Plasmonic nanostructures : fabrication, optical properties and anti-counterfeiting application

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(On the Spine)

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**PLASMONIC NANOSTRUCTURES:
FABRICATION, OPTICAL PROPERTIES AND
ANTI-COUNTERFEITING APPLICATION**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2017

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Table of Contents

SUMMARY	1
1 INTRODUCTION.....	3
1.1 LOCALIZED SURFACE PLASMON RESONANCE	4
1.2 FABRICATION OF PLASMONIC NANOPARTICLES.....	6
1.2.1 Chemical Synthesis	7
1.2.2 Lithography	22
1.3 PARAMETERS TUNING PLASMONIC PROPERTIES	23
1.3.1 Physical Features of Plasmonic Nanoparticles	23
1.3.2 Assembly of Plasmonic Nanoparticles	29
1.4 CHARACTERIZATION OF PLASMON RESONANCES.....	34
1.4.1 Far-Field Optical Studies	35
1.4.2 Near-Field Mapping of Plasmons	37
1.5 APPLICATIONS OF PLASMONIC NANOPARTICLES	41
1.5.1 Surface-Enhanced Raman Scattering.....	42
1.5.2 Plasmonic Anti-counterfeiting Security Label.....	49
1.5.3 Plasmonic Platforms for Data Storage	51
1.6 MOTIVATION AND OBJECTIVES.....	53
1.7 REFERENCES	55
2 PRECISION SYNTHESIS: DESIGNING HOT SPOTS OVER HOT SPOTS**	73
2.1 INTRODUCTION	75
2.2 RESULT AND DISCUSSION	77
2.3 CONCLUSION.....	105

2.4 MATERIALS AND METHODS.....	106
2.5 ACKNOWLEDGEMENT	110
2.6 REFERENCES	110
3 PLASMON MAPPING OF COUPLING WITHIN AG NANOCUBE DIMERS**	
.....	115
3.1 INRODUCTION.....	116
3.2 RESULTS AND DISCUSSION	119
3.3 CONCLUSION.....	130
3.4 MATERIALS AND METHODS.....	132
3.5 ACKNOWLEDGEMENT	133
3.6 REFERENCES	133
4 PLASMONIC NANOPILLAR ARRAYS ENCODED WITH MULTIPLEX	
MOLECULAR INFORMATION FOR ANTI-COUNTERFEITING	
APPLICATIONS**	139
4.1 INTRODUCTION	140
4.2 RESULT AND DISCUSSION	141
4.3 CONCLUSIONS.....	160
4.4 MATERIALS AND METHODS.....	161
4.5 ACKNOWLEDGEMENT	163
4.6 REFERENCES	164
5 THREE DIMENSIONAL FLEXIBLE PLASMONIC ANTI-COUNTERFEITING	
SECURITY LABELS BASED ON SURFACE-ENHANCED RAMAN	
SCATTERING**	167
5.1 INRODUCTION.....	169
5.2 RESULTS AND DISCUSSION	172
5.3 CONCLUSION.....	187

5.4 MATERIALS AND METHODS.....	188
5.5 REFERENCES	190
6 SUMMARY AND OUTLOOK.....	195
6.1 SUMMARY	195
6.2 OUTLOOK	198
6.3 REFERENCE.....	201
7 LIST OF ACRONYM.....	203
8 LIST OF PUBLICATION.....	205

Summary

This thesis involves my four-year graduate research studies on fabrication, optical properties and anti-counterfeiting applications of plasmonic nanostructures. In the beginning, recent works are summarized focusing on synthetic methods used to engineer the morphologies, parameters used to tune the plasmonic properties and applications of plasmonic nanoparticles (chapter 1). Two challenges are generalized in the field of plasmonic nanostructures: (i) to efficiently tune and understand the surface plasmonic properties of plasmonic nanoparticles at single-particle level and in the coupled system; (ii) to develop novel platforms using plasmonic nanoparticles for practical applications. Based on that, I aim to efficiently enhance the intensity and enlarge the densities of hot spots on individual plasmonic nanoparticles via precision synthesis (chapter 2), to understand the plasmon resonances that occur in the Ag nanocube dimers (chapter 3) and to develop plasmonic anti-counterfeiting platforms on both rigid (chapter 4) and flexible substrates (chapter 5).

We efficiently increase the volumes and intensities of localized fields on individual nanoparticles by introducing a “hot spots over hot spots” strategy that selectively depositing plasmonic active nanodots on edge and tip hot spots regions (chapter 1). Moreover, combining CL and EELS maps on Ag nanocube dimers, we acquire knowledge on localized surface plasmon resonances (LSPRs) that occur in Ag nanocube dimers and directly visualize how plasmon modes evolve with alteration of dimer orientations with nanoscale spatial resolution (chapter 3). Besides, we broaden the applications of plasmonic nanoparticles by introducing a novel anti-counterfeiting platform encoding five identifying layers in the form of SERS, fluorescence and their signal intensities on a single platform (chapter 4). We also

develop a flexible plasmonic anti-counterfeiting platform giving stable SERS readouts over applying several cycles of external bending forces for practical applications (chapter 5). In the end, outlook of these research works in this field is proposed (chapter 6).

1 Introduction

ABSTRACT. Plasmonic nanoparticles confine lights into volumes at sub-wavelength scale and convert them into enhanced EM fields or other energies. This ability is brought about by localized surface plasmon resonances (LSPRs) of metal nanoparticles, arising from the collective oscillation of the conduction band electrons. Light-matter interactions can be tailored for varieties of applications. In this chapter, we introduce synthetic methods to engineer the morphologies, the parameters being used to tune the plasmonic properties and characterization methods to study the optical properties of plasmonic nanoparticles. In the end of this chapter, we review some current platforms consisting of plasmonic nanoparticles for SERS detection, anti-counterfeiting and data storage.

1.1 LOCALIZED SURFACE PLASMON RESONANCE

Metallic nanoparticles possess unique abilities to confine light and manipulate light-matter interactions at nanometer scale. This property arises from the localized surface plasmon resonance (LSPR) of metallic nanoparticles.^{1,2} In definition, surface plasmon resonance (SPR) is a coherent oscillation of free electrons which is excited by electromagnetic (EM) radiating (light, fast electrons *etc.*) on a metal surface. Under light radiation, the electrons in the metal conduction bands are perturbed from their equilibrium positions and coherently oscillate with incident light at a resonance frequency. For LSPR, light interacts with a metallic nanoparticle whose size is smaller than its incident wavelengths, so that the resulting oscillation of free electrons is confined to a limited volume surrounding the nanoparticles (Figure 1.1).^{1,3} The metallic nanoparticles supporting LSPR are known as plasmonic nanoparticles, such as Ag and Au nanospheres. Figure 1.1 illustrates the LSPR supported by plasmonic nanospheres.¹ The electrons being accumulated at one end of the particle and move to the other end, creating a net dipole.^{1,3} This dipolar plasmon resonance is the main LSPR mode for Ag and Au nanospheres whose sizes are less than 30 nm. Within larger nanospheres and nanoparticles with less symmetry than nanosphere, high-order plasmon modes containing more diploes appear.⁴ For example, quadrupole plasmon resonance which contains two negatively charged poles is supported by 140-nm Ag nanospheres.⁵

Figure 1.1. Scheme illustrating localized surface plasmon resonance. Reprinted with permission from Ref [1]. Copyright © 2007, Annual Reviews.

Plasmonic nanoparticles supporting LSPR are interesting for research because of their potential applications. The Lycurgus cup exhibiting changing colors is an ancient application of plasmonic nanoparticles. The cup appears green when lit from front for viewing the scattering light while it shows red when lit from behind for observing the transmission. Analysis on composition of the Lycurgus cup reveals that it contains 70-nm nanoparticles made of Ag-Au alloy. This phenomenon results from enhanced far-field scattering and absorption at the LSPR frequencies of these nanoparticles which are ~500-550 nm (green light region). Moreover, LSPR frequencies are sensitive to the changes in local dielectric environment and thus can be used for sensing.⁶⁻¹² For example, LSPR positions of Au nanoparticles shift when being conjugated with bio-molecules, making Au nanoparticles to be sensitive probes for bio-sensing.^{13,14} Al nanoclusters exhibit high spectral sensitivity to dielectric changes so that the presence of analyte can be detected via color changes.¹⁵

On the other hand, due to the surface plasmon oscillations at the LSPR frequency, the electromagnetic (EM) fields are strongly concentrated at the surfaces of nanoparticles and this near-field is greatly enhanced as compared with the incident fields which induce LSPR. These regions with greatly localized and enhanced EM fields are known as “hot spots”. The strong near-field greatly enhances the electronic transitions of optical absorbers and emitters placed in the vicinity of the nanoparticles. For instance, the cross section of Raman scattering from molecules which are placed near the plasmonic nanoparticles is reported to be proportional to the square of the EM field intensity and the Raman signal enhancement of such molecules is well-known as surface-enhanced Raman scattering (SERS) enhancement.^{16,17} Moreover, the fluorescent emission intensity of the fluorophore placed near the plasmonic nanoparticle surfaces is enhanced with enhancement factors ranging from 2-1000, arising from the concentrating of light and the decrease in the fluorescence lifetime induced by the LSPR.¹⁸ On the basis of the surface-enhanced Raman and

fluorescence signals, hot spots of plasmonic nanoparticles are investigated for analytical applications, such as ultrasensitive detection and sensing of toxic chemicals as well as biological systems.¹⁹⁻²⁶ Furthermore, plasmonic nanostructures localizing EM fields to sub-wavelength region serve as optical antennas to efficiently localize and convert light into energy.² With this capability, the plasmonic nanostructures with abundant hot spots can be used to improve performances of photodetector, energy harvesting, bio-imaging and nonlinear signal conversions including harmonic generation and two-photon luminescence.²⁷⁻³¹

In general, the capability of plasmonic nanoparticles on concentrating light within sub-wavelength volume has been widely used in many fields on the basis of LSPR, such as sensing, detection, wave-guiding, lasing, imaging and light harvesting, etc.^{6-9,15,32-44} For manipulating the light-matter interactions at nanometer scale, a number of synthetic methods emerge to fabricate plasmonic nanoparticles (details in section 1.2). Studies are also conducted to understand the relationship between plasmonic properties and the physical features (size, shape, composition and *etc.*) of these nanoparticles (details in section 1.3). Moreover, numerous novel characterization methods appear to understand LSPR of plasmonic nanoparticles and distributions of localized EM fields with sub-wavelength spatial resolution (details in section 1.4). Furthermore, on the basis of these optical studies, plasmonic-nanoparticle platforms are developed for novel applications (details in section 1.5).

1.2 FABRICATION OF PLASMONIC NANOPARTICLES

The capability of manipulating the morphologies of plasmonic nanoparticles is essential for investigating plasmonic properties and developing potential applications. To date, plasmonic nanoparticles with different physical features such as shapes, sizes and compositions are fabricated via wet-chemical synthesis and lithography methods.

1.2.1 Chemical Synthesis

Chemical syntheses are prevalently utilized for fabricating nanoparticles in large scale and with high yields. The morphologies of both mono-metallic and bi-metallic nanoparticles can be manipulated via thermodynamic and kinetic control over the chemical reaction. In this section, we focus on introducing the polyol reduction and seed-mediated methods, which are frequently used in this thesis. Galvanic replacement reaction will be briefly introduced. Moreover, we emphasize on discussing recent synthetic methods about controlling the morphologies of bi-metallic nanostructures using anisotropic deposition or etching.

1.2.1.1 Polyol Reduction Synthesis

Typically, the polyol reduction synthesis includes the reduction of metal salt precursors using polyol at high temperature.^{26,45,46} Capping agents and precursors are injected into the polyol which is heated to an elevated temperature in advance. Polyol such as ethylene glycol and 1,5-pentanediol is the solvent and reductant in this reaction. The reducing capability of polyol is activated by pre-heating it in the presence of air. For example, ethylene glycol heated in ambient at 150 °C generates glycolaldehyde which is a stronger reductant than ethylene glycol.⁴⁶ As a result, polyol reduction process is highly sensitive to the temperature.

Polyol reduction process is typically used for producing different shapes of fcc Ag nanocrystals.⁴ During the synthetic process, there are three stages. At the beginning, small clusters of Ag atoms are formed through reduction. Then these Ag clusters grow larger and become seeds. In the last stage, more Ag atoms deposit at the active sites on the seeds and grow into nanostructures with well-defined morphologies. Figure 1.2 shows the scheme of these three stages.⁴ In the second stage, four different seeds are generated, including single crystalline, singly twinned, multiply twinned seeds and plate with stacking faults. Different seeds are grown into nanostructures with different morphologies. For example, single

crystalline seeds evolve into octahedra, cuboctahedra and cubes while singly twinned seeds are grown into right bipyramids.

Figure 1.2. Scheme of three stages of growing to fcc metal nanocrystals having different shapes. Reprinted with permission from ref [4]. Copyright © 2009 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

Oxidative etchant and capping agents are used to obtain high yield of single morphology. The role of trace amount of the oxidative etchant, such as Cl^- ions, in the shape control is to remove the unwanted seeds. For example, Cl^-/O_2 can dissolve all but the single crystalline seeds and thus Cl^- are added when synthesizing polyhedral nanoparticles.⁴⁷ Capping agents such as poly(vinylpyrrolidone) (PVP) are normally used to prevent aggregation by stabilizing the freshly formed surfaces. For shape control, capping agents which are selectively bound to certain facets are used to lead the growth along a single

direction. For instance, PVP is reported to be preferentially capped on {111} facets of the Ag seeds containing a mix of {100} and {111} facets, forcing the further Ag growth along (100) direction.⁴⁸ In the typical synthetic procedure of Ag polyhedra, PVP and Ag precursors are separately injected with controlled amounts and injecting rates.⁴⁸ Whether the dominating morphology is cubes, cuboctahedra or octahedra strongly depends on the ratio between growth rate along the (100) and (111) directions. Generally, polyol reduction synthesis is a simple one-pot method. No foreign metal ions are introduced into the final products and the precursors are directly added without pretreatments. The limitation of this synthetic method lies in the strict conditions including temperature, injection speed and amount of chemicals. Slight deviation from the optimal conditions results in generation of unwanted morphological products, reducing the reproducibility of this method.

1.2.1.2 Seed-mediated Method

Seed-mediated method includes reducing metal salts into seed nanoparticles and growing the seed nanoparticles into desired shapes. Compared with polyol reduction methods, seed-mediated method separates the generation of seed nanoparticles from the growth step, and is more versatile in controlling the nanoparticle shape, size and composition. Various kinds of monometallic and bimetallic nanoparticles are synthesized in large scale by using this method.⁴⁹⁻⁵⁵ The tunable parameters for shape control include morphology of the seeds, injecting speed of the metal salts (precursor), amount ratio between seeds and precursors, reducing power and amount of reducing agents, foreign ions as well as surfactants.⁴⁹⁻⁵⁵

1.2.1.2.1 Monometallic Nanoparticles

Seed-mediated method involves two steps. In the first step, seed nanoparticles with arbitrary morphologies are produced. These seeds are normally synthesized by reduction process in which metal salts are reduced by reducing agents. In the second step, these seeds

are added into a growth solution containing metal salts, mild reducing agents and surfactants. The metal salts will be reduced on the surfaces of seeds and then these seeds grow into the final morphology.

Surfactants or capping agents are added in this step to control the growth directions and thus the final morphology. This is a concerted effect with the non-homogeneous surface energies which are distributed on the seeds. Normally, surfactants or capping agents bind to the faces with higher surface energies and thus inhibit the further growth on these faces.⁵⁶ Surface energies are the highest at regions with defects and stacking faults. For the single-crystalline seeds which are fcc metal nanocrystals, the energy rule is $E\{110\} > E\{100\} > E\{111\}$.⁵⁷ For example, cetyltrimethylammonium bromide (CTAB) is used in the synthetic process of Au nanorods.⁵⁸ In this process, Au decahedral nanoparticles are produced as seeds in the first step. The crystal structure of this seed consists of five $\{100\}$ facets at side-edges and ten $\{111\}$ facets at the end-faces. Because of the higher surface energy of $\{100\}$ than $\{111\}$, CTAB preferentially binds to the $\{100\}$ facets and inhibits the nucleation of Au on the side. As such, Au salts are reduced and grown on $\{111\}$ facets at the end-faces to form Au nanorods.

In addition, external ions can be introduced in the second step to form active sites on seed nanoparticles and alter the growth directions. For example, in the synthetic procedure of Au spiky nanoparticles, Au nanoparticles serving as seeds are produced by reducing HAuCl_4 . Ag^+ is introduced to form AgCl on the seed surfaces. Freshly grown AgCl are active sites for further Au growth, inducing the formation of spikes.⁵⁹

1.2.1.2.2 Bimetallic Nanoparticles

Seed-mediated method is always used to fabricate bimetallic nanoparticles. Depositing a secondary metal on the seeds is the second step of generating bimetallic nanoparticles, which is different from synthesizing monometallic nanoparticles. Epitaxial growth of the secondary metal is obtained when the lattice match of seed and the secondary metal is

close.⁴ The lattice is well matched between Ag and Au ($d_{\text{Ag}}=4.090 \text{ \AA}$ and $d_{\text{Au}}=4.089 \text{ \AA}$), so Ag-Au-Ag nanorods can be synthesized via directed overgrowth on Au decahedral seeds (Figure 1.3).^{60,61} In this work, PVP which serves as capping agents preferentially binds to $\{100\}$ rather than $\{111\}$ surface, directing the growth of Ag segments along the longitudinal direction.⁶⁰

Figure 1.3. Directed anisotropic growth. (a) Scheme illustrating the growth of Ag-Au-Ag nanorods from Au decahedra and nanorods. (b and c) SEM images of Ag-Au-Ag heterogeneous nanorods synthesized using (b) Au decahedra and (c) nanorods as seeds, respectively. All scale bars are 500 nm. Reprinted with permission from Ref [60]. Reprinted with permission from Ref [60]. Copyright © 2008, American Chemical Society.

Besides, the secondary metals can be uniformly grown on the seeds or selectively deposited on tips, edges and faces of the seed nanoparticles by kinetic control over the reaction. The capability of controlling the growth results from the difference in the surface energies of the template nanoparticles and in the affinities of certain surfaces with capping agents or foreign ions. Generally, the metal salts are readily reduced on sites with higher surface energies.

By tuning the Pt/Au ratio, Pt nanodots can be selectively grown on the edges or randomly deposited over entire faces of Au nanorods.⁵¹ When Pt/Au ratio is less than 0.2,

Pt nanodots are mainly grown on the end-tips and edges of the Au nanorods while when Pt/Au ratio is larger than 0.2, random deposition of Pt nanodots are observed on the nanorods. The nanodot-density increases as the Pt/Au ratios increase and Au nanorods are grown with conformal Pt layers when the ratio reaches to 2. In this work, edges with more structural defects and end-caps with fewer CTAB are high-energy surfaces on nanorods and thus Pt deposition preferentially happens at these sites at low Pt/Au ratio.

The effect of foreign ions on deposition of secondary metal is investigated by depositing Pt on Au nanocube, nanooctahedra and nanosphere using controlled Pt/Au ratios and Ag^+ serves as the foreign ions (Figure 1.4).⁵² At low Pt/Au ratios, the Pt are readily deposited on the faces of nanocubes while on the tips and edges of nanooctahedra (Au {100} facets). When the Pt/Au ratio reaches sufficiently high, the Pt begins to deposit on corners of nanocubes and planar faces of nanooctahedra (Au {111} facets). In the case of Au nanosphere, the Pt deposits on the entire surfaces at any Pt/Au ratios. XPS measurements on freshly synthesized Au nanocubes and nanooctahedra demonstrate more residual Ag existing on gold nanocubes, probably arising from the higher concentration of silver nitrate used in the Au nanocubes synthesis. The residual Ag are preferentially adsorbed to the {100} facets rather than to the {111} facets. The Pt are more preferentially deposited on Au {100} facets because Ag on the {100} facets provide electrons which facilitate the Pt reduction.

Figure 1.4. Scheme illustrating the controlled overgrowth of Pt on a Au nanocube (top), octahedron (middle) and sphere (bottom), respectively. Reproduced from Ref [52] with permission from the PCCP Owner Societies. Copyright © 2009, Royal Society of Chemistry.

Apart from tuning the surface energies of different facets on seeds using capping agents and foreign ions, the growth rate can be used to control the final product morphologies and thus LSPR frequencies. The growth rate is normally manipulated by tuning the amount of reducing agents, pH value and injection rate of precursors of the secondary metals. For instance, the LSPR frequencies for Au@Pt nanorods are varied with Pt thicknesses during the Pt deposition, achieved by changing the ratios of ascorbic acid (AA) which serves as reducing agents and Pt precursor (Figure 1.5).⁵¹ When the AA/Pt ratio is less than 10, the LSPR red shifts with the increase of AA/Pt ratio while the LSPR turns to blue shift with further increase of AA/Pt ratio when the ratio is larger than 10. It arises from the difference between growth rate of Pt at the end and at the side of nanorods when changing the AA/Pt ratios. Increasing the AA/Pt ratios induces more Pt being deposited at the side and thus smaller aspect ratio of the final nanorods, which results in blue shift of LSPR.

Figure 1.5. Absorption spectra of (a) Au NRs and (b-h) the Au-Pt NRs with AA/Pt molar ratios of 1, 5, 10, 25, 50, 100, and 200, respectively. Reproduced with permission from Ref [51]. Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In another work, pH value is adjusted to maneuver the growth rate of Pd and determines the formation of multiple Pd nucleation sites on the Pt nanocubes, instead of conformal overgrowth (Figure 1.6).⁵³ Ascorbic acid is used as reducing agent for Pd salts. PH value is

increased by adding NaBH_4 . With higher pH value, ascorbic acid will be deprotonated to accelerate the reaction. Higher reaction rate favors multiple nucleation sites rather than conformal overgrowth of a thin Pd shell. In the end, single, double and multiple nucleation are produced, predominantly at the corners. Moreover, controlled growth of Au on edges of Ag decahedral nanoparticles is achieved by tuning both pH and injection rate of Au precursors (Figure 1.7).⁵⁴ The selective deposition is achieved by reducing the growth rate of Au. At low growth rate, Au is preferentially deposited on high-energy sites. In this work, Decahedral Ag nanoparticles are selected as seed for Au deposition because of their well-defined edges connecting 10 (111) facets. (111) facets possess low surface energies relative to the edges, making edges the preferred locations for deposition. In contrast, on nanocubes which contains edges connecting (100) facets, (100) are more reactive and Au can be uniformly deposited on the faces even at low growth rate.

Figure 1.6. TEM images of (a) Pt/Pd nanoparticles, (b) an interface of Pt and Pd, (c) high Pd coverage and (d) low Pd coverage of Pt/Pd nanoparticles, respectively. Reprinted with permission from Ref [53]. Copyright © 2008, American Chemical Society.

Figure 1.7. TEM images of Au nanoframes and nanocages upon depositing Au onto decahedral Ag nanoparticles and subsequently etching Ag using H_2O_2 . (a) Decahedral Ag nanoparticles (b) Decahedra after selective deposition of Au. (c-h) Images of the nanoframes and nanocages after dissolving Ag with etchant H_2O_2 . The Au/Ag ratios used in the sythesis were 20, 15, 7, 5, 3, and 1 mol %, respectively. Scale bars represent 50 nm. Reprinted with permission from Ref [54]. Copyright © 2011, American Chemical Society.

1.2.1.3 Galvanic Replacement Reaction

In definition, galvanic replacement reaction is a spontaneous redox reaction in which electrons from the valence band of metal reduce the other metal ions with more positive reduction potential.⁶² In this one-step reaction, metal with less potential dissolves with the deposition of another metal. Galvanic replacement reaction is generally used to fabricate hollow nanostructures such as nanocages and nanoframes. This synthetic process of nanostructures contains a sacrificial template particle and precursors. For example, Au nanocages are generated using Ag nanocubes as sacrificial templates. HAuCl_4 has redox potential (0.99V vs SHE) more positive than the Ag^+/Ag (0.80 vs SHE) pair.⁶² During this synthetic process, HAuCl_4 solution, which serves as Au precursor, are titrated into Ag

nanocubes at an elevated temperature. This reaction consists of alloying and dealloying stages (Figure 1.8).⁶² In the alloying process, Ag nanoparticles are continuously dissolved based on three Ag atoms being displaced by one Au atom. As such, pinholes are formed on the Ag nanocube surfaces. At the temperature higher than 100 °C, inner Ag atoms diffuse to the surfaces and alloy with the freshly formed Au, generating nanoboxes with hollow interiors, smooth surfaces and homogeneous Au-Ag alloy walls. In the dealloying process, Ag in the Ag-Au alloy walls are removed. The dealloying process is performed by adding more Au precursors to the system, and thus allowing replacement reaction to continue to dissolve more Ag. Ostwald ripening induces morphological reconstruction, enlarges the holes on the wall and finally generates Au nanocages. Besides, external etchants such as H₂O₂ or Fe(NO₃)₃ can be used to remove the Ag in the alloy.^{63,64} Unlike introducing more HAuCl₄ which induces concurrently Au deposition, external etchants make the dealloying process easily to be controlled. Nanoframes with variable wall thicknesses are fabricated using Fe(NO₃)₃ as etchant. In addition, Pt and Pd nanocages as well as Pd/Au/Ag nanocages can be fabricated using this method.^{62,65}

Figure 1.8. Process of generating Au nanoframes using galvanic replacement reaction. SEM images of (A) Ag nanocubes and products generated after (B-D) 0.30 mL, 0.5 mL, and 2.25 mL of HAuCl₄ aqueous solution (1 mM) reacting with a 5-mL of Ag nanocube suspension (0.8 mM), respectively. Electron diffraction (inset in A) indicates that they are single crystals. Insets shown in B and C are TEM images of corresponding products. (E) Schemes summarizing morphological changes. Reprinted with permission from Ref [62]. Copyright © 2004, American Chemical Society.

Moreover, galvanic replacement reaction between Ag templates and Au precursors is exploited for fabricating Au-Ag nanocages with long 130-nm-length spikes in order to achieve strong field localization (Figure 1.9).⁶¹ In this work, Ag octahedra are used as seeds and oxidized by HAuCl₄ in the presence of large-molecular-weight PVP. PVP with large molecular weight forms highly viscous matrix surrounding the Ag seeds. This matrix decreases the mobility of free Ag⁺ and Cl⁻ ions, promoting the formation of AgCl. These insoluble AgCl crystals subsequently deposit on surfaces of Ag seeds and serve as seeds for non-epitaxial growth of Au due to the large lattice mismatch between AgCl and Au ($d_{\text{AgCl}}=5.549 \text{ \AA}$ and $d_{\text{Au}}=4.080 \text{ \AA}$). Concurrently, Ag from the core diffuses to the surface for galvanic replacement reaction with Au ions. As such, long spikes are grown on AgCl sites with the generation of Ag-Au nanocages.

Figure 1.9. Formation of Au-Ag spiky nanoparticles. (A) Schemes illustrating the growth of Au-Ag spiky nanoparticles. SEM images, TEM images, camera pictures, and histogram of spikes' lengths of (B) Ag octahedra, and (C and D) Ag-Au spiky nanoparticles with an average spike lengths of 50 and 130 nm, respectively. Reprinted with permission from Ref [61]. Copyright © 2013, American Chemical Society.

In general, galvanic replacement reaction is versatile, simple for operation and free of reducing agents. It happens when the standard electrode potential of the sacrificial material is sufficiently lower than that of the target material. However, in the seed-mediated process of synthesizing Au-deposited Ag nanoparticles with solid cores, galvanic replacement reaction is always acting as competing reaction which is to be prevented. For example, coating Ag nanoparticles with Au is always competitive with the galvanic replacement. In the process of depositing Au on Ag nanoprisms, ascorbic acid is used to reduce the Au precursors and protect the Ag nanoprisms from galvanic replacement reaction.⁵⁵ Moreover, citrate is used as capping agent to minimize the damage to nanoprisms during the coating

process. At low Au/Ag ratios (about 0.08 to 0.17) a thin layer of Au is deposited on the edges of the nanoprisms without the structural damage caused by galvanic replacement reaction. With more Au salts, galvanic replacement dominates and makes the nanoprism hollow.

1.2.1.4 Electrochemical Deposition

Electrochemical deposition can be used to fabricate bi-metallic nanoparticles on the substrate. For example, Torimoto *et al.* have obtained the Au-framed Ag nanocubes by electrochemical depositing Au onto the edges and vertices of Ag nanocubes which are immobilized on HOPG substrate.⁶⁶ Linear sweep voltammograms for Au deposition on various substrates were obtained in the phosphate buffer solution containing $\text{Au}(\text{CN})_2^-$ ions, based on the equation below.

Figure 1.10 shows using this strategy for synthesizing both Au nanoframe and an Au nanobox. In the case of fabricating Au nanoframe, Ag nanocubes are functionalized with 1-octanethiol (OT).⁶⁶ Discontinuity of the OT layer appears at edges and vertices of nanocubes, inducing defects where Au deposition selectively happen. After chemical etching of Ag, Au nanoframes are formed on the substrate. In contrast, for fabricating Au nanobox, PVP-Ag nanocubes are immobilized on the HOPG surface used as working electrode. Au is electrodeposited on the entire surfaces of PVP-Ag. After chemically etching, nanoboxes are generated.

Figure 1.10. Scheme showing the strategy for synthesis of an (a) Au nanobox and an (b) Au nanoframe, respectively. Reproduced from Ref [66] with permission from the Royal Society of Chemistry. Copyright © 2009, Royal Society of Chemistry.

1.2.1.5 Selective Etching Induces Selective Growth

Apart from exploiting the original active sites on the seeds, the nucleation sites can be created by selective etching in advance of secondary deposition. A series of Pt hollow nanostructures is synthesized using Au polyhedra as seeds (Figure 1.11).⁶⁷ The key step is using iodide to etch the edges of polyhedron where highly active sites are formed, inducing the selective deposition of Pt on the Au edges. The Pt layer protects the Au on the etched edges against further etching. Subsequently, the Au on {111} facets which are free of protection will be etched away and finally nanorings would be formed.

Figure 1.11. Scheme showing process of selective-etching inducing selective growth. Pt ring is fabricated using Au decahedron as seed. Reprinted with permission from Ref [67]. Copyright © 2012, American Chemical Society.

1.2.1.6 Light-induced Deposition

Light can be used to fabricate plasmonic nanoparticles on semiconductor templates via photoreduction. Metal-tipped semiconductor nanorods provide a charge transport path through the long axis of rod. In this case, electrons from the CdS rodlike shell move to the gold tip under UV excitation. The hole left behind facilitates the reduction of metal salts in solution and induces selective deposition on the tips (Figure 1.12).⁶⁸

Figure 1.12. Scheme of light-induced deposition. Reprinted with permission from Ref [68]. Copyright © 2011, American Chemical Society.

