the capability to encode multiplex information which are read out by exerting specific stimuli, achieved by simply changing the microstructure material to the stimuli-responsive polymer.

We take Poly(N-isopropylacrylamide) (Poly-NipAAm) as example, which is known as an efficient temperature responsive material. The as encoding binary information will be decoded 010010001001000100100010010 from the middle height of the microstructure at room temperature. However, heated over the conversional temperature, the shrinkage of NipAAm makes the structure become shorter and smaller, leading to a possible read out of 0100000001000000001000000010 for instance (Scheme 2). Thus, controlled by stimuli, our information storage platform could be much harder to be counterfeited and decoded by anyone without the knowledge.

Scheme 2. The proposal to utilize temperature as stimuli to control the tagging information of binary numbers.

Furthermore, the anisotropic nanoparticles obtained by using strategies shown in the chapter 2 and 3 can be utilized for fabricating the 3D SERS substrate. As reported by *Xia et al.*, breaking the symmetry of nanocubes directly changed the plasmon resonance and further tuned the Raman intensities by changing the polarization of laser.⁹ Thus, by combining the anisotropic nanoparticles with the 3D SERS substrate, in the future we are able to encode the polarization-dependent SERS intensities as another dimension in terms of data storage and anti-counterfeiting, apart from the focus planes. Consequently, we can realize a much more complex and versatile platform for information encoding by

combining the symmetry broken nanoparticle and fabrication of 3D SERS substrate.

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