THE FABRICATION AND APPLICATION OF PLASMONIC NANOPATTERNS BY SHADOW NANOSPHERE LITHOGRAPHY

by

WHITNEY INGRAM

(Under the Direction of Yiping Zhao)

ABSTRACT

Nanoplasmonic materials are metals with nanoscale dimensions that possess strong localized electric fields at specific resonance wavelengths. Such a fascinating optical property can be exploited in numerous applications such as chemical and biological sensors, solar cell technology, metamaterials (cloaking technology), localized heating, biological imaging methods, *etc*. The ability to control and tune the plasmonic resonance of nanomaterials is critical, and depends strongly on the material's design and fabrication technique. For practical applications, the design procedures shall be simple and straightforward while the fabrication method must be scalable and inexpensive. In this dissertation, we utilize a simple, inexpensive, and scalable nanofabrication technique known as shadow nanosphere lithography (SNSL), which combines the nanosphere lithography with the dynamic shadow growth method, to design several new plasmonic structures/materials.

Based upon the principles of SNSL, we introduce four specific strategies for designing plasmonic nanopatterns with tunable plasmonic properties: silver (Ag) films on nanospheres, Ag triangular networks, Ag double triangles, and Ag-Cu alloy nanopatterns. Each structure possesses unique morphologies that can be predicted through numerical simulations based on the shadowing effect of the nanosphere template. By systematically changing the nanopattern's morphology or

material composition, the localized surface plasmon resonance can be tuned to specific wavelengths. The relationship between the nanopattern morphology and its plasmonic properties are understood through finite-difference time-domain simulation, while the effect of composition variation on the optical properties are predicted by an empirical equation derived from bulk materials.

Finally, we establish that by tuning the localized surface plasmon resonance of these plasmonic nanomaterials, the sensitivity of these structures can be optimized for sensors based on surface enhanced Raman spectroscopy and localized surface plasmon resonance principles.

INDEX WORDS: Plasmonic nanomaterials, shadow nanosphere lithography, localized surface plasmon resonance, self-assembled colloid monolayer, dynamic shadow growth

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DEDICATION

I would also like to dedicate this to my family: my father, Timothy Ingram, mother, Dianna Ingram, and older sister, Janay Ingram. This would have not been possible without the support they gave me.

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CHAPTER 1

OVERVIEW OF PLASMONIC NANOMATERIALS

1.1 Introduction

Plasmonics is the study of the optical properties of metals with nanometer scale dimensions. Particularly, this research field focuses on a metal's ability to generate plasmons when excited by light, a property also observed in large scale (or bulk) metals. Plasmons are the collective movement of free electrons within a metal. At the boundary between a metal and a dielectric (such as air), plasmons couple with light to produce a wave that propagates along the metal/dielectric interface known as surface plasmons polaritions (SPP). When the dimensions of the metal are confined to nanometer-length, SPP no longer propagate. Its motion is restricted by the boundary of the metal's surface. Instead, a standing wave forms inside the confined metal surface called localized surface plasmon (LSP). Due to LSP, nanoscale metals possess optical



Figure 1.1.1 An example of stained glass made from gold and silver nanoparticles. [1]

features that are not observed in their bulk counterparts. For instance, they can change in color. Such properties have been employed by mankind for centuries. Medieval artisans, for instance, unknowingly mixed gold nanoparticles with molten silica to create beautiful red stained glass, and similarly used silver nanoparticles to create yellow stained glass as illustrated **Figure 1.1.1**. [1] The cause of the optical changes in these materials was unknown until the beginning of the 20th century. In 1908 Gustav Mie analytically solved Maxwell's equations for the interaction of a plane EM wave and a spherical particle. [2,3] His theory predicted that a conductive nanoparticle can scatter light intensely at specific wavelengths, which can make it appear in a different color. Currently, the optical properties of nanoscale metals that Mie predicted are now understood to be the result of their LSP. In short, when metal nanomaterials are excited by light at a specific LSP frequency, a strong localized electromagnetic (EM) field is generated at the metal surface that can intensely absorb and/or scatter light. This optical phenomenon is an important property known as localized surface plasmon resonance (LSPR).

The ability to absorb or scatter light at specific visible wavelengths makes plasmonic nanomaterials attractive for many applications. In fact, plasmonic nanomaterials play a crucial role in chemical and biological sensing techniques like LSPR sensing [4-6] and surface enhanced Raman spectroscopy (SERS) [7-9], solar cell technology [10-12], metamaterials, [13,14], localized heating [15,16], and optical imaging techniques. [17-19]

However, many applications require the LSP to resonate at a specific wavelength range and to reach a certain strength. SERS, for instance, is a sensory technique that detects scattered light due the vibrations of molecules adsorbed on a plasmonic nanomaterial's surface. When the nanomaterial is excited at its LSPR wavelength, the strong localized electric field generated can amplify the Raman scattering signal induced by the molecule [4-6,20] Similarly, in studies of plasmonic nanomaterials coated on solar cells, the nanomaterials must be made to enhance and expand the absorbance of visible light. [10-12] Therefore, plasmonic nanomaterials with tunable LSPR wavelengths have become increasingly important for those practical applications.

The LSPR wavelength of a plasmonic nanomaterial can be tuned by its composition, size, shape, proximity to other plasmonic materials, and surrounding dielectric environment, which can be controlled by the material's fabrication technique. [4] In general, nanofabrication techniques can be divided into two categories: top-down and bottom up methods. For practical applications, these nanofabrication methods should easily tune the morphology of a nanomaterial and be inexpensive, quick, and scalable. However, many methods suffer from limitations that prevent practical use.

Shadow nanosphere lithography (SNSL) is a promising method to fabricate plasmonic nanomaterials in a simple and practical manner. It is the combination of a bottom-up strategy called dynamic shadow growth (DSG) and a top-down method called nanosphere lithography (NSL). SNSL is simple, inexpensive, and scalable fabrication method that can generate predictable and controllable nanomaterial patterns. In this dissertation, SNSL is used to fabricate new plasmonic nanomaterial patterns. For each nanopattern, the LSPR wavelength can be tuned by systematically changing the material's morphology and/or composition. We show that this strategy is an effective method to optimize the sensitivity of SERS and LSPR sensing strategies.

In this chapter, the fundamental concepts, applications, and an overview of a commonly used nanofabrication techniques for plasmonic materials are introduced. Specifically, in **Section 1.2.**, the basic theory of plasmonics, factors that affect the LSPR wavelength, and LSPR sensing principles are discussed. In **Section 1.3**, SERS detection is elaborated. Then, in **Section 1.4**, the

dynamic shadowing growth and nanosphere lithography are discussed in detail. Lastly, an overview of the dissertation is given in **Section 1.5**.

1.2 Fundamentals of Plasmonics

1.2.1 Basic theory

Maxwell's equations in matter

The interaction between metals and EM fields can be understood through classical electrodynamics (quantum effects are not significant so long as the metal dimensions are above 10 nm). [21] Classical EM behavior is governed by the Maxwell's equations,

$$\nabla \times \boldsymbol{D} = \rho_{ext},\tag{1.1}$$

$$\nabla \cdot \boldsymbol{B} = \boldsymbol{0}, \tag{1.2}$$

$$\nabla \times \boldsymbol{H} = \boldsymbol{J}_{ext} + \frac{\partial \boldsymbol{D}}{\partial t}, \qquad (1.3)$$

$$\nabla \times \boldsymbol{E} = \frac{\partial \boldsymbol{B}}{\partial t},\tag{1.4}$$

where D is the displacement field, E is the electric field (E-field), ρ_{ext} is the free charge density in the material, J_{ext} is the current density in the material, H is the magnetic field, and B is the magnetic induction field.

For homogeneous and isotropic media, the four fields are related by the following constitutive relations,

$$\boldsymbol{D} \equiv \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = \varepsilon_0 (1 + \chi_e) \boldsymbol{E} = \varepsilon \boldsymbol{E}, \qquad (1.5)$$

$$H \equiv \frac{1}{\mu_0} B - M = \frac{1}{\mu_0} (1 + \chi_m)^{-1} B = \frac{1}{\mu} B, \qquad (1.6)$$

where P is the polarization, χ_e is the electric susceptibility, ε_0 is the permittivity of free space, ε is the dielectric function, **M** is the magnetization, χ_m is the magnetic susceptibility, μ_0 is the

permeability of free space, and μ is the relative permittivity. For the plasmonic materials discussed below, they are usually assumed to be nonmagnetic, thus $\mu = 1$.