1.2.1.7 Top-down Etching Method

The above discussed approaches are bottom-up synthetic methods, in which secondary deposition happens on seeds and templates. In contrast, instead of deposition and growth on the seed nanoparticles, top-down shaping is to etch the seeds. Octahedra with concave edges and octapod structures are synthesized by selectively etching {100} surfaces of Ag octahedra. Roughened Ag nanowires are obtained via mildly etching.⁶⁹ In addition, novel morphologies can be enriched by etching bi-metallic nanostructures.⁵² For instance, Pt-Au nanocubes with concave edges are fabricated by combining bottom-up deposition and top-down etching. Pt is selectively deposited on faces of Au nanocubes and the resulting products are etched by CN^- . Pt on the cube faces serves as protective masks and the exposed Au edges are selectively etched by CN^- .⁷⁰ In this method, etching kinetics is strictly controlled by tuning reaction rate of the etchant and time for etching.

1.2.2 Lithography

Aside from the chemical syntheses, lithography followed by metal deposition allows the arrangements and structures of plasmonic nanostructures being precisely controlled. Generally, lithography fabricates nanostructures in a way of generating polymer mask for deposition or etching using resist. Electron-beam lithography (EBL) and focused ion beam lithography (FIB) utilizes electron beam and ions to selectively scan over the regions according to programmed patterns, respectively.⁷¹⁻⁷⁴ For the regions exposed to the focused electrons or ions, the resists become soluble (positive resist) or insoluble (negative resist) to certain solvents called developer. For instance, poly(methyl methacrylate) (PMMA) resist turns soluble under the electron beam and can be removed from the mask.⁷⁵ After that, Ag can be deposited to fill the voids on the mask. Ag nanostructures with desired shapes are formed on substrates after removal of the remaining PMMA. So far, a number of optical antennas with sub-10 nm gap sizes are fabricated using FIB and EBL, such as Yagi-Uda antenna, gap antenna and split-ring resonator.² High resolution of tens of nm can be achieved using EBL and FIB, but they are time-consuming and can only be used to fabricate disk-like structures.

In contrast, two-photon lithography based on the laser-induced two-photon excitation renders absorption with high spatial resolution in three dimensions.⁷⁶⁻⁷⁸ The two-photon induced polymerization of photoresist can be confined down to 150 nm and complex three-dimensional structures can be obtained through the direct laser writing, such as helical structures, 3D photonic crystals, pillars and wires.^{77,79,80} Two-photon lithography is a direct laser writing technique. A piezoelectric scanning stage is used to precisely move the photoresist in x, y and z directions relative to the laser focusing points where the photoresist are polymerized, according to programmed patterns.⁸¹ Typically, polymeric nanostructures are formed layer-by-layer starting from the interface of the resist and substrate. The resulting nanostructures are then metalized by using thermal evaporation.

1.3 PARAMETERS TUNING PLASMONIC PROPERTIES

Plasmonic nanoparticles with arbitrary size, shape and compositions are synthesized by using the above-mentioned fabrication methods, which enables the researchers studying their plasmonic properties at single-particle level and assembly state. In this section, we generalize the parameters for tuning plasmonic properties involving frequencies of LSPR modes, far-field absorption and scattering as well as EM near-field localization and enhancement. These properties can be tuned by engineering plasmonic nanoparticles' physical features at single-particle level and by manipulating plasmon coupling in the assembly of nanoparticles.

1.3.1 Physical Features of Plasmonic Nanoparticles

1.3.1.1 Size

The simplest way to engineer the LSPR frequencies and thus the optical properties of nanoparticles is to tune their sizes. For instance, the colors of colloidal Ag nanospheres can be engineered from transparent light yellow to yellow, dark-yellow and cloudy silver colors by changing the sizes from ~3.1 nm to ~13.4, ~46.4 and ~ 91.1 nm.⁸² More vivid color changes are observed by changing the sizes of Au nanospheres.⁸³ The extinction spectra (scattering + absorption) of these nanoparticles demonstrate that the sizes of nanoparticles determine the locations and numbers of the plasmon modes. The major plasmon resonance peaks red-shift with the increase of the sizes, arising from the larger charge separation and thus lower frequency of the electron collective oscillations for the larger particles.^{84,85} This trend can be widely applied to plasmonic nanostructures with nonspherical shapes, such as nanocubes,⁴⁶ octahedra,⁸⁶⁻⁸⁸ prisms^{89,90} and pillars.⁹¹ Moreover, for extinction of Ag nanospheres, a shoulder peak at 384 nm other than the dipolar mode at 440 nm appears when the sizes reach ~91.1 nm, indicating the emergence of additional plasmon modes for larger nanoparticles.⁸² Furthermore, the ratio of absorption to scattering is also determined

by the dimensions of nanoparticles.^{18,92} The absorption and scattering cross sections proportional to R^3 and R^6 (R represents the radius of the nanoparticle) if R is smaller than the light wavelength.¹⁸ As such, the absorption dominates scattering in the small nanoparticles ($R < 30$ nm) while the scattering dominates over absorption in the large nanoparticles.⁹² In general, increasing the nanoparticle sizes red-shifts the major plasmon mode positions, brings additional plasmon modes other than dipolar modes, and enhances the scattering efficiency.

1.3.1.2 Shape

Compared with nanosphere in which the electron confinements are the same in three dimensions, the anisotropic shape exhibits more plasmon modes and additional tunable parameters other than sizes. Experimental and theoretical investigations on LSPR of nanoparticles with different morphologies show that the geometry, corner sharpness as well as symmetry have large effect on the frequencies of LSPR.^{4,48,56,93-95}

Firstly, the number of plasmon resonance modes increases as the structural symmetry decreases. Xia *et al.* has compared the LSPR among Ag nanoparticles with the same sizes (40 nm), including Ag nanosphere, nanocube, tetrahedron and octahedron, using the results of discrete dipole approximation (DDA) calculations.⁹⁵ The calculated spectra for Ag nanocube demonstrate the emergence of more peaks when compared with Ag nanospheres. The additional peaks originate from the lower symmetry of the cubes than spheres which enables electrons polarizing in more than a single manner. This trend is also applicable for octahedra and tetrahedra. Moreover, the LSPR frequencies are also related to the corner sharpness of nanoparticles. For instance, the major plasmon modes for Ag nanocubes with sharp corners are red-shifted from 410 nm to 500 nm and the tetrahedra with the sharper corners has the more red-shifted plasmon resonances when compared with nanocubes.⁹⁵ This phenomenon arises from the accumulation of surface charges at the sharp corners. The charges aggregating at the corners increases the charge separation and thus reduces the

restoring force, manifesting as red shift of the plasmon resonances. Furthermore, the SPR frequencies of anisotropic nanoparticles are sensitive to slight changes in particle geometries and thus the optical properties of these nanoparticles are tunable across the entire visible, near-infrared (NIR) and infrared region. For example, the absorption of Au nanorods can be tuned to NIR via changing the aspect ratios, for enhancing the contrast in the photoacoustic imaging of bacteria.⁹⁶ The high sensitivity of the SPR to the geometry of nanoparticles also enables their applications for optical recording and photorealistic printing at the optical diffraction limit.^{33,97,98}

Apart from the frequencies and number of LSPR modes, the electromagnetic fields enhancements are also related to the shapes of nanostructures. EM fields are most intensely localized and enhanced at the tiny features with small curvatures, such as sharp tips and edges, on the individual nanoparticles.^{2,61,99,100} These regions are commonly known as hot spots. For example, the EM field is reported to be enhanced by factor of 10^2 at the gap regions of nanosphere dimers due to the plasmon coupling effect.¹⁰¹ Moreover, the field intensity can be enhanced to ~4500 times the applied fields at the tips of Ag nanorods arising from the “lightening rod” effect.¹⁰¹ As such, morphologies with sharp tips, such as nanoflowers, nanostars, spiky nanoparticles, and nanostructures with intra-particle gaps are reported to enhance the local EM fields by up to $\sim 10^4$ of magnitude.^{45,61,102-105} These nanostructures with dense hot spots are exploited for applications in diverse fields, including plasmon-enhanced fluorescence, light harvesting, surface-enhanced Raman scattering (SERS) sensing and detection.³⁴⁻⁴¹ In addition, plasmon mapping on individual nanocubes and octahedra shows that the edges are also localized with enhanced EM fields but the intensities are much lower relative to the tips.^{61,106} The edge regions of nanoparticles are promising for designing large-area hot spots because of the large surface area of edges relative to tips and high curvature.

1.3.1.3 Composition

According to Mie theory which is used to calculate the extinction cross-section C_{ext} of a metal nanosphere (equation 2), the strength of the surface plasmons that a metal nanoparticle can support depends on the dielectric constant ϵ of the metal consisting of a real part ϵ_r and an imaginary part ϵ_i , relative dielectric constant of the medium surrounding the nanosphere ϵ_m , radius R and the excitation wavelength λ .¹⁰⁷ The equation shows that the extinction reaches the maximum when the denominator of the bracket in equation 2 approaches zero, indicating that the material with ϵ_r close to $-2\epsilon_m$ and ϵ_i approximating zero can support strong surface resonance. As such, metals like Ag, Au, Cu and Al satisfy these conditions at certain wavelength regions.

$$C_{ext} = \frac{24\pi^2 R^3 \epsilon_m^{3/2}}{\lambda} \left[\frac{\epsilon_i}{(\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2} \right] \quad (2)$$

Moreover, researchers use the quality factor (Q) to compare the strength of surface plasmons for different materials at certain regions and the strength is proportional to Q.¹⁰⁸ It is reported that Q value should be larger than ~10 for high-performance plasmonic applications.¹⁸ Figure 1.13 presents the quality factors of several metals over the UV-Vis-NIR regions, demonstrating that Ag supports strongest surface plasmon strength across the Vis-NIR region.^{18,108} For Au and Cu, their interband transitions at 500 and 600 nm restrict the LSPR excitation wavelengths to the regions above 500 and 600 nm, respectively. As a result, Ag nanoparticles are always engineered for plasmonic applications, especially when the excitation wavelength is ~500 nm. However, silver oxide and silver sulfide are readily formed on the surfaces of Ag nanostructures, degrading some plasmonic properties. Ag is also considered toxic. In contrast, Au is stable and bio-inert, making the Au nanostructures more suitable for in vivo applications than Ag.⁸³ Some researchers work on fabricating Ag@Au core-shell nanoparticles to solve the instability and toxicity issues of Ag.^{109,110} Al as another plasmonic material is normally applied in plasmon supported photonics, SERS

and other plasmon related spectroscopy in the UV range.¹¹¹⁻¹¹³ Nowadays, studies show that the plasmon resonances of Al nanostructures can be tuned to the visible and NIR regions through increasing the sizes, aspect ratios and coupling arrays or holes.^{15,114,115} Due to the formation of alumina oxide on the surfaces, the resonances can be further tuned to even longer wavelengths.¹¹⁶ Combined with natural abundance and low cost, these properties make Al nanostructures promising material for plasmonic applications in the entire optical region which is wider than the applicable range of Ag. The LSPR of Al nanoparticles are more sensitive to the physical features, such as sizes and shapes, as compared with Ag and Au, thus it is a challenge to give reproducible signals when using the Al nanoparticles.

Figure 1.13. Quality factor (Q) of the LSPR for different metal/air interfaces. Reprinted with permission from ref [18]. Copyright © 2011 American Chemical Society.

In addition to using mono-metallic nanoparticles with different materials to tune the LSPR, higher tunability and novel optical properties can be achieved in bi-metallic and multi-metallic nanoparticles. For example, the Ag-Au nanocages formed by galvanic replacement reaction exhibit LSPR which are tunable from visible to NIR region by changing the Au/Ag ratios while the LSPR of Ag nanocubes can only be tuned in the visible range via manipulating particle sizes.¹¹⁷ Moreover, the LSPR properties of several types of bi-metallic core-shell structures are investigated.^{109,110,118} Their LSPR properties are

different from a mixture of mono-metallic nanoparticle. It is reported that the SERS of Ag-Au core-shell nanoparticles are greatly enhanced compared with Ag or Au nanospheres.¹⁰⁹

1.3.1.4 Solid and Hollow

Another method to manipulate the LSPR is to hollow the metal nanostructures, normally achieved by using a solid nanostructure as sacrificial template or layering plasmonic material on dielectric cores.^{104,119,120} The major plasmon resonances can be significantly red-shifted while retaining small sizes. For example, the LSPR of Ag nanoshells with the sizes below 100 nm can be tuned to the NIR region.¹²¹ In contrast, solid Ag nanoparticles supporting LSPR in the NIR region are normally bigger than 200 nm. The LSPR red-shift arises from the plasmon coupling between the inner and outer surfaces of the metal layer.^{117,122-124} This coupling in turn enhances the EM fields localized at the hollow structures and amplifies the absorption and scattering cross sections of the particles. Nanoshells with large absorption and scattering cross-section in the NIR region are attractive for photo-thermal and bio-imaging applications.¹¹⁷ Typically, the extent of LSPR shift is strongly related to the thickness of the metal shell. The LSPR red-shifts with the decrease of the shell thickness, due to the stronger coupling resulting from greater charge separation in the thinner shells.^{117,123,124}

Moreover, hollow structures with morphologies other than spherical shapes are fabricated for investigating the optical properties. A series of Au nanocages are synthesized by using small Ag nanocubes (~40 nm) as sacrificial templates.¹¹⁷ The LSPR positions of the Au nanocages are tunable across the visible and to NIR region, by increasing the Au/Ag ratio and decreasing the wall thicknesses. This high tunability and large extinction cross section makes Au nanocages promising for colorimetric sensing and biomedical applications.¹²⁵ Au nanocages with an inner edge length of 30 nm and a wall thickness of 5 nm have been used as contrast enhancement agents for photoacoustic tomography, due to

the absorption cross-section estimated as $\sim 20 \times 10^{-15} \text{ m}^2$ at 710 nm, which is much greater than traditional organic dyes.¹²⁵

Furthermore, extreme hollowing of the solid cores generates nanoframes in which only the skeletal structures remained. Nanoframes introduce the ratio of edge lengths and ridge thickness as additional parameter for tuning LSPR. Surface resonances of nanoframes with thinner wall or longer edge length are red-shifted to longer wavelengths.¹²⁶ Compared with nanocages, plasmon coupling is rather strong in the nanoframes, leading to strongly localized EM fields and thus greatly enhanced SERS capabilities.¹²⁶⁻¹²⁸ The LSPR of nanoframe in the NIR region is also beneficial for SERS-based detection with low fluorescence background. Recently, it is reported that the LSPR and SERS capabilities of nanoframes can be manipulated by tuning the crystallite sizes and porosity at the ridge places, further enriching the family of hollow structures and their applications.¹⁰⁴

1.3.2 Assembly of Plasmonic Nanoparticles

To manipulate light at the nanoscale through surface plasmon resonance, apart from tuning the shape and size of individual nanoparticle, assembly of these components based on plasmon coupling is prevalently investigated.

1.3.2.1 Plasmon Coupling

Currently, many of the applications are based on the assemblies of plasmonic nanoparticles, such as wave-guiding, lasing, detection, sensing and *etc.*^{6-9,15,32,42-44,129-134} These applications are strongly dependent on interparticle interactions in the near-field. The plasmon resonance modes of one particle are capable of coupling with those on particles in vicinity, giving rise to new plasmon modes and enhancing electromagnetic near fields by 2-3 orders of magnitude.⁹ Nanosphere dimers are the simplest plasmon coupling systems because individual nanospheres only exhibit dipolar plasmon modes. The dipolar plasmon mode of a single nanosphere splits into two modes via coupling to another nanosphere,

manifesting as a red-shifted and a blue-shifted plasmon band in the LSPR spectrum.¹³⁵ This interaction is understood in terms of plasmon hybridization, in which the dipolar modes of two particle surfaces hybridize to give a lower-energy bonding mode and a higher-energy anti-bonding mode.¹³⁵⁻¹³⁸ For nanosphere dimers as coupling systems, the bonding modes which are symmetrically aligned are so-called “bright” modes because they have a net dipole moment and can be excited by light. “Bright” plasmon modes are correlated with strongly radiative optical properties, such as plasmon colors.^{33,139,140} On the contrary, the anti-bonding modes within nanosphere dimers are asymmetrically aligned resulting in zero dipole moment. These modes are referred to as “dark” modes because they interact weakly with the incident light.¹⁴¹ Because of low radiative losses, the dark modes are fundamentally studied for applications like wave-guiding, lasing and sensing.^{42-44,142}

On the other hand, the nature of plasmon coupling is more complicated within more complex plasmonic nanostructures than nanosphere dimers. In some coupled systems with specific symmetry, such as plasmonic heptamer structures and dolmen structures, plasmon hybridization and Fano resonance co-exist.^{11,15,143,144} In a heptamer structure, hybridization of plasmon modes of the central particle and the outer particles results in a bright bonding mode and a dark anti-bonding mode. Then, Fano resonance arises from the interference between the bonding and anti-bonding modes.¹¹ In a dolmen structure, near-field coupling between the plasmon modes in the monomer and dimer gives rise to a bonding mode and an anti-bonding mode. The interference between these two hybridized modes induce to Fano resonance.¹¹ Both plasmon hybridization and Fano resonance can induce a mode splitting into two peaks but the contribution of each coupling phenomenon to the near-field enhancement is dependent on the plasmonic structures.¹⁴⁴ For example, Fano resonance is reported to dominate the near-field enhancement on a plasmonic heptamer while the bonding and anti-bonding modes within a dolmen structure arising from plasmon hybridization dominate the near-field enhancement.¹⁴⁴ In general, it is difficult to

distinguish the contribution of plasmon hybridization and Fano resonance in the far-field extinction or scattering spectra but the contribution of these two components to the near-field enhancement can be differentiated by analyzing the near-field spectral properties. Researchers generalize two differences between these two phenomena arising from plasmon coupling.¹⁴⁴ Plasmon hybridization is strong in coupling strength compared with Fano resonance. Moreover, the widths of two resonance modes (splitting modes) are drastically different when the plasmon coupling is dominated by Fano resonance. In contrast, the plasmon coupling is described by hybridization when the widths of two modes are similar.

Moreover, the strength of plasmonic coupling between pairs of nanoparticles damps with the increases in gap sizes. The gap-dependent plasmonic coupling and EM-field enhancements scale with the particle sizes as such the same EM enhancements can be obtained at larger gaps for larger nanoparticles.^{9,145} Plasmonic coupling also strongly depends on polarization of incident light and orientation of nanoparticles.^{9,134,146,147} Dimer nanoparticles have been prevalently used for sensing, analyte detection, and SERS enhancement for many years, because of the high localization of fields at the inter-particle gap regions.^{6-9,129-134} Recent studies of the dimer coupling system are focused on the dependence of SERS enhancement factors or sensitivity factors on its orientation and gap sizes.^{130-134,147-153} In addition, other optical phenomena, such as Fano resonance and extraordinary optical transmission, are supported by clusters consisting of larger number of nanoparticles.^{10-12,154-159} Their optical properties are strongly related to the orientation and arrangements of the particles.

1.3.2.2 Gap and Orientation

Plasmonic coupling results in intense EM field enhancement in the spaces between neighboring nanoparticles.^{9,160} Optical properties originating from this field enhancement can be further manipulated by controlling the orientation and spacing of nanoparticles in a finite cluster. For instance, the SERS enhancement factors of octahedral dimers can be

maximized at their face-to-face configurations relative to tip-to-tip and edge-to-edge configurations.¹³⁴ Moreover, the uniformity and diameter of the gaps in the polyhedral assemblies greatly influence the SERS enhancements and homogeneity. Inter-particle gap sizes in these polyhedral nanoparticle clusters can be controlled by the thickness of surfactant.¹³⁴ Furthermore, the orientation of nanoparticle pairs determines the inter-particle distances where the plasmonic coupling exists.¹⁴⁷ Besides, the morphology of the narrow gap modifies the plasmon responses.¹⁵⁰

In contrast to dimers, clusters with other special configurations exhibit more complex and interesting optical properties. For example, Fano resonance behavior which shows a distinct dip in the spectrum, is supported by a plasmonic heptamer which is assembled from Au nanoshells.¹⁵⁷ When the central nanoparticle is close to the surrounding hexamer at gaps smaller than 60 nm, the hybridization of dipolar plasmonic mode of central nanoparticle and that of the hexamer ring generates a broad bright mode and a narrow dark mode. The destructive interference between the two modes gives rise to the Fano resonance dip in the spectrum. The distinct line shape combined with the high sensitivity to the changes in geometry and local environment enable the nanostructure supporting Fano resonance to be potentially used as chemical or biological sensor.^{10,11}

When more building blocks are assembled in large scale, different superlattices are achieved. Compared with close-packed lattices, open lattices with less dense arrangements have been demonstrated more interesting properties in photonics,^{161,162} catalysis and response to mechanical stress.¹⁶³ Besides, open lattices of metallic nanoparticles always construct arrays of holes in nanoscale with varied sizes and shapes, which are responsible of extraordinary optical transmission (EOT).^{154,158,159} For example, enhanced light transmission is observed in the arrays of tiny holes on an opaque metal film when hole sizes are smaller than the light wavelength.¹⁵⁸ Periodic metallic arrays of holes can trap light on their surfaces, lengthening the interaction time of the light with the

molecules adsorbed and thus enabling applications in signal enhancement in Raman or fluorescence spectroscopy.¹⁵⁴⁻¹⁵⁶ Moreover, the light transmission through holes arrays is sensitive to the dielectric media contacting with the surface, making it a promising material for molecule detection.¹² The wavelength at which the most efficient transmission occurs is controlled by the shape and size of the holes arrays, as well as the depth.¹⁵⁴

The strong dependence of LSPR and corresponding optical properties on the arrangement of building blocks makes it interesting to control the assembly of plasmonic nanoparticles. It is a challenge to assemble nanoparticles in an efficient and reproducible way. Nowadays, many arrays in nanoscale are obtained by top-down method, such as nanolithography,^{154,156,164} which is advantageous in its simplicity in generating patterns of nanoscale features. However, dimensions of the features and their gaps are larger than that could be achieved by colloidal method and the surface roughness cannot be easily controlled.¹³⁴ Shaped nanoparticles synthesized by colloidal methods are monodisperse in sizes and their surfaces are atomically smooth. In this case, they can be used as building blocks to assemble reproducible crystalline superlattices with nanoscale gaps and holes. In colloidal assembly of nanoparticles, different interparticle interactions are utilized, including chemical bonding, electrostatic and molecular interaction. In general, there are mainly two factors regarding to control the direction, range and strength of the interaction between nanoparticles.¹⁶⁵ The first factor is the property of the particle, including its composition and chemical functionality on the surface.¹⁶⁶ The second factor is the environmental parameters, such as ionic strength,¹⁶⁷ temperature¹⁶⁸ and external force.¹⁶⁹ For example, capillary force assembly is the simplest way to obtain dimers and other arrays of building blocks. Nanoparticle suspension is drop-cast on a substrate and self-assembly of these particles is driven by the capillary force generated in the drying process.¹⁸

1.4 CHARACTERIZATION OF PLASMON RESONANCES

In order to understand and engineer the surface plasmons at the nanoscale for intended applications, it is essential to be able to characterize the position, intensity and distribution of the LSPR modes. As such, researchers have developed numerous experimental methods to investigate both far-field and near-field optical properties of plasmonic nanoparticles. Traditional techniques which are based on light-induced LSPR, such as UV-Vis-NIR spectrometry and dark-field microscopy, are easy to operate and always used to characterize the LSPR of novel morphologies and to monitor the shape changes in the synthetic progress.^{46,48} However, the resolution of these techniques are restricted by the light diffraction limit. For instance, we can hardly differentiate individual nanocube and nanocube dimers under these optical microscopes. In contrast, techniques such as cathodoluminescence (CL) and electron energy-loss spectroscopy (EELS) use fast electrons as excitation source, yielding truly nanometer spatial and spectral resolution and thus enabling the mapping of different LSPR modes and near-field distributions at nanometer scale.¹⁷⁰ The LSPR distribution in a single particle can be visualized by using these near-field mapping.

These experimental characterizations are always combined with the simulation results to investigate the nature of each plasmonic mode. Numerical methods including Mie theory, discrete dipole approximation (DDA), finite difference time domain (FDTD) and boundary element method (BEM) are used to solve the Maxwell's equations for the interaction of light or electrons with the matter over the nanoparticle volume.^{136,141,171-175} Apart from matching the simulation with the existing experimental spectra to study the origins of LSPR modes, simulation results can be also used to predict the plasmonic properties of nanostructures which have not been fabricated yet, motivating the synthetic efforts. In this section, we focus on introducing the experimental characterization methods which are used in our works, coupled with brief discussion of some related simulation methods.

1.4.1 Far-Field Optical Studies

UV-Vis-NIR spectrometry is one of the simplest and most prevalent methods to characterize LSPR, based on the fact that the metallic nanoparticles exhibit strong absorption and scattering at the LSPR frequencies resulting in extinction peaks in the spectra. Extinction (absorption + scattering) spectra are obtained in the UV-Vis-NIR measurements.¹ As discussed in the previous section 1.2, the positions and intensities of the peaks shown in the extinction spectra are strongly dependent on the nanostructures' physical features, such as materials, sizes, shapes, orientations and gap sizes. Moreover, the equipment is relatively fast to operate and low-cost, making the UV-Vis-NIR a conventional way to check the uniformity, sizes and morphologies of the particles in the solution during the synthesis process. For example, Yang *et al.* have demonstrated the extinction spectral evolution from Ag nanocubes to cuboctahedra and octahedra, thus extinction spectra can be used to monitor the synthesis process in order to obtain high yield of morphologies in any stages.⁴⁸ Xia *et al.* use the extinction spectra to evaluate the edge lengths of the Ag nanocubes using a calibration curve that plotting the dipole mode position against the edge length of cubes.¹⁷⁶ However, UV-Vis-NIR spectrometry can be only used to characterize LSPR for an ensemble of nanoparticles in the solution, resulting in an averaged extinction of nanoparticles with slight differences in sizes and morphologies which are unavoidable in the colloidal reactions.¹⁷⁷

To rule out the morphological variations and possible interparticle interactions among ensembles, optical properties are always investigated in the single-particle level. Dark-field optical microscopy is normally used to study the plasmonic properties of individual nanoparticles which are sparsely dispersed on the substrates and scattering spectra are obtained in the measurements.¹⁷⁷ This technique is based on the elastic scattering in plasmonic nanoparticles and such scattering strongly depends on the wavelength and is enhanced at the LSPR frequencies.¹ Typically, the sample is illuminated using a high

numerical aperture condenser with the central light path blocked. The light scattered by nanoparticles are collected by objective with small numerical aperture, resulting in particles appearing as bright spots on a dark background (Figure 1.14).¹⁷⁷ Nanoparticles with different shapes and sizes exhibit varied LSPR, manifesting different colors in the dark-field images.⁴⁵ Dark-field scattering images are prominently used to indicate the LSPR positions. For example, Ag nanocubes with edge lengths of ~ 80 nm strongly scatter the green light, in line with their major LSPR peak at 500-550 nm. Shape evolution of the Ag nanocubes to truncated cubes and octahedra shifts the scattering color to yellow and orange, respectively.⁴⁸ Moreover, scattering spectra of single particles enables the correlation of plasmonic properties with the physical features, such as sizes, shapes and composition (as shown in the section 1.2). Furthermore, this technique also allows for investigating the plasmonic coupling effect among different nanoparticle configurations, such as dimers, chains, Fano structures, 2D and 3D assemblies.^{160,178-180} However, dark-field microscopy is not suitable for monitoring the nanostructures whose extinction are dominated by absorption, such as nanoparticles with sizes less than 30 nm. To measure pure absorption at single-particle level, researchers conventionally use indirect detecting techniques including ground-state depletion microscopy and photothermal microscopy.^{181,182}

Figure 1.14. Scheme of dark-field microscope (left) and dark-field image of colloidal nanoparticles (right). Reproduced from Ref [171] with permission from the PCCP Owner Societies. Copyright © 2013, Royal Society of Chemistry.

1.4.2 Near-Field Mapping of Plasmons

Characterization on LSP behavior as function of the locations on structure is the foundation of precisely manipulating light for its potential application in SERS detection, imaging, energy conversion and laser.^{27-31,42-44,129} Moreover, the local electromagnetic field enhancement normally is restricted to less than 50 nm ranges.¹⁷⁰ As such, it is critical to spatially characterize LSPR and their distributions with nanometer scale resolution. However, there are technical challenges to obtain nanoscale spatial and spectral resolution. Far-field optical microscopy like dark-field microscopy provides advantageous spectral resolution using simple instrument.^{45,183,184} However, due to the diffraction limit, optical microscopes can hardly be used to spatially map plasmon modes with resolution below 200 nm. Near-field scanning optical microscopy (NSOM)¹⁸⁵ is capable of achieving resonances mapping with ~20-nm resolution but is restricted by the signal interference of sharp tips used in this technique.¹⁸⁶ On the other hand, fast electron based microscopy including cathodoluminescence (CL)^{5,186-188} and electron energy loss spectroscopy (EELS)¹⁸⁹ circumvent these limitations and achieve the nanometer-scale spatial mapping of surface plasmons. Furthermore, near-field excitation by electron beam enables easily excitation of dark modes (sub-radiant modes) on nanoparticle surfaces. Higher-order plasmon modes as well as dark modes can also be excited by far-field excitation when the particle size becomes large due to phase retardation effect or through plasmon coupling among adjacent nanoparticles, but the excitation probability of higher-order modes is larger by near-field excitation.¹⁷⁰ As such, near-field techniques such as electron energy loss spectroscopy (EELS) are always used to investigate dark modes.

1.4.2.1 Cathodoluminescence (CL)

Cathodoluminescence (CL) is typically the electron-induced photon emission. The scheme shown in Figure 1.15 illustrates the excitation process of CL and mechanism behind EELS.¹⁷⁰ In general, fast electrons generate localized surface plasmons for metallic

nanoparticles. The LSPs decay in the form of coupling to radiations, giving rise to the generation of cathodoluminescence (CL). Electronic excitations of electron-hole pairs can also induce CL emissions, resulting from the recombination of electrons and holes. Here, we focus on the LSP-mediated CL emission for plasmonic nanoparticles. CL spectra directly indicate the LSPR frequencies for the nanoparticle, because CL depends on the excitation of LSPs and the spectra are determined by the energy of the scattered photon.

Figure 1.15. Scheme illustrating some excitation process including CL and EELS triggered on a solid by a swift passing electron. Reproduced with permission from Ref [164]. Copyright © 2010, American Physical Society.

CL is typically combined with scanning electron microscope (SEM) or scanning transmission electron microscope (STEM), in which the focused electron beam can be used in a scanning mode.^{5,186-188} By raster scanning the electron beam over the nanoparticle surfaces, a 2D intensity map of photons within a given energy window can be achieved, exhibiting the distribution of plasmon modes and enhanced EM fields localized on the particle. In our work, we use hyperspectral CL imaging in which CL spectra can be retrieved at each spatial positions in the scan.⁸⁸

CL with high-quality beam provides spatial resolution at sub-10 nm.^{170,188} For instance, by combining a transmission electron microscopy (TEM) with a high-energy resolution of a photon detection system, CL spectra and spatial maps of plasmonic modes supported by Ag nanospheres is obtained for the first time.⁵ With the increase of the sizes of nanospheres from 90 to 140 and 285 nm, high-energy modes like quadrupolar and hexapolar modes

sequentially appear on the CL spectra. The experimental results agree with the calculated simulation using the Mie theory. This work also demonstrates that the CL emissions are dependent on electron beam positions relative to the nanosphere surfaces. Moreover, anisotropic nanostructures like Ag triangular nanoparticles are characterized by cathodoluminescence spectroscopy and the results meet well with finite-difference time-domain numerical simulations.¹⁸⁸ It is reported in this work that the electron beam excites both in-plane and out-of-plane modes while light can only excite in-plane modes. In addition, by measuring CL, researchers have achieved spatial investigations of plasmonic modes on decahedron gold nanoparticle, Ag nanocube, Au nanoprism, Ag nanorod, ring-shaped nanocavity and complex nanoparticle structures such as dimers, bow-tie structures and nanodisks supporting Fano resonances.^{175,186-188,190-193}

1.4.2.2 Electron Energy Loss Spectroscopy (EELS)

When fast electrons impinge on plasmonic nanoparticles, the induced localized EM field excite and couple to the plasmon modes on the surfaces of nanoparticles, causing the loss in electron energies (Figure 1.15). EELS measures the loss in the scattered electron energy.¹⁹⁴ The electron-beam energies are normally higher than 10 keV, allowing the excitation of plasmon modes with different energies. Normally, EELS is combined with scanning transmission electron microscope (STEM) in which the high-energy electron beam is focused to a small excitation spot and scanned over the surfaces of plasmonic nanoparticles. Spatial plasmonic mapping is obtained by relating the spatial origins of the scattered electrons to the energy losses, generating intensity maps of scattered electrons with certain energy windows. Moreover, EELS spectrum can be retrieved from each point on the nanoparticle surfaces with the sub-10 nm spatial resolution.¹⁹⁴

To compare with CL, EELS is restricted to the use of electron transparent sample whose thickness is normally no more than 150 nm while CL is a complement to this drawback.¹⁸⁶ In addition, EELS can be used to characterize both radiative (bright) and non-radiative

modes (dark modes) while CL only provides information on radiative modes.^{141,174,194} Dark modes can be excited by electrons but are weakly radiative with the optical radiations because they have no net dipole moment.¹⁴¹ However, since the dark modes suppress radiative losses, they are promising for uses in plasmonic waveguides and SERS.^{42,43,195} As such, it is equivalently important to investigate bright and dark plasmon modes. Plasmonic properties of Au nanosphere chains from 1 to 5 particles are investigated by spatial mapping both bright and dark modes using EELS and BEM modeling.¹⁴¹ These results demonstrate the presence of super-radiant modes, transverse modes as well as subradiant modes in the chains. It is observed N of modes and a transverse mode in EELS mapping of a chain containing N particles. As the chain increases, all the N modes are delocalized along the chain and form a broadband resonance, which links the localized and travelling plasmons. This work focuses on studying the evolution of subradiant modes with increasing the chains lengths, because this mode giving low loss is important for waveguiding applications. In addition, EELS is used to study the plasmonic properties of anisotropic nanoparticles such as nanocube, nanorods and nanoprism.^{106,174,175} Currently, combined CL and EELS experiments can be conducted on the same nanostructures to compare their differences. EELS and CL are simultaneously measured on a same particle by using a homemade system which integrates CL and EELS detection with a scanning transmission electron microscope (Figure 1.16).¹⁷⁴ CL and EELS experiments performed on the same particle for each measurement can rule out spectral changes arising from morphological variations, such as sizes and edge rounding.^{94,174} By measuring EELS and CL on the same Au nanoprism, radiative and non-radiative modes are directly sorted out. Moreover, the far-field extinction and scattering are linked to the EELS and CL measurements, respectively.¹⁷⁴

Figure 1.16. Combining EELS and CL measurements. (a) Scheme showing a scanning transmission electron microscope integrated with EELS and CL detection systems. (b) Combined HAADF imaging (top), EELS (middle), and CL (bottom) spatially resolved data sets. Reprinted with permission from Ref [168]. Copyright © 2015, American Chemical Society.

1.5 APPLICATIONS OF PLASMONIC NANOPARTICLES

With the ability to tailor the light-matter interaction at nanoscale, plasmonic nanoparticles have benefited many fields including anti-counterfeiting, data storage, sensing, detection, photodetector, energy harvesting, bio-imaging and nonlinear signal conversions *etc.*^{6-12,23,24,27-31,80,196} Current applications of plasmonic nanoparticles based on localized surface plasmon resonance can be classified into three categories. In the first category, applications are based on tuning LSPR positions in the visible range, such as colorimetric sensing and structural colors. The second category of applications are based on manipulating the optical properties of nearby molecules via localizing and converting light into intense EM fields, such as SERS and SEF. In the third category, the applications are based on converting light into other energies, such as photovoltaic cells which harvest light for electrical energy generation and photo-thermal therapy which converts absorbed NIR-

light to heat. In this thesis, we focus on discussing the capabilities of plasmonic nanoparticles in surface-enhanced optical properties of nearby molecules, especially for surface-enhanced Raman scattering (SERS). The related theories, some existing platforms and practical applications based on them will be elaborated. Moreover, we extend to discuss some current researches using plasmonic nanostructures for anti-counterfeiting and data storage applications.

1.5.1 Surface-Enhanced Raman Scattering

1.5.1.1 Theory

Raman scattering is an inelastic scattering relative to Rayleigh scattering (elastic scattering). Raman spectroscopy relying on Raman scattering is used to study the vibrational, rotational and other low-frequency modes, providing an insight into chemical structures of molecules.¹⁰⁸ However, the uses of Raman spectroscopy is restrained by the weak signals of Raman scattering for molecules with small Raman cross-section and the Raman spectra of dye molecules with large Raman cross-section can be overwhelmed by fluorescence. Since the first observation of enhanced Raman signals on the roughened Ag electrode surfaces in 1973, surface-enhanced Raman scattering on plasmonic nanostructures has been investigated extensively.¹⁹⁷ Compared with normal Raman scattering, plasmonic nanostructures supporting SPR are prerequisite for SERS system. In-depth understanding of SERS promotes the applications of this vibrational spectroscopy in many fields, including surface studies, trace sensing and detection, molecular information encoding, etc.^{19-26,80}

In general, there are two parts of contributions to enhance Raman signals of molecules nearby the plasmonic nanoparticles, including electromagnetic enhancement (EM) and chemical enhancement (CE).^{16,198} Figure 1.17 presents the EM enhancement in SERS.¹⁶ Typically, when illuminated with light which can excite the LSPR, the nanoparticles serve

as optical antennas to concentrate and convert light into enhanced EM fields which are localized at the nanoparticle surfaces. The enhanced EM fields ($E_{\text{loc}}(\omega_{\text{inc}})$) excite the inelastic scattering of nearby molecules and in turn the nanostructures absorb the energy emitted by these molecules (Stokes Raman scattering, $E(\omega_{\text{inc}} - \omega_{\text{vib}})$) which is radiated by the nanostructures into the far-field. The SERS intensity is related to both of the two fields which are “incoming” ($E_{\text{loc}}(\omega_{\text{inc}})$) and “outgoing” ($E(\omega_{\text{inc}} - \omega_{\text{vib}})$) field shown in Figure 1.17.¹⁶ In all, $I_{\text{SERS}} = |E_{\text{loc}}(\omega_{\text{inc}})|^2 |E(\omega_{\text{inc}} - \omega_{\text{vib}})|^2$. If ω_{inc} is far above ω_{vib} , SERS intensity is approximately equal to $|E_{\text{loc}}|^4$. As such, slight enhancement in EM fields, for example to a 10-fold EM enhancement would induce 10^4 -fold SERS enhancement. Regarding to the induced dipole moment of the SERS probe molecules, $\mu = \alpha_{\text{molecule}} E_{\text{loc}}(\omega_{\text{inc}})$, where α_{molecule} and $E_{\text{loc}}(\omega_{\text{inc}})$ represent polarizability of the molecule and local EM fields.¹⁶ Signal intensities are increased by increasing the dipole moment. EM enhancement contribution enhances the Raman scattering by increasing the intensities of local EM fields. In contrast, chemical enhancement contributes by increasing the electronic polarizability by means of charge transfer (CT) between the metal and the molecule.¹⁹⁹ For example, additional signal enhancement takes place for adsorbed dye molecules with electronic adsorption bands near the plasmon bands of the nanoparticles, known as surface-enhanced resonance Raman scattering (SERRS).²⁰⁰

Figure 1.17. Scheme illustrating electromagnetic enhancement in SERS. A) Excitation of a dipolar localized surface plasmon resonance (LSPR) on a Au nanosphere. B) “Incoming” field (ω_{inc} , green) and the “outgoing” field ($\omega_{inc} - \omega_{vib}$, orange) are both enhanced by the LSPR supported by Au nanosphere. Reproduced with permission from Ref [16]. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The SERS enhancement factor (EF) relative to the normal Raman scattering can be calculated by using the equation shown below.¹⁰⁸ I_{SERS} and I_{Normal} represent the SERS intensity and the normal Raman intensity measured in solution, respectively. N_{SERS} and N_{Normal} are the number of molecules on the surface (SERS) and in solution (normal Raman), respectively. It is fair to compare the performances among different nanostructures as SERS substrates by calculating the corresponding SERS EF since the intensities of SERS and normal Raman scattering are normalized to the number of molecules. Moreover, it is theoretically and experimentally validated that the SERS intensity scales with r^{-12} (r represents the distance to the surface), indicating that SERS is highly surface-selective.¹⁸

$$EF = \frac{I_{SERS}}{I_{Normal}} \times \frac{N_{Normal}}{N_{SERS}} \quad (3)$$

Generally, EM enhancement is a more dominant contribution than CE for SERS enhancement, with standard SERS EFs in the range of 10^3 - 10^{10} while CE enhancements are normally 10 - 10^3 .¹⁸ In this thesis, we focus on the EM contributions to the SERS

enhancement. According to the EM enhancement theory, the SERS enhancement is strong at the so-called hot spot regions (sharp tips, edges and nanoscale gaps) where the EM fields are intensely enhanced, motivating the synthetic routes to obtain novel nanoparticles with high-density of hot spots at the single-particle level and assembly methods to increase the volume of hot spots both in two- and three- dimensions.

1.5.1.2 Single-Particle SERS Platform

High-performance SERS substrates can be obtained by fabricating substrates with high-density hot spots. Prior to large-area hot spots fabrication, many researchers investigate the SERS enhancements for novel nanostructures on a single-particle level. Single-particle SERS studies are essential for investigating the relationship between SERS enhancement factor and the physical features of the nanoparticles, ruling out the contribution from inter-particle coupling effect.¹⁷⁷

Many researchers make synthetic efforts to obtain anisotropic nanoparticles with sharp tips and edges for the single-particle SERS applications. For example, Ag nanocubes and octahedra with well-defined tips and edges are synthesized by using polyol reduction method.^{46,48} The enhanced EM fields of these two morphologies are reported to be localized at the tip and edge areas. The single-particle SERS EF of Ag nanocube and octahedra are $\sim 3.7 \times 10^5$ and $\sim 4.8 \times 10^5$, enhanced by ~ 6.5 - and ~ 8.4 -fold compared with spherical nanoparticles, respectively.²⁰¹ Moreover, Au nanostars are fabricated and the reported SERS EF is $\sim 10^{10}$ for Au nanostars sitting on Au plate, arising from the strongly enhanced EM fields at the tips.¹⁰³ Other plasmonic nanoparticles with abundant tips have been synthesized, including nanoflower, spiky nanoparticles and mesoparticles.²⁰²⁻²⁰⁴ Their SERS EF is $\sim 10^8$. Furthermore, nanometer scale gaps can be achieved on single particles to greatly enhance SERS signals. For example, anisotropic etching on Ag octahedra generates etched particles with intraparticle gaps, outperforming the octahedra by 5-50 fold for SERS enhancement.⁴⁵ Intense SERS EF ($\sim 10^8$) has also been detected on DNA-anchored

nanobridged nanogap particles in which 1-nm interior gaps are observed.¹⁰⁵ In addition, hot spots densities can be increased by creating nanometer scale roughness on the single-crystalline nanoparticles. For example, mildly etching the Ag nanowires increases the hot spots densities from the end-tips of nanowires to the entire nanowire surfaces.²⁰⁵

1.5.1.3 Large-scale SERS Platform

To further increase the hot spots volume via inter-particle plasmonic coupling and fabricate large-area SERS substrates for practical uses, methods to fabricate two- and multi-dimensional SERS platforms are developed. Light irradiation, nanosphere lithography and self-assembly are three typically used methods for fabricating large-scale SERS platforms.^{1,206-210} In the light irradiation method, the number of the hotspots is increased in the form of knobs and corners between the branches on the branched nanowires upon exposure to light.²⁰⁶ This is a simple method to produce high density hotspots in large scale. However, the hotspots are rather randomly distributed and are dependent on the arrangements of the nanowires. This lacks reproducibility in terms of hotspot location and density, thus impeding the application of these platforms for SERS based sensing. Ordered SERS substrates fabricated via nanosphere lithography (NSL) overcome this randomness but the fabrication process is multistep and the Q-factor is lower due to the polycrystallinity of the metal used.¹ As such, self-assembly of chemically synthesized nanoparticles is prevalent to obtain large-scale SERS substrate with high utility and reproducibility.

Self-assembling of Ag nanoplates with high density on the substrate increases the number of clusters where nanometer gaps between adjacent nanoparticles potentially serve as hotspots.^{207,211} Aside from nanoplates, particles of other morphologies including Ag nanocubes, octahedra, nanorods have also been assembled to fabricate SERS substrates.^{209,210} Besides, the hot spots volume and reproducibility can be further increased by tuning the orientation of the nanoparticles in the assemblies. For example, self-assembly of Au nanorods into vertically aligned monolayer can push the edge-to-edge gap sizes to

sub-nanometer level, which induces strong and uniform electric field enhancement at $\sim 10^6$.²¹⁰ Recently, our group achieve three 2D superlattices of Ag octahedra including hexagonal close-packed, open hexagonal and square standing arrays by tuning wettability of the particle surfaces (Figure 1.18).²¹² The area of a single hot spot in the square standing array is ~ 130 -fold larger in the hexagonal array, resulting in a 7.5-fold higher SERS enhancement factors (Figure 1.19).²¹²

Figure 1.18. A series of superlattices of Ag octahedra obtained by adjusting the surface wettabilities of particle surfaces. (a) Increased contact angles of Ag films' surfaces when functionalized with different ligands. (b) Structural evolution of self-assembly from hexagonal close-packed superlattice to the open hexagonal structure and finally to the square superlattice, achieved by using Ag octahedra with increased hydrophobicity. The scale bars represent 200nm. (c) Schemes illustrating the evolution of superlattices. Reprinted with permission from Ref [206]. Copyright © 2015, Rights Managed by Nature Publishing Group.

Figure 1.19. Localized electromagnetic field distributions of three superlattices. All scale bars represent 100 nm. Reprinted with permission from Ref [206]. Copyright © 2015, Rights Managed by Nature Publishing Group.

1.5.1.4 Practical Applications in Detection

SERS can be used in molecular detection for its three advantages: (i) SERS spectra provides insight into the chemical structures of molecules and increase the accuracy of the detection; (ii) Greatly enhanced SERS signals lower the detection limit; (iii) band-width of a characteristic peak in SERS spectra is much narrower than conventional spectroscopic technique like fluorescence, decreasing the cross-talk and thus improving the detection accuracy and sensitivity. As a result, a number of SERS platforms are developed for detecting toxic chemicals and chemical sensing. Generally, ideal SERS substrates used for detection are uniform, chemically stable, easy to fabricate and providing strong and reproducible signals.

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is reported to operate SERS detection in a noncontact mode, in which Au nanospheres are covered by silica or aluminium oxide shell.²¹³ The detected molecules are isolated from the Au surfaces, preventing the signal disturbance arising from the interactions between these two. The particles are spread onto probe surfaces for detection, thus the SHINERS can be used on surfaces with any topography and in situ measurements. Moreover, assembly monolayer of Ag octahedra is used in detecting trace amount of arsenic substances in contaminated water and the arsenate detection at 1 ppb is achieved.²¹ Recently, our group achieve trace amount sensing of rhodamine 6G with detection limit down to 10^{-16} M using the superhydrophobic Ag nanocube array. This platform combines the analyte concentrating effect and plasmonic SERS enhancement.²⁴ Superhydrophobic-oleophobic Ag nanowire SERS platform is also fabricated for ultratrace detection (0.1 fmol for melamine and Sudan I) and quantification of toxins in both aqueous and organic solutions.²⁶

In addition to SERS platforms providing only one signal readout, there are multiplex SERS platforms in which more than one type of signals can be detected in the single platforms. For example, the work on star-shaped gold colloidal nanoparticles studies the

SERS, resonant SERS, and surface-enhanced fluorescence (SEF) performance of gold nanostars and their potential to use this SERS-fluorescence dual platform for ultradetection of unfunctionalized analytes in a sandwich configuration.²¹⁴ The addition of fluorescence broadens the windows for detection and thus increases the sensitivity. Moreover, our group fabricates the plasmonic liquid marble using 1H,1H,2H,2H-Perfluorodecanethiol (PFDT) functionalized Ag nanocubes, enabling the multiplex ultratrace detection of molecules in two phases (Figure 1.20).²³

Figure 1.20. Plasmonic liquid marbles used for multiplex interfacial SERS detection. A) Scheme and B) SERS spectra for the multiplex interfacial detection of methylene blue and coumarin. Reprinted with permission from Ref [23]. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.5.2 Plasmonic Anti-counterfeiting Security Label

Anti-counterfeiting entails encoding information that can only be accessed by the authorized parties. To reveal these information, advanced and complicated spectroscopic techniques are used so that they are not readily accessible by the general public. Conventionally, security labels used for anti-counterfeiting are made of unique physical

features, such as holograms, watermarks and security inks, which are difficult to forge.²¹⁵⁻
²¹⁷ These features are fabricated by using photonic structures, stimuli-responsive materials and up-conversion particles and can only be visualized under corresponding external stimuli, such as heat, magnetic fields, humidity or light.²¹⁸⁻²²² Some of the technologies are known to the public and are easy to copy by counterfeiters. To improve the security level, new techniques are developed so that only the authorized party can read the hidden information and new generations of security labels are always equipped with more than one layer of identifying readouts.¹⁹⁶ Plasmonic nanoparticles and nanostructures are promising materials for information encryption and anti-counterfeiting applications because of their small sizes and unique optical properties revealed by using advanced analytical instruments serving as identifications.

Multiplexing can be used in anti-counterfeiting labels to increase the identifying layers by incorporating multiple features in a single platform which can be individually read out. LSPR of plasmonic nanoparticles is sensitive to the physical features, such as sizes, shapes, gaps and orientations, endowing the multiplexing capabilities to the security labels made from plasmonic nanostructures (first category of plasmonic nanostructure application). For example, ~300 plasmonic colors are manifested in metallic nanodisk arrays where tunable colors are achieved by manipulating optical resonances supported by nanodisks with variable diameters and inter-particle gaps.^{33,139,140} Moreover, plasmonic enhanced surface properties can be used on anti-counterfeiting security labels (second category of plasmonic nanostructure application). Our group initiates introducing SERS into the anti-counterfeiting by exploiting the polarization-dependent SERS imaging on Ag nanowires (Figure 1.21).¹⁹⁶ Changing the polarization angle of excitation laser selectively reveals the SERS readouts, with high imaging specificity arising from the narrow SERS bandwidth. The multiplexing ability in the plasmonic nanowire platform is achieved by developing a sandwich structure in which more than one molecular information can be embedded into

the system. Cheng et al. introduced a dual-coded plasmonic nanosheets as anti-counterfeiting security labels in which plasmonic signatures and molecular fingerprints in the SERS spectra are used as two readouts. In addition, fluorescence and photoluminescence are other commonly used techniques for security labels. For anti-counterfeiting applications, the major challenge in the multiplexing strategy is to prevent signal interferences among multiple features and to obtain readouts with low error probabilities.

Figure 1.21. Plasmonic anti-counterfeiting security label relying on polarization-dependent SERS. (i) SEM, (ii) x - and (iii) y -polarized SERS images of (A) Ag nanowires with horizontal and vertical orientation, (B) superimpose of upright and inverted “A”s, (C) an “A” written using horizontal and vertical nanowires, and (D) overlaid letters of NTU and CBC. Scale bars represent 10 μm . Reprinted with permission from Ref [190]. Copyright © 2013, Royal Society of Chemistry.

1.5.3 Plasmonic Platforms for Data Storage

The vast amount of digital information generated daily ($\sim 2.5 \times 10^{18}$ bytes) in modern society drives the immediate urgency in developing high-density data storage platforms.²²³ Current information storage technologies are based on variations in electrical charges, magnetic or optical properties of the storage material, with the binary (two-state) system most widely used commercially.^{33,80,98,139,140,224-226} To increase the information density in a

data storage platform, researchers are focusing on diminishing the sizes of the encoding units or increasing the number of data storage digits. As such, small dimensions and multiplexing capabilities of plasmonic nanoparticles and nanostructures make them popular for optical data storage: their small dimensions enable higher density of readable information to be stored within a given area.

Currently, spatially encapsulating fluorescent dyes in polymer nanoparticles are popular strategies for multiplexing in the data-storage platforms, since the methods enable flexible patterning of layered images, but the multiplexing ability is restricted by the broad bandwidth of dye fluorescence and the number of the dyes which can be individually read out (~17 fluorescent colors by using recent advancing technique like multi-color flow cytometry).^{227,228} In other strategies, up-conversion nanoparticles with narrow emission bands are inkjet-printed on A4 paper or embedded in barcoded microparticles by stop-flow lithography.^{222,229,230} Up to 10000 distinguishable codes with the combination of color, intensity and lifetime of up-conversion nanoparticles can be individually read out under NIR-laser-excitation or time-resolved scanning by tuning the compositions,²³¹ but the inkjet-printing and stop-flow lithography technically restrict the printing resolution to micrometer-sizes. Furthermore, in the above-mentioned strategies, excited/unexcited state of each type of encoded nanoparticles serve as binary digits. Multiple-digit data storage platform can be obtained using adjustable SERS intensities on Ag nanowires as data storage elements. The quantifiable SERS intensities are manipulated by the orientation of Ag nanowires (Figure 1.22).⁸⁰

Figure 1.22. Multiple-digit data storage platform based on SERS. (A) SEM images; (B, C) x- and y-polarized 2D SERS images of Ag nanowires at orientation angles changing from 0° to 90°. (D, E) Respective x- and y-polarized SERS spectra collected from Ag nanowires with orientation angles in the range $\theta = 0$ –90°. (F, G) Plots of simulated and normalized experimental SERS intensity versus Ag nanowire orientation angle when polarized in the x- and y-directions, respectively. All scale bars are 5 μm . Reprinted with permission from Ref [76]. Copyright © 2014, American Chemical Society.

1.6 MOTIVATION AND OBJECTIVES

Plasmonic nanoparticles supporting LSPR confine lights into volumes at nanometer scale and convert them into enhanced EM fields or other energies. Light-matter interactions can be tailored for a variety of applications. In this chapter, we have introduced synthetic methods to engineer the morphologies, the parameters being used to tune the plasmonic properties and characterization methods to study the optical properties of plasmonic nanoparticles. Some of the plasmonic nanoparticle platforms for applications in SERS detection, anti-counterfeiting and data storage are also summarized in the end of this chapter.

In general, there are two challenges in this field: (i) to develop ways that efficiently tuning the surface plasmonic properties of plasmonic nanoparticles; (ii) to develop novel platforms using plasmonic nanoparticles for practical applications. In order to tailor surface

plasmonic properties, there are mainly two ways including engineering the physical features of nanoparticles in single-particle level and manipulating the plasmon coupling in the coupled system of nanoparticles.

On the basis of these two challenges, our objectives are to efficiently enhance the EM-field of plasmonic nanoparticles on single-particle level, to understand plasmonic behaviors of particle dimer which is the simplest coupled system and to develop plasmonic nanoparticle platforms for anti-counterfeiting and data storage applications. In our works, we focus on Ag nanoparticles because Ag supports high strength of surface plasmon resonances without damping induced by interband transition in the visible range. Cathodoluminescence hyper-spectral imaging is employed as characterization method to directly visualize EM fields' localization at nanometer scale. SERS is the potential application and we use it to develop novel plasmonic platforms for anti-counterfeiting and data storage.

. In the beginning, we demonstrate the high efficiency of enhancing EM fields and thus SERS enhancement in the single particle level via precisely depositing hot spots over hot spots (chapter 2). Plasmonic-active nanodots are exclusively decorated on the hot spots areas which are tips and edges of Ag nanoparticles. We validate the high efficiency of our “hot spots over hot spots” strategy for SERS enhancement by our cathodoluminescence hyperspectral imaging and DDA simulations. In addition, there is to date no in-depth understanding of the local electromagnetic field distribution and the types of plasmonic resonances that occur between the dimer particles with different orientations. As such, we utilize Ag nanocube pairs as model systems to study LSPRs that occur between nanoparticle dimers and to directly visualize how surface plasmon modes and fields localization evolve with alteration of dimer orientations (chapter 3). Highly-resolved (<10 nm spatial resolution) plasmon maps of Ag nanocubes are acquired by combining CL and EELS. Besides, novel anti-counterfeiting and data-storage platforms are developed using Ag nanopillar arrays

encoded with multiplex molecular information (chapter 4). Our platform encodes multiple identifying features in the form of SERS, fluorescence and their signal intensities on a single platform. These information can be decoded with no interferences using hyper-spectral imaging technique. In the end, we introduce a flexible and a 3D anti-counterfeiting platforms combining SERS and plasmonic nanostructures, aiming to develop security labels giving stable SERS readouts over applying external bending forces and to develop novel security labels based on Z-dependent SERS (chapter 5). In the future, we are going to study the nature of each plasmon modes of Ag nanocube and to understand the underlying physics behind plasmonic coupling by correlating the experimental results with numerical simulation using the boundary-element method (BEM). Based on the findings in chapter 1 and 2, we would investigate the plasmonic properties on dimers of selective gold deposited polyhedral nanoparticles with different orientations. The aim is to find the dimers with the most intense localized fields and efficiently enhance SERS. Assemblies of these selective gold deposited Ag nanoparticles giving strong SERS would be combined with the multiplex strategy introduced in chapter 4 and with flexible anti-counterfeiting platform in chapter 5. In current platforms in chapter 4 and chapter 5, plasmonic properties are given by the Ag film which is deposited on the polymeric nanostructures using thermal evaporation. To replace the Ag film with assemblies of selective gold deposited Ag nanoparticles, we believe the SERS signals would be more intense and easily to be initiated by using less strict excitation conditions, such as lower excitation power. This makes these strategies and platforms more applicable for real-world applications.

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2 Precision Synthesis: Designing Hot Spots over Hot Spots**

ABSTRACT. Plasmonic hot spots are typically confined to highly localized regions on metal nanoparticles. A major challenge is to be capable of efficiently increasing the hot spot volumes on single metal nanoparticles for stronger signals in plasmon-enhanced applications. In this work, we demonstrate an efficient enhancement of the plasmonic hot spot volumes on single metal nanoparticles by selective edge gold-deposited Ag octahedra (SEGSO) using a two-step seed-mediated protocol. Such “hot spots over hot spots” strategy is attributed to our precise synthesis of plasmonic-active nanodots onto the edge and tip hot spots regions of nanoparticles. We probe the localized surface plasmon responses of the selective gold-deposited octahedra using cathodoluminescence hyperspectral imaging at the single-particle level with a spatial resolution of ~10 nm. The hot spot areas on the Ag octahedra are clearly enlarged after Au deposition, with an increase in emission intensities observed across the visible wavelengths. Single-particle surface-enhanced Raman scattering (SERS) measurements demonstrate an order of magnitude increase in the SERS enhancement factor of the SEGSO as compared to pure Ag octahedra, and a 3-fold increase as compared with non-selective gold-deposited Ag octahedra (NSEGSO). The practicality of designing hot spots selectively over hot areas is also demonstrated using theoretical simulations, where the local electromagnetic field enhancement of our edge-deposited particles is 15 times and 1.3-fold times stronger than pure Ag octahedra and facet-deposited particles, respectively. The synthetic mechanisms underlying the growth of such designer nanoparticles are also discussed together with a demonstration of the versatility of this

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synthetic protocol to create a library of selective gold-deposited Ag-based nanoparticles, which can be subsequently etched to cages as well as frames.

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2.1 INTRODUCTION

Understanding and tailoring light-matter interactions at the nanoscale is one major focus of current research. Noble metal nanoparticles (Au, Ag) represent an important class of nanomaterials in this field due to their ability to confine light into sub-wavelength volumes to generate tremendous enhancement of local electromagnetic fields.¹ This phenomenon is brought about by localized surface plasmon resonances (LSPRs) of metal nanoparticles, arising from the collective oscillation of the conduction band electrons.² Many studies have shown that the local electromagnetic fields are most enhanced along nanometer gaps, sharp tips and well-defined edges of metal nanoparticles and these regions are commonly known as hot spots.²⁻⁵ Hot spots of metal nanoparticles have been exploited for applications in diverse fields, including plasmon-enhanced fluorescence, surface-enhanced Raman scattering (SERS) sensing, and light harvesting.⁶⁻¹³ Methods including light irradiation, nanosphere lithography and self-assembly are applied to fabricate large-area hot spots, but increasing both hotspot utility and SERS efficiencies on a single-particle level prior to large-area fabrication gives more potential for high-sensitive SERS substrate.^{1,14-18} Nanoparticles such as prisms, cubes, octahedra, and nanorods can generate huge enhancements in local electromagnetic fields. However, plasmonic hot spots with the most intense electromagnetic field enhancements are typically highly confined spatially to nanometer level, usually in the 0-10 nm range, and the field enhancement decreases exponentially with increasing distance from the metal surface.³ This in turn leads to non-trivial challenges in hot spot fabrication and readout signals that can be hard to reproduce, thus severely impeding the potential of the aforementioned applications.

The synthesis of designer nanoparticles in high yields via wet-chemical ‘precision synthesis’ approaches has arisen as a possible solution to increase the hot spot density as well as hot spot volumes on metallic nanoparticles. Akin to lithography on the nanoscale,

precision synthesis of such designer nanoparticles enables selective and precise control over the resulting particle morphology in large quantity that is not achievable using top-down lithographic approaches.² By subjecting different types of Ag nanoparticles to mild oxidative etching, the SERS enhancement factor of mildly etched Ag octahedra is enhanced by an order and the hot spots densities on Ag nanowires are increased from the wire tips to span the entire length of the nanowires.^{19,20} However, the reaction kinetics of such oxidative etching is challenging to control, thus increasing the difficulty of synthesizing designer nanoparticles in high yields. Aside from etching, the selective deposition of Au along the edges of Ag nanoparticles has also been successfully achieved on several types of nanoparticles, including decahedra, prisms, and nanocubes.²¹⁻²⁵ However, the optical properties as well as the structure-to-function relationship of many of these designer nanoparticles have not been thoroughly investigated to date, especially at the nanoscale. Furthermore, the edges of anisotropic nanoparticles possess greater surface areas than the tips and possess high curvatures, implying that the edge areas exhibit huge potential for large area hot spot design. The motivation for the study of selectively deposited nanoparticles lies in the potential discovery of more efficient or even novel properties arising from specifically decorating “hot spots” at “hot spot areas”.