Bulk Plasmons

The unique optical property of plasmonic nanomaterials is determined by their dielectric function, which is closely related to their bulk counterparts. The dielectric function of metals is related to the motion of its free electrons in the presence of an EM field. In metals, free electrons move independently against a stationary lattice of positive ion cores. But, when an EM wave interacts with a metal, the free electrons are accelerated due to the EM force. This force causes the electrons to oscillate. A quanta of the collective oscillation is called a plasmon. The harmonic motion of free electrons can be described analytically by the following kinematic equation,

$$m\ddot{\boldsymbol{x}} + m\gamma\dot{\boldsymbol{x}} = -e\boldsymbol{\boldsymbol{E}}(t),\tag{1.7}$$

where *m* is the mass of the electron, *e* is the charge of the electron, γ is a damping coefficient, *x* is the displacement of the electron, and the dot represents a time derivative.

For a time-dependent *E*-field, $(E(t) = E_0 e^{-i\omega t})$, where ω is angular frequency) the displacement of free electrons is also time harmonic, and the solution to **Equation (1.7)** is

$$\boldsymbol{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)} \boldsymbol{E}(t).$$
(1.8)

Such a displacement of free electrons contributes to a polarized field $\mathbf{P} = -ne\mathbf{x}$, where *n* is the number density of electrons. Thus, **Equation (1.8)** can be as,

$$\boldsymbol{P} = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)}\boldsymbol{E}(t). \tag{1.9}$$

Then, according to Equation (1.5), \mathbf{P} is related to D and E,

$$\boldsymbol{D}(t) = \varepsilon_0 \left[1 - \frac{ne^2}{m(\omega^2 + i\gamma\omega)} \right] \boldsymbol{E}(t) . \qquad (1.10)$$

According to **Equations (1.5)** and (1.10) the dielectric constant of a metal, $\varepsilon(\omega)$, can be derived as

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \qquad (1.11)$$

where, ω_p , called the bulk plasma frequency, is defined as $\omega_p = \frac{ne^2}{m\varepsilon_0}$.

Equation (1.11), also known as the Drude model, describes the complex dielectric function of a metal as a function of ω . It can be written as a real and an imaginary component $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2},$$
 (1.12)

and

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau^2}{\omega(1+\omega^2 \tau^2)},\tag{1.13}$$

where $\tau = 1/\gamma$ is called the relaxation time. According to **Equations (1.12)** and (**1.13**), when $\omega > \omega_p$, the ε is predominately real (and negative), and light can propagate through the metal. When $\omega < \omega_p$, the ε is predominately imaginary (and positive) and light is attenuated through metal absorption or scattering. **Table 1.2.1** shows the ω_p and τ for some common metals. In addition to EM waves, these relations also hold for plasmons (longitudinal waves) in the metal. Plasmons that propagate throughout the volume of the metal are called bulk plasmons.

Element	$\omega_p(PHz)$	τ(ps)
Ag	2.32	0.18
Cu	2.12	0.04
Au	2.07	0.22
Al	3.57	0.05
Pt	1.24	0.06

Table 1.2.1 The plasma frequency (units of Peta (10^{15}) hertz (PHz)) and relaxation time (units of pico (10^{-12}) seconds (ps)).[22-24]

Surface Plasmon Polaritions

At the boundary between a metal and dielectric (*i.e.* air, water, *etc.*), plasmons can be excited and propagate along the metal/dielectric interface, known as surface plasmon polaritions (SSP). Figure 1.2.1 illustrates SSP propagating along an interface: the metal with a dielectric constant $\varepsilon_m(=\varepsilon_1 + i\varepsilon_2)$, is located at z < 0, whereas a dielectric with ε_d is located at z > 0. The SSP propagates along the metal/dielectric interface in the along *x*-direction, with a wave vector k_x , along the metal-dielectric interface. The wave is continuous at the boundary (z = 0). Note, that both ε_d and ε_m are assumed to be homogeneous in the *x*-*y* plane.

Conceptually, SPPs can be treated as a "hybrid wave" that results from the coupling between light and free electron displacement on the metal/dielectric surface. To describe SPP mathematically, a common strategy is to define a wave equation that can allow the propagation of light at the metal/dielectric interface, i.e., the wave must have an E-field component normal to the interface (E_z), but must also have a component in the propagation direction (for SPP to propagate, E_x). Thus, only transverse magnetic (TM, or p-polarization) light under certain conditions can



Figure 1.2.1. A diagram of SPP propagating in the x-direction along the metal (ε_m) and dielectric (ε_d) interface.

excite the SPP as shown in **Figure 1.2.1** [25,26]. By solving the wave equation (derived from **Equations (1.3-1.4)**) for a TM plane wave propagating along the *x*-direction, the electric and magnetic fields can be written as[25]:

$$H(r,t) = A_1 \, j e^{i(k_x x - \omega t)} e^{-k_1 z} \,, \tag{1.14}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = \left(A_1 \frac{ik_1}{\omega\varepsilon_0\varepsilon_d} \hat{\boldsymbol{\iota}} - A_1 \frac{k_x}{\omega\varepsilon_0\varepsilon_d} \hat{\boldsymbol{k}}\right) e^{(k_x x - \omega t)} e^{-k_1 z} \quad , \tag{1.15}$$

for z > 0 (dielectric), and

$$H(r,t) = A_2 \,\hat{j} e^{i(k_x x - \omega t)} e^{k_2 z},\tag{1.16}$$

$$\boldsymbol{E}(\boldsymbol{r},\boldsymbol{t}) = \left(-A_2 \frac{ik_2}{\omega\varepsilon_0\varepsilon_m} \hat{\boldsymbol{\iota}} - A_2 \frac{k_x}{\omega\varepsilon_0\varepsilon_m} \hat{\boldsymbol{k}}\right) e^{i(k_x \boldsymbol{x} - \omega \boldsymbol{t})} e^{k_2 \boldsymbol{z}},\tag{1.17}$$

for z < 0 (metal), where A_1 and A_2 are the magnitude of the fields in the dielectrics and metal, respectively, k_1 and k_2 are the *z*-components of the wave vector in the dielectric and metal, respectively.

Continuity of the EM fields at z = 0 of the interface requires that $A_1 = A_2$ and,

$$\frac{k_1}{k_2} = \frac{\varepsilon_d}{\varepsilon_m}.$$
(1.18)

Additionally, the wave vectors must follow the relationships [26],

$$k_1^2 = k_x - \frac{\omega^2}{c^2} \varepsilon_d, \tag{1.19}$$

and

$$k_2^2 = k_x - \frac{\omega^2}{c^2} \varepsilon_m, \tag{1.20}$$

where *c* is the speed of light in a vacuum. By combining **Equations** (1.18-1.20), the dispersion relationship for a SPP wave can be obtained as,

$$k_{\chi}^{2} = \left(\frac{\varepsilon_{m}\varepsilon_{d}}{\varepsilon_{m}+\varepsilon_{d}}\right)\frac{\omega^{2}}{c^{2}}.$$
(1.21)

Equation (1.21) describes the frequency-dependent coupling between the excitation light and SPP waves. At frequencies close to the bulk plasma frequency ω_p , the surface plasmons will not be able to directly couple with the incident light. As a result the SPP frequency will approach an upper limit value called the surface plasma frequency [27],

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1+\varepsilon_d}}.$$
(1.22)

According to **Equation (1.22)**, resonance of SPP waves depends upon the ε_d . In air (where, $\varepsilon_d = 1$), for instance, SPP resonance occurs at $\frac{\omega_p}{\sqrt{2}}$. At resonance, SPP no longer propagates, but becomes standing waves called surface plasmons.

Localized Surface Plasmons

When the dimensions of a metal are about or smaller than the skin depth l_s of an EM wave that was defined as [28],

$$l_{s} = \frac{\omega}{c} \left[Re \left(\frac{-\varepsilon_{m}^{2}}{\varepsilon_{m} + \varepsilon_{d}} \right)^{1/2} \right]^{-1}, \qquad (1.23)$$

an EM wave can propagate throughout the entire volume of the metal. Free electrons oscillate in response to the E-field creating surface plasmons that are spatially confined to the nanomaterial in the form of standing waves called localized surface plasmons (LSP). **Figure 1.2.2** illustrates the behavior of free electrons in a metal nanosphere. As the EM field propagates along the *x*-direction, displaced free electrons result in opposite charge distribution along the metal surface. Since the E-field is proportional to surface charge density, such a concentrated electric charge will generate an enhanced localized E-field near the surface of the nanosphere.

G. Mie derived an analytical solution for the interaction of EM waves with a metal nanoparticle. A detailed derivation and explanation of Mie's theory can be found in Ref. [29]. In short, Mie's theory shows that the total scattering (σ_{sca}), extinction (σ_{ext}), and absorption (σ_{abs})



Figure 1.2.2 An illustration of localized surface plasmon resonance (LSP), which shows the coupling of an electromagnetic field and metal nanospheres.

cross-sections from a conducting nanosphere are given as,

$$\sigma_{sca} = \frac{2\pi}{|k|^2} \sum_{L=1}^{\infty} (2L+1)(|a_L|^2 + ||b_L|^2|), \qquad (1.24)$$

$$\sigma_{ext} = \frac{2\pi}{|k|^2} \sum_{L=1}^{\infty} (2L+1) \left(Re(a_L + b_L) \right), \qquad (1.25)$$

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca}, \tag{1.26}$$

where L=1, 2, 3... is an integer representing the dipole and higher multipoles of the nanoparticle, a_L and b_L represent parameters that are composed of the Bessel functions ψ_L and χ_L ,

$$a_L = \frac{u\psi_L(u\eta)\psi'_L(x) - \psi'_L(u\eta)\psi_L(\eta)}{u\psi_L(\eta x)\chi'_L(\eta) - \psi'_L(u\eta)\chi_L(\eta)},$$
(1.27)

$$b_{L} = \frac{\psi_{L}(u\eta)\psi_{L}'(\eta) - u\psi_{L}'(u\eta)\psi_{L}(\eta)}{\psi_{L}(u\eta)\chi_{L}'(\eta) - u\psi_{L}'(u\eta)\chi_{L}(\eta)},$$
(1.28)

where $u \equiv \tilde{n}_m/n_d$ where \tilde{n}_m is the complex index of refraction of the metal ($\tilde{n}_m = n_r + i\kappa$), n_d is the index of refraction in the dielectric medium, $\eta \equiv k_d r$, where k_d is the wavenumber in the dielectric medium and *r* is the radius of the conductive nanoparticle.

Equations (1.25) can be simplified by approximating the Bessel functions as a power series. By only considering the dipole term, the σ_{ext} can be expressed as [27],

$$\sigma_{ext} = \frac{9\omega\varepsilon_d^{3/2}V}{c} \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_d]^2 + \varepsilon_2(\omega)},$$
(1.29)

where V is the volume of the particle, and ε_1 and ε_2 are the real and imaginary components of ε_m .

In Equation (1.29), σ_{ext} is maximized when the frequency ω_0 satisfies $\varepsilon_1(\omega_0) = -2\varepsilon_d(\omega_0)$. At ω_0 , the oscillating electrons generate a strong localized EM field. This phenomenon is called the localized surface plasmon resonance (LSPR). Based on the Drude model (Equation (1.12)), and assuming $\omega_p \gg \gamma$, ε_1 can be simplified as,

$$\varepsilon_1 \approx 1 - \frac{\omega_p^2}{\omega^2},\tag{1.30}$$

where this relation assumes $\omega_p \gg \gamma$. Therefore, ω_0 can be approximated as,

$$\omega_0 = \frac{\omega_p}{\sqrt{2\varepsilon_d + 1}},\tag{1.31}$$

or

$$\lambda_0 = \lambda_p \sqrt{2\varepsilon_d + 1},\tag{1.32}$$

where the LSPR wavelength $\lambda_0 = \frac{2\pi c}{\omega_0}$. According to **Equations (1.31)** and (1.32), the λ_0 is clearly dependent on the dielectric environment. However, there are other factors that can affect the resonance wavelength. They include the composition ε_1 and ε_2 , size *V*, shape, and proximity of the nanomaterial to other nanomaterials. Each of these factors are discussed in more detail in the following sections.

1.2.2 The LSPR Wavelength Dependence

Metal Composition

The composition of the metal is an intrinsic factor that can influence λ_0 . Equation (1.31) clearly demonstrates that ω_0 is proportional ω_p , the bulk plasmon frequency. Based on the values listed in **Table 1.2.1**, different materials have different ω_p . Figure 1.2.3 shows the extinction spectra of silver (Ag), copper (Cu), and gold (Au) triangular nanopatterns of the same size. The spectra show that the λ_0 redshifts for metals with higher λ_p . Other metals can also shift the LSPR resonance, but their λ_0 is usually in the IR wavelength range. [30]

In addition, the imaginary dielectric component of the metal, ε_2 , can also affect the extinction magnitude at λ_0 . The strongest σ_{ext} values occur when $-\varepsilon_1 \gg \varepsilon_2$. In order to reduce the optical loss, ε_2 needs to be small in magnitude. In fact, a term called the quality factor, Q_{LSP} , is used to estimate the relative σ_{ext} value of a specific metal at the LSPR, [22]



Figure 1.2.3 The normalized extinction spectra for Ag, Cu, and Au nanotriangles. Inset shows an SEM image of the triangular nanopattern.[31]

$$Q_{LSP} \equiv \frac{-\varepsilon_1}{\varepsilon_2}.$$
 (1.33)

The maximum Q_{LSP} can be determined by substituting the Drude model in **Equation (1.11)** and solving for Q_{LSP} as a function of ω . The maximum Q_{LSP} , Q_{LSP}^{max} , is defined as [22]

$$Q_{LSP}^{max} = \frac{2(\omega_p^2 - \gamma^2)^{3/2}}{3\gamma\omega_p^2\sqrt{3}}.$$
 (1.34)

Figure 1.2.4 shows the Q_{LSP}^{max} and corresponding frequency at which Q_{LSP}^{max} occurs (in eV) for most metals on the periodic table. The optical constants used to evaluate Q_{LSP}^{max} were calculated from experimental measurements (see Ref.[22]). Among all metals shown in **Figure 1.2.4**, Ag possess the highest Q_{LSP}^{max} . Other metals that have high Q_{LSP}^{max} are highlighted in blue, including Cu, Au, aluminum (Al), and the alkaline metals.

In most plasmonic research, Au and Ag are used frequently because of their high Q_{LSP}^{max} and optical response in the visible wavelength range. However, for mass production, both Ag and Au are expensive. Copper is also considered as a promising plasmonic material. Not only does it have a relatively high Q_{LSP}^{max} , but it is also more abundant and less expensive compared to Ag and Au. Unfortunately, Cu rapidly oxidizes into Cu₂O and CuO when exposed to air, which greatly attenuates its LSPR response. [30] Recent studies show that the oxide layer can be temporarily removed with acetic acid. [31] Another strategy to reduce or prevent the Cu oxidation process is by covering the Cu surface with graphene, polymers, or corrosion inhibitors. [32-34] These treatments make it possible for Cu to be used as a plasmonic material. An alternative strategy to reducing the Cu oxidation layer is to alloy Cu with another metal. Li, *et al.* showed that the oxidation of copper thin films can be reduced by alloying it with metals such as titanium (Ti), nickel (Ni), chromium (Cr), *etc.* [35] Similarly, Tsuji *et al.*, shows that plasmonic Cu-Ag coreshell nanoparticles suppress oxidation. [36]

Li	Be		Element									в	С	Max Q	sp Key
0.14*	0.20												0.00	-2.99	
28.82	3.58		Freque	ency of	* wmax is at the limit of the available data								3.00	3.00-3.99	
Na	Mg	1	Max QLSP # low requency data not included							AI	Si	4.00-6.99			
1.44	4.00		Мах	imum								11.00		7.00-9.99	
35.09	9.94		QL	SP							13.58		10+		
к	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
1.05	0.65*	0.3*	0.20	0.36	0.30	0.07*	0.10*	0.10*	0.15	1.75	3.60#	8.30			
40.68	3.63	1.02	2.58	4.27	2.16	1.16	2.48	2.69	2.71	10.09	3.59	3.41			
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те
0.81	0.36*	1.48*	3.00	0.55	0.38		0.10*	0.30	0.10*	1.14	0.65#	5.10	2.25	3.50	
21.90	2.85	1.41	1.16	3.39	5.38		2.03	2.10	6.52	97.43	3.63	4.60	3.50	1.33	
Cs	Ba	Lan	Hf	Та	w	Re	Os	lr	Pt	Au	Hg	ΤI	Pb	Bi	Po
0.51*	1.91		0.52*	0.58	0.30	0.10*	0.10*	0.40	0.35	1.40	4.20	3.20	5.95	3.50	
11.20	0.91		0.79	5.25	4.96	4.99	6.12	2.55	1.96	33.99	2.20	2.71	3.07	1.15	

Figure 1.2.4 A plot of the periodic table of elements showing the maximum quality factor (Max QLSP) value and frequency (in eV) for selected metals. [22]

In addition to oxidation protection, noble metal alloys or mixed phase materials can be used to change the λ_0 . By changing the composition of the alloy or mixed phase material, the λ_0 will shift. [30,37-43] Nanomaterials fabricated from alloys can also produce unique plasmonic responses not observed in pure metals. For instance, Gong *et al.* fabricated Ag-Cu, Au-Cu, and Ag-Au plasmonic thin film alloys. [43] They showed that at specific compositions the alloy possessed higher surface plasmon polarization than that of the corresponding pure metals.