Here we develop a large scale ‘precision synthesis’ to selectively deposit Au nanodots over the edge and tip of Ag octahedra and study their optical properties at the nanometer lengthscale. The aim is to optimally enhance and enlarge the hot spot densities of Ag octahedra by spatially decorating the plasmonic-active Au nanodots over the edge and tip hot spot areas. In the first part of this paper, we demonstrate that a library of related nanoparticles can be obtained via a seed-mediated kinetically-controlled growth process, including selective edge gold-deposited silver octahedra (SEGSO), which can be subsequently etched to octahedral cages as well as octahedral frames. Next, we characterize the optical properties of these nanoparticles both at the ensemble and at the single-particle

levels. By mapping the plasmon modes of single nanoparticles using cathodoluminescence hyperspectral imaging with a spatial resolution of ~ 10 nm, we demonstrate the contrasting difference in plasmonic response of the Ag octahedra with and without Au deposition. We then use SERS as an application to further demonstrate the advantages of our designer nanoparticles in comparison to both randomly deposited and un-deposited Ag octahedra. The experimental observations also corroborate well with theoretical simulations.

2.2 RESULT AND DISCUSSION

Precise Synthesis of Selective Edge Gold-deposited Silver Octahedra (SEGSO), Octahedral Cages and Octahedral Frames

We use a kinetically-controlled seed-mediated method containing two steps to generate selective edge gold-deposited silver octahedra (SEGSO). In the first step, Ag octahedra are first synthesized via the polyol reduction method using PVP as the capping agent.¹⁹ The average edge lengths of the as-synthesized Ag octahedra are 322 ± 5 nm (Figure 2.1A, B). In the second step, using Ag octahedra as seeds, edge-selective growth of Au is achieved by dropwisely injecting aqueous Au precursors with a syringe pump to a solution containing PVP and ascorbic acid maintained at a pH of ~ 2 . The final suspension after the reaction appears reddish dark grey (Figure 2.2B).

Figure 2.1. SEM images of (A, B) Ag octahedra and (C, D) selective edge gold deposited silver octahedra (SEGSO), respectively.

Figure 2.2. Digital images of (A) Ag octahedra, (B) SEGSO and (C) Octahedral cages, respectively.

Au nanodots of average diameters of $\sim 32 \pm 5$ nm are selectively deposited along the tips and edges of the Ag octahedra (Figure 2.1C, D, and confirmation on the metallic Au formation is discussed in the last section). Some Au nanodots are occasionally deposited on the facets of the Ag octahedra, but there are generally no more than two dots on a single facet. The yields of such particles reach nearly 100% in our reactions (Figure 2.3). The average edge length of the decorated octahedra is noted to increase to 380 ± 13 nm after the growth process, with no loss of particle monodispersity observed (Figure 2.1C, D).

Figure 2.3. (A) Zoom-out and (B) zoom-in SEM images of SEGSO, respectively.

The growth of SEGSO arises from the non-homogeneous distribution of surface energies across the different facets/regions on the Ag octahedra, with the $\{100\}$ tips and $\{110\}$ edges having higher surface energies and hence increased reactivity than the more stable $\{111\}$ facets (*vide infra*).²⁶ Consequently, our synthesis protocol is generic and can be broadly applied to other particles with facets having non-homogeneous surface energies.

As a first example, we change the seed particles to Ag cuboctahedra which have clearly defined $\{111\}$ and $\{100\}$ facets, corresponding to the hexagonal-shaped and square faces, respectively (Figure 2.4A, B). Selective deposition of Au nanodots on square $\{100\}$ facets and $\{110\}$ edges of the Ag cuboctahedra is observed, but not on the hexagonal-shaped $\{111\}$ facets (Figure 2.4C and D). We make a comparison between selective Au nanodots deposition on Ag octahedra and Ag cuboctahedra (Figure 2.5). The nanoparticles used in our work is made up of three main crystal facets: $\{111\}$, $\{100\}$, and $\{110\}$. The surface energy of these facets decreases in the sequence of $\{110\} > \{100\} > \{111\}$.²⁶ Ag octahedra are bound with 8 triangular-shaped $\{111\}$ facets, with $\{110\}$ facets on the edges and $\{100\}$ facets on the tips.²⁷ Selective deposition of Au dots on the tips and edges of Ag octahedra occurs on the more reactive $\{110\}$ and $\{100\}$ facets under controlled conditions in our experiments (Figure 2.5, top). On the other hand, Ag cuboctahedra are bound with two kinds of facets comprising 8 hexagonal-shaped $\{111\}$ facets and 6 square-shaped $\{100\}$ facets. The facets on the edges of this kind of cuboctahedron are $\{110\}$. The $\{100\}$ facets are much larger in the Ag cuboctahedra than in Ag octahedra. Using Ag cuboctahedra, we demonstrate the selective deposition of Au nanodots on both the edge $\{110\}$ and square $\{100\}$ facets, thus leaving the hexagonal $\{111\}$ unreacted (Figure 2.1D, 2.2D and Figure 2.5, bottom). The difference in morphological appearance post-selective deposition arises from the difference in the size of the various crystalline facets of the seed particles (Ag octahedra vs. Ag cuboctahedra). Furthermore, selective deposition of Au nanodots is also demonstrated using Ag truncated tetrahedra and Ag nanoplates (Figure 2.6). These are all demonstrations of the universality of our synthetic protocol for Ag nanoparticles containing different crystalline facets. Detailed studies on the formation of the selective deposition of Au nanodots are discussed in the following section of this work.

Figure 2.4. SEM images of Ag cuboctahedra (A, B) before and (C, D) after selective Au deposition, respectively.

Figure 2.5. Scheme and SEM images showing selective Au deposition process of Ag octahedron (top) and Ag cuboctahedron (bottom) with different facets, respectively.

Figure 2.6. Selective Au deposition also achieved on (A) truncated tetrahedron; (B) hexagonal plate and (C) cuboctahedron, respectively.

The structural diversity of our nanoparticles can be further enriched by transforming the selectively deposited Ag octahedra from solid particles to octahedral cages and frames through selective etching of the Ag component (Figure 2.7A). The addition of hydrogen

peroxide as a Ag-selective etchant into the reddish grey dispersion of SEGSO changes the dispersion to light bluish grey (Figure 2.2C). SEM and TEM characterization depicts a hollowed-out Ag octahedra core (Figure 2.7B, C and Figure 2.8B). The Au nanodots on the octahedra are unaffected by the etching process. The yield of the octahedral cages is nearly 100% (Figure 2.7B). In addition, octahedral frames are produced by adding excess iron (III) nitrate to the SEGSO deposited on Si substrate. In this procedure, the Ag cores are almost etched off, leaving Au nanodots to form intact octahedral frames (Figure 2.7D, E). In spite of the near 100% yield, the quantity of the octahedral frames produced is not comparable to the solution-phased etching by H_2O_2 . The use of H_2O_2 is postulated to lead to the formation of a thin layer of $\text{Ag}_2\text{O}/\text{AgOH}$ on the Ag surface, thus preventing the complete removal of Ag and leading to the formation of cages.²⁸ In our experiment, the $\text{Ag}_2\text{O}/\text{AgOH}$ formed on the octahedra surface give the particles a rough morphology (Figure 2.9A) and are then removed by heating the aqueous dispersion of cages at 100 °C for 10 min, giving octahedral cages with smooth surface (Figure 2.9B).

Figure 2.7. (A) Scheme illustrating the transformation of the SEGSO to octahedral cages and octahedral frames through selective etching of the Ag component by H_2O_2 and $\text{Fe}(\text{NO}_3)_3$, respectively; SEM images of (B, C) octahedral cages and (D, E) octahedral frames.

Figure 2.8. TEM images of (A) SEGSO and (B) octahedral cage, respectively.

Figure 2.9. SEM images of octahedral cages (A) before and (B) after heating at 100 °C in water, respectively. Note the fussy SEM image in (A) is due to the charging during SEM imaging caused by the presence of non-conductive Ag_2O and AuOH .

Optical Characterization

The ensemble extinction spectra of various octahedra highlight a progressive red-shift in localized surface plasmon resonance with the selective deposition of Au and with the etching of the octahedral core (Figure 2.10). The extinction spectrum of the Ag octahedra (edge length = 322 ± 5 nm) shows one major plasmon resonance at 932 nm and multiple resonance modes within the range of 400-600 nm, and they are assigned to quadrupolar resonance and higher order resonance modes respectively.²⁷ These higher-order plasmon modes appear in the extinction spectra because of the phase retardation effect arising from the large sizes of Ag octahedra.^{27,29} For SEGSO, these plasmon resonances are red-shifted to 1196 nm and 723 nm. This red-shift of 264 nm arises from both the increase in size of the octahedra and the change in dielectric upon Au growth.^{1,30,31} As a comparison, the quadrupolar resonance of Ag octahedra with identical dimensions as the SEGSO (edge length 380 ± 5 nm) is located at 1034 nm. This indicates that among the total red-shift of

264 nm, a 102-nm red-shift can be ascribed to size increase of the octahedra and that the subsequent red-shift of 162 nm can be ascribed to dielectric changes brought about by Au deposition. The ensemble extinction of octahedral cages exhibits featureless LSPR modes within the wavelength window measured, indicating a possible further red-shift of all the plasmon modes stemming from the hollow structure.³² We are not able to examine the extinction of frames because they are prepared on substrate. The extinction spectra of Ag octahedra and SEGSO corroborate well with those simulated using discrete dipole approximation (DDA) (Figure 2.11).

Figure 2.10. From top to bottom, extinction spectra of Ag octahedra with average edge lengths of 322 nm (black) and 380 nm (orange), SEGSO (blue) and octahedral cages (brown).

Figure 2.11. Comparison of extinction spectra between experimental results (solid line) and DDA simulated data (dash line) for Ag octahedra (black) as well as edge SEGSO (blue).

To spatially obtain plasmon mapping of the various plasmonic nanoparticles at the single-particle level and at the nanometer length-scale, we use cathodoluminescence (CL) hyperspectral imaging with sub-wavelength resolution.³³⁻³⁵ Using a low-energy electron beam as the excitation source, this spectroscopic technique enables the radiative plasmon modes of individual plasmonic nanoparticles to be identified spectrally and spatially simultaneously with ~10-nm resolution through raster-scanning the probe particles.³⁶ Cathodoluminescence emission arises from the electronic excitation of the plasmon modes and can be correlated to the electromagnetic field localization on the nanoparticles.^{37,38} Thus, the areas with strong cathodoluminescence emission correspond to the plasmonic hot spots and their spatial distribution can be indexed to the respective plasmon mode order.³⁸

The cathodoluminescence spectra from the tips, edges, and faces of both the pure Ag octahedra and the SEGSO are first analyzed (Figure 2.12A, B). Four emission peaks are observed from both particles with their spectral positions color-coded according to different wavelength windows, i.e. 620 nm (650 nm for SEGSO), 460 nm (515 nm for SEGSO), 400 nm (430 nm for SEGSO) and 345 nm. In general, the emission wavelengths of SEGSO are red-shifted relative to Ag octahedra due to the dielectric change brought about by Au deposition. For both particles, the highest CL emission intensities are collected from the tips and edges in the wavelength windows of the 400 nm (430 nm for SEGSO) and 460 nm (515 nm for SEGSO), indicating the hot spots are located at both tips and edges. In comparison, the photon emission intensity of our SEGSO at the edge location is at least ~40 counts (1.6-fold) higher compared to the pure Ag octahedron (Figure 2.12A, B – edge), signifying a drastic increase in the hot spot intensity contributed by the selective addition plasmonic-active Au nanodots over edge hot spot area. On the other hand, we note that in both cases, the octahedral facets give rise to relatively broad featureless spectra with very weak emission at 345 nm. This suggests that the octahedra facets are the ‘cold spots’, unlike the hot spots observed on the edges and tips of the octahedra.

Figure 2.12. Site-specific cathodoluminescence emission spectra of (A) Ag octahedra and (B) SEGSO collected from the (a) tip, (b) edge, and (c) face of the particles. The various emission peaks are deconvoluted from the main cathodoluminescence emission spectra and are highlighted by the green columns. Monochromatic cathodoluminescence emission maps of (C) Ag octahedron taken at wavelength windows centered at (ii) 400 nm, (iii) 460 nm, (iv) 620 nm, (D) SEGSO recorded at wavelength windows centered at (vi) 430 nm, (vii) 515 nm and (viii) 650 nm, respectively. CL maps recorded at windows of wavelengths centered at (i, v) 345 nm are shown in Figure 13. Left side shows correlated SEM images overlapped with composite CL maps. All scale bars represent 100 nm.

In addition, the spatial information of these plasmon modes can be clearly illustrated in the cathodoluminescence spectral images of pure Ag octahedra collected at three wavelength windows (Figure 2.12C). At 400-nm wavelength window, the entire tip-to-edge regions are in strong resonance (Figure 2.12C-ii); whereas at 460-nm wavelength window, bright CL emissions are alternatingly observed along the tips and edges. At 620-nm wavelength window, only the three tips are lit up (Figure 2.12C-iv). The complex

cathodoluminescence emission patterns observed suggest that the emission originates from the electromagnetic oscillation of higher-order plasmon modes, highlighting that these confined regions are where the electromagnetic fields are most concentrated on the octahedron.³⁷⁻⁴¹ Notably, the contribution of the octahedra facets to the emissions at these wavelength windows is negligible, evident from the absence of bright regions from the facets at all the wavelengths probed, in line with the featureless emission spectrum observed. When the photon emission wavelength is centered at 345 nm, the whole particle is lit-up, albeit dimly (Figure 2.13). We ascribe this emission to arise from the bulk plasmon mode of Ag.^{39,42,43}

Figure 2.13. CL maps of Ag octahedron (top) and SEGSO (bottom) recorded at windows of wavelengths centered at 345 nm, respectively.

In contrast, the cathodoluminescence spectral images of the SEGSO obtained at 650 nm, 515 nm, and 430 nm wavelength windows display a common similarity: the edges and tips of the deposited Ag octahedra light up at these wavelengths (Figure 2.12D). This indicates the hot spot distribution is enlarged across all the edges of the octahedra post-deposition, and these hot spots remain bright across all the measured wavelengths. This is a definitive demonstration of the advantages of precisely controlling the locations at which

Au dots are deposited on Ag, leading to an efficient overall increase in hot spot density on a single particle. The bulk plasmon mode of Ag at 345 nm remains unchanged since the emission does not arise from the octahedra surface. Due to the polycrystalline nature of the Au deposition, we are unable to assign the individual plasmon emission modes of the SEGSO. The results of CL mapping and spectra of Ag octahedron and SEGSO are highly repeatable over different samples (Figure 2.14).

Figure 2.14. Monochromatic cathodoluminescence emission maps of (A,B, C) Ag octahedron taken at wavelength windows centered at (i) 345 nm, (ii) 400 nm, (iii) 460 nm, (iv) 620 nm and (D, E, F) SEGSO recorded at wavelength windows centered at (v) 345 nm, (vi) 430 nm, (vii) 515 nm and (viii) 650 nm, respectively. Left side shows correlated composite CL maps.

Singe-particle surface-enhanced Raman scattering (SERS) experiments are conducted as a direct application for the advantages arising from the strategic increase in hot spot densities and enhanced electromagnetic fields on the SEGSO. The SERS capabilities of SEGSO are compared against pure Ag octahedra, octahedral cages, as well as non-selectively gold-deposited octahedra (NSEGSO). For NSEGSO, Au nanodots ~5 nm in sizes are randomly deposited on the entire surface of Ag octahedra. After the Au deposition, the surfaces of the Ag octahedra seeds are roughened by Au nanodots instead of coated with a uniform Au film (Figure 2.15D). NSEGSO are prepared by using the same amount of Au precursor and experimental parameters as producing SEGSO, except that the pH value is tuned to pH=8 before adding the Au precursor (please refer to the mechanistic study section for the details). SERS measurements are carried out using 4-methylbenzenethiol (4-MBT) as the non-resonant analyte molecules at an excitation wavelength of 532 nm. 4-MBT is chosen because it forms self-assembled monolayers (SAMs) on the surface of Au and Ag⁴⁴ as a result of highly specific coordination bond between thiol and Ag, and this is important for the subsequent quantification of analyte molecules to derive a more accurate SERS enhancement factor.

A highly diluted solution of the nanoparticle dispersion is drop-casted onto an indexed Si substrate for both SEM imaging and SERS mapping to ensure that only single particles are measured each time. Overlaying the SERS image produced with the 1079 cm⁻¹ mode with the SEM image ascertains that only SERS signals from single particles are measured each time (Figure 2.15A, C, and E). Typical SERS spectra of 4-MBT obtained from the four types of nanoparticles show two characteristic vibrational modes at 1079 cm⁻¹ and 1584 cm⁻¹ (Figure 2.15G). The peak at 1079 cm⁻¹ is the signature of the phenyl ring-breathing mode, C-S stretching and C-H in-plane bending, whereas the peak at 1584 cm⁻¹ arises from phenyl stretching motion. The SEGSO exhibits the highest SERS signals (1513 ± 333 counts),

followed by NSEGSO (498 ± 75 counts), octahedral cages (235 ± 78 counts), and lastly pure Ag octahedra (121 ± 39 counts).

Figure 2.15. Overlaid SEM and SERS images, and SEM images of isolated (A, B) Ag octahedron, (C, D) non-selective gold-deposited silver octahedra (NSEGSO) and (E, F) SEGSO. The white boxes indicate the locations of particles in (B), (D) and (F). Colors are assigned by the relative intensity of the vibrational mode at 1080 cm^{-1} . (G) Single-particle surface-enhanced Raman scattering (SERS) spectra and (H) SERS enhancement factors of SEGSO, NSEGSO, octahedral cage and Ag octahedron, respectively.

The SERS enhancement factors of every particle type are calculated to directly compare the SERS enhancements, and are calculated based on the SERS intensity of the peak at 1584 cm^{-1} (details on calculation are listed in the end of this section). The SERS enhancement factors (EF) of the SEGSO is 1.1×10^5 (Figure 2.15H), while that of the NSEGSO is nearly three times weaker at 2.6×10^4 . The SERS enhancement factors of octahedral cages and bare Ag octahedra are calculated to be 1.04×10^4 and 0.9×10^4 , respectively. The SERS enhancement factors of the Ag octahedra that we measure here is lower as compared to literature values,¹⁹ due to the different experimental conditions adopted in our studies including laser excitation wavelengths and probe molecules used.

A 10-fold increase in SERS signals are observed from the SEGSO compared to pure Ag octahedra. It should be noted that this 10-fold increase in SERS enhancement factor is averaged over the entire particle and the actual SERS enhancement is much higher along

the edges decorated with Au dots. Moreover, the enhancement factor from the SEGSO is an underestimated value due to the simplified model used to estimate the increase in surface area arising from the Au deposition. The advantage of precision synthesis is clearly evident in the comparison of SERS enhancement factors between SEGSO with that of the NSEGSO. Even though the same amount of Au is used for the growth of Au nanodots, the SERS enhancement factor of SEGSO is three-fold higher than NSEGSO. For NSEGSO, the random Au deposition on Ag octahedron brings secondary roughness to the whole particle. From the SEM image of NSEGSO (Figure 2.15D), we observe tiny Au nanodots deposited on the surfaces. These plasmonic-active tiny curvatures and junctions between two nanodots in fact give rise to additional hotspots as compared to the smooth pure Ag octahedron.⁴⁵ In addition, hybrid nanostructures containing both Ag and Au are proven to be more efficient SERS performers than their monometallic counterparts, in line with the higher SERS enhancement factor of NSEGSO than pure Ag octahedra observed in our study.⁴⁶ In our NSEGSO particles, every Au nanodot on the Ag surface is a new hotspot. However, it is important to strategically add the hotspots to the “most efficient areas”, where the electromagnetic fields are most intense. On the SEGSO, the Au nanodots are selectively deposited on the original hotspots regions of Ag octahedron, efficiently enhancing the hotspot densities and electromagnetic field enhancements. Consequently, this further increases the SERS signals as compared with NSEGSO. This accounts for the SERS enhancement factor of the various particles to decrease in the order of SEGSO>NSEGSO>Ag octahedron.

These experiments collectively demonstrates the successful increase in hot spot densities as well as the extent of electromagnetic field localization at the nanoscale via the precise and efficient synthetic protocol of tip- and edge-selective Au nanodot growth on Ag octahedra. This is further confirmed by investigating the electromagnetic field enhancements of SEGSO through DDA simulations using an incident excitation of 532 nm.

The electromagnetic field intensities of the cut-planes of both pure Ag octahedra and SEGSO (Figure 2.16) clearly indicates an increase in areas of electromagnetic field enhancement from the particle tips in pure Ag octahedra to the entire triangular edge framing the octahedra in SEGSO. The electromagnetic field enhancement along the edges of SEGSO is increased up to 15-fold relative to the pure Ag octahedra at the non-resonant wavelength of 532 nm.

Figure 2.16. Simulated total field intensity for (A) Ag octahedron and (B) SEGSO, using an incident excitation wavelength of 532 nm. The intensity enhancement bars are shown as color bars.

The importance and significance of synthesizing designer nanoparticles such as SEGSO over non-selectively deposited nanoparticles is also demonstrated through the DDA simulations. The electromagnetic field enhancement of eight individual Au nanodots deposited on each of the eight edges is compared against those deposited on each of the eight facets (Figure 2.17). Every single Au particle deposited on the octahedra edge leads to a 33% increase in electromagnetic field enhancement compared against the Au particle deposited on the octahedra facet.

Figure 2.17. Simulation on the electric field intensity enhancement for (A) Ag octahedra, (B) SEGSO, (C) individual Au nanodot deposited on the edges and (D) individual Au nanodot deposited on the facets, illuminated at 532 nm. The enhancement intensity bars are shown as color bars.

Calculation of enhancement factor (EF)

The enhancement factor is calculated by using the equation below:

$$EF = \frac{I_{SERS}}{I_{Normal}} \times \frac{N_{Normal}}{N_{SERS}} \quad (1)$$

We choose the peak at 1584 cm^{-1} to calculate enhancement factor.

$I_{SERS} = 1513$ (on SEGSO; measured using $100 \times$ objective lens, XY Scanning, 1s integration time)

$I_{Normal} = 122/60s = 2.03$ (based on 1 M benzenethiol solution, $100 \times$ objective lens, point, 60 s integration time)

$N_{Solution} = \text{number of molecules in solution within the measured laser spot} = V_{\text{solution}} \times \text{Concentration of molecules} \times \text{Avogadro's number}$

$V_{\text{Solution}} = \pi \times a \times b \times h$ ($a=0.91/2=0.455 \text{ um}$, $b=0.68/2=0.34 \text{ um}$, $h=4.32 \text{ um}$) $= 3.142 \times (455 \text{ nm}) \times (340 \text{ nm}) \times (4320 \text{ nm}) = 2.1 \times 10^9 \text{ nm}^3$

$$N_{\text{Solution}} = 2.1 \times 10^9 \text{ nm}^3 (= 2.1 \times 10^{-18} \text{ m}^3) \times 1 \text{ M} (= 1000 \text{ mol/m}^3) \times 6.022 \times 10^{23} = 1.26 \times 10^9$$

N_{Surface} = number of molecules on the surface of nanoparticles within the measured laser spot

For Solid Selective Gold Deposited Octahedra (SEGSO)

$I_{\text{SERS}} = 1513$ (on SEGSO; measured using $100 \times$ objective lens, XY Scanning, 1s integration time)

Laser beam diameter = 721 nm ($100 \times$ objective lens) > diameter of nanoparticles

Surface area within the measured laser spot = sum surface area of a nanoparticle

Regarding SEGSO as edges semi-spheres attached octahedra, the surface areas where 4-MBT molecules are adsorbed contain 7 triangle faces (edge length = 322 nm) and 9 edges with 6 semi-spheres (diameter = 32 nm) attached on each edge.

$$S_{\text{Semi-sphere}} = 4\pi \times r^2/2 = 4 \times 3.142 \times (32/2)^2/2 = 1608.7 \text{ nm}^2$$

$$S_{\text{Triangle-face}} = \sqrt{3}/4 \times a^2 \text{ (a = 322 nm)} = 4.5 \times 10^4 \text{ nm}^2$$

$$S_{\text{Sum}} = 7S_{\text{triangle-face}} + 9 \times 6 \times S_{\text{Semi-sphere}} = 4 \times 10^5 \text{ nm}^2$$

$$\text{Surface area of 4-MBT} = 2.3 \times 2.3 \text{ \AA}^2/\text{molecule} = 0.0529 \text{ nm}^2/\text{molecule}$$

$$N_{\text{Surface}} = 4 \times 10^5 / 0.0529 \text{ nm}^2/\text{molecule} = 7.6 \times 10^6 \text{ molecules}$$

$$EF = [1513/2.03] \times [1.26 \times 10^9 / 7.6 \times 10^6] = 1.2 \times 10^5$$

For octahedral cages

ISERS = 235 (on octahedral cage; measured using 100 × objective lens, XY Scanning, 1s integration time)

$$S_{\text{Sum}} = 2 \times 7 S_{\text{triangle-face}} + 9 \times 6 \times S_{\text{Semi-sphere}} = 7.2 \times 10^5 \text{ nm}^2$$

$$\text{Surface area of 4-MBT} = 2.3 \times 2.3 \text{ \AA}^2 / \text{molecule} = 0.0529 \text{ nm}^2 / \text{molecule}$$

$$N_{\text{Surface}} = 7.2 \times 10^5 / 0.0529 \text{ nm}^2 / \text{molecule} = 1.4 \times 10^7 \text{ molecules}$$

The N_{Surface} is considered the inner side surface

$$\mathbf{EF} = [235/2.03] \times [1.26 \times 10^9 / 1.4 \times 10^7] = 1.04 \times 10^4$$

For Silver Octahedra (Edge length = 375 nm)

ISERS = 121 (on Ag octahedron; measured using 100 × objective lens, XY Scanning, 1s integration time)

$$S_{\text{Sum}} = 7 \times S_{\text{triangle-face}} = 4.3 \times 10^5 \text{ nm}^2$$

$$\text{Surface area of 4-MBT} = 2.3 \times 2.3 \text{ \AA}^2 / \text{molecule} = 0.0529 \text{ nm}^2 / \text{molecule}$$

$$N_{\text{Surface}} = 4.3 \times 10^5 / 0.0529 \text{ nm}^2 / \text{molecule} = 8 \times 10^6 \text{ molecules}$$

$$\mathbf{EF} = [121/2.03] \times [1.26 \times 10^9 / 8 \times 10^6] = 0.9 \times 10^4$$

For Non-selective Gold Deposited Octahedra (NSEGSO)

ISERS = 498 (on NSEGSO; measured using 100 × objective lens, XY Scanning, 1s integration time)

Regarding a NSEGSO as a structure where the surface of an octahedron was totally covered with a layer of semi-spheres, the sum surface areas of this nanoparticle is two times

of that of silver octahedron at edge length of 300 nm (since $S_{\text{semi-sphere}}/S_{\text{circle}} = [4\pi \times r^2/2] / [\pi \times r^2] = 2$)

$$S_{\text{Sum}} = 2 \times 7 \times S_{\text{triangle-face}} = 6.3 \times 10^5 \text{ nm}^2$$

$$N_{\text{Surface}} = 6.3 \times 10^5 / 0.0529 \text{ nm}^2/\text{molecule} = 1.2 \times 10^7 \text{ molecules}$$

$$EF = [498/2.03] \times [1.26 \times 10^9 / 1.2 \times 10^7] = 2.6 \times 10^4$$

Mechanistic Study on SEGSO Formation

To investigate the inner structure and composition of SEGSO, we also section the nanoparticles using ultracut-microtome. The nanoparticles are casted in an epoxy, and sliced into a 80-nm thin section. Figure 2.18A shows the typical morphology of a microtome-sectioned SEGSO (edge length of 375 nm), which is cut in the direction parallel to the {111} facet. The TEM image clearly exhibits roughened edges with grainy curvatures. Energy dispersive X-ray spectroscopy (EDS) mapping of this section reveals that the deposited dots on edges are Au (Figure 2.18B-D).

Figure 2.18. (A) microtome-sectioned TEM image and (B, C, D) Ag, Au, and Ag-Au composite EDS maps of a microtome section that cut through (111) plane; (E, F) Ag 3d and Au 4f X-ray photoelectron (XPS) spectra of SEGSO.

Further EDS performed on the un-sectioned SEGSO estimates the presence of $\sim (90 \pm 2) \%$ Ag and $\sim (10 \pm 2) \%$ Au (Table 1). X-ray photoelectron (XPS) measurements are also performed to determine the chemical compositions of the SEGSO (Figure 18E, F). The high resolution scan of Ag 3d indicates one main doublet at 366.5 and 372.5 eV, representing Ag 3d_{5/2} and Ag 3d_{3/2}, respectively (Figure 18E). The binding energy difference between Ag 3d_{5/2} and Ag 3d_{3/2} is 6.0 eV, and the intensity ratio of these two peaks is 2:3, confirming the presence of Ag(0).^{47,48} The high resolution Au 4f spectrum also shows a main doublet at 83.5 and 87.2 eV, corresponding to Au 4f_{7/2} and Au 4f_{5/2}, respectively (Figure 18F). The difference in binding energy between the doublet peaks is 3.7 eV with a 4:3 intensity ratio, and can be indexed to Au (0). In addition to metallic Ag and Au, two smaller sets of doublets can be discerned at 367 and 373 eV (for Ag) and 83 and 87 eV (for Au), indicating the presence of small amounts of Ag-Au alloy.⁴⁹ The peak area ratio of the sum of the Au (0) and Ag (0) peaks to the total peak area indicates that 89 % of the Au and Ag remain in the

metallic state, and 11 % in the alloy state. The EDS and XPS analyses tally quantitatively with each other, unambiguously identifying the dots to be predominantly Au (0).

Table 1. Atomic percentages of selective Au deposited silver octahedra (SEGSO), octahedral cages, octahedral frames, as obtained from EDS mapping analysis.

Element	Atomic %		
	SEGSO	Octahedral cage	Octahedral frame
Au	10 ± 2	27 ± 6	57 ± 7
Ag	90 ± 2	73 ± 6	43 ± 7

The composition of the octahedral cages and frames is examined by both EDS and XPS. EDS analyses estimate the Ag content to be approximately (70 ± 6) % for the octahedral cages and decreases to (43 ± 7) % for the frames, with Au comprising the remaining component (Table 1). XPS data reveals ~79 % Ag for the octahedral cages and ~48% for the octahedral frames (Figure 2.19). The incomplete removal of Ag in the frames is likely due to the formation of Ag-Au alloy. In Ag 3d XPS scan of frames, the main doublet is shifted to 363 and 373 eV, indicating that the remaining Ag is mainly in alloy form in the frames (Figure 2.19). The Au 4f XPS scan of frames indicates that the main doublet remains at 83.5 and 87.2 eV, again validating that pure metallic Au as the dominating composition in the deposited dots.

Figure 2.19. XPS spectra of (A, B) octahedral cages and (C, D) octahedral frames, respectively.