Overall, varying material and/or composition plays a significant role in determining and controlling the LSPR.

Size

The size V of a nanomaterial can affect its λ_0 . This relationship can be understood by examining Mie's theory for a conductive spherical particle. In **Equation** (1.29), σ_{ext} is proportional to the volume of the nanoparticle V. Thus, as the radius of the particles becomes larger, the optical extinction will increase.

Another consequence of increasing V is that the particle can no longer be approximated by its dipole approximation, which is the assumption to derive in **Equation** (1.29). Higher order resonant modes, such as quadrupole resonances, become important. This effect can be seen by including the quadrupole contribution to **Equation** (1.29), [44]

$$\sigma_{ext} \approx \frac{4d}{\pi r^2} \left(g_d + \frac{d^2}{12} g_q + \frac{d^2}{30} (\varepsilon_2 - 1) \right), \tag{1.35}$$

where g_d is the dipole contribution, $g_d = \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m - 2\varepsilon_d}$, g_q is the quadrupole contribution, $g_q = \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m - 3/2\varepsilon_d}$, $da = \frac{2\pi r(\varepsilon_d)^{-\frac{1}{2}}}{\lambda}$, where *r* is the radius of the spherical nanoparticle, and $\lambda = \frac{2\pi c}{\omega}$.

From Equation (1.35), one can see that as r increases, the contribution of the quadrupole term becomes more significant. Moreover, at resonance, there will be two λ_0 , one from the dipole resonance, λ_{0d} , and one from the quadrupole resonance, λ_{0q} . To illustrate and determine the effect



Figure 1.2.5. The E-field enhancement for Ag spheres with (a) r = 30 nm and (b) r = 60 nm excited by p-polarized light. (c-d)The extinction spectra (black line) and the average enhanced electric field spectra (blue, red, and green lines, respectfully) for (c) r = 30 nm and (d) r = 60 nm[44]

of *r*, **Figure 1.2.5** (a-b), shows the simulated E-field enhancement, $|E^2|$ of a single Ag sphere with r = 30 and 60 nm excited by *p*-polarized light. [44] As light excites the 30 nm-radius sphere, a strong E-field is generated. This response is due primarily to the dipole component, which is located along the upper and lower regions of the sphere. The E-field enhancement for the 60 nm - radius sphere, on the other hand, shows a dominant quadrupole resonance, which is indicated by the four distinct enhancement regions surrounding the sphere.

The corresponding plot of the extinction spectra, the average E-field, and localized E-field at specific locations (indicated as Point 1 and 2) are plotted in **Figure 1.2.5 (c-d)**. By comparing the extinction spectra (the solid black line) from each diameter, one can see that the 30 nm diameter particle has a single dipole resonance peak, while the 60 nm diameter particle has two resonance peaks associated with the dipole and quadrupole effect. **Figure 1.2.5 (c-d)** also shows the field enhancement at the dipole and quadrupole locations for each particle. In the figure, Point 1 indicated the dipole field, while Point 2 represents the quadrupole field. Theoretically, the λ_{0d} for



Figure 1.2.6 (a) The extinction spectra of Ag nanoparticles with different diameter d. (b) The dipole resonance wavelength plotted as a function of d [45]
both sized spheres should be the same, but the coupling effect between the dipole and quadrupole resonance depolarizes the dipole plasmon resonance, resulting in a smaller average field and redshifted peak. [44,46] Thus, the simulation results illustrate that as r increases, the effects of higher order modes, λ_{0q} in this case, become important, and can redshift and broaden λ_{0d} .

The above calculations are consistent with experimental studies. Figure 1.2.6 (a), for instance, shows the extinction spectra of Au spherical nanoparticles with diameters ranging from 10 nm to 100 nm. The spectra show that as r (or d, the diameter) increases, the magnitude of σ_{ext} at λ_{0d} increases, and the λ_{0d} redshifts. The λ_{0q} can be observed when d > 70 nm. Figure 1.2.6 (b) plots λ_{0d} versus d, and clearly shows that the λ_{0d} redshifts with increasing d. And although λ_{0q} is not plotted, this peak also redshifts with d. This example is a simple case of the size-dependent effect of λ_0 , but similar trend has been observed in other shaped plasmonic materials. [27,47,48]

Shape

The effect of a nanomaterials' shape on λ_0 can be understood through the example of a spheroid-shaped nanoparticle. Gan's theory generalizes Mie theory for the case of an ellipsoid of any aspect ratio. Analogous to **Equation (1.29)**, the σ_{ext} of a nanospheriod can be expressed as [49,50]

$$\sigma_{ext} = \frac{2\pi\omega V \varepsilon_d^{3/2}}{3c} \sum_j \frac{\left(1/P_j^2\right) \varepsilon_2}{\left(\varepsilon_1 + \frac{1-P_j}{P_j} \varepsilon_d\right)^2 + \varepsilon_2^2},\tag{1.35}$$

where P_j (with the indexes j = a, b, c) is the depolarization factor that corresponds to the three primary axes from a general equation of an ellipsoid, $\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$. In the case of a spheroid with a > b = c, P_j can be written as [51],

$$P_a = \frac{1 - e^2}{e^2} \left[\frac{1}{2e} \ln \left(\frac{1 + e}{1 - e} \right) - 1 \right],$$
(1.34)

and

$$P_b = P_c = \frac{1 - P_a}{2}, \tag{1.35}$$

where e is the eccentricity defined as,

$$e = \sqrt{1 - \left(\frac{b}{a}\right)^2}.$$
(1.36)

Equation (1.35) shows the depolarization factors, P_j will determine number of λ_0 , which depends upon the nanomaterial shape. Since there are two P_j terms, the spheroid will have two λ_0 ; one that corresponds to *a*, the long axis of the spheroid, is often referred to as the longitudinal mode, λ_{0L} ; and the other that is related to *b*, the short axis, is called the transverse mode, λ_{0T} . Figure 1.2.7 (a) shows the calculated extinction spectra of a spheroid with an aspect ratio, R = 3.3 (where R = a/b). Both λ_{0L} and λ_{0T} are labeled in the spectrum. By changing the shape of the spheroid, i.e., the aspect ratio R = b/a, both λ_{0L} and λ_{0T} will also change. Figure 1.2.7 (b) shows the extinction spectra of spheroid nanoparticles with different *R*. As the *R* increases, both λ_{0L} and λ_{0T} redshift, and their corresponding σ_{ext} peaks increase. The inset in Figure 1.2.7(b) shows a plot of λ_{0L} as a



Figure 1.2.7. Numerical calculations for an ellipsoid by Gans Theory. (a) Absorbance spectra of a spheroid with R = 3.3 and (b) ellipsoids with different aspect ratio R. [51]

function of *R*, which indicates a linear relationship between λ_{0L} and *R*. Link *et al.*, used numerical method to determine the relationship between λ_{0L} and *R*, and derived the following empirical expression for λ_{0L} ,

$$\lambda_{0L} = (\beta_1 - \beta_2 R)\varepsilon_d + \beta_3, \tag{1.37}$$

where β_1 , β_2 , and β_3 are constants. By fitting **Equation** (1.37) with λ_{0L} as a function of *R* (Figure 1.2.7 (b)), β_1 , β_2 , and β_3 were determined to be 33.34, 46.31, and 472.31, respectively. Similar results has been obtained for λ_{0T} .