In our synthesis method, the reaction rate is the key determining factor to achieve SEGSO. This can be explained by the differences in the surface energy between the $\{100\}$, $\{110\}$, and $\{111\}$ facets present on Ag octahedra, which are slightly truncated at the tips and edges. The crystal structures of the triangular facets on these octahedra are $\{111\}$, whereas the tips and edges are dominated by higher energy $\{100\}$ and $\{110\}$ facets, respectively.²⁷ When Au^{3+} are added into the reaction mixture containing Ag octahedra, they are more likely to be adsorbed to the $\{100\}$ and $\{110\}$ sites prior to being reduced.⁵⁰ This leads to the selective reduction of Au^{3+} and subsequent growth of Au nanodots along the tips and edges of Ag octahedra. As we will show in our subsequent experiments, this mechanism accounts for the selectivity of Au deposition under several experimental conditions: relatively lower Au^{3+} concentrations, lower injection speeds, and reduced reducing rate of ascorbic acid at $\text{pH} < 3$. These conditions lead to mild kinetics, with Au^{3+} adsorbing selectively onto the preferred $\{100\}$ and $\{110\}$ facets of Ag octahedra.

The selective growth of Au nanodots is highly dependent on the concentration and injection rate of Au precursor. Selective growth of Au nanodots is achieved when Au

precursor is ≤ 0.3 mM, with Au nanodot size controlled from 21-32 nm (Figure 2.20). An increase in Au precursor's concentration to ≥ 0.4 mM leads to non-selective growth with nanodots randomly deposited on the Ag octahedra (Figure 2.21A-H). By keeping the molar amount of Au precursor constant at 1.5×10^{-6} mol (i.e. 0.3 mM and 5 mL), non-selective growth of Au nanodots on Ag octahedra is also observed at an injection rate of 1 mL/min. However, highly selective growth is observed at a lower injection rate of 0.76 mL/min (Figure 2.22). The presence of excess Au precursors in the Ag octahedra dispersion during the growth process, either by increasing the Au precursor concentration or injection speed, reduces the selectivity of Au growth on Ag octahedra.

Figure 2.20. Correlation of diameters of Au nanodots on SEGSO with concentrations of Au precursor

Figure 2.21. Influence of Au precursor concentration on SEGSO. SEM images of nanoparticles when concentration of Au precursor is (A, B) 0.1 mM; (C, D) 0.2 mM; (E, F) 0.3 mM and (G, H) 0.5 mM, respectively.

Figure 2.22. Influence of injection speed of Au precursor on the selectivity of depositing Au nanodots on tips and edges of Ag octahedra. SEM images of nanoparticles at injection speeds of (A, B) 1 mL/min and (C, D) 0.76 mL/min, respectively.

The use of ascorbic acid in the growth process also implies that the selective deposition of Au nanodots on Ag octahedra is pH-dependent, with increasing selectivity observed at acidic pH. SEGSO are clearly observed at pH values of 2, whereas random non-selective growth of Au nanodots occurs over all the facets of Ag octahedra is observed at pH 8 (NSEGSO, Figure 2.23). This is attributed to the pH-dependent reducing ability of ascorbic acid. In the experiments, the anionic ascorbate form is the active reducing agent. At pH 8, nearly all of the ascorbic acid molecules are deprotonated to anionic ascorbate ions (ascorbate ions molar percentage calculations are listed under Figure 2.23), therefore significantly increasing its reducing power and the corresponding kinetics of Au^{3+} reduction in the reaction solution.⁵¹ However, at pH 2-3, only 5.9 % of the ascorbic acid molecules are in their anionic form, translating to nearly 17-fold decrease in the reducing power of ascorbic acid at acidic pH. The lower reducing power and decreased rate of Au^{3+} reduction enables selective growth of Au nanodots at acidic pH. Despite the decreased reducing power of ascorbic acid at low pH, it is still able to reduce Au^{3+} into elemental Au nanoparticles, as indicated in the control experiments (Figure 2.24). The colorless reaction solution in the absence of Ag octahedra seeds turns purplish-red upon the introduction of Au precursors and this solution exhibits an extinction peak at 580 nm, characteristic of Au nanoparticles (Figure 2.24).¹³

Figure 2.23. Influence of pH on the the selectivity of depositing Au nanodots on tips and edges of Ag octahedra. SEM images of nanoparticles obtained when the pH of the reaction solution is tuned at (A) pH 2-3, (B) pH 4, and (C) pH 8, respectively.

Ascorbate ions molar percentage calculations

Deprotonation of ascorbic acid is shown in equation (1):

In different pH, the ratio can be calculated from the Henderson Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \text{Log} (\text{base/acid}) \quad (3)$$

At pH = 8, $[\text{B}]/[\text{A}] = 7943/1$, molar percentage of $[\text{B}] = 99.9\%$

At pH = 5, $[\text{B}]/[\text{A}] = 8/1$, molar percentage of $[\text{B}] = 89\%$

At PH= 3. $[\text{B}]/[\text{A}] = 1/15.8 = 5.9\%$

Figure 2.24. (A) SEM image, (B) extinction spectrum and (C) digital of Au nanoparticles produced in the control experiment in the absence of Ag octahedra seeds.

Furthermore, the selective growth of Au nanodots can also be achieved by using other weak reducing agents such as hydroquinone (Figure 2.25). In contrast, the use of a strong

reducing agent such as NaBH_4 leads to direct formation of Au nanoparticles even in the presence of Ag octahedra seeds (Figure 2.25), further highlighting the importance of the reducing strength of the reducing agent in the selective growth of Au nanodots.

Figure 2.25. (A, B) SEM images of SEGSO achieved by using 0.3 mM of hydroquinone as reducing agent instead of ascorbic acid; (C) SEM image of products when NaBH_4 is used as reducing agent; (D) extinction spectrum of the upper solution obtained after centrifuging of the resulting mixture.

The ascorbic acid/ Au^{3+} molar ratio is typically maintained at a slight excess of 2 rather than the stoichiometric ratio of 1.5 in our experiments to ensure that selective deposition is dominant over the competing galvanic replacement reaction (Figure 2.26). Under such experimental conditions, the Ag octahedra seeds remain as solid particles over the course of selective Au nanodots deposition instead of becoming hollow particles that are typically observed from galvanic replacement reactions (Figure 2.26).^{52,53} When the molar ratio of ascorbic acid/ Au^{3+} is ≤ 1.5 , the octahedra cores are partially empty, indicating that some of the Au^{3+} are reduced via galvanic replacement reaction (Figure 2.26A, B). It is noteworthy that the amount of ascorbic does not influence the morphology of the final product or selectivity of Au deposition (Figure 2.26D-F). In the complete absence of ascorbic acid,

spiky structures form over the entire octahedra (Figure 2.27), brought about by the galvanic replacement of Ag by Au^{3+} to form AgCl, which subsequently act as seeds for the formation of the spikes.⁵ The reduction of Au^{3+} to Au (0) by ascorbic acid is more thermodynamically favored than galvanic replacement reaction even at low pH value, and can be rationalized by the reduction potentials of the participating reactants, with $E(\text{Au}^{3+}/\text{Au}) = 0.99 \text{ V}$, $E(\text{AA}/\text{oxidized form of AA}) = 0.000281 \text{ V}$, and $E(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$, respectively (equations are listed under Figure 2.26).^{51,53} Galvanic replacement reaction is thus kept to a minimum in our system, supported by the presence of only 11 % of Au-Ag alloy, with the remaining 89 % composed of metallic Au and Ag from the XPS measurements.

Figure 2.26. Influence of AA/Au on selective deposition. TEM and SEM images of the products when final concentration ratio of AA/Au is at (A, D) 0.6, (B, E) 1.5 and (C, F) 3, respectively.

The reduction of Au^{3+} by AA is stoichiometric at a molar ratio AA: Au^{3+} of 1.5, as shown in the equation below:

Figure 2.27. Spiky nanoparticles are obtained in a control experiment where only galvanic replacement reaction occurs between Au precursor and Ag octahedra at room temperature.

2.3 CONCLUSION

In summary, we have demonstrated a simple and versatile way to selectively deposit Au nanodots on tips and edges of Ag octahedral nanoparticles, to fabricate the hotspots exclusively on the areas where the electromagnetic fields are localized. The significance of finely designing hotspots at original hotspots regions for SERS are directly supported by our cathodoluminescence hyperspectral imaging and further confirmed by investigating the electromagnetic field enhancements of SEGSO through DDA simulations. Every single Au particle deposited on the octahedra edge leads to a 33% increase in electromagnetic field enhancement compared against the Au particle deposited on the octahedra facet. The advantage of precision synthesis is clearly evident in the single-particle SERS measurement which demonstrates 3-fold enhancement on the precisely designed SEGSO over the randomly deposited NSEGSO, even though using the same amount of Au for the growth of Au nanodots. By carefully designing additional hot spots at the hot regions of nanoparticles, the SEGSO particles can function as highly sensitive single-particle SERS substrates,

opening a new pathway to maximize the SERS performance by synthesizing various designer nanoparticles. The generality of our protocol can be applied to many additional particle morphologies. In addition, to further enhance the SERS signals, the SEGSO nanoparticles can also be assembled into various 2D/3D arrays for the substrate-based detection of analytes, enabled by the high synthetic yields and narrow size-distribution of this protocol.

2.4 MATERIALS AND METHODS

Materials. 1,5-pentanediol, silver nitrate (99+%), poly(vinylpyrrolidone) (PVP, average $M_w = 55,000$ Kg/mol), L-ascorbic acid, auric acid trihydrate ($\geq 99.9\%$), and sodium citrate tribasic dehydrate ($> 99\%$) were purchased from Sigma-Aldrich. 37% Hydrochloride acid was purchased from Schedelco and 30% H_2O_2 from QREC (ASIA). Copper(II) chloride was from Alfa Aesar. Iron(III) nitrate nonahydrate (98+%) was from Strem Chemicals. All the chemicals were used without further purification. Milli-Q water (> 18.0 M Ω ·cm) was purified with a Sartorius Arium 611 UV ultrapure water system.

Synthesis and purification of silver octahedra. Silver octahedra were synthesized based on previously reported literature.¹⁹ In brief, 0.083 g of copper(II) chloride, 0.20 g of silver nitrate and 0.20 g of PVP ($M_w = 55$ Kg/mol) were dissolved in 10 mL of 1, 5-pentanediol through sonication and vortex. In the 100 mL round-bottomed flask, 20 mL pentanediol was heated at 190 °C for 20 min. Then the two precursor were injected into the hot round-bottomed flask at following rates: 500 μ L silver nitrate was quickly injected for every 1 min and PVP solution drop-wisely added for every 30 sec. For cubes, the addition of precursor lasts 16 min, while another 60 min was required for the synthesis of octahedra. For the purification of Ag nanooctahedra, pentanediol was first removed through centrifugation and dispersed in 10 mL ethanol. The Ag octahedra suspension was then dispersed and preserved in PVP solution (100 mL, aqueous, 0.2 g/L). The resulting solution

was vacuum filtered using PVDF filter membranes with pore sizes ranging from 5 μm , 650 nm and 450 nm. The filtration was repeated for several times with each pore size.

Selective deposition of Au nanodots. 1 mL of Ag octahedral nanoparticles was injected slowly into 7.5 mL of 1 mg/mL aqueous PVP solution. After that, 161.6 μL of 28.96 mM ascorbic acid was injected into the solution according to AA/Au molar ratios at 3. 20 μL of 2.98 mol/L HCl (aq) was added to adjust the pH of the solution to 2. 5 mL of 0.3 mM HAuCl₄ solution was injected by syringe pump with injection speed at 0.76 mL/min. The reaction happens at 25 °C and stirring speed at 500 rpm. After the addition of HAuCl₄, the round bottomed flask was heated at 100 °C for 5-10 min. The nanoparticles were finally dispersed and stored in ethanol.

Hydrogen peroxide etching to form hollow nanostructures. 30% H₂O₂ was added into selective gold-deposited octahedra in ethanol solution. The volume ratio 1:1, and the mixture is stirred at room temperature with speed at 500 rpm for 30 min. The mixture was centrifuged and washed in water for 3 times to remove excess H₂O₂ and the nanoparticles were re-dispersed in water. The aqueous suspension was then heated at 100 °C for 5-10 min.

Iron (III) nitrate etching to form octahedral gold nanoframe. Selective gold-deposited octahedra were dried on silicon wafer. The substrate was then soaked into 60 mM iron(III) nitrate solution for 24 hours, and subsequently washed with water and ethanol.

Non-selective deposition of Au nanodots. 1 mL of Ag octahedral nanoparticles was injected slowly into 7.5 mL of 1 mg/mL aqueous PVP solution. After that, 161.6 μL of 28.96 mM ascorbic acid was injected into the solution according to AA/Au molar ratios at 3. Drops of trisodium citrate (aq) were added to adjust the pH of the solution to 8. 5 mL of 0.3 mM HAuCl₄ solution was injected by syringe pump with injection speed at 0.76 mL/min. The reaction happens at 25 °C and stirring speed at 500 rpm. After the addition of HAuCl₄, the round bottomed flask was heated at 100 °C for 10 min.

Cathodoluminescence hyperspectral imaging experiments. Quantitative cathodoluminescence was carried out using an Attolight Rosa 4634 microscope, which 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). Cathodoluminescence was spectrally resolved with a Czerny-Turner spectrometer (Horriba-JY iHR320, 320 mm focal length, 150 grooves/mm grating) and measured with an Andor Newton EM-CCD (EM-970P-BV). Electron beam energies of 8 kV were used to excite the samples. The beam dwell time was set to 0.2 s.

Surface-enhanced Raman scattering (SERS) measurements. Substrates drop-casted with nanoparticles were immersed into 10 mM 4-MBT in ethanol solution for overnight. 4-MBT is expected to form a self-assembled monolayer (SAM) on the nanoparticles due to the strong Ag-S coordination bond. Then, these substrates were rinsed with ethanol, and dried in nitrogen gas to remove extra 4-MBT and solvent. SERS spectra and SERS intensity maps were obtained using Ramantouch microspectrometer (Nanophoton, Osaka, Japan). A 532-nm laser was used as an excitation laser. The laser light was focused into a line on a sample using a cylindrical lens and an air objective lens (LU Plan Fluor 100× NA 0.9). The back-scattered Raman signal coming from the line-illuminated site was collected through the same objective lens, and a one-dimensional Raman image (1D space and Raman spectra) was acquired with a two-dimensional image sensor (pixis 400 BR, -70 °C, 1340 × 400 pixels) at once. Two-dimensional (2D) Raman spectral images were obtained by scanning in a single direction using the line-shaped laser. The excitation laser power on the sample plane was 0.09 mW. The exposure time for each line and slit width of the spectrometer were 1s and 50 μm for 2D Raman imaging. The line scan mode was used for x-y imaging with the resolution of y direction around 300 nm. 10 particles were measured for each sample.

Simulation Methodology. The simulations were carried out using the discrete dipole approximation (DDA) using the open source program DDSCAT 7:3.⁵⁴ The DDA has been

recently applied to the simulation of various shaped plasmonic nanoparticles excited optically and by electron beams.^{41,55} The octahedral shape is non-standard and was generated with a python script. The Ag octahedron of width 320 nm is composed of 471 781 discrete dipoles that are situated on a uniform grid. To generate the extinction spectra, four individual spectra (for two orthogonal incident polarizations and two different orientations of the octahedron with respect to the propagation vector) are averaged. In the first orientation, the octahedron central axis is parallel to the propagation vector and in the second orientation, one of its faces is perpendicular. The second orientation arise by a rotation of 35:26 of the first one. The SEGSO consists of 30 nm Au spheres located on the edges. The dielectric permittivity data for both Au and Ag are based on experimental tabulated data.⁵⁶

For the Raman excitation at wavelength 532 nm, the DDA simulation region is extended by 20% around the structural region. The intensity enhancement with respect to the incident intensity is plotted. A cut-plane located on one of the faces of the octahedron is also shown. For easier visualization, the minimum visible value is altered to highlight the hot spots in the structure. In all the field plots, the electric field excitation occurs with the propagation vector along the -z direction and E-field parallel to the y axis and the octahedron axis is parallel to z axis.

Characterization. Nanoparticles dispersed in ethanol are drop-casted on a clean silicon substrate, dried with nitrogen and analyzed using a JEOL-JSM-7600F scanning electron microscopy with an accelerate voltage of 5kV. Energy dispersive X-ray spectroscopy (EDS) analysis (JEOL-JSM-7600 Oxford X-max 50 mm²) as performed used the SEM at a higher accelerating voltage of 30 kV. For transmission electron microscopy (TEM), nanoparticles dispersed in ethanol were drop-casted on a clean copper grid and characterized using (JEOL-JEM-1400) at an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) spectra are measured by using a Phoibos 100 spectrometer coupled with a

monochromatic Mg X-ray radiation source. Binding energies are calibrated to the energy of C1s peak at 284.5 eV. For thin film sectioning, the nanoparticles were first embedded in epoxy resin then sectioned using a Leica Ultramicrotome with diamond knife under cryogenic condition. The 80-nm thin sections were collected and examined using high-resolution (HR) TEM-EDS (JEOL-2100) at an accelerating voltage of 200 kV.

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3 Plasmon Mapping of Coupling within Ag Nanocube Dimers**

ABSTRACT. This project aims to acquire knowledge on localized surface plasmon resonances (LSPRs) that occur in Ag nanocube dimers and to directly visualize how fields' localization evolves with alteration of dimer orientations. Highly-resolved (<10 nm spatial resolution) plasmon maps of these nanostructures are obtained using both cathodoluminescence and electron energy-loss spectroscopies. In total, there are four plasmon modes supported by isolated Ag nanocubes and five modes supported by nanocube dimers. A “dark” mode distributed on edges is sorted out by comparing CL and EELS results and this mode is observed in both Ag nanocube monomer and dimer. Upon plasmonic coupling, a “mode splitting” phenomenon is observed that a low-energy mode at 2.10 eV in isolated nanocube disappear with the appearance of two separate modes at 1.85 and 2.30 eV in dimer. Moreover, the localizations of all the plasmon resonance modes in the range of 1.5-3.5 eV are observed at the tip, edge and gap regions of a dimer. The distributions of the two “splitting” modes are influenced by the symmetry of dimer configuration while that of the high-energy modes is independent. Furthermore, percentage of high-energy modes within a nanocube dimer is adjustable and increased in the process of geometrical shifting from face-to-face to edge-to-edge configurations, indicating that localized electromagnetic field within Ag nanocube dimers can be maximized at their edge-to-edge configurations

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3.1 INTRODUCTION

Plasmonic coupling is the interaction of the surface plasmon resonances (SPR) supported by at least two nearby nanoparticles to generate new plasmon modes and strikingly enhance the intensity as well as density of local electromagnetic near-fields.¹ Instead of tailoring shapes and sizes of nanoparticles, plasmonic coupling efficiently manipulates light-matter interaction to finely tune the resonance frequency and electromagnetic (EM) fields' localization by simply playing with gaps, orientations and organizations of assembly using single particle morphology. For example, the plasmonic coupling behaviors within metallic nanoparticle chains,²⁻⁶ bow-tie structures,⁷⁻¹¹ nanodisk arrays¹²⁻¹⁴ are promising for applications including waveguide,^{5,6} laser,¹¹ printing,¹² and sensing.^{14,15} Dimer nanoparticle consisting of two nearby nanoparticles is the simplest coupled system, prevalently being used for sensing,^{1,16-18} detection,¹⁹ and SERS enhancement^{7,20-23} for many years, because of the high field localization at the inter-particle gap regions (hot spots). On the basis of simulation, interaction between nanospheres is understood in terms of the hybridization of plasmon modes that the dipolar modes of two particle surfaces hybridize to give a lower-energy mode and a higher-energy mode compared to the single-particle plasmon mode.

Fundamental studies which are conducted on dimers of nanodisks, nanospheres and on bow-tie structures by measuring extinction spectra demonstrate that the strength of plasmonic coupling exponentially decays with increasing gap distances.^{7,20,24} However, for nanostructures with less symmetry than these nanoparticles, orientation of particles in a dimer becomes another important parameter to consider. A theoretical simulation is conducted to study plasmonic coupling behaviors of Ag nanocube dimers with face-to-face and edge-to-edge configurations.²⁵ Calculated results for edge-to-edge nanocube dimer show 40% greater EM field intensity and stronger localization of oscillating dipoles near the gap region relative to face-to-face dimer. The large density of oscillating dipoles induces

high intensity ratio of high-energy modes in the calculated extinction spectra of edge-to-edge dimer. Moreover, SERS intensities of probe molecules are used as “hot spots” indicators on nanoparticle dimers to exhibit that the intensity of EM fields are varied with the configurations.^{7,20-23,26,27} To date, there is no direct observation on the changes of field localization with orientations of nanoparticle dimers. In addition, in-depth understanding of plasmon resonances that occur between the dimer particles and study on evolution of SP modes with the alteration of dimer orientations are currently lacking, especially for experimental investigations. The major challenge lies in spatially mapping of surface plasmon modes because they appear at sub-wavelength scale which are inaccessible to optical microscopes due to the diffraction limit.

Fast electron-based spectroscopic techniques including cathodoluminescence (CL)²⁸⁻³¹ and electron energy loss spectroscopy (EELS)³² circumvent the limitation on resolution and can achieve spatial mapping of surface plasmon modes at nanometer scale. In brief, fast electrons excite the surface plasmon resonances and transfer energy to the nanoparticles through electromagnetic interaction.^{33,34} Measuring the amount of energy allows us to experimentally explore the plasmonic behavior of the nanostructures. CL measurements detect the emitted light resulting from the electron-matter interaction and thus are related to the radiative plasmon modes which strongly couple to radiation. They are correlated to enhanced emission and scattering and known as “bright modes”.^{12,35,36} EELS measures the sum of energy loss of the electrons arising from interaction with the sample and detect both radiative and non-radiative modes. In contrast of radiative modes, non-radiative modes couple weakly with radiation and known as “dark modes”.¹⁰ These “dark modes” mainly decay in a manner of absorption and are fundamentally studied for applications like wave-guiding, lasing and sensing because of their low energy losses.^{5,6,11,37} As such, it is equivalently important to spatially investigate bright and dark plasmon modes within a nanostructure.

Combining EELS and CL measurements provides a complete understanding of plasmon modes and allows one to experimentally distinguish and compare “bright”/“dark” modes. For example, by measuring EELS and CL on the isolated Au nanoprism, radiative and non-radiative modes are directly sorted out. Direct comparison on radiative mode frequency in EELS and CL spectra enables the correlation of EELS and CL to the far-field extinction and scattering, respectively.³⁸ Plasmonic properties of isolated Au nanodecahedron are also investigated by combining EELS and CL.³⁹ Field localization of two dipolar modes on corners of Au nanodecahedron is directly visualized with sub-10 nm resolution.³⁹ We believe that combining these two high-performance techniques would provide insights into the plasmonic coupling within a nanoparticle dimer but such a study is currently lacking in the field. Even though EELS alone has been used to study plasmon resonances supported by dimers of Au nanosphere and Au nanoprism, these work focus on the “dark” plasmon modes within the dimer and has not investigated the plasmon modes evolution from isolated particle to a dimer.^{2,10} Plasmonic study on split-ring resonator and a bow-tie antenna experimentally exhibits the signature of coupling that plasmon modes hybridize to give two separate modes.^{40,41} However, there is no study on the effect of orientation to the plasmonic properties of dimers.

In this work, we use Ag nanocube dimer as a model system to investigate their plasmonic properties and obtain highly-resolved (<10 nm spatial resolution) plasmon maps of Ag nanocube dimers with different orientations. This project aims to experimentally obtain knowledge on plasmon resonances that occur between the dimer particles and to directly visualize plasmon modes and fields’ localization evolving with the dimer geometrical alteration. From both cathodoluminescence (CL) and electron energy-loss spectroscopies (EELS) results of Ag nanocube monomer and dimer, we directly observe a “mode splitting” which indicates the plasmon coupling within Ag nanocube dimers. We predict from CL mapping that these two coupling modes are radiative. To compare CL and

EELS results, a plasmon mode at ~ 3.45 eV is sorted out as a “dark” mode in both Ag nanocube monomer and dimer. Resonances at 3.45 eV are localized at the edges. Moreover, CL spectra are taken at gap, tip and edge region of the four configurations shifting from face-to-face to edge-to-edge configurations. The intensities of the high-energy modes gradually increase at these three regions during the shifting process. The percentage of high-energy modes for edge-to-edge dimer increases by 30%, 97% and 35% at the gap, tip and edge regions relative to the face-to-face dimer. High-energy modes are typically ascribed to high-order modes which are formed by two or more oscillating dipoles. Thus, we expect that edge-to-edge dimers support a increased density of dipoles which indicates intense EM fields on edge-to-edge relative to face-to-face dimers. Furthermore, CL intensity maps exhibit that the EM fields are localized at the tips, edges and gaps of all these four configurations. Spatial distribution of the two “splitting modes” are influenced by the symmetry of dimer configuration while the distributions of the high-energy modes are independent.

3.2 RESULTS AND DISCUSSION

CL and EELS Experimental Results for Ag Nanocube Monomer

To investigate the evolution of plasmon modes supported by Ag nanocube via coupling, we first study the plasmon modes and their distributions for Ag nanocubes under isolated condition. Hyper-spectral Cathodoluminescence (CL) and Scanning Transmission Electron Microscopy-Electron Energy Loss Spectroscopy (STEM-EELS) imaging are performed on single-particle Ag nanocubes seated on Si_3N_4 TEM grid. By using hyper-spectral imaging, we acquire a full set of spectra and maps at each spatial position as the electron beam raster-scans the particle. Plasmon modes of individual plasmonic nanoparticles can be identified spectrally and spatially simultaneously with spatial resolution of ~ 10 nm in the later analysis. Single-crystalline Ag nanocubes with the edge length of ~ 110 nm are synthesized through

the polyol reduction method. The synthesized Ag nanocubes are uniform in sizes and morphologies after purification, reducing the probability of spectral changes arising from morphological variations, such as sizes and edge rounding for each measurements.^{38,42} We spatially investigate the plasmonic behaviour at the tip and edge areas where the enhanced electromagnetic fields are normally localized. For CL and EELS maps, the surface plasmon modes are analyzed by fitting each spectrum to a sum of Gaussian functions and each Gaussian peak can be associated with a specific plasmon mode.^{43,44}

CL spectra taken from the nanocube edges (P1) and tips (P2) show three plasmon modes, respectively (Figure 3.1A). In total, there are four distinct modes including 2.10, 2.70, 3.10 and 3.35 eV, by fitting these two CL spectra. We then investigate the distributions of these four distinct SPR modes through the CL intensity maps. At 2.10 eV, both tips and edges are in strong resonances (Figure 3.1D-ii). Similar emission intensity levels are observed at tips and edges. At 2.70 eV, emission is stronger at the four tips than at the edges (Figure 3.1D-iii). At 3.00 eV, only the four tips are lit up (Figure 3.1D-iv) while emission at 3.35 eV is too weak to be recognized. Comparing the CL spectra extracted from edge and tips, the frequencies of the first and second plasmon modes are almost the same but the intensity ratio of the second plasmon mode (2.70 for P1 and 2.78 for P2) to the first mode (2.10 for P1 and 2.15 for P2) is higher on the tips (P2) than on the edges (P1).

For EELS spectra measured at both edges and tips, there are also four plasmon modes which are located at ~1.90, 2.70, 3.20 and 3.45 eV (Figure 3.1B). EELS maps obtained at 1.90, 2.70 and 3.20 eV demonstrate that both tips and edges are in resonances with stronger energy-loss at the tips (Figure 3.1Eii-iv). At the energy window of the 3.45-eV mode, only the edges are in resonances.

Figure 3.1. CL and EELS experimental results for Ag nanocube monomer. (A) CL and (B) EELS spectra taken from (i) P1 position at tip and (ii) P2 position at edge of Ag nanocube, respectively. (C) Comparison of CL (blue) and EELS (red) taken at (i) tip and (ii) edge, respectively. (D) (i) SEM image and (ii-v) CL maps of modes shown in (A). (E) (i) EELS-HAADF image and (ii-v) EELS maps of modes shown in (B). All scale bars represent 100 nm.

To compare the experimental results of CL and EELS, the intensity of high-energy modes are different. Four distinct SPR modes supported by individual nanocube can be generalized from both CL and EELS spectra (2.10 (1.90), 2.70, 3.10(3.20) and 3.35(3.45) eV). The 3.45 eV mode in the EELS spectra taken from edges is strikingly strong and the EELS map of this mode demonstrates resonance distributed on the edges (Figure 3.1E-v). In contrast, this mode in the CL spectra is of rather low intensity and the related CL maps show weak emission along the edges. According to the previous studies on CL and EELS,

CL results indicate the presences of radiative plasmon modes (bright modes) while EELS results exhibit both radiative and non-radiative modes (dark modes).^{2,45} As such, the high-energy mode at ~3.4 eV arises from non-radiative surface plasmon resonances. Moreover, the intensity of this dark mode in EELS spectra is much higher than the two radiative modes. For example, in the EELS spectra taken from edges, the intensity of the 3.45-eV modes is 7 times higher than the 1.83-eV mode and 6 times higher than the 2.68-eV mode. The strength of this high-energy dark mode is higher than the low-energy bright modes in Ag nanocubes, but this part of the energy is inelastically absorbed instead of being scattered. To validate our hypothesis and investigate origins of each plasmon modes, we will correlate the experimental results with simulation in the future.

CL and EELS Experimental Results for Ag Nanocube Dimer

Next, in order to spatially investigate the plasmonic coupling of Ag nanocubes at the nanometer scale, we conduct CL and EELS measurements on individual Ag nanocube dimer which is the simplest coupling system of Ag nanocubes. Two nanocubes are perfectly face-to-face aligned in the nanocube dimer, observed from the SEM and HAADF images (Figure 3.2). Apart from analyzing the CL and EELS spectra taken from tips and edges, we study the plasmonic behaviour at the gap regions.

Figure 3.2. CL and EELS experimental results for Ag nanocube dimer. (A) CL and (B) EELS spectra taken from (i) P1 position at gap (ii) P2 position at tip and (iii) P3 position at edge of Ag nanocube, respectively. (C) Comparison of CL (red) and EELS (blue) taken at (i) tip and (ii) edge, respectively. (D) (i) CL-HAADF image and (ii-v) CL maps of modes shown in (A). (E) (i) EELS-HAADF image and (ii-vi) EELS maps of modes shown in (B). All scale bars represent 100 nm.

We can fit four plasmon modes from each CL spectrum which are taken at the gap (P1, Figure 3.2-i), tip (P2, Figure 3.2-ii) and edge (P3, Figure 3.2-iii). They are centered at 1.85, 2.30, 2.60 and 3.00 eV. CL intensity maps of these four energy windows also illustrate different field distributions of the corresponding modes (Figure 3.2D). More specifically, at the energy window of 1.85 eV, two ends along the long axis show strong resonance,

presenting the distribution of a dipolar mode (Figure 3.2D-ii). At the energy window of 2.30 eV, all tips and edges are lit up but the emission from tips at two ends are relatively strong (Figure 3.2D-iii). At 2.60 eV, CL emission are merely observed at the end tips and gap region (Figure 3.2D-iv). All the tips and edges are at resonances again at 3.00 eV, but the emissions are relatively intense at the tip and gap regions.

On the other hand, five distinct plasmon modes (1.38, 2.28, 3.00, 3.25 and 3.45 eV) are fitted into the EELS spectra taken at the gaps, tips and edges. EELS maps obtained at the energy window of 1.38, 2.28, 3.00 and 3.25 eV (Figure 3.2Dii-v) show similar distribution of the modes with the corresponding CL maps (Figure 3.2Eii-v). The only exception is that we observe resonances along the edges at 3.45 eV in EELS maps while no obvious emission is presented in the related CL maps (Figure 3.2D-vi and 2E-vi). The intensity of the 3.45-eV mode is also relatively high in the EELS spectra. These results collectively indicate that this mode is a dark mode.

Comparison on Ag nanocube monomer and dimer: CL and EELS

Evolving from Ag nanocube monomer to dimer, both CL and EELS spectra exhibit disappearance of one broad mode and it is likely “splitting” into two separate modes in the low energy range (1.5-2.5 eV). For CL, the 2.10-eV mode in monomer disappears via coupling and two separate modes at 1.85 and 2.40 eV appear in the dimer structure. For EELS, the “mode splitting” is also observed at low-energy range. The 1.90-eV mode supported by a monomer splits into 1.38 and 2.28-eV modes supported by a dimer. Such a “mode splitting” phenomenon coincides with the results of previous numerical and EELS studies on plasmon hybridization within dimers of nanosphere,⁴⁶ split-ring resonator⁴⁰ and a bow-tie antenna.⁴¹ This is the first time whereby such a signature of plasmon coupling is observed within nanocube dimers. It is noteworthy that these two new modes probably arise from coupling of two low-energy modes (i.e. dipole-dipole coupling) or from coupling of

one low-energy mode and one high-energy mode (i.e. dipole-multipole coupling) supported by individual nanocubes. Plasmon hybridization and Fano resonance can both induce to the two splitting modes in the spectra. The contribution of these two plasmon coupling phenomena to the near-field enhancement is unknown at the current stage, but we hypothesize that plasmon hybridization dominates the near-field enhancement on Ag nanocube dimers based on the similar widths of the two bands shown in the EELS spectra.⁴⁷ Moreover, the lower-energy mode in dimer is detected at 1.38 eV in EELS spectra which is red-shifted by ~ 0.42 eV when compared with the mode detected in CL. The reason inducing to this big red-shift in EELS is unknown from the experimental results. For high-energy modes (2.5-3.5 eV), much smaller shifts than low-energy modes are observed upon coupling. Future work here will involve correlating the experimental results with numerical simulation, in order to understand the underlying physics of the “mode splitting” phenomenon and to theoretically investigate the evolution of plasmon modes from monomer to dimer.

Figure 3.3. Comparison of Ag nanocube monomer and dimer. CL spectra of (A) Ag nanocube monomer and (B) Ag nanocube dimer, taken from (i) tip and (ii) edge position, respectively. EELS spectra of (C) Ag nanocube monomer and (D) Ag nanocube dimer, taken from (i) tip and (ii) edge position, respectively.

Investigation on the Effect of Orientation to the CL Results

CL measurements are also carried out on Ag nanocube dimers with various extents of misalignment ranging from face-to-face to edge-to-edge configurations. It is to investigate the effect of dimer orientations on their optical properties and to observe the evolution of plasmon modes with the shifting of two nanocubes from the perfectly aligned face-to-face dimer (Figure 3.3). The extend of shift (S) is calculated by using the equation $S = X/L$, where X is the distance by which the nanocubes shift from the perfectly aligned position and L is the edge length of the nanocube (Figure 3.3A). We measure CL on four dimer configurations with S ranging from 0 (face-to-face) to 0.15, 0.40 and in the end to 1 (edge-to-edge).

Figure 3.3. CL spectra taken on different configurations of Ag nanocube dimers. (A) Scheme of shifting the face-to-face configuration to edge-to-edge configuration. CL spectra are taken from (i) gaps, (ii) tips and (iii) edges of configurations with (B) $S1 = 0$, (C) $S2 = 0.14$, (D) $S3 = 0.4$ and (E) $S4 = 1$, respectively. (iv) in (B-E) shows SEM images of corresponding dimers and P1, P2, P3 indicate the locations where the CL spectra in (i)-(iii) are taken from. All scale bars represent 100 nm.

Four gaussian peaks can be fitted in the CL spectra which are taken from gaps (P1), tips (P2) and edges (P3) of these four dimer configurations. During the configuration shifting, no obvious differences are observed in the frequencies of these four modes but the intensities of these modes are gradually changing. To compare the contribution of each

mode in these configurations, we calculate the percentage of each gaussian peak in a CL spectrum. Slight shifting from face-to-face configuration ($S=0$) to where $S = 0.15$, the percentage of high-energy modes (2.7 and 3.1 eV) increases by 11.6% in the CL spectra of gap region (Figure 3.3B and C). When S increases from 0.15 to 0.4, this percentage is unchanged (Figure 3.3C and D). When S increases from 0.4 to 1, the percentage of high-energy modes increases by 17%, 110% and 68% at gap, tip and edge respectively (Figure 3.3D and E).

In general, shifting from face-to-face to edge-to-edge configurations, the contribution of the high-energy modes increases by 30%, 97% and 35% at the gap, tip and edge regions, respectively (Figure 3.3B and E). El-Sayed *et al.* have reported in a numerical study that the interaction of two Ag nanocubes occurs at a longer distances for edge-to-edge dimers than face-to-face dimers. The increased interaction at a greater distance is ascribed to the increased contribution of the higher-order modes within a edge-to-edge dimer. This theoretical result coincides with and further supports our CL mapping result. On the other hand, their theory is experimentally validated by our CL measurements for the first time. High percentage of the higher-order modes which are formed by two or more oscillating dipoles supports relatively high density of free electrons and intense localized electromagnetic fields. As such, we hypothesize that localized electromagnetic field within Ag nanocube dimers can be maximized at their edge-to-edge configurations.

In addition, we compare the distribution of the four plasmon modes among these four configurations to observe the field localization evolving with the configuration shifting. (Figure 3.4). Two “splitting” modes located at 1.85 and 2.30 eV present in the CL spectra of dimers at each stages of orientation changes (Figure 3.4). At 1.85 eV, intense emissions are always observed at the two ends of the long axis (Figure 3.4Ci-Fi). In general, resonance areas of this modes evolve from four tips and two edges to six tips and four edges, during the shift from face-to-face to edge-to-edge configurations. At 2.30 eV, all tips and edges are

lit up with relatively strong emission at the tips located at the end of the long axis (Figure 3.4Cii-Fii). In the shifting process, asymmetric resonance appear when the symmetry of the dimer is broken ($S = 0.15$, Figure 3.4D-i and -ii) while the resonance returns to be symmetric when the symmetry of dimer is recovered ($S=1$, Figure 3.4F-i and -ii). For the distribution of high-energy modes, at 2.70 eV, we observe strong CL emission at the end tips and weak emission at the tips beside the gap region (Figure 3.4Ciii-Fiii). At 3.10 eV, all the tips and edges are at resonances in which the emissions are relatively intense at the tips (Figure 3.4Civ-Fiv). At these two high-energy modes, the areas at resonances remain the same and the distributions are independent with the symmetry when shifting from face-to-face to edge-to-edge configurations. For these four configurations, distributions of plasmon modes are observed at the tip, edge and gap region. It is noteworthy that the emission is stronger at the tips than at the gap region for plasmon modes in the range of 1.5-3.5 eV.

Figure 3.4. CL maps of plasmon modes supported by different configurations of Ag nanocube dimers. (A) Scheme of shifting the face-to-face configuration to edge-to-edge configuration. (B) CL maps of Ag nanocube monomer at (i) 2.10, (ii) 2.70 and (iii) 3.10 eV, respectively. (C-F) CL maps of nanocube dimers with (C) $S1 = 0$, (D) $S2 = 0.14$, (E) $S3 = 0.4$ and (F) $S4 = 1$ at (i) 1.80, (ii) 2.30 (iii) 2.70 and (iv) 3.10 eV, respectively. (v) in (C-F) shows SEM images of corresponding dimers. All scale bars represent 100 nm.

3.3 CONCLUSION

In summary, we have experimentally investigated plasmon resonances that occur between the dimer particles and directly visualized the evolution of surface plasmon modes

and fields' localization with the shift of dimer orientation, using both highly-resolved (<10 nm spatial resolution) plasmon maps of cathodoluminescence and electron energy-loss spectroscopies. In the range of 1.5-3.5 eV, combining CL and EELS measurements demonstrates that four plasmon modes are supported by Ag nanocube monomer and five plasmon modes are supported by nanocube dimer. Upon plasmon coupling, the lowest-energy mode in monomer disappear with the appearance of two separate modes at 1.85 and 2.30 eV, while frequencies of the other three high-energy modes have no striking changes. By comparing CL and EELS, a "dark" mode at 3.45 eV is sorted out for Ag nanocube monomer and dimer. This "dark" mode is mainly distributed on the edges. Moreover, the localizations of all the plasmon resonances in the range of 1.5-3.5 eV are observed at the tip, edge and gap regions of a dimer. The distribution of the two "splitting" modes can be influenced by the symmetry of dimer configuration while that of the high-energy modes is independent with the configuration. Furthermore, the percentage of high-energy modes within a nanocube dimer is tunable and increased in the process of shifting from face-to-face to edge-to-edge configurations. This experimental result is coincide with the numerical study reported by El-Sayed *et al.* and we hypothesize that intensity of localized electromagnetic field within Ag nanocube dimers can be maximized at their edge-to-edge configurations. This work provides insights of plasmon resonance behaviour within a coupling system of Ag nanocube via experiments. The methods combining CL and EELS can be used to investigate plasmonic properties of other morphologies and coupling systems. To investigate the nature of each plasmon modes and to understand the underlying physics of plasmonic coupling of Ag nanocubes, we will correlate the experimental results with simulation in the near future.

3.4 MATERIALS AND METHODS

Materials. Silver nitrate, poly(vinylpyrrolidone) (PVP, average $M_w = 55,000$), copper chloride and 1-hexanethiol were purchased from Sigma Aldrich. Milli-Q water ($>18.0 \text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system. Low stress 30-nm-thick SiN TEM windows were purchased from Norcada Inc.

Synthesis and purification of Ag nanocubes. In brief, 0.083 g copper chloride was dissolved in 10 mL 1, 5-pentanediol by sonication and vortex. In another vial 0.20 g PVP ($MW = 55000 \text{ amu}$) was dissolved in 10 mL pentanediol and then 0.20 g silver nitrate and 35 μL copper chloride was added in 10 mL pentanediol. 20 mL pentanediol was stirred and heated at 190°C for 20 min in a round-bottomed flask (100 mL). 500 μL silver nitrate was quickly injected into round-bottomed flask, followed by drop-wise injection of 235 μL PVP, then injecting silver nitrate solution for every 1 min and PVP solution for every 30 sec. The reaction is stopped at 30 min. In the process of purification, the Ag nanocubes were first separated with pentanediol through centrifugation. After removing the pentanediol, Ag nanocubes were dispersed in 10 mL ethanol. Then, Ag nanocube solution was dispersed and preserved in the PVP solution (aqueous, 100 mL, 0.2 g/L). The resulting solution was vacuum-filtered using PVDF filter membranes with pore sizes ranging from 5 μm , 650 nm, 450 nm and 200 nm. The filtration was repeated for several times with each pore size.

Ligand exchange reactions. 0.5 μL of concentrated Ag nanocube suspension was washed for once and re-dispersed into 1.5 mL of mixture of H_2O and IPA (volume ratio is 1:1). Then 1 μL of 1mM 1-hexanthiol was injected into the suspension under stir (500 rpm). After 3 hours, the liquid mixture was removed through centrifugation and nanocube was re-dispersed into another 1.5 mL of mixture of H_2O and IPA. 1 μL of 1mM 1-hexanthiol was injected into the suspension under stir (500 rpm) for another 4 hours before removing the liquid mixture through centrifugation. Powder of nanocube functionalized with hexanthiol

was preserved in the N₂ box. 1-hexanethiol was supposed to form a self-assembled monolayer (SAM) on the Ag nanostructures due to a strong coordination bond Ag-S.

Self-assembly of silver nanocubes: 1 μ L of nanocube powder was dispersed in 1 mL of ethanol. The nanocube suspension was diluted for 10000 times before being dropped onto the SiN TEM window. The thickness of the SiN membrane is 30 nm.

Cathodoluminescence hyperspectral imaging experiments. Quantitative cathodoluminescence was carried out using an Attolight Rosa 4634 microscope, which 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). Electron beam energies of 9 kV were used to excite the samples. The beam dwell time was set to 0.2 s.

Characterization. Scanning electron microscopy (SEM) (JEOL-JSM-7600F) was performed with an accelerating voltage of 5 kV.

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4 Plasmonic Nanopillar Arrays Encoded with Multiplex Molecular Information for Anti-counterfeiting Applications**

ABSTRACT. A major challenge in information security and developing anti-counterfeiting platform is to encode multiple identification features which can be decoded with no interference on a single platform. Here, we demonstrate a progressively complex anti-counterfeiting platform using a multiplex fabrication strategy. This multiplex strategy enables us to realize the spatially selective encapsulation of dye molecules within a Ag nanopillar array, embedding covert molecular information which are revealed in the form of fluorescence, surface-enhanced Raman scattering (SERS), and signal intensities. A total of five identification layers can be used to authenticate genuine products in our nanopillar platform. Moreover, two spectroscopic techniques are required to fully decode the various covert layers encoded within the same nanopillar array, thereby greatly enhances the information security. Hyperspectral imaging technique precisely generates unique SERS fingerprints of molecules encapsulated in each nanopillars, making our anti-counterfeiting platform extremely difficult to be forged when combining with high information density of ~17,000 pillars per inch (ppi). Our encoding platform enables high security, large information density and low-error decoding.

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4.1 INTRODUCTION

There is vast amount of digital information generated daily ($\sim 2.5 \times 10^{18}$ bytes) in modern society.¹ Effective protection of these data against unwanted or accidental information thefts is increasingly important in a digital era. Information security entails encoding information such that only authorized parties can read it; decoding involves the use of advanced and complicated spectroscopic techniques which are not readily accessible by the general public. On the other hand, fast-growing product forgery causes enormous financial damage and threatens public health, driving immediate urgency in developing complex anti-counterfeiting platforms. Nanoparticles and nanostructures are promising materials for information security and anti-counterfeiting: their small dimensions and unique optical properties enable encoding of high-density information which can be read out by using advanced analytical instruments as identification. For example, structural colors,²⁻⁷ fluorescence/photoluminescence,⁸⁻¹⁰ and surface-enhanced Raman scattering (SERS)¹¹⁻¹³ are some commonly used techniques for security labels. However, the optical signal outputs of the stored information in these nanostructures depend strongly on their physical features (morphology and structural orientations). Minor changes in physical features during fabrication can lead to false signals. Furthermore, these physical features are easily discernible under optical or electron microscopy, implying that these platforms are unable to securely hide the data stored.

To further secure information and deter forgery, additional optical features are always embedded within the physical features. Multiplexing is an attractive approach to incorporate multiple features within a single platform which can subsequently be selectively and individually read out. These optical features are independent of nanostructure morphology, and can only be fully decoded using any of the aforementioned spectroscopic techniques chosen by the authorized parties.¹⁴⁻¹⁹ However, these systems primarily use one read-out

technique per platform. Security level can be further increased by using a platform with multiple layers of identification features to distinguish between authentic and fake products. To achieve a multiple-layer encoding platform using a multiplexing strategy, the major challenge is to prevent signal interferences among multiple features and obtain low-error readouts using various spectroscopic techniques in the multiplex system.

Here, we demonstrate a multiple-layer anti-counterfeiting platform with enhanced information security using a multiplex fabrication strategy. The aim is to develop an information encoding platform with large information density, high security and low-error decoding. A progressively complex anti-counterfeiting platform is achieved by utilizing arrays of nanopillars fabricated using two-photon photolithography, where multiple identification layers of molecular information are read out in the form of fluorescence, SERS, and their signal intensities. In addition, we create covert nanoscale patterns by devising a protocol to selectively encapsulate multiple dye molecules (multiplex) over different areas of the same substrate. These images can only be fully decoded using both fluorescence and SERS hyperspectral imaging. Decoding accuracy is enhanced due to the independence of optical readouts from the physical features. Furthermore, the combination of the high information density that is $\sim 17,000$ pillars per inch with hyperspectral imaging technology indicates that $\sim 17,000$ complete spectral information can be fully decoded within every inch. This further enhances accuracy of data outputs and the information security.

4.2 RESULT AND DISCUSSION

Nanopillar Fabrication

We fabricate arrays of structurally identical nanopillars for our anti-counterfeiting platform using two-photon photolithography. A benzylidene ketone-based photoresist serves as both photo-initiator and monomer (Scheme 1). Dye molecules such as rhodamine

6G (R6G) and eosin Y (EY) can be easily encapsulated within the nanopillars by mixing the dye solution with the photoresist prior to the laser writing process. Following photopolymerization, the nanopillars are rendered SERS-active by thermally evaporating 25 nm of Ag layer (Scheme 4.1). The SERS signals are detected because of the nanoscale asperities serving as hot spots generated by the thermal evaporation process and 532-nm laser generates sufficient near-field enhancements to enhance the Raman signals on these nanoscale asperities.^{11,19} Photolithography enables us to achieve high structural fidelity and precision in the fabrication of the dye encapsulated nanopillar arrays (Figure 4.1A, B). The diameters of the Ag coated nanopillars are 520 ± 20 nm (Figure 4.1A, B), with average heights of 1.1 ± 0.1 μm (Figure 4.1C, D). The plasmon bands of these Ag coated nanopillars with large sizes and dielectric cores are predicted to be in the near- and mid-infrared region.²⁰⁻²² Thermal evaporation of Ag generates nanoscale asperities serving as hot spots for SERS detection on the surfaces of nanopillars.^{11,19} In addition, the presence of dye molecules does not affect the fabrication of the nanopillars (Figure 4.2).

Scheme 4.1. Fabrication of Ag nanopillars using two-photon photolithography. Left, resin comprising the photoresist and probe molecules (rhodamine 6G, R6G; eosin Y, EY) is drop-cast on a glass slide. The resin is polymerized into pre-defined nanopillar morphology via direct laser writing. Right, Ag nanopillars are fabricated via thermal evaporation. Probe molecules are incorporated into the nanopillars during the laser writing process. Two types of Ag nanopillars (R6G- and EY-encapsulated nanopillars) can be fabricated.

Figure 4.1. Dual spectroscopic readout on a single-dye encapsulated nanopillar array. (A, B) SEM and (C, D) AFM images of a 5×6 array of nanopillars deposited with Ag film, respectively. (E) Fluorescence spectra and (F) images taken from R6G- (red) and EY-encapsulated nanopillars (blue), respectively. (G) SERS spectra and (H) images taken from R6G- (red) and EY-encapsulated nanopillars (blue), respectively. Scale bar in (B) represents 200 nm and other scale bars represent 2 μm .

Figure 4.2. Comparison on morphologies of photoresist nanopillar and dye-encapsulated nanopillars. SEM images of (A) photoresist nanopillar, (B) R6G-encapsulated nanopillars, and (C) EY-encapsulated nanopillars, respectively. Scale bar represents 5 μm .

We then investigate the information encoding capability of the nanopillar arrays, making use of 2D hyperspectral imaging spectroscopy to retrieve the embedded fluorescence and SERS information. The fluorescence images of the R6G- and EY-encapsulated nanopillars demonstrate uniform fluorescence intensity when the emission peaks of R6G and EY are selected at 560 nm and 630 nm, respectively (Figure 4.1E, F, 3A and B). In addition to fluorescence read-out, the xy SERS images of R6G-encapsulated nanopillars show the nanopillars exhibiting similar brightness when the characteristic vibrational mode of R6G at 622 cm^{-1} is selected for image generation (Figure 4.1G, H and 3Ci). Similarly, identical brightness is observed for the EY-encapsulated nanopillars using the 1639 cm^{-1} vibrational fingerprint of EY (Figure 4.1G, H and 3Cii). A complete vibrational mode assignment of the SERS spectra is given in Tables 4.1-2.²³⁻²⁵ The photoresist does not complicate the SERS spectra as compared to commercially available photoresists such as IPL-780 (Figure 4.4). Nanopillars produced by using the commercial photoresist IPL-780 create non-homogeneous and disordered SERS signals (Figure 4.4A), because IPL-780 is composed of two ingredients as monomer and photo-initiate separately. Different polymerization extents generate various molecular structures, giving rise to the non-homogeneous SERS signals. Moreover, selecting at 1607 cm^{-1} which is the common peak shown in all SERS spectra gives rise to non-uniform SERS images (Figure 4.4A), thus IPL is not a suitable base material for SERS applications in our current system. On the other hand, SERS measurement on the nanopillar arrays fabricated by using our photoresist with a single component gives rise to clean SERS spectra with three main vibrational modes at 1180 , 1370 and 1607 cm^{-1} (Figure 4.4D). Selecting at 1607 cm^{-1} homogeneously illuminates the entire array in SERS images.

Figure 4.3. Homogeneity of SERS and fluorescence signals on dye-encapsulated nanopillars. (A) Fluorescence images taken from the (i) R6G- and (ii) EY-encapsulated nanopillars at 560 (for R6G) and 630 nm (for EY). (B) Cross-sectional fluorescence intensity profile along lines 3 and 4, labeled in (A). (C) SERS images of (i) R6G- and (ii) EY-encapsulated nanopillars created by selecting their respective vibrational bands at 622 (for R6G) and 1639 cm^{-1} (for EY). (D) Cross-sectional SERS intensity profile along lines 1 and 2 in (C). Scale bar represents 2 μm .

Figure 4.4. SERS spectra comparison between commercial photoresist IPL-780 and our photoresist. (A) SERS spectra of Ag-coated pure IPL structures taken at points I, II, and III. (B) bright-field microscopic and (C) SERS images of Ag-coated pure IPL-780 arrays using the 1607 cm^{-1} vibrational peak. (D) SERS spectra taken from Ag-coated pure photoresist

arrays using our photoresist. (E) bright-field microscopic and (F) SERS images of Ag-coated pure photoresist arrays. The colors are assigned by relative intensity of the spectrum at 1607 cm^{-1} . Scale bar represents $5\text{ }\mu\text{m}$.

Table 4.1. Assignment of major vibrational peaks in SERS spectra of R6G-encapsulated nanopillars.

SERS band (cm^{-1})	Band assignment
622	xanthene ring/phenyl ring
785	in-plane deformation of the xanthene ring
1180	benzene ring stretches/symmetric CO_2 stretch
1321	$\text{C}=\text{C}$ stretching vibration
1370	xanthene ring stretches/carboxylate stretches
1519	xanthene ring
1583	$\text{C}=\text{O}$ stretching vibration/ $\text{C}=\text{C}$ symmetric stretching motion in phenyl group
1607	phenyl ring stretches
1660	$\text{C}=\text{C}$ symmetric stretching mode in xanthene ring

Table 4.2. Assignment of major vibrational peaks in SERS spectra of EY-encapsulated nanopillars.

SERS band (cm^{-1})	Band assignment
656	xanthene breathing/benzene ring breathing
779	xanthene ring stretches
1180	xanthene and benzene ring stretches/symmetric $-\text{COO}$ stretch
1337	xanthene and benzene ring $\text{C}-\text{C}$ stretches

1370	xanthene ring stretches/carboxylate group stretch
1420	xanthene ring stretches
1560	xanthene ring stretches
1607	benzene ring stretches
1639	xanthene ring stretches

These observations collectively indicate that our nanopillar platform is capable of using both fluorescence and SERS as read-out techniques for deterring forgery. Notably, this is also the first time in which SERS/fluorescence dual readouts are used for anti-counterfeiting and potentially data storage. Using two spectroscopic readouts in a single anti-counterfeiting platform enhances the complexity of our anti-counterfeiting platform and thus increases the level of security. Compared with the detection-based platforms which can also simultaneously detect SERS and fluorescence, our encoding platform is capable of hiding and locating the dye molecules within the arrays consisting of nanopillars with the same physical features.²⁶⁻²⁹ The independency of multiple readouts with physical features enhances the decoding accuracy and increases the security level. Moreover, the encoding strategy is simple and straightforward as compared with the bio-analysis systems.³⁰⁻³² Fluorescence and SERS serve as two layers of identification features in our anti-counterfeiting platform and increase the security levels compared with conventional platforms where merely SERS or fluorescence is read out. Furthermore, imaging technique precisely generates unique SERS spectra of molecules encapsulated in each nanopillar, serving as fingerprints of each nanopillar for authentication. Thus, security level can be further enhanced by maximizing the number of nanopillars which can be fully resolved in the hyper-spectral images. This number is defined as information density.

Information Density & Grayscale-covert Array

An information density of 17,000 pillars per inch can be achieved in a nanopillar array encapsulated with one probe molecule, in which each nanopillar encoded with the molecular information. This information density is determined by the minimum distance between the individual nanopillars which can be fully imaged in the fluorescence/SERS images without significant changes in signal intensities. We determine the information density of our platform by fabricating square arrays of R6G-encapsulated nanopillars with inter-pillar gaps of 3.5, 1.5, 1.0 and 0.5 μm (Figure 4.5A-D and Figure 4.6A-D). The corresponding xy SERS/fluorescence images demonstrate that the dye-containing nanopillars need to be spaced at least 1 μm apart from each other (Figure 4.5C and Figure 4.6C). Otherwise, at smaller inter-pillar gaps (0.5 μm), the fluorescence/SERS measurements on the array demonstrate un-resolved images and higher signal intensities compared with other arrays with larger inter-pillar gaps (Figure 4.5D and Figure 4.6D). We separately measure the resolution limit of our hyper-spectral imaging technique and the results show two nanopillars should be separated over the length of 0.8- μm in order to be fully resolved in SERS imaging (Figure 4.7). Below the resolution limit, we observe a signal “spillover” effect that the signals from the side nanopillars are accumulated within the gap region to induce the entire area lighting up as one block (Figure 4.5D, 4.7A and B). In all, a density of 17,000 dot per inch is achieved by using our strategy, with each nanopillar representing a dot (Figure 4.5C and Figure 4.6C). Our platform outperforms commercial techniques such as inkjet printing, which typically achieves a density of only 1000 – 10000 dot per inch.^{33,34}

Figure 4.5. Information density and intensity grayscale. (A-D) SEM (left) and SERS (right) images of R6G-encapsulated nanopillars with different inter-pillar gaps. The distances between the pillars are (A) 3.5 μm , (B) 1.5 μm , (C) 1 μm and (D) 0.5 μm . An inter-pillar gap of (C) 1 μm is required to fully distinguish the pillar morphology in the SERS images. (D) Un-resolved SERS images and higher signal intensities are obtained at pillar array with smaller inter-pillar gaps, arising from plasmonic coupling and resolution limit of the hyperspectral imaging technique. However, we can make use of this to achieve a three-level signal output to create (E-H) an intensity grayscale. (E) SEM and (F) SERS images of nanopillar array consisting of R6G-encapsulated nanopillars and blank nanopillars. (G) Cross-sectional SERS intensity profiles at diagonal line labeled in (F). (H) Overlaid SERS image and SEM image. The colors in SERS images are assigned by the vibrational signature of R6G at 622 cm^{-1} . All scale bars represent 5 μm .

Figure 4.6. Fluorescence intensity grayscales of the nanopillar array. (A-D) Fluorescence images of R6G-encapsulated nanopillars with different inter-pillar gaps. The distances between the pillars are (A) 3.5 μm , (B) 1.5 μm , (C) 1 μm and (D) 0.5 μm . (E) Fluorescence image and cross-sectional SERS intensity profile along (F) line 1 and (G) line 2 labeled in (E), respectively. Scale bar represents 5 μm .

Figure 4.7. Influence of gap distance in the R6G-encapsulated nanopillar dimer. (A-D) SEM and (E-H) Overlapping SERS images of R6G with SEM images of Ag nanopillar dimers with inter-pillar gap distances of 200, 500, 800 and 1100 nm, respectively. The colors in SERS images are assigned by the vibrational signature of R6G at 622 cm^{-1} . All scale bars represent 1 μm .

Based on the abovementioned inter-pillar-gap dependent outputs, more sophisticated information encoding can be achieved by adding the signal intensities (SERS and fluorescence) as additional information read-out channels in addition to SERS and fluorescence read-outs. To demonstrate this, we fabricate a 25×25 array of nanopillars

spaced 0.5 μm apart (Figure 4.5E). From SEM images, we observe no morphological difference among these nanopillars. In fact, this array consists of R6G-encapsulated nanopillars as the information containing nanopillars and blank nanopillars which act as the ‘dummy filler’ to shield the positions of real data stored within the nanopillar matrix. The covert information can only be revealed by hyperspectral SERS/fluorescence imaging techniques. The center of this large array is a 3×3 array of R6G-encapsulated nanopillars (Figure 4.5H-i). This is followed by an 11×11 array of R6G-encapsulated and blank nanopillars, where the R6G-encapsulated nanopillars are alternately spaced apart by the blank nanopillars and the separation distance between two R6G-encapsulated nanopillars is 1.5 μm (Figure 4.5H-ii). Beyond this, the R6G-encapsulated nanopillars are separated from each other by three blank nanopillars, with a separation distance of 3.5 μm (Figure 4.5H-iii).

The corresponding xy-SERS image of this array forms a layered concentric square when the 622 cm^{-1} vibrational fingerprint of R6G is selected, showing three levels of intensity output (Figure 4.5F). The strongest signals are observed in the center 3×3 array of R6G-encapsulated nanopillars at ~ 453 counts per second (cps). The next strongest signal is recorded from the regularly spaced R6G-encapsulated nanopillars in the outer layers at ~ 237 cps (Figure 4.5G). Compared with outer-layer arrays (Figure 4.5H-ii and -iii), the stronger SERS intensity detected from the center 3×3 array (Figure 4.5H-i) results from SERS enhancement of double amount of R6G loaded in this array and the “spillover” effect of resolution limit. No R6G signal is observed from the blank nanopillars (Figure 4.8). By normalizing the SERS intensities from the maximum, a gradient of SERS values at 1, 0.5 and 0 are obtained. A similar signal intensity-based grayscale image (1, 0.5, and 0 intensities) can also be observed in the fluorescence image by selecting the emission peak of R6G at 560 nm (Figure 4.6E). Thus, we are able to arbitrarily locate these grayscales with three read-outs of information (fluorescence, SERS and signal intensities), by using blank

nanopillars which give no R6G signals to control the gaps. Furthermore, these intensity grayscale images are covert pieces of information, where normal characterization such as SEM is unable to decode the concentric squares at all (Figure 4.5E, F). Consequently, the intensity grayscale images as well as their locations serve as additional identification information of complicated security labels to distinguish between authentic and fake products.

Figure 4.8. Intensity profile of the grayscale nanopillar array. (A) Overlaid SERS and SEM images. (B) Cross-sectional SERS intensity profile along line 1 in (A). Scale bar represents 5 μm .