For shapes such as cubes or triangles, edge effect can lead to additional plasmon resonances. Fruch *et al.* theoretically and experimentally studied the optical properties of cube-shaped particles, and showed that, when excited, the edges of the cube become strongly charged and each corner induced a resonance peak. [52] Experimentally, the extinction spectra of cubical metal particles showed multiple, but broad resonance peaks. The edge effect observed in Fruch's work is consistent with the results for other shaped plasmonic materials published in literature.[4]

Nearest Neighbor Proximity

The proximity between two nanoparticles/patterns is another factor that can shift λ_0 , which is the result from the EM coupling. The EM coupling effects of plasmonic nanomaterials can be easily understood by simulations. As an example, Clarkson *et al.* calculated the scattering spectra of two spherical Ag nanoparticles (dimer) with fixed center-to-center separation distance L (=200 nm), and varying radius r (from 10 to 100 nm) as shown in **Figure 1.2.8** (a). [53] The spectra show that for small r/L (or smaller spheres, since L is fixed) ratio, a dipole resonance peak, λ_{0d} , is observed. As r/L increases, a second peak due to the quadrupole resonance λ_{0q} is observed. As r/L increases both resonances redshift. Since the size of the nanoparticles and their separation distance changes, it is important to distinguish which property causes the shift of λ_0 . **Figure 1.2.8**



Figure 1.2.8 (a) The calculated scattering spectra of Ag dimers with fixed center-to-center separation distance L, and varying radius, r.(b) A plot of the LSPR resonance peak as a function of r/L for dipole and quadrupole resonances for dimer(or particle-pair) and its corresponding single particle with the same r.[53]

(b) plots the λ_{0d} and λ_{0q} for the dimer and individual particle as a function of r/L. Note that the values of λ_{0d} and λ_{0q} for the individual particle of radius r are plotted alongside the dimer at r/L for comparison purposes. The plot shows that when r/L > 0.350, the shift of λ_{0d} becomes faster than that of the individual particles. Such a result is assumed to be due to a coupling effect, while the emergence of λ_{0q} is a size induced effect. Based on the data in **Figure 1.2.8** (b), Clarkston *et al.* derived an empirical relationship between λ_{0d} and r/L, [53]

$$\lambda_{0d}(\varsigma) = (C_0 + \lambda_{10}) + Ae^{-\varsigma/_s}, \tag{1.38}$$

where C_0 is a constant, A is a scaling factor, $\varsigma = L/2r$, and s is the decay constant. [53] Thus the interparticle spacing plays an important role in λ_{od} , which is consistent with other studies as well.[4,5]

It is well known that the coupling between nanomaterials can also generate a strong localized E-field between two spheres, called "hot spots". For example, **Figures 1.2.9** (**a-b**) shows the simulated E-field distribution of a single and a pair of Au 100 nm diameter spheres. [54] The



Figure 1.2.9 (a) The E-field distribution of a 100 nm-diameter Au nanoparticle. (b)The E-field distribution of an Au dimer with a gap distance of 75 nm. (c) Enhancement factor of the E-field versus the gap distance. [54]

gap distance for the dimer is 25 nm. Compared to the E-field distribution of the single nanoparticle, the E-field distribution between the pair of Ag particles is much stronger. This trend can be expressed quantitatively by a term called the field enhancement factor, defined as $\frac{|E|}{|E_0|}$, where E_0 and *E*, are the E-field the magnitudes of the single and pair of particles, respectively. **Figure 1.2.9** (c) shows the enhancement factor of the particle-pair as a function of separation distance. Clearly, as the spacing distance increases, the field enhancement factor becomes smaller.

Dielectric Environment and LSPR Sensing

It is easy to see from **Equation** (1.32) that λ_0 is directly correlated to ε_d , the surrounding environment of the plasmonic material. Therefore, it is expected that the change in dielectric medium can shift λ_0 , *i.e.*, increasing ε_d will redshift λ_0 . According to **Equation** (1.32),

$$\lambda_0 = \lambda_p \sqrt{2\varepsilon_d + 1} \approx \sqrt{2}\lambda_p n_d, \tag{1.39}$$

where n_d is the real component of the index of refraction for a dielectric medium. Thus, **Equation** (1.41) indicates that λ_0 increases almost linearly with n_d . Figure 1.2.10 shows the simulated extinction spectra of Au nanoparticles in different dielectric medium. The insert in the figure confirms the linear relationship between λ_0 and n_d .

The change of λ_0 with respect to n_d can be used as a sensing mechanism to produce a socalled LSPR sensor. The LSPR sensing has been developed rapidly in the past 20 years, and can be divided into two categories: the bulk refractive index sensing and molecular sensing, illustrated in **Figure 1.2.11**. For the bulk refractive index sensing, the surrounding bulk dielectric medium is changed. It is used to quantitatively evaluate the sensitivity of a plasmonic material or to detect variations in the dielectric environment due to changes in the media concentration. [27,55-57] For molecular sensing, the local dielectric environment immediately surrounding the plasmonic material is changed due to molecular adsorption onto the material surface. It is commonly used for biological sensing. In this case, plasmonic nanomaterials are functionalized with probe molecules that can be selectively bonded to the desired target. As the target molecules attaches to the captured molecule, the local dielectric environment of the plasmonic nanomaterial will change, which redshifts its λ_0 . Molecular sensing has been used to quantitatively detect anti-body interaction,



Figure 1.2.10 The absorbance spectra of nanopatterns with different dielectric environments (symbolized by their index of refraction n). [58]

Bulk Refractive Index Sensing



Figure 1.2.11. An illustration of LSPR sensing methods: (a) Bulk index of refraction sensing and (b) molecular sensing. [27]

DNA hybridization, protein recognition, bacteria adsorption, hydrogen peroxide concentrations, and biomarkers for disease, *etc.* [57,59,60]

One of the current challenges for LSPR sensing, especially for molecular sensing, is that small molecules that bind to plasmonic nanomaterials do not significantly shift λ_0 . The sensitivity *S* of the LSPR sensor is defined as,

$$S = \frac{\Delta \lambda_0}{\Delta n_d}.$$
 (1.40)

In addition, the performance of the sensor also depends on the LSPR peak width. As the size of the plasmonic particles increase, the width of their extinction peak becomes broader due to multipolar resonances. Therefore, a second parameter, the figure of merit (FOM), is also used to describe the quality of the sensor,

$$FOM = \frac{S}{FWHM} = \frac{\Delta\lambda_0}{\Delta n_d \times FWHM}$$
(1.41)

where *FWHM* is the full-width at half-maximum of the LSPR peak. The explicit expression of *S* can provide some possible ways to improve the response of the LSPR sensor, [56]

$$S = \frac{\frac{d\varepsilon_1}{dn}}{\left(\frac{d\varepsilon_1}{d\lambda_0}\right)_{\lambda_d}} = -\frac{2\chi n}{\left(\frac{d\varepsilon_1}{d\lambda_0}\right)_{\lambda_d}},\tag{1.42}$$

where χ is a shape factor (related to the aspect ratio) of the nanomaterial. According to **Equation** (1.42), in order to increase *S*, one can increase the χ . This can be done by increasing the aspect ratio of the nanomaterial. In general, nanomaterials with high aspect ratios tend to have sharper, narrower resonance peaks. For instance, nanorods and nanocubes have been shown to have much higher sensitivity than that of spherical nanoparticles. [61-63] The other way is to reduce the dependence of ε_1 on λ_0 , *i.e.*, decreasing the value of $\frac{d\varepsilon_1}{d\lambda_0}$. This can be achieved by alloying the nanomaterial with another metals. For instance, by alloying a metal such as Au, which has a strong LSPR peak, with Cu or Ti, which shows weaker LSPR response, the dependence of ε_1 on λ_0 can be reduced. Jeong *et al.* demonstrated that the LSPR sensitivity of Ag nanoparticles could be improved by alloying them with Ti. [56]

1.3 Surface Enhanced Raman Spectroscopy

Raman Spectroscopy

Raman spectroscopy is a vibrational scattering technique used to detect inelastically scattered light. [64] When photons, with energy $\hbar\omega$, interact with a molecule vibrating at a frequency ω_1 , the scattered photons can have three possible energies. **Figure 1.3.1** (a) illustrates the possible scattering phenomena generated by this interaction. Most of the photons will be scattered with the same energy as the incident photon, $\hbar\omega$, called Rayleigh elastic scattering, which is indicated by the green arrow in the figure. Photons can also scatter with energies that are higher with $\hbar(\omega + \omega_1)$, called Anti-Stokes Raman scattering. Or, the scattered photons can have lower energies with $\hbar(\omega - \omega_1)$, called Stokes Raman scattering. The energies gained or loosed by the scattering photons in Stokes and anti-Stokes Raman scattering are the characteristic vibrational



Figure 1.3.1 (a) A diagram of the interactions between a photon and molecule. (*b*) The Raman spectra of benzene (DMMB), 4-(mercaptomethyl)ethynyl benzene (MMByne) and 4-(mercaptomethyl)nitrobenzene (MMBNO). [65]

energies of the molecular bonds, which reveal information about distinct composition of the molecule concerned. Such a scattered intensity versus the shifted energy of the scattered photons can be used as "molecular fingerprint" to identify specific molecules. **Figure 1.3.1 (b)** shows representative Raman spectra of some organic molecules. Although Raman spectroscopy is a good analytic chemical tool to study and detect molecular composition, the intensity of Raman scattered light is very low. This effect is primarily due to the low Raman cross-section of most molecules (approximately 10⁻²⁵ to 10⁻³⁰ cm²). [66] Thus Raman spectroscopy cannot be used as an optical sensor.

Surface Enhanced Raman Spectroscopy

Nearly 30 years ago it was discovered the "roughened surface" of Ag could enhance the Raman signal from molecules adsorbed onto it. [7,8,67,68] This phenomenon was attributed primarily to the chemical interactions of molecules with Ag, and the plasmonic properties of Ag, and is now known as surface-enhanced Raman spectroscopy (SERS). Currently, SERS has

developed into a promising optical chemical and biological sensing technique. For instance, SERS has been used to detect biomarkers for cancer, inorganic pollutants, explosives, proteins, DNAs, *etc.* [69-73] Compared to Raman spectroscopy, SERS has a much better sensing capability. The ratio of the enhanced Raman signal to a regular Raman signal is called the enhancement factor *EF*,

$$EF = \frac{I_{SERS}/N_{Vol}}{I_{RS}/N_{SERS}},\tag{1.43}$$

where I_{RS} and I_{SERS} are the scattering intensity of the regular Raman and SERS, N_{SERS} and N_{RS} are the number of adsorbed molecules on a SERS substrate probed by the excited laser beam and the number of molecules within the scattering volume for regular Raman. Overall, the *EF* of SERS substrates can have values ranging from 10⁵ to 10¹⁰. [74,75]

There are two known SERS enhancement mechanisms. The first is an EM (EM) field enhancement due to the plasmonic properties of the metal substrate. [9] The second mechanism is chemical (CM) enhancement, which is due to the chemical bonding or charge transfer (CM) between the metal and the molecule. [9,76]

EM enhancement is related to the plasmonic properties of the nanomaterial. Specifically, when an EM field $E_0(\omega)$ irradiates the surface of a plasmonic metal, a localized E-field $E_{loc}(\omega)$ is generated on the surface of the material. This enhanced E-field can increase the probability of the incident photons interacting with a molecule, and also force the molecule to vibrate at a large magnitude. Based on both classic and quantum theory, the Raman scattered intensity I_{SERS} can be described quantitatively as [9],

$$I_{SERS} = |E_0(\omega)|^2 |E_{loc}(\omega - \omega_1)|^2 .$$
 (1.44)

The maximum I_{SERS} will occur when $E_{loc}(\omega)$ reach the highest value, *i.e.*, at a hot spot, $\omega - \omega_1 = \omega_0$. According to previous discussion, since $\omega \gg \omega_1$, at the maximum I_{SERS} , $I_{SERS} \approx |E_{loc}(\omega_0)|^4$

Chemical enhancement, on the other hand, is related the affinity of a molecule to adsorb or interact with the plasmonic metal's surface. [9] Molecules can chemically interact with a plasmonic material via charge transfer. For this interaction, coupling between the metal and molecule creates metal-ion bonds that have intermediate vibrational states that can be easily excited and scatter light. [76]

Among the two enhancement mechanisms, the EM mechanism can have an EF up to 10^8 or higher, while CM enhancement could contribute up to 10^3 in EF.[76,77] Therefore, EM enhancement is the dominant contribution to SERS. Thus, a significant amount of studies focus amplifying SERS signals by designing nanomaterials to have better EM-based signal enhancement.

There are two ways to improve EM enhancement of a nanomaterial. First, the wavelength of the excitation laser must be tuned near the LSPR wavelength of the nanomaterial as discussed above. In fact, experimentally, Greeneltch *et al.* verified such a condition. [57] **Figure 1.3.2** plots the SERS *EF* as a function of the excitation wavelength λ for benzenethiol and Ag nanorods



Figure 1.3.2. SERS enhancement factor versus the LSPR wavelength [20]

substrates maximum EF is obtained when $\lambda \approx \lambda_0$. Another method is to increase the density of hot-spots (see Section 1.1.2, nearest neighbor proximity). With a high hot-spot density, more targeted molecules will have an opportunity to fall into the hot-spot locations, thus improve I_{SERS} . [4,5] High hot-spot densities can be created by designing nanopatterns that have small separation distances.

1.4 Nanofabrication and Synthesis

1.4.1 Plasmonic nanofabrication overview

There are numerous techniques reported in literature to fabricate plasmonic nanomaterials. These methods can be divided into two general catalogs: top down and bottom up nanofabrication techniques. [78] Top down methods commonly use a template to fabricate nanomaterials onto a surface, while bottom up methods assemble atoms or molecules into nanomaterials by using chemical or physical processes. Methods associated with each technique have advantages and disadvantages that can be used for practical production.

Electron beam lithography (EBL) is a commonly used top-down method to fabricate plasmonic nanomaterials. This technique, illustrated in **Figure 1.4.1 (a-f)**, uses a focused beam of electrons to write nanopatterns onto an electron sensitive material referred to as "resist." After writing, the resist is immersed in a solution that selectively removes E-beam exposed photoresist. Then the developed substrate is coated with a desired material, and the underlying polymer is chemically removed. EBL can produce nanomaterial arrays with feature sizes less than 5 nm, and gives excellent control over the aspect ratio of the nanomaterial shape. [79] However, this method is time consuming, expensive, non-scalable, and low throughput. Another popular top-down method is nanoimprint lithography (NIL). [80,81] As shown in **Figure 1.4.2 (a-e)**, a polymer melted above its glass transition is pressed into a mold and is allow to cool down. Once the polymer



Figure 1.4.1(a-e) An illustration of the steps in the EBL strategy. (Condensed matter Group, University of Leeds). (g) Au and (h) Ag nanopatterns fabricated by EBL. [82,83]

has solidified, the mold is lifted, leaving a template on the substrate surface. Similar to EBL, material is deposited onto the template, and then the template is removed. An example of NIL fabricated nanopatterns is shown in **Figure 1.4.2 (b)**. Due to its relatively simple and quick fabrication strategy, NIL is a promising technique to fabricate plasmonic nanopatterns in an inexpensive and scalable manner. [81] However, NIL still has some limitations. The mold may experience stress due to the repeated heating and cooling, which could distort the mold over time and affect the reproducibility of nanopatterns. In addition, the viscosity of the polymer used in the molding process can limits the feature size and precision of the nanopatterns. [79]

One type of bottom-up nanofabrication method is chemical synthesis, which are wetchemical reactions where molecules or atoms self-assemble into nanoparticles. [30,37,40,84] One particular synthesis technique, called chemical reduction, is a widely used method where metal salts are mixed with strong reducing agents to form metal or metal alloy nanoparticles, as shown in **Figure 1.4.3** (a). These methods can generate nanomaterials with a variety of shapes, including



Figure 1.4.2 (a-e) An illustration of the steps in the NIL strategy. [81](*f*) SEM images of gold nanodisks [85], and (*g*)gold antennas prepared via NIL. [80]

nanospheres, cubes, stars, sheets, *etc.* as illustrated in **Figure 1.4.3** (b-c). [30,86] Chemical synthesis methods are an attractive method to prepare plasmonic materials because it is considered as a quick and scalable technique. But, these techniques lack the freedom to easily and freely manipulate the shape of the nanomaterials. [87]. Another fabrication method is physical vapor deposition (PVD). PVD techniques use a physical process such as melting or physically ablating to deposit materials into thin films or nanopatterns. [78] **Figure 1.4.4** (a) shows an example of a PVD method, the sputtering deposition method, where titanium (Ti) and Cadmium (Cd) sources are physically ablated to coat a substrate. **Figure 1.4.4** (b-c) show corresponding Ag nanoparticles and Au films fabricated by the sputtering deposition. For practical applications, PVD is an ideal nanofabrication method because it is scalable, high throughput, and fairly inexpensive. There are



Figure 1.4.3 (*a-c*) An illustration of the chemical synthesis. (*a*) Reducing agent is added to a heated metal precursor solution. (*b*)The continuous mixing between the precursor and reducing agent generates small clusters of nanoparticles and over time,(*c*) the size of the nanoparticle clusters increase. (*d*) The SEM images of Ag nanocubes [88]and Ag nanotriangles made by chemical reduction methods. [89]



Figure 1.4.4 (a) A diagram of a DC magnetron sputtering system where two sources, Ti and Cd, are sputtered simultaneously in argon and oxygen plasma environment.. [90] (b) SEM images of Au nanoparticles and (c) Ag film fabricated by DC magnetron sputtering. [91]

numerous PVD strategies to design nanopatterns by manipulating material flow during the deposition. However, nanopatterns made from PVD tend to be random. Therefore, to design nanopatterns with controllable features, such as size, shape, and separation distance, PVD is often combined with template-based methods.

1.4.2 Dynamic shadow growth

Dynamic shadowing growth (DSG) is a PVD method where nanomaterials are fabricated by controling the material vapor flux relative to the substrate position. In this method, material is melted inside a pressure controlled chamber. Once the metal vaporizes, some of the adatoms of the material condense onto a substrate mounted inside the chamber. A shadowing effect occurs when some of the initially deposited adatoms, called nucleation sites, block the vapor flux, which prevents material from accumulating in specific regions. This concept is the foundation of DSG. As an example, columnar nanorods can be formed when the angle θ between the incident vapor flux and the substrate normal is an oblique angle. This is a type of DGS method commonly known as oblique angle deposition (OAD). [92] **Figure 1.4.5(a)** shows a typical deposition set-up. During the deposition, the vapor flux is often monitored by a quartz crystal microbalance (QCM) and a rotating state can control both θ and its azimuthal orientation φ . Figure 1.4.5 (b) shows the initial nucleation sites of metal vapor deposited at a large incident angle θ . As the deposition continues, the adatoms of the material (metal, for instance) only deposit and grow in the unshadowed regions as shown in Figure 1.4.5 (c). A representative SEM image of tiled nanorods fabricated by OAD is shown in Figure 1.4.6 (a). Alternatively, other nanostructures can be prepared by rotating the substrate position in both φ and θ directions known as Glancing-Angle deposition (GLAD). Figures 1.4.6 (b-c) shows vertical Ag nanorods and helical nanorods



Figure 1.4.5 (a) The illustration of a deposition system. (b) An illustration of nucleation sites that form at the beginning of the deposition and the (c) columnar growth due to the shadowing effects of neighboring particles.



Figure 1.4.6 SEM images of nanopatterns fabricated DSG techniques: (a) tilted nanorods, [93]
(b) nanohelixes, [94], and (c) vertical nanorods.[93] fabricated by GLAD with randomly seeded nucleation site. (d-f) Illustrations of helical, [94], seeded vertical nanorods, [95], and tilted nanorods using seeded nucleation sites. [96]

fabricated by this way. A template-based method can be used to create artificial nucleation sites to control the direction and location of columnar growth, as shown in **Figure 1.4.6** (**d-f**). The use of templates for DSG can provide a distinctive shadowing profile used to generate a variety of nanopatterns.

1.4.3 Shadow nanosphere lithography

Shadow nanosphere lithography (SNSL) is a template-based DSG technique that uses a colloid monolayer template made of polymer or silica nanospheres. Figure 1.4.7 (a-c) describes the general SNSL strategy. First (Figure 1.4.7 (a)), a monolayer of close-packed hexagonally arranged nanospheres is deposited onto a substrate. This monolayer is created from a self-assembly method, then it is coated on a substrate surface. A brief review of self-assembly methods will be given in Chapter 2. Figure 1.4.8 (a) shows an SEM of a typical polystyrene (PS) colloid monolayer. After the monolayer is coated, the mask can be modified by etching or annealing, which the shape of resulting nanopatterns can be changed. After colloid monolayer assembly and coating, the second step is to coat the substrate with a material using bottom up method such as PVD technique. Control over θ and φ during the deposition can change the nanomaterial design



Figure 1.4.7 An illustration of the SNSL method. (a) The colloid monolayer is coated onto a substrate. (b) Metal is deposited onto the substrate. (c) The mask can be chemically or physically removed exposing the underlying nanopattern on the substrate.



Figure 1.4.8 (a) The SEM image of 500 nm-diameter PS colloid monolayer mask and (b) the SEM image of triangular patterns. [97]

during the deposition. After the deposition, the monolayer mask can be removed or the metal coated template can remain.

SNSL is a variation of a simplified technique called nanosphere lithography (NSL). NSL is a templating technique pioneered by Van Duyne *et al.*[97] They demonstrated that by depositing metal normal to the substrate, then removing the colloid template, one could produce triangular nanopatterns. [98] **Figure 1.4.8** (b) shows an SEM image of the triangular nanopatterns fabricated by Van Duyne *et al.* In later work, they also showed that the morphology of the triangular nanopatterns could be easily modified by changing the colloid size, shape (by annealing), or number of monolayer layers. [55,97-100] This strategy is a simple technique to make nanopattered arrays. However, the variety of shapes this method can produce is limited.

SNSL combines NSL with DSG by manipulating the vapor incident angle θ , the position, and the azimuthal orientation φ of the colloid template. [101,102] There are numerous strategies to manipulate θ with respect to the substrate. **Figure 1.4.9 (a-c)** shows nanopatterns templated on the nanosphere surfaces. **Figure 1.4.9 (a)** shows Ag nanopatterns on colloid monolayers where Ag was deposited at a fixed θ . **Figure 1.4.9 (b)** shows the "patchy pattern" by coating Ag on close-



Figure 1.4.9 Examples of nanopatterns fabricated by SNSL. SEM images of (*a-c*) *nanopatterns on colloid nanospheres* [103-105] *and* (*d-f*) *nanopatterns on substrates.* [106-108]

packed nanospheres at a fixed θ by Pawar *et al.*[104]To create more complex patterns, the colloid monolayer templates may be modified by reactive ion etching (RIE) or annealing. By removing the colloid template, the shadowing of the nanospheres can produce patterns directly on the substrate surface. For example, Nemiroski *et al.* used SNSL combined with RIE to produce complex assemblies of metasurfaces with both single and multiple materials. [107]. **Figures 1.4.9** (**d-f**) show examples of nanopatterns after the colloid layers are removed. Overall, SNSL is a relatively new, but versatile nanofabrication technique. It is also considered as an inexpensive and scalable nanofabrication technique. [109,110] Therefore, in this thesis, innovative and simple SNSL-based nanofabrication methods are used to systematically tune the LSPR wavelength of a nanomaterial by changing its size, shape, separation distance, and composition.

1.5 Overview of Dissertation

This dissertation describes the fabrication and applications of plasmonic nanopatterns prepared by SNSL. **Chapter 1** provides the fundamental theory related to plasmonic

nanomaterials. The chapter also includes applications of plasmonic nanomaterial, and an overview of DSG and SNSL fabrication methods. In Chapter 2, the fundamentals colloid self-assembly are discussed, and a review of different self-assembly methods is provided. Additionally, the specific self-assembly and experimental methods used to fabricate the SNSL nanopatterns are discussed. The morphological and optical characterization techniques are also described. In **Chapter 3**, Ag films on nanospheres (Ag FONs) are introduced. These structures are Ag nanopatterns coated on surface of the colloid nanospheres. By systematically changing the size and shape of the nanopatterns, we can optimize SERS sensitivity. These structures could also be used for quantitative SERS. In Chapter 4, Ag triangular network nanopatterns are described. A simple strategy to fabricate tunable strictures is introduced, where the LSPR wavelength can be tuned by changing the shape of the nanopatterns. In Chapter 5, double triangle (DT) nanopatterns are presented. These DT nanopatterns are fabricated by a co-deposition SNSL method to simultaneously create different Ag nanopatterns. In this method, the LSPR wavelength is tuned by changing the size and separation distance of the nanopatterns. Then, in Chapter 6, Ag-Cu mixed phase nanopatterns were fabricated. It is shown that the LSPR wavelength of these structures can be tuned by changing the composition and the size of the nanopatterns. Lastly, in Chapter 7, I provide some overall conclusions and future outlook for the SNSL techniques used in this thesis.

CHAPTER 2

MONOLAYER SELF-ASSEMBLY TECHNIQUE AND EXPERIMENTAL METHODS

2.1 Introduction

As discussed in **Section 1.4.3**, the SNSL method consists of multiple steps. First, polymer or silica nanospheres are self-assembled into a close-packed monolayer and coated onto a flat substrate. There are numerous ways to assemble nanosphere monolayers depending upon the nanosphere material, *i.e.*, polystyrene or silica. **Section 2.2.1** provides a review of the assembly principles and methods used to make the colloid masks. Due to their ease of assembly and popularity, we limit the review of assembly methods to nanospheres made of polystyrene (PS). Each method has advantages and disadvantages related to monolayer coverage on the substrate, self-assembly speed, domain quality, scalability and throughput. Among all the techniques discussed in **Section 2.2.1**, the air-water interface method provides an excellent substrate coverage, is scalable, and has a high throughput. For these reasons, we have developed a semi-automatic airwater interface assembly technique, described in **Section 2.3.1**, to coat PS nanosphere monolayers onto Si and glass substrates. Not only does this method provide high quality domains over large areas, but also it is semi-automatic, making it more convenient than other available methods.