Multiplex Array

Next, we develop a multiplex encoding strategy to further enhance the complexity of our nanopillar platform. We selectively encapsulate R6G and EY on different areas of the same nanopillar array using a two-step polymerization process (Figure 4.9A), starting with the fabrication of R6G-encapsulated nanopillars. To do so, the individual nanopillars are encoded with their own molecular information. A 4-nm layer of alumina is then deposited over the R6G-encapsulated nanopillars using atomic layer deposition to prevent the R6G molecules from leaching out of the nanopillars. EY-encapsulated nanopillars are subsequently fabricated, followed by thermally evaporating 25 nm of Ag to render the entire substrate SERS active (Figure 4.10). It is noteworthy that we deposit 25-nm thickness of Ag layer to give both strongly SERS-active and fluorescence-active nanopillars in the multiplex array. In the typical experiment to optimize the Ag thicknesses, three multiplex

arrays of nanopillars encapsulated with R6G and EY are fabricated by using the same protocol demonstrated above. Different thicknesses of Ag film are deposited on these multiplex arrays, increasing from 5 nm, 25 nm, to 50 nm. From SERS measurements of R6G on R6G-encapsulated nanopillars, we observe that the SERS signals of R6G increase with the thickness of Ag film (Figure 4.10A and C). However, the fluorescent emissions are reduced when the thickness of Ag film is increased (Figure 4.10B and D). Stronger SERS/fluorescence signals lead to a greater contrast between the nanopillars and the background in corresponding images, with more accurate information readouts. In our encoding platform, both SERS and fluorescence of the encapsulated dye molecules are encoded information which are supposed to be clearly read out. In the multiplex array deposited with 5-nm Ag, the fluorescence information is clearly read out but the SERS spectra/image can be hardly discerned. In the multiplex array coated with 50-nm Ag, the SERS spectra/image can be resolved but the fluorescence is rather dim. Thus, we select 25 nm as the optimal thickness of Ag film to enable accurate decoding of both SERS and fluorescence information.

Figure 4.9. Multiplex encoding strategy based on spatially selective encapsulation of two dye molecules. (A) Scheme demonstrating the two-step fabrication to selectively encapsulate different probe molecules on the same nanopillar array. (B) (i) bright-field microscopic and (ii) fluorescence images cannot fully reveal the covert structures. (C) (i) SERS spectra and respective SERS images created by selecting at the vibrational bands at (ii) 622 (for R6G), (iii) 1639 (for EY) and (iv) 1180 cm^{-1} , respectively. All scale bars represent 5 μm .

Figure 4.10. Influence of Ag thickness in the multiplex array. (A) SERS and (B) fluorescence images of R6G in the multiplex arrays which are deposited with 5 nm, 25 nm and 50 nm of Ag films, respectively, derived using the 622 cm⁻¹ mode for R6G. (C) SERS and (D) fluorescence spectra taken from R6G-encapsulated nanopillars in the multiplex arrays which are deposited with 5 nm, 25 nm and 50 nm of Ag films, respectively.

Covert information of this multiplex platform can only be fully recovered using hyperspectral SERS imaging. The R6G and EY nanopillars appear structurally identical under normal bright-field microscopic characterization (Figure 4.9Bi). The nanopillars light up in the corresponding fluorescence characterization (Figure 4.9Bii), indicating that fluorescence can serve as the first identification layer. The covert patterns cannot be fully revealed through fluorescence in this system because of the spectral overlap of broad emission peaks of R6G and EY (Figure 4.11). Nevertheless, the fluorescence image shows that the emission from the center diamond is stronger than the four corners, because the fluorescence quantum yield of R6G is higher than EY. In contrast, when the vibrational

fingerprint of R6G is selected at 622 cm^{-1} , a distinct diamond array can be discerned from the R6G-encapsulated nanopillars; whereas the remaining EY-encoded nanopillars remain invisible (Figure 4.9Cii). Conversely, four sets of three nanopillars aligned in a right-angle triangular orientation light up when the vibrational fingerprint of EY at 1639 cm^{-1} is separately selected (Figure 4.9Ciii). The entire square array is formed when a common vibrational mode is selected at 1180 cm^{-1} (Figure 4.9Civ). In anti-counterfeiting terms, the individual SERS images of R6G- and EY-encapsulated nanopillars serve as the second and third identification layers of a security label made by using our nanopillar platform, while the combined image serves as the fourth identification layer to authenticate products. Combining with the tunable intensity grayscales, five identification layers can potentially be used to authenticate genuine products.

Our multiplex nanopillar platform exhibits a high level of decoding accuracy. The cross-sectional SERS intensity profile at 622 cm^{-1} and 1639 cm^{-1} show uniform signal intensity for both R6G- and EY-encapsulated nanopillars (Figure 4.12B). Furthermore, we observe no vibrational-mode difference when comparing between the SERS spectra of single dye-encapsulated nanopillars and in the multiplex system (Figure 4.13). This signal uniformity clearly indicates that the encoded spectral information can be precisely read out without any signal cross-talk in the two-step fabrication process.

Figure 4.11. Fluorescence spectra taken from R6G- (red) and EY-encapsulated nanopillars (blue) in the multiplex nanopillar array, respectively.

Figure 4.12. SERS taken from the multiplex nanopillar array. (A) Vibration-mode-selective SERS images created by selecting at band 622 cm^{-1} (red, for R6G), 1639 cm^{-1} (For EY) and 1180 cm^{-1} , respectively; (B) cross-sectional SERS intensity profiles at position 1-3, labeled in (A), respectively. All scale bars represent $5\text{ }\mu\text{m}$.

Figure 4.13. Comparison on SERS taken from the multiplex system and single-dye system. SERS taken from R6G-encapsulated nanopillars in (i) multiplex and (ii) single-dye system, respectively. SERS taken from EY-encapsulated nanopillars in (iii) multiplex and (iv) single-dye system, respectively.

Patterning Flexibility

To demonstrate the patterning flexibility of our encoded nanopillars and the high security level of this encoding strategy for potential applications like anti-counterfeiting, we fabricate a “yin-yang” pattern with two symmetric halves comprising R6G- and EY-encapsulated nanopillars. Bright-field microscopic characterization reveals only a solid circle consisting of identical nanopillars (Figure 4.14A). Fluorescence image shows the illumination of the whole pattern in which the R6G half is brighter than the EY half, arising from the higher fluorescence quantum yield of R6G. However, SERS image generated using the 622 cm^{-1} peak for R6G can selectively exhibit the left half of ‘yin-yang’ (Figure 4.14C), whereas selecting at 1639 cm^{-1} for EY exclusively gives rise to the right half of the ‘yin-yang’ (Figure 4.14D). It is note-worthy to highlight that the peak difference between 1639 cm^{-1} for EY and 1660 cm^{-1} for R6G is only 21 cm^{-1} , corresponding to $\sim 1\text{ nm}$ spectral gap in the wavelength scale (Figure 4.15). Thus, the narrow bandwidth of the SERS bands gives rise to a sensitive and accurate anti-counterfeiting platform. The two-layer optical information encoded in this pattern is more complex than security labels revealed by either SERS or fluorescence alone. Furthermore, the hyperspectral imaging technique generates unique SERS fingerprints for every individual R6G- and EY-encapsulated R6G- and EY-encapsulated nanopillar, and this serves as another layer of encryption further deters forgery.

Figure 4.14. Multiplex plasmonic security label consisting of R6G- and EY-encapsulated nanopillars. (A) bright-field microscopic image and (B) fluorescence image cannot fully reveal the covert ‘Yin-yang’ symbol. On the other hand, the SERS images created by selecting at (C) 622 cm^{-1} and (D) 1639 cm^{-1} can fully reveal the respective halves of the ‘Yin-yang’ symbol. All scale bars represent 10 μm .

Figure 4.15. Zoom-in SERS taken from R6G- (orange) and EY-encapsulated nanopillars (blue) in ‘yin-yang’ pattern, respectively. The peak difference between 1639 cm^{-1} for EY and 1660 cm^{-1} for R6G is only 21 cm^{-1} .

Data Storage Capability

In addition to information security, SERS images of the multiplex array demonstrate that the R6G- and EY-encapsulated nanopillars can be individually read out without signal interferences, validating the data storage capability of our nanopillar platform. In total, three well-defined states can be achieved depending on whether it has R6G, EY or no dye molecules encapsulated in nanopillars. To calculate the possible states in terms of data

storage, N well-defined states on a data storage platform generate up to N^P combinations with P digits. In our platform, N is 3 and P is the number of nanopillars per inch square. Combined with the 17,000 pillar per inch density, our multiplex nanopillar platform is able to provide the total possible states to be $3^{289,000,000}$ states/in². We can simultaneously achieve high storage density and secure data protection on a single platform.

4.3 CONCLUSIONS

In conclusion, we demonstrate a complicated and high-density anti-counterfeiting platform with multiple identification layers which is capable of enhancing information security and deterring product forgery. Molecular Information is hidden behind the same physical features and read out in the form of SERS, fluorescence, and their corresponding signal intensities by using hyperspectral imaging technique. We highlight a spatially selective encapsulation strategy to design various unique and covert patterns within a single array of nanopillars. Full decoding of these patterns require the use of fluorescence and SERS images, and the ability to spectrally resolve 1 nm between extremely closely-spaced vibrational signatures is superior to most conventional optical encryption platforms. Moreover, the use of hyperspectral imaging technology enables retrieving unique SERS spectra from each nanopillars and thus further enhances the security of our platform. Our multiplex nanopillar array is also a potential data storage platform providing the total possible states to be $3^{289,000,000}$ states/in². In all, we have shown a progressively complex information encoding platform with large information density, low-error decoding, high flexibility and security. The security level and data storage density can both be enhanced through the use of even more probe molecules or the fabrication of more complex structures.

4.4 MATERIALS AND METHODS

Materials. Rhodamine 6G, eosin Y and dimethyl sulfoxide were purchased from Sigma Aldrich. Milli-Q water ($> 18.0 \text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system.

Synthesis of photoresist.

Methyl 2-(methyl(phenyl)amino)acetate

In a 100 mL flask, 3.05 mL of methyl bromoacetate, 3.975 g of sodium carbonate and 2.725 mL of N-methylaniline were dissolved in 37.5 mL of methanol. The reaction mixture was stirred under reflux at 75°C for 3.5 h. Then the solution was filtered off, the solid residue was washed with ethylacetate (EA, $3 \times 30 \text{ mL}$). The solution was washed with water ($3 \times 100 \text{ mL}$) and brine ($1 \times 100 \text{ mL}$). The organic layer was dried over sodium sulfate, filtered and concentrated. Purification by column chromatography (Hexane: EA=20:1) yielded 2.473 g (66%) of the desired products as light yellow oil.

$^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ): 7.51 – 7.10 (m, 2H), 6.85 – 6.74 (m, 3H), 4.14 (s, 2H), 3.77 (s, 3H), 3.13 (s, 3H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , δ): 171.6, 148.8, 129.2, 117.4, 112.3, 54.3, 51.9, 39.5; GS-MS m/z : 179.20, 120.16, 91.11, 77.08.

Methyl 2-((4-formylphenyl)(methyl)amino)acetate

1.15 mL of phosphorous oxychloride (25 mmol) were dropwisely added to 10 mL of dry DMF at 0°C . After 30 min, 2.24 g of methyl 2-(methyl(phenyl)amino)acetate (25 mmol) were added to the reaction mixture, which was subsequently heated to 75°C for 4h. Then

the solution was cooled and poured into ice water (250 mL) with vigorous stirring overnight. The mixture was extracted with methylene chloride (3×50 mL) and the combined organic layers were washed with water (3×50 mL) and brine (1×50 mL). Then the organic layer was dried over sodium sulfate. The solvent was evaporated and the crude product was purified by column chromatography (Hexane: EA=2:1) to yield 1.8 g (69%) of products as white solid. Mp: 75-78 °C.

$^1\text{H-NMR}$ (200 MHz, CDCl_3): δ (ppm) = 9.68 (s, 1H), 7.66 (d, $J = 8.9$ Hz, 2H), 6.62 (d, $J = 8.9$ Hz, 2H), 4.09 (s, 2H), 3.66 (s, 3H), 3.07 (s, 3H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): δ (ppm) = 190.39, 170.26, 153.34, 131.98, 126.34, 111.37, 53.84, 52.25, 39.65. GS-MS analysis: (m/z) = 207.28, 148.22, 118.20, 77.10.

Sodium 2-((4-formylphenyl)(methyl)amino)acetate

A mixture of methyl 2-((4-formylphenyl)(methyl)amino)acetate (1g, 4.82 mmol) and NaOH powder (0.6g, 15 mmol) in 20 mL of EtOH was stirred overnight at room temperature. The solvent was removed in vacuum and the crude product was used directly for the next step without further purification.

Photoresist monomer

With protection of Al foil, 0.01 g of sodium hydroxide, 0.978 g of the benzaldehyde compound and 0.181 g of freshly distilled cyclopentanone were dissolved in 10 mL of water. The reaction was stirred at 80 °C for 4 h and then cooled to room temperature. 20 mL of

EtOH and 1 M HCl were added consequently until no precipitate formed. The red solids were collected by centrifugation and dried in vacuum. The obtained solids were put into 20 mL of water and 0.1 M NaOH was added dropwise until pH 8.5 was reached (monitored with pH meter). The undissolved solids were filtered off and water was removed via freeze-drying to yield desired products 0.966 g (88% of two steps).

Surface-enhanced Raman scattering (SERS) measurements. SERS spectra and SERS mapping were obtained using Ramantouch microspectrometer (Nanophoton, Osaka, Japan). The excitation laser is a 532-nm laser. The laser power used for the measurements is 10 μ W. The damage power to the substrate is 20 μ W where the organic molecules are burnt. The exposure time for each line and slit width of the spectrometer were 1 s and 50 μ m for 2D Raman imaging. The line scan mode with the resolution of y direction around 300 nm was used for x-y imaging.

Fluorescence measurements. The excitation laser is a 532-nm laser with the power of 10 μ W. The excitation laser light was focused into a line on a sample through a cylindrical lens and an air objective lens (LU Plan Fluor 100 $\times$ NA 0.9). The exposure time for each line of the spectrometer were 1 s. The line scan mode with the resolution of y direction around 300 nm was used for x-y imaging.

Characterization. Scanning electron microscopy (SEM) (JEOL-JSM-7600F) was performed with an accelerating voltage of 5 kV.

4.5 ACKNOWLEDGEMENT

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5 Three Dimensional Flexible Plasmonic Anti-counterfeiting Security Labels based on Surface-enhanced Raman Scattering**

ABSTRACT. Anti-counterfeiting platforms using plasmonic nanostructures effectively encode high-density information and protect these data from theft by exploiting the unique optical properties of plasmonic nanostructures. For real-world application, the security labels have to be wrapped on objects with arbitrary shapes and to provide reproducible signals over various mechanical strains. In this work, we introduce a flexible anti-counterfeiting platform using plasmonic nanowires to achieve polarization-dependent SERS and a three dimensional (3D) plasmonic security label exploiting z-dependent SERS. Labels composed of vertical and horizontal nanowires are directly written on the flexible films using two-photon lithography. These security labels fabricated on flexible substrates can be wrapped on both flat and curved surfaces without reducing the decoding accuracy. This fabrication method is simple, straightforward and can be used to pattern onto arbitrary images and trade marks. Furthermore, this flexible anti-counterfeiting SERS substrate exhibits excellent tolerance to bending and the layered information can be decoded with low error using hyper-spectral SERS imaging under 100 cycles of convex, concave and twist bending. Besides, the z-dependent SERS measured from this flexible SERS substrate validates its potential usage for selective data decryption. Based on that, a 3D anti-counterfeiting platform is developed combining nanopillars and slopes with different inclination angles. Molecular information are encoded in nanopillars located at different

** I would like to acknowledge Dr. Yan Cui for designing the pattern and doing parts of the SERS measurement for the flexible plasmonic substrates based on PET.

heights and they can be selectively decoded by measuring SERS at certain z values. Security levels and efficiency in space utilization can be further enhanced by using slopes with larger inclination angle

** I would like to acknowledge Dr. Yan Cui for designing the pattern and doing parts of the SERS measurement for the flexible plasmonic substrates based on PET.

5.1 INRODUCTION

Anti-counterfeiting platforms using plasmonic nanostructures effectively encode high-density information and protect these data from theft by exploiting the unique optical properties of plasmonic nanostructures, such as plasmonic colours,¹⁻⁶ SERS,⁷⁻¹⁰ fluorescence and other emissions.¹¹⁻¹⁹ These optical properties are always covert to the general public and can only be deciphered by the authorized party using sophisticated spectroscopic techniques. Moreover, the security level of authentic products can be enhanced using the plasmonic security labels which are encoded with multiple additional layered hidden information as identifying codes.^{5,10,20,21} Apart from information encryption in two dimensions (2D), plasmonic nanostructures can be used to fabricate three-dimensional (3D) anti-counterfeiting platforms so that densities of encoded information as well as the number of identifying codes are further increased by extending encoding spaces to three dimensions.^{22,23} As such, security labels made of plasmonic nanostructures are endowed with enhanced security levels for protecting the consumer value and integrity of branded goods, compared with conventional commercial security labels which protects products using unique physical features, such as holograms, watermarks and security inks.^{21,24,25} However, all the above-mentioned plasmonic security labels are fabricated on the rigid substrates such as glass slides. Real-world application requires the security labels to be wrapped on both planar and curved surfaces. Moreover, rigid substrates are too fragile to sustain various mechanical strains and thus reduce the reproducibility of the read-out signals from the plasmonic structures built on them. Thus, it is essential to develop a strategy to fabricate flexible plasmonic security labels.

The advantages of flexible SERS-active substrates over the rigid counterparts lies in their capability to adapt to the underlying objects with any sizes and shapes, being applied to detection,²⁶⁻³⁰ sensing^{31,32} and real-time reaction monitor.³³ Ag and Au nanoparticles decorated on flexible bases have been used to detect trace amount of toxins on surfaces of fish and fruit by directly swabbing the substrates on the testing samples.^{28,30} Compared with rigid substrates, more SERS-active sites on the flexible substrates can contact with the probe molecules on samples in this way and thus increase the testing sensitivity. Despite their great potential, the challenge in applying the flexible substrates for practical usage is fabricating substrate rendering reproducible SERS signals and low-error readouts over several rounds of mechanical strains. None of the above-mentioned works show such a capability. Besides, these SERS substrates are fabricated by evaporating Ag and Au on roughened soft substrates or by self-assembly of nanoparticles onto the poly(dimethylsiloxane) (PDMS) and poly(methyl methacrylate) PMMA films.²⁶⁻³³ The techniques and strategies can hardly be used to make arbitrary patterns, hindering their usage as security labels which always contain complex images. To make SERS substrate with user-designed patterns, multiple steps including self-assembly of particles, laser engraving, scotch tape peel-off/transfer and metal sputtering are involved into a single strategy which is too complicated and tricky.³⁴

Three dimensional SERS substrates are interesting because they enhance the detecting sensitivities by exploiting the hot spots in z dimension and by fully utilizing the effective confocal volume of the excitation laser.²² Conventionally, 3D SERS substrates are fabricated through self-assembly,^{22,35-38} template deposition^{39,40} and electron-beam lithography.⁴¹ In these works, there lacks studies on vertical space utilization. Moreover, these methods involving multiple steps are time-consuming. On the other hand, flexible SERS substrates are promising for studies on 3D SERS detection because they can be simply wrapped onto arbitrary shaped surfaces to make any 3D surfaces to be SERS-active.

Here, we introduce flexible and 3D anti-counterfeiting platforms combining SERS and plasmonic nanostructures, aiming to develop security labels giving stable SERS readouts over applying external bending forces and to develop novel security labels based on z-dependent SERS. In this work, we develop novel strategies to fabricate Ag nanowires which are selectively encrypted with molecular information on the free-standing poly(ethylene terephthalate) (PET) films. The encrypted information can only be fully read out using selective molecular Raman imaging, which is obtained by manipulating the polarization of excitation light in the SERS measurements. These flexible plasmonic SERS security labels can be wrapped onto curved objects. The molecular information is accurately decoded through SERS imaging from both curved and planar surfaces which are wrapped with the security labels. Moreover, SERS measurements on the flexible SERS security labels under bending strains show high stability of the SERS signals under external mechanical forces and the encrypted information can be read out with low error after 100 of bending cycles. Combining with the high security, this new generation of flexible plasmonic SERS security labels with high mechanical stability are promising for real-world applications. This first demonstration of flexible SERS anti-counterfeiting platform marks an important step forward in the practical application of SERS security labels. Besides, we observe an interesting z-dependent SERS phenomenon that distributions of SERS intensities vary with the laser focus planes in z direction, when the pattern on PET film is wrapped onto a small-radius cylinder ($\sim 590\text{ }\mu\text{m}$) and the pattern centers are away from the top-most point. Based on this observation, we design a three-dimensional (3D) security label by locating nanopillars-array onto slopes with different tilting angles. On these 3D security labels, molecular information are encoded at different heights and they can be selectively decoded by measuring SERS at certain z values. 3D security labels made of larger inclination angles are endowed with higher security levels and more efficient in vertical space utilization. In the future, 3D plasmonic security labels would be combined with flexible substrates.

5.2 RESULTS AND DISCUSSION

Fabrication of flexible plasmonic anti-counterfeiting security labels

Poly(ethylene terephthalate) (PET) films are popularly used materials for producing flexible devices due to their high mechanical strengths and flexibility. We use two-photon lithography to fabricate polymer nanowires on the films. Two-photon lithography is a direct laser writing technique allowing for building structures with spatial resolution down to nanometer scale. A piezoelectric scanning stage is used to precisely move the photoresist in x, y and z directions relative to the laser focusing points where the photoresist are polymerized, according to programmed patterns. Using this technique, we can fabricate arbitrary patterns with nanometer-scale resolution. Typically, IP-Dip is dropped onto the substrate, serving as photoresist and immersion. Objective lens is directly dipped into the photoresist in an inverted scheme (Figure 5.1) which is called dip-in lithography (DiLL) configuration. Then, polymeric nanostructures are formed layer-by-layer starting from the interface of the resist and substrate. These nanostructures can be anchored on the flexible substrate only when the correct interface of the resist IP-Dip and substrate is located. In this technique, the interface is automatically found when the sufficient refractive-index mismatch $n_{\text{substrate}} - n_{\text{(IP-Dip)}} > 0.03$ exists. Below this value of mismatch, the autofocus system does not work and structures cannot be directly written.

Figure 5.1. Process of fabricating flexible anti-counterfeiting label on poly(ethylene terephthalate) (PET) film. SEM image of a unicorn pattern formed by arrays of vertical lines and horizontal lines on PET film is put on the right. Scale bar represents 10 μm.

For PET film, the refractive-index mismatch is 0.11 ($n_{\text{PET}} = 1.63$ and $n_{(\text{IP-Dip})} = 1.52$) which is sufficiently for the autofocus and thus the polymeric nanostructures can be fabricated on PET through direct laser writing (strategy A). After that, nanowires on these flexible substrates are endowed with SERS activities via metallization using Ag and functionalization with 4-methylbenzenethiol (4-MBT). The polymerized nanowires are coated with a 100-nm Ag film/molecule/100-nm Ag film sandwich layer which is achieved via metallization, molecule functionalization and secondary metallization.¹⁰ We construct these sandwich structures to maximize the SERS signals taken from the flexible anti-counterfeiting substrate. It is reported in our previous work that the 100 nm Ag/4-MBT/100 nm Ag layout generates the strongest 4-MBT signals for arrays of nanowires.¹⁰ By using this strategy, a unicorn pattern with the size of $\sim 50 \times 50 \mu\text{m}^2$ are fabricated on PET film. From SEM images of patterns on the PET substrate, we observe unicorn heads composed of horizontal and vertical nanowires with the width ~ 500 nm. The nanowires fabricated on PET is well-defined. Horizontal wires are observed at the eyes and nostrils of the unicorn while the other parts are made of vertical wires (Figure 5.1).

SERS performance of PET flexible substrate on a curved object

Then, we examine the SERS capability of using these flexible substrate on both planar and curved surfaces. Figure 5.2 illustrates the setup for SERS measurements on flexible substrates being wrapped on the curved pillar with a radius of $\sim 3000 \mu\text{m}$. (Figure 5.2A and B). SEM image shows a combination of horizontal and vertical lines and does not clearly reveal a defined unicorn head (Figure 5.2C). For measuring SERS, 4-MBT serving as probe molecules are embedded in the sandwich structures which are fabricated on the PET film. SERS measurements show typical SERS spectra of 4-MBT containing two characteristic vibrational modes at 1079 cm^{-1} and 1584 cm^{-1} . The peak at 1079 cm^{-1} is attributed to a combination of the phenyl ring-breathing mode, C-H in-plane bending, and C-S stretching,

whereas the peak at 1584 cm^{-1} arises from phenyl stretching motion. Upon irradiating with x-polarized laser, the vertical lines give active SERS (bright) while horizontal lines give inactive SERS (dark) signal, originating from the directionally enhanced EM-fields localized on Ag-coated nanowires. This arises from the momentum mismatch between incident light and the propagating plasmons supported by nanowires.^{7,8,10,35,42} As such, SERS intensity imaging at 1079 cm^{-1} exhibits the lightening of all the vertical lines constituting a unicorn pattern while the eye and nostrils of the unicorn which consisting of horizontal lines remain dark. In general, the molecular information embedded in the pattern cannot be distinguished using SEM. The encrypted information can only be fully read out using selective molecular Raman imaging using x-polarized incident light.

Figure 5.2. Comparison of SERS measurements on PET based flexible anti-counterfeiting label between planar and curved surfaces. (A) Setup of SERS measurement from a curved surface. (B) The enlarged picture of a flexible anti-counterfeiting label wrapping on a plastic cylinder which is indicated using a red cycle in (A). (C) SEM image of a unicorn pattern consisting of vertical and horizontal nanowires. X-polarized 2D SERS images created by selecting at 1080 cm^{-1} measured from (D) a planar surface and (E) a curved surface, respectively. (F) SERS intensities of peak 1080 cm^{-1} measured from (a) focused area and

(b) unfocused area, as indicated in (E). (G) 3D SERS image of the unicorn pattern wrapped on the curved surface. The z-distance from the top most layer to the bottom most layer is $\sim 5\mu\text{m}$. Scale bars are $10\mu\text{m}$.

To compare the SERS measurements on the planar and curved surfaces, SERS images show the same unicorn pattern. Under polarized laser irradiation, there is no significant difference between SERS imaging on planar and curved surfaces, indicating that the capability of decoding the embedded polarization-dependent identification is not hindered by the curved surfaces. It is note-worthy that SERS intensities on parts of the unicorn (Figure 5.2E-b) become weaker than other areas (Figure 5.2E-a) when measuring SERS on the curved surface because these parts are beyond the laser focus plane. Quantitative analysis of the SERS intensities taken from area “a” and “b” demonstrates that the SERS intensities at these two areas are ~ 366 and ~ 130 counts, respectively. The SERS intensity drops $\sim 64\%$ on area “b” relative to “a” (Figure 5.2F). However, the relatively weak signal from area “b” still can show strong contrast to the backgrounds and thus the embedded information in this security label can be accurately revealed using SERS. To fully decode the image of structures on curved surfaces, we can use 3D SERS images which are obtained by compiling a few of XY-scanning images taken on different focus planes (Figure 5.2G). This finding shows high possibility on practically applying the plasmonic SERS anti-counterfeiting platform to varieties of objectives, from planar items like documents, banknote and CD to curved items such as irregular packages, medicine vials and luxury products.

Effect of cyclic bending strains on the flexible PET anti-counterfeiting label

Next, we investigate the capability of the flexible SERS security label on withstanding the mechanical strains, by monitoring the effect of cyclic bending strains on SERS read-out of the flexible anti-counterfeiting substrates. 100 bending cycles in total have been exerted

on these substrates and SERS is measured for every 20 cycles. In each cycle, three forces including a tension force, a compression force and a torsion force are exerted on the film (Figure 5.3A and B).

Figure 5.3. Cyclic bending strain test on PET-based flexible anti-counterfeiting label. (A) Schemes demonstrating three forces which are exerted on flexible substrates in each bending cycle. (B) Photos of PET based flexible anti-counterfeiting label under tension force, compression force and torsion force. (C) Bright-field and (D) 2D SERS images of unicorn pattern under bending of (i) 0, (ii) 20, (iii) 40, (iv) 60, (v) 80 and (vi) 100 cycles, respectively. The polarization is along x-axis. (E) SERS intensities of peak 1080 cm⁻¹ for every 20 bending cycles in the entire process. SEM image of unicorn pattern (F) before and (G) after 100 cyclic bending, respectively.

From bright-field images of the unicorn pattern under cyclic strains, we observe that wrinkles appear on non-patterned area after 60 bending cycles but the nanowires remain as well-defined structures under the 100 cycles of strains. Moreover, clear and high-contrast

SERS images are observed for every 20 bending cycles in the entire process. In each SERS image, the polarization-dependent underlying information is precisely revealed as the eyes and nares of the unicorn are dark (horizontal wires) when other areas are bright (vertical wires), indicating that the encryption capability and high security remained undamaged under a large number of strain forces.

Furthermore, SERS signals are reproducible and stable, illustrated by the bar graph of SERS intensities of the 1080 cm^{-1} peak as the function of the number of bending cycles (Figure 5.3E). In the graph, the SERS intensities are retained almost constantly at ~ 400 cps with a maximum decrease of $\sim 16\%$. It is note-worthy that the SERS intensity does not constantly reduce with the number of bending cycles, in which the intensity drop to its minimum after 40 cycles and increase $\sim 27\%$ after additional 20 cycles. This may probably arise from the fine wrinkles formed on the surfaces during the bending which induce additional hot spots for SERS enhancement. The wrinkles can also be observed from the SEM images of the pattern after 100 bending cycles even though they do not affect the information decoding via SERS imaging.

These results collectively indicate that the embedded information can be decoded with low-error under 100 cycles of mechanical deformation using our flexible SERS anti-counterfeiting platform. The flexible anti-counterfeiting security label exhibits a good tolerance to bending, making it an effective plasmonic security label for practical uses.

Strategy to fabricate security labels on PDMS film

We develop another strategy to fabricate security labels on poly(dimethylsiloxane) (PDMS) films using direct-laser-writing. As introduced above, the interface is automatically found in the dip-in lithography when sufficient refractive-index mismatch $n_{\text{substrate}} - n_{\text{(IP-Dip)}} > 0.03$ exists, but the mismatch between refractive index of PDMS and IP-Dip is -0.12 ($n_{\text{PDMS}} = 1.40$). Thus, the autofocus system does not work and nanostructures

cannot be directly written on substrate like PDMS. To increase the refractive-index difference for direct laser writing, we deposit a layer of 10-nm alumina on PDMS. Then, the nanostructures can be directly written on the PDMS films. In the end, this flexible substrate is endowed with SERS activities via being coated with a 100-nm Ag film/molecule/100-nm Ag film sandwich layer which is achieved via metallization, molecule functionalization and secondary metallization (Figure 5.4). From SEM images of the pattern fabricated on a PDMS film, we observe a unicorn which is composed of well-defined vertical and horizontal nanowires. The width of the nanowire is ~500 nm which is the same as the nanowire fabricated on the PET film (Figure 5.4).

A PDMS film with higher elasticity than PET can resume its normal shape after being stretched.^{43,44} By using our strategy to directly write nanostructures on PDMS, the gaps between nanostructures can be accurately controlled by stretching the PDMS film, enabling the study of gap-dependent SERS of plasmonic nanostructures in the future. The adjustable outputs of SERS intensities via stretching could serve as additional layer of encryption, which would further enhance the security level by using this anti-counterfeiting platform.

Figure 5.4. Process of fabricating flexible anti-counterfeiting label on poly(dimethylsiloxane) (PDMS) film. SEM image of a unicorn pattern formed by arrays of vertical lines and horizontal lines on PDMS film is put on the bottom-right. Scale bar represents 10 μm .

To fabricate plasmonic nanodots-array on flexible substrates

Apart from nanowires, we can fabricate nanopillar arrays on PET films by using our strategy combining two-photon lithography and Ag thermal evaporation. We fabricate a 7×11 array consisting of structurally identical nanopillars. These nanopillars are uniform in shapes and sizes owing to the high precision of two-photon lithography technique. The diameters of these Ag-coated nanopillars are ~ 500 nm, observed from SEM images (Figure 5.5A-C). In order to investigate the capability of decoding molecular information from the nanopillars-array on curved surfaces. We wrap the film with nanopillar structures onto the plastic cylinder shown in Figure 5.2B and then measure SERS on this nanopillars array. SERS measurement demonstrates a homogeneous SERS image at 1080 cm^{-1} with similar brightness, indicating that our fabricating strategy could be applied in nanopillars-array patterns without deterring the decoding accuracy. Compared with nanowires, nanopillars with smaller sizes in 2 dimensions increases the information capacity within unit areas (500 nm of a nanopillar versus tens of micrometers of a nanowire in y directions) and enhances the patterning flexibility. Future works would involve designs of nanopillar patterns on flexible substrates.

Figure 5.5. SERS measurement for a plasmonic nanopillars-array on PET-based substrate. (A-C) SEM images of a 7×11 nanopillars array. (A) Zoom-out top-view, (B) zoom-in side-view (with 30° -tilted angle) and (C) zoom-in top-view SEM images. (D) SERS intensity image of peak 1080 cm^{-1} for the 7×11 nanopillar array placed on a curved surface. The scale bars in (A) and (D) represent $10\text{ }\mu\text{m}$ while the scale bars in (B) and (C) represent $5\text{ }\mu\text{m}$.

Above SERS measurements on curve surfaces are conducted by placing the center of pattern at the top-most point of the underlying cylinder (position A in Figure 5.6A) and the radius of cylinder is $\sim 3000\ \mu\text{m}$. In this case, no big difference in SERS images is observed for measuring a $50\ \mu\text{m} \times 50\ \mu\text{m}$ pattern on planar or curved surfaces (Figure 5.2 and Figure 5.5).

Interestingly, we observe a Z-dependent SERS phenomenon that distributions of SERS intensities vary with the laser focus planes in Z direction, when the pattern on PET film is wrapped onto a cylinder with radius of $\sim 590\ \mu\text{m}$ and the pattern centers are away from the top-most point (position B and position C in Figure 5.6A, Figure 5.6C and D). In the typical experiment, two unicorn patterns with the same sizes of $50\ \mu\text{m} \times 50\ \mu\text{m}$ are sequentially written on a PET film with a $100\text{-}\mu\text{m}$ distance. This film is wrapped onto the cylinder to make the first unicorn being located at position B which is $100\text{-}\mu\text{m}$ away from position A and the second unicorn is located at position C (Figure 5.6A). SERS for these two unicorn patterns are first measured by focusing the laser at the nanowire with the lowest Z value and we set this plane as $Z_1=0\ \mu\text{m}$. SERS measurements on position B and C reveal only parts of the unicorn patterns focusing at different planes (Figure 5.6C and D).

To explain this phenomenon, we hypothesize that the Z-dependent SERS arises from that the height differences between nanowires induced by the curves are out of the effective laser spot volume. In our SERS measurements, excitation laser is focused into a line through a cylindrical lens and a $100\times$ air objective lens with a numerical aperture of 0.9. When focusing at a certain plane (Z), x-y SERS hyper-spectral image is acquired by scanning the sample using line-shaped laser in the y direction on this plane. The size of confocal laser spot is $\sim 0.81\ \mu\text{m}$ in the Z axis, so that SERS signals from hot spots within this height can be detected in the process of x-y SERS imaging.²² The height difference between the most top and the most bottom nanowire is $\sim 0.1\ \mu\text{m}$ for the unicorn pattern placed at the top-most

point of cylinder with radius of $\sim 3000\text{ }\mu\text{m}$ (Figure 5.2). This height difference is negligible when compared with the confocal laser spot volume, so that SERS measurement on this curve surface can reveal a full unicorn pattern. Moving to position B and C, the inclination angles with respect to x-y plane increase to 19° and 39° from 0° for position A (please refer to the schemes above Figure 5.6C and D). For a $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ pattern, the height differences caused by inclination angles are $16\text{ }\mu\text{m}$ and $31\text{ }\mu\text{m}$ for position B and C, respectively. These height differences are far beyond the volume of the laser spot and thus the SERS signals are highly dependent on the focus planes.

Figure 5.6. SERS measurements on unicorn patterns located at different locations. (A) Scheme illustrating the set-up for SERS measurement on a flexible plasmonic PET film which is wrapped onto a cylinder surface. Unicorn patterns are located at position B and C. Position A indicates the top-most center point of the cylinder. The diameter of the underlying cylinder is 0.59 cm. Distances between A and B as well as B and C are 100 μm . (B) SEM image of an unicorn pattern comprising horizontal and vertical nanowires. SERS intensity images of peak 1080 cm^{-1} for unicorn patterns located at (C) position A. SERS intensity images of peak 1080 cm^{-1} for unicorn patterns located at (D) position B and (E) position C, measured at three corresponding focus planes in Z directions, respectively. All scale bars represent 10 μm .

Preliminary studies on three-dimensional (3D) plasmonic security label based on z-dependent SERS

Based on the z-dependent SERS observations in the above experiments, we design a three-dimensional (3D) security label locating nanopillars-array onto slopes with different tilting angles. The aim is to create 3D security labels encoded with molecular information that is dependent on its height, and to study the effect of slope angles with respect to the SERS signals. In order to rule out further height differences caused by the curves of flexible substrates, we fabricate these 3D security labels on rigid glass slides. Both the slope and nanopillars-arrays are produced as polymer structures through direct-laser-writing (DLW) process using two-photon lithography. These substrates are endowed with SERS activities by coating a 100-nm-Ag/4-MBT-monolayer/100-nm-Ag sandwich layer. We fabricate nanopillar arrays with distances between neighbored pillars $\sim 4\ \mu\text{m}$ (Figure 5.7). These arrays are located at a triangular prism with slope angle designated at 5 degree and 14 degree, respectively. Rows of nanopillars are sequentially located from bottom to top of slopes, with each row comprising ten nanopillars. From SEM images, we observe that the nanopillars are uniform in diameters ($\sim 500\ \text{nm}$). The underlying slopes do not affect shapes and sizes of the nanopillars (Figure 5.7).

We measure SERS on these three 3D security labels by focusing laser planes on nanopillar rows with the lowest heights (set as $z=0$, as indicated using blue dot-lines in Figure 5.7). SERS image on a flat platform shows homogeneous brightness span the entire arrays indicating the uniform SERS intensities of peak $1080\ \text{cm}^{-1}$ for 4-MBT (Figure 5.7A-iii). In contrast, inhomogeneous signals are observed in SERS images on triangular prisms with varying degree of slope (Figure 5.7B-iii and 5.7C-iii). For the array on 5-degree slope, SERS image demonstrates a gradual decrease in intensity from the bottom to the top, with the darkness at the last row (Figure 5.7B-iii). For the array on 14-degree slope, SERS image

merely exhibits the first two rows of nanopillars at the bottom indicating the big contrast in SERS signal intensities among nanopillars at different z on the 14-degree slope (Figure 5.7C-iii). In this case, the molecular information embedded into the first two rows are selectively readout by focusing laser at $z = 0$. It is note-worthy that some ridges like structures are produced on the slopes in the direct-laser-writing process (Figure 5.7B-ii and 5.7C-ii). Currently, we are yet to circumvent this issue using our existing methodology. Nevertheless the SERS measurements demonstrate that these roughnesses do not affect the images of nanopillars (Figure 5.7B-iii and 5.7C-iii).

Figure 5.7. Comparison on SERS measurements on nanopillars-arrays which are fabricated on flat stage, 5-degree slope and 14-degree slope. (i) Scheme, (ii) SEM and (iii) SERS images of nanopillars-arrays on (A) flat stage, (B) 5-degree slope and (C) 14-degree slope, respectively. The blue dot-lines indicate where the planes of laser are focused. All scale bars represent 10 μm .

Next, we investigate the effect of gaps between rows to the SERS readout on slopes with varied angles, in order to increase the decoding selectivity so that every single rows of

nanopillars can be individually revealed at specific height, z . Here, the gap indicates the distance between two nearby rows located at different z (Figure 5.8A). To calculate the minimal gap sizes for selective read-out from each nanopillar row, we have to take into account the shapes and sizes of the confocal laser spot. When focusing at the z of the first nanopillars-row, the pillars in the second row should be out of the effective volume of laser spot in order to prevent the interferences from the second row (Figure 5.8A). The confocal laser spot is estimated to be $\sim 0.81 \mu\text{m}$ in z axis.²² As shown in the scheme, the gap is estimated at $(1+0.81)/\sin(\text{angle})$ to circumvent the interferences (Figure 5.8A).

We fabricate two 3D security labels by adding nanopillars on 15-degree and 30-degree slopes (Figure 5.8B and C). On the 15-degree slope, we fabricate nanopillars with the gap sizes of $8 \mu\text{m}$ because the minimal gap is calculated to be $7 \mu\text{m}$ ($1.81/\sin 15^\circ$). SEM images demonstrate the slopes and nanopillars are well-defined in shapes (Figure 5.8B-i). Then, we measure SERS by focusing laser on planes with different z values. SERS images demonstrate that the first and second rows of nanopillars can be selectively readout without error by focusing excitation laser at z at $1.8 \mu\text{m}$ and $6.0 \mu\text{m}$, respectively (Figure 5.8B-iv and -v). Hence, based on our design of the 3D security label, the complete image of the security label can only be fully and successfully decoded by compiling several XY-scanning SERS images taken on different focus planes with z ranging from 0 to $8 \mu\text{m}$ (Figure 5.8B-iii).

For the 30-degree slope, the minimal gap is calculated at $3.6 \mu\text{m}$ ($1.81/\sin 30^\circ$). Hence, the gaps between two rows of nanopillars are set at $4.5 \mu\text{m}$ (Figure 5.8C). From SEM images, we observe that these nanopillars are uniform in shapes and sizes. The shape of the 30-degree slope is well-defined (Figure 5.8C-i). Similar to the results for 15-degree slope, SERS of the first, second and third rows of nanopillars can be individually revealed by focusing line-shaped laser at $z=1.4$, 4.0 and $6.0 \mu\text{m}$, respectively (Figure 5.8C-iv-vi). 3D SERS images reveals the full map of three rows of nanopillars by compiling 2D images

taken at planes ranging from $z=0$ to $z=7.0\text{ }\mu\text{m}$ (Figure 5.8C-iii). It is noteworthy that the height of the last row of nanopillars is the same as the upper edge of the slope, so that the SERS image at corresponding z combines the nanopillars and the edge. As such, we exclude the SERS image taken from that plane.

These results verify the capability of selective decoding information by measuring SERS at certain z values on our 3D plasmonic security labels. These z values which are unknown to anyone but authorized party serve as identifying layers to protect the encoded information. With more of planes (z) which can be individually read out via measuring SERS, an additional identifying layer has been create to better secure the data in our tailor-designed 3D plasmonic security label. Here, the security label with 15-degree slope provides three layers for identification, which includes a 3D image and two of selective-revealed 2D images at different z planes. Comparing with the 15-degree slope, the 3D security label with 30-degree slope is encoded with an additional identifying layer in the range from $z=0$ to $z=6.0\text{ }\mu\text{m}$, arising from the smaller gap which is allowed for larger inclination angles (Figure 5.8B and C). As such, 3D security labels made of larger inclination angles are endowed with higher security levels and more efficient in vertical space utilization. In the future, 3D plasmonic security labels would be combined with flexible substrates to investigate the z -dependent SERS on curved substrates and to promote the uses of 3D security labels to the real-world application.

Figure 5.8. Z-dependent SERS for nanopillars-arrays on slopes with different angles. (A) Scheme illustrating the cross-section of nanopillars-arrays on slopes. (B) (i) SEM image, (ii) scheme, (iii) 3D SERS image and (iv and v) 2D SERS images acquired at focusing plane (iv) $Z=1.8\ \mu\text{m}$ and (v) $Z=6.0\ \mu\text{m}$ for nanopillars-arrays on a 15-degree slope, respectively. (C) (i) SEM image, (ii) scheme, (iii) 3D SERS image and (iv and v) 2D SERS images acquired at focusing plane (iv) $Z=1.4\ \mu\text{m}$, (v) $Z=4.0\ \mu\text{m}$ and (v) $Z=6.0\ \mu\text{m}$ for nanopillars-arrays on a 30-degree slope, respectively. All scale bars represent $10\ \mu\text{m}$.

5.3 CONCLUSION

In summary, we have demonstrated a flexible anti-counterfeiting SERS platform with enhanced security, high flexibility and capability of resisting mechanical deformation. The fabrication methods are simple, straightforward, and can be used to pattern into arbitrary images and trademarks, which are superior to some multiple-step approaches based on peeling-off and transfer. Combining the plasmonic nanowire supporting polarization-dependent plasmon resonances and SERS, molecular information can be selectively hidden

at the different polarization. The layered identification strengthens the security level compared with conventional anti-counterfeiting platforms embedded with only one identification layer. Moreover, our security labels fabricated on free-standing PET and PDMS substrates can be wrapped on both flat and curved surfaces without reducing the decoding accuracy. Such a high flexibility breaks the barrier of applying the anti-counterfeiting platform based on SERS to non-rigid surfaces, such as documents, banknotes, irregular packages and medicine vials, outperforming the plasmonic security labels on rigid substrates in this aspect. Furthermore, this flexible anti-counterfeiting SERS substrates exhibits excellent tolerance to bending and the layered information can be decoded with low error using hyper-spectral SERS imaging under 100 cycles of convex, concave and twist bending. The robustness of our flexible plasmonic security labels based on SERS makes them promising for real-world applications and broadens the usages of flexible SERS substrates. Besides, the z -dependent SERS measured from this flexible SERS substrate validates its potential usage for selective data decryption. Based on that, a 3D anti-counterfeiting platform is developed combining nanopillars and slopes with different inclination angles. Molecular information are encoded in nanopillars located at different heights and they can be selectively decoded by measuring SERS at specific z planes. These z values serve as multiple layers of identification that secures the information. It is also concluded that 3D security labels made of larger inclination angles are endowed with higher security levels and more efficient in space utilization. In the future, 3D plasmonic security labels would be combined with flexible substrates to investigate 3D SERS detection on arbitrary shaped surfaces.

5.4 MATERIALS AND METHODS

Materials. IP-Dip photoresist with refractive index $n \approx 1.52$ (Nanoscribe Inc, Germany) was used for two-photon lithography in dip-in laser lithography (DiLL) configuration.

Ethanol, 4-methylbenzenethiol (4-MBT, 98%), isopropyl alcohol (IPA) and propylene glycol monomethyl ether acetate (PGMEA) were purchased from Sigma-Aldrich. Silicone elastomer curing agent and silicone elastomer base (Sylgard 184) were purchased from Dow Corning. 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. Poly(ethylene terephthalate) (PET) films with the thickness of $50 \text{ }\mu\text{m}$ were donated from Innova Higa Singapore PTE. LED.

Fabrication of polymeric anti-counterfeiting structures on PET film. Polymeric nanostructures were fabricated by using a direct laser writing system (Nanoscribe Inc., Germany). Typically, IP-Dip monomer was drop-casted on a PET film then polymerized when exposed to a computer-assisted femto-second pulsed fiber laser with a center wavelength of 780 nm . Polymeric structures were formed according to the pre-defined graphic programs. In the Dip-in Laser Lithography (DiLL) process, an inverted microscope with an oil immersion lens ($100\times$, NA 1.4), and a piezoelectric stage were used. The average laser power around 6 mW for DiLL and a writing speed at $30 \text{ }\mu\text{m/s}$ were used. Then, the substrate with polymerized structures was immersed in PGMEA for 10 min , and then rinsed with IPA for another 5 min to remove un-polymerized photoresist.

Fabrication of polymeric anti-counterfeiting structures on PDMS stamp. Two precursors, silicone elastomer curing agent and silicone elastomer, were carefully mixed in a 1: 10 volume ratio and evenly poured onto a polytetrafluoroethylene (PTFE) holder with 16 squares feature. Then the holder with precursors was put in oven at 80°C for overnight. Cured PDMS stamp was peeled off from PTFE hold and cut into pieces for further uses. A $10 \text{ nm Al}_2\text{O}_3$ film was deposited onto the PDMS stamps via atomic layer deposition to increase the refractive index differences between photoresist and PDMS substrates.

Metallization of the nanowire arrays. Deposition of Ag film on the substrates was conducted using a thermal evaporator. The deposition rate of Ag was 0.5 Å/s. Ag tablets with 99.99% purity was purchased from Advent Research Materials, UK.

Ligand exchange reactions. Modification of 4-MBT monolayer was performed by immersing substrates with plasmonic structures in 100 mM 4-MBT ethanol solution for 6 hours. Then, samples were rinsed with ethanol to remove extra 4-MBT and dried in nitrogen gas. 4-MBT was expected to form a self-assembled monolayer on the Ag nanostructures. Another layer of Ag film was deposited to form metal-molecule-metal sandwich structure.

Surface-enhanced Raman scattering (SERS) measurements. SERS spectra and Raman mapping were obtained by using Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan). Wavelength of excitation laser is 532 nm. The excitation laser power was 0.09 mW with 5-s exposure time for each line. Slit width of the spectrometer was 50 µm. The line-scan mode with the resolution of y direction around 300 nm was used for x-y imaging. To switch the polarization of incident light from y- to x-direction, a combination of a polarizer and a half wave plate was used. The SERS intensities were obtained from the longitudinal body of nanowires at different orientation angles (excluding the Raman intensity from the respective tips).

Characterization. Scanning electron microscopy (SEM) (JEOL-JSM-7600F) was performed with an accelerating voltage of 5 kV.

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6 Summary and Outlook

6.1 SUMMARY

Plasmonic nanoparticles supporting localized surface plasmon resonances (LSPR) are able to confine lights into sub-wavelength scale and convert them into highly localized electromagnetic fields or other energies. Tailoring the light-matter interactions can be achieved by manipulating the optical properties of plasmonic nanoparticles on the basis of LSPR, which has already benefited wide range of fields, such as surface-enhanced Raman scattering, analyte detection, sensing, wave-guiding, lasing, anti-counterfeiting, data storage and *etc.* In this field, there are two challenges: to efficiently manipulate the interaction of light with surface plasmon resonances supported by plasmonic nanostructures and to develop novel platforms using plasmonic nanoparticles for practical applications. To tailor surface plasmonic properties, there are mainly two ways including engineering the physical features of nanoparticles in single-particle level and manipulating the plasmon coupling in the coupled system of nanoparticles. Motivated by these two challenges, my works during these four years focus on tailoring optical properties of plasmonic nanoparticles via fabricating novel morphologies, investigating optical properties of coupled nanoparticles through plasmon mapping with nanometer scale resolution, and developing plasmonic nanostructure platforms for anti-counterfeiting/data storage applications on both rigid and flexible substrates.

In chapter 2, we demonstrate a “hot spots over hot spots” strategy to efficiently increase intensities and volumes of hot spots on single-particle level. In this strategy, plasmonic nanodots are exclusively deposited on hot spots areas which are tips and edges of nanoparticles using a wet-chemical synthetic protocol. The great significance of precisely

designing hotspots at original hotspots regions for SERS are directly confirmed using the cathodoluminescence hyperspectral imaging and DDA simulations on electromagnetic field (EM) enhancements. EM field intensities are enhanced by 33% by depositing every single Au nanodot on the edges of Ag octahedra relative to deposit Au nanodots on the faces of octahedra. The advantage of precision synthesis is clearly evident in the single-particle SERS measurement which demonstrates 3-fold enhancement on the precisely designed SEGSO over the randomly deposited nanostructure, even though using the same amount of Au for the growth of Au nanodots. By carefully designing additional hot spots at the hot regions of nanoparticles, the SEGSO particles can function as highly sensitive single-particle SERS substrates, opening a new pathway to maximize the SERS performance by synthesizing various designer nanoparticles. Besides, the synthetic mechanisms underlying the growth of such designer nanoparticles are also discussed together with a demonstration of the versatility of this synthetic protocol to create a library of selective gold-deposited Ag-based nanoparticles, which can be subsequently etched to cages as well as frames for future applications.

In addition to fabricate novel morphologies, plasmon coupling efficiently manipulates light-matter interaction in a way that introduces novel optical properties and upgrades performances by simply playing with orientations and assemblies of single morphologies. Thus, in chapter 3, we use Ag nanocube dimers as model systems to acquire knowledge on localized surface plasmon resonances (LSPRs) that occur between Ag nanocube dimers and to directly visualize how SP modes and fields localization evolves with alteration of dimer orientations. Highly-resolved (<10 nm spatial resolution) plasmon maps of Ag nanocube dimers are obtained by combining CL and EELS measurements. In this work, we experimentally observe a “mode splitting” phenomenon that a low-energy mode at 2.10 eV in isolated nanocube disappear with the appearance of two separate modes at 1.85 and 2.30 eV in dimer via coupling. Moreover, the localizations of plasmon resonances in the range

of 1.5-3.5 eV are observed at the tip and edge regions of dimers with four configurations. The percentage of high-energy modes within a nanocube dimer is tunable and increased in the process of shifting from face-to-face to edge-to-edge configurations. This increase in percentage of high-energy modes indicates that localized field within Ag nanocube dimers can be maximized at their tip-to-tip configurations.

To develop novel platforms to broaden the applications of plasmonic nanoparticles and SERS, in chapter 4, we demonstrate a multiple-layer anti-counterfeiting platform with enhanced information security based on combining plasmonic nanopillars, SERS and fluorescence. The multiplex strategy enables us to realize the spatially selective encapsulation of dye molecules within a Ag nanopillar array, embedding covert molecular information which are revealed in the form of fluorescence, surface-enhanced Raman scattering (SERS), and signal intensities. In this encoding platform, five identification layers with no interferences can be arbitrarily hidden within the arrays consisting of Ag nanopillars behind the same physical features. These encrypted information is then located and revealed only when SERS and fluorescence hyper-spectral imaging are conducted. Multiple readouts are independent with the physical features and hyperspectral imaging technology provides complete spectral information with high spectral and spatial resolution, both enhancing the decoding accuracy and security level. Moreover, we can simultaneously achieve high storage density and secure data protection on a single platform by using multiplex arrays while the information storage capability of conventional platforms are limited to the binary 'excited/ground' states. High information density of $\sim 17,000$ pillars per inch (ppi) can be achieved by using our strategy.

Aiming towards to use the plasmonic anti-counterfeiting platforms in the real-world application, we introduce a flexible anti-counterfeiting platform combining polarization-dependent SERS and plasmonic nanostructures, aiming to develop security labels giving stable and reproducible SERS readouts over applying external bending forces. We are able

to fabricate Ag nanowires which are selectively encrypted with molecular information on the flexible poly(ethylene terephthalate) (PET) films. Combining the plasmonic nanowire supporting polarization-dependent plasmon resonances and SERS, molecular information can be selectively hidden at the different polarization. The layered identification strengthens the security level compared with conventional anti-counterfeiting platforms embedded with only one identification. Moreover, our security labels fabricated on PET substrates can be wrapped on both flat and curved surfaces without reducing the decoding accuracy. Furthermore, this flexible anti-counterfeiting SERS substrates exhibits excellent tolerance to bending and the layered information can be decoded with low error using hyper-spectral SERS imaging under 100 cycles of convex, concave and twist bending. Besides, the Z-dependent SERS measured from this flexible SERS substrate validates its potential usage for selective data decryption. Based on that, a 3D anti-counterfeiting platform is developed combining nanopillars and slopes with different inclination angles. Molecular information are encoded in nanopillars located at different heights and they can be selectively decoded by measuring SERS at certain Z values. These Z values serve as multiple layers of identification that secures the information. It is also concluded that 3D security labels made of larger inclination angles are endowed with higher security levels and more efficient in space utilization. In addition, we develop another strategy to fabricate security labels on poly(dimethylsiloxane) (PDMS) films. A PDMS film with higher elasticity than PET can resume its normal shape after being stretched, enabling its future uses on studying gap-dependent SERS by fabricating plasmonic nanostructures on PDMS and stretching the film to control the gap.

6.2 OUTLOOK

We demonstrate efficient enhancements of localized field on Ag octahedra by using “hot spots over hot spots” strategy that precisely depositing plasmonic active nanodots onto

tips and edges hot spots regions of nanoparticles. This precision synthetic method and mechanical studies on the secondary “hot spots” growth are applicable to efficiently add “hot spots” densities on any other morphologies bearing facets with inhomogeneous surface energies, such as nanocubes and nanoflowers. Moreover, we experimentally visualize the distribution of plasmon modes at nanometer scale within nanoparticle pairs and the results exhibit that the electromagnetic fields’ localization is strongly related to the orientation of the dimer. Based on the results of these two works, in the future we would investigate the plasmonic properties on dimers of selective gold deposited polyhedral nanoparticles with different orientations. The aim is to find the dimers with the most intense localized fields and efficiently enhance SERS enhancement for detection. Apart from dimers, to further enhance the SERS signals, the selectively deposited nanoparticles can also be assembled into various 2D/3D arrays, thanks to the high synthetic yields and narrow size-distribution of this protocol. Assemblies of these selective gold deposited Ag nanoparticles giving strong SERS would be combined with the multiplex strategy introduced in chapter 4 and with flexible anti-counterfeiting platform in chapter 5. In current platforms in chapter 4 and chapter 5, plasmonic properties are given by the Ag film which is deposited on the polymeric nanostructures using thermal evaporation. To replace the Ag film with assemblies of selective gold deposited Ag nanoparticles, we believe the SERS signals would be more intense and easily to be initiated by using less strict excitation conditions, such as lower excitation power. This makes these strategies and platforms more applicable for real-world applications.

In addition, regarding to the plasmon mapping of coupled system, future work here will involve correlation of the experimental results with numerical simulation results, in order to study the nature of each plasmon modes of Ag nanocube and to understand the underlying physics behind plasmonic coupling. Spatially resolved CL and EELS probabilities can be simulated by using the boundary-element method (BEM), which enables the calculation of

arbitrary morphologies.¹⁻⁴ Moreover, we have demonstrated the capability of combining CL and EELS to investigate optical properties of coupling systems. In the future, we can extend the study of optical properties at nanometer scale to a more complex coupled system of Ag nanocubes, such as clusters consisting of three and above number of nanoparticles. More possibilities of configurations and larger versatilities of plasmonic behaviors can be predicted relative to dimers.

Regarding to develop novel plasmonic anti-counterfeiting platforms, this multiplex strategy with simultaneous encryption and data storage capability in chapter 4 can be combined with the flexible anti-counterfeiting platform in chapter 5. The objective here is to promote the information encoding platform with large information density, high security and low-error decoding to practical uses. The multiplex security labels with data storage capability would be fabricated on PET or PDMS films. Resulting labels can adapt to non-rigid surfaces, such as documents, banknotes, irregular packages and medicine vials, making them promising for real-world applications. In addition, a systematic stability testing can be conducted on these multiplex security labels to evaluate their performance under drastic changes in temperature, moisture and acidity. To lengthen platform durability for practical uses, we will deposit an additional thin layer of polymer like PDMS onto the plasmonic structures to further insulate them against air, moisture and heat.

Moreover, we have also demonstrated a 3D plasmonic security label based on Z-dependent SERS in chapter 5. Flexible SERS substrates are promising for studies on 3D SERS detection because they can be simply wrapped onto arbitrary shaped surfaces to make any 3D surfaces to be SERS-active. In the future, 3D plasmonic security labels would be combined with flexible substrates to investigate 3D SERS detection on arbitrary shaped surfaces.

Furthermore, to reduce the cost of mass-producing this plasmonic security label, we can replace the Ag with Al. Nowadays, studies show that the plasmon resonances of Al

nanostructures can be tuned to the visible and NIR regions through increasing the sizes, aspect ratios and coupling arrays or holes. Due to the formation of alumina oxide on the surfaces, the resonances can be further tuned to even longer wavelengths. Combined with natural abundance and low cost, these properties make Al nanostructures promising for fabricating security label based on SERS. Besides, it is well-known that the SERS intensities are highly dependent on the gap sizes. A PDMS film with higher elasticity than PET can resume its normal shape after being stretched.^{5,6} By using our strategy to directly write nanostructures on PDMS, the gaps between nanostructures can be accurately controlled by stretching the PDMS film, enabling the study of gap-dependent SERS of plasmonic nanostructures. The adjustable outputs of SERS intensities via stretching could serve as additional layer of encryption, which would further enhance the security level by using this anti-counterfeiting platform.

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7 List of Acronym

Acronym	Definition
LSPR	localized surface plasmon resonance
SPR	surface plasmon resonance
SP	surface plasmon
EM	electromagnetic
SERS	surface-enhanced Raman scattering
SEF	surface-enhanced fluorescence
SERRS	surface-enhanced resonance Raman scattering
PVP	poly(vinylpyrrolidone)
CTAB	cetyltrimethylammonium bromide
AA	ascorbic acid
NR	nanorod
SHE	standard hydrogen electrode
OT	1-octanethiol
HOPG	highly-orientated pyrolytic graphite
EBL	electron-beam lithography
FIB	focused ion beam lithography
NSL	nanosphere lithography
PMMA	poly(methyl methacrylate)
DDA	discrete dipole approximation
FDTD	finite difference time domain
BEM	boundary element method
CL	cathodoluminescence

EELS	electron energy-loss spectroscopy
NSOM	near-field scanning optical microscopy
SEM	scanning electron microscopy
EDS	energy dispersive X-ray spectroscopy
TEM	transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
SERS EF	surface-enhanced Raman scattering enhancement factor
CE	chemical enhancement
CT	charge transfer
SHINERS	shell-isolated nanoparticle-enhanced Raman spectroscopy
PFDT	1H,1H,2H,2H-perfluorodecanethiol
SEGSO	selective edge gold-deposited silver octahedra
NSEGSO	non-selective edge gold-deposited silver octahedra
4-MBT	4-methylbenzenethiol
SAM	self-assembled monolayer
PPI	pillar per inch
R6G	rhodamine 6G
EY	eosin Y
3D	three-dimensional
PDMS	poly(dimethylsiloxane)
PET	poly(ethylene terephthalate)
DILL	dip-in lithography

8 List of Publication

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