After the monolayer is coated onto a substrate, one has the option to modify the nanosphere mask by annealing or etching. Reactive ion etching (RIE) is a popular modification method used to reduce the diameter while keeping the space of the nanospheres. To accurately control the

nanosphere diameter, the etch rate of nanospheres must be accurately determined. In **Section 2.3.2**, we perform a detailed study to determine how the PS bead shape deforms during the RIE etching for different exposure durations. Based upon the results, an empirical model is developed to estimate the etch rate of the nanospheres.

After modification of the monolayer mask, desired materials, silver for instance, can be deposited onto substrates to form the targeted nanopatterns. In **Section 2.3.3**, we describe two custom-built deposition systems that are used to create the SNSL nanopatterns.

Finally, in **Section 2.3**, the methods and equipment used to characterize the morphology, composition, optical property, and sensing capabilities of the SNSL plasmonic nanopatterns are described.

2.2 Review of Monolayer Self-Assembly Techniques

2.2.1 Self-assembly principles

Two PS nanospheres, which have a surface charge of about - 40 mC, can experience an attractive or repulsive force depending upon their separation distance. [111] These interactions can be described by the well-known Lenard-Jones (LJ) potential,

$$V(r) = \frac{A_0}{r^{12}} - \frac{B_0}{r^6},\tag{2.1}$$

where *r* is the separation distance between two adjacent nanoparticles, $A_0 = 4\delta\sigma^{12}$ and $B_0 = 4\delta\sigma^6$, σ is the distance at which the potential is zero, and δ is the minimum potential. Figure 2.2.1 illustrates a LJ potential. The nanoparticles experience short range repulsive force and a long range attractive force. The combined effect of the attractive and repulsive terms constitutes the LJ model, as shown in the plot by the solid red line. To create a stable PS nanosphere monolayer, the nanospheres must be brought close enough to experience the attractive forces. Thus, there must be a mechanism to push the particles close enough together. Most assembly methods rely on external



Figure 2.2.1 The LJ potential between two particles with a separation distance r (red curve). The two dashed curves represent the repulsive and attractive potential terms. The separation distance at the minimum of the potential is called Van der Waals (vdw) radius. [112]

attractive capillary forces or electrostatic forces due to the surface charge of the particles.

There are two types of capillary forces: flotation and immersion forces. [113] Flotation capillary forces occur when two particles are floating in a fluid, while immersion forces occur



Figure 2.2.2 An illustration of the attractive capillary forces: Flotation capillary forces and immersion capillary forces. [113]

when nanospheres are partially submerged in a fluid. **Figure 2.2.2** illustrates the attractive flotation and immersion capillary forces. Both flotation and immersion forces are attractive forces that result from the meniscus that forms around the PS nanospheres. When two particles on a liquid surface become close enough, their respective meniscus will merge together, and create lower gravitational potential that draws the two particles together. Kralchevsky *et al.* theoretically derived the force equations for flotation and immersion forces.[113] While both immersion and flotation forces are similar, they have different dependencies on their separation distance. Immersion forces are highly dependent upon the particle's surface charge, while flotation forces are primarily dependent upon the particle's size.[113,114]

2.2.2 Common Self-Assembly Methods

In general, five different monolayer self-assembly methods are used in the literature.

Table 2.2.1 gives an illustration of each method and summarizes some of their advantages and disadvantages.

Drop coating/Drop casting: Drop casting is considered to be the earliest PS nanosphere monolayer self-assembly method. In this method, a fixed amount of PS nanospheres, water, and surfactant (such as sodium dodecyl sulfate) are mixed to create the colloid suspension. Then a specific volume of suspension is dispensed onto the substrate and allowed to dry, as illustrated in **Table 2.2.1**. As the water begins to evaporate, immersion capillary forces between the nanospheres cause them to compress into a monolayer. If the concentration of PS nanospheres is optimized, one can create a monolayer of close-packed nanospheres. Drop casting, which is a variation of drop coating, was first reported by Michelleto *et al.* [115] In this technique, droplets of the nanosphere suspension are dispensed onto a tilted substrate. By allowing the substrate to dry while

Self-Assembly Technique	Illustration	Advantages (Adv) /Disadvantages (Dis)	References
Drop coating/casting	Top-view Side view	Adv: quick and simple assembly method Dis: poor quality, limited coverage, requires hydrophilic substrates, not scalable, low throughput	[115-119]
Convective Assembly	Assembly by evaporation Stationary substrate	Adv: good coverage Dis: long assembly time, time consuming, requires hydrophilic substrates, not scalable	[120-123]
Spin Coating		Adv: quick assembly, good substrate coverage, scalable Dis: Only hydrophilic substrates, small domain sizes.	[124-126]
Air water Interface	a b	Adv: Large coverage, good quality crystal domains, scalable, high throughput Dis: Long assembly time,	[127-131]
Electric-Field Assembly	A Apply do field Repeat Deposit more particles Lower field Haise field Repeat Lower field Lower field Lower field Lower field	Adv: Quick assembly time, good coverage, Dis: Only conductive substrates, small domains	[132-134]

 Table 2.1.1 Summary of the most common colloid self-assembly methods for PS nanospheres.

the droplets sliding across the substrate, one can accelerate the drying of the nanosphere suspension and still maintain the attractive capillary forces necessary to self-assemble the monolayer. Both the drop coating and casting techniques are the simplest and quickest methods to prepare nanosphere monolayers, but they suffer from poor coverage and bad colloid crystal quality.

Convective Assembly: Convective assembly is the self-assembly technique based on the controlled evaporation of nanosphere suspension. In this method, illustrated in Table 2.2.1, a suspension of PS nanospheres in water is wedged between two substrates typically made of glass. One substrate is laid flat, the other substrate is tilted at an angle, and is attached to a motor. The assembly process begins when the tilted substrate moves in a direction that thins the suspension until a meniscus forms between the substrates. When the meniscus is thinner than the diameter of the nanospheres in the suspension, attractive capillary forces assemble nanospheres into a monolayer. There are many advantages to the convective assembly method. It has good coverage and crystal quality. It is also possible to form multilayered structures. However, this technique has a slow assembly time because the motor must move slowly enough for the suspension to dry as it is deposited onto a substrate. For these reasons, convective assembly has low throughput and is not scalable. Methods to improve the assembly speed has been realized recently. For instance, Kim et al. was able to demonstrate that heating the suspension during the assembly process increased the assembly speed. [120] In addition, this method requires that the two substrates used to assemble the monolayer need to be hydrophilic.

Spin coating: In this procedure, droplets of PS nanosphere suspension are first dispensed onto a hydrophilic substrate.[124,125] Then the substrate is spun at a low speed to spread the suspension over the entire substrate. Next, the rotation rate of the substrate is accelerated to increase the evaporation rate of the liquid, which induces immersion capillary forces on

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neighboring nanospheres to form a monolayer. By carefully controlling the rotation speeds and suspension concentration, spin coating can be optimized for good coverage over large areas (> 10 cm²). Furthermore, this technique can also be used to prepare multilayered photonic crystals and non-close-packed arrays. [124,126] Overall, this method is high throughput and scalable with a quick assembly time and good coverage. However, this technique only works on hydrophilic substrates. Also it is highly inefficient because most of the suspension are spun off from the substrates during rotation acceleration. [125]

Air/water interface method: A monolayer of PS nanospheres can also be assembled on the water surface. To achieve such an assembly, PS nanospheres are directly dispersed and floated onto the water surface; then the nanospheres are compressed using a physical or chemical method until they are close enough to experience flotation capillary forces. For example, nanospheres can be compressed physically by a sliding bar that floats on the water surface. This method is commonly known as the Langmuir-Blodgett technique. [127,131,135]. They can also be compressed by changing the surface tension of the water. When surfactants, such as sodium dodecyl sulfate and Triton-X, are dispensed upon the water surface, they can lower the overall surface tension of the water which increases the flotation capillary force between neighboring nanospheres. [130]

Self-assembly at the air/water interface is a popular technique that can produce single crystal monolayers with domains greater than > 5 cm². [128] This technique is high throughput and scalable. However, it can have a relatively long self-assembly time.

Electric field induced self-assembly: For electric field induced assembly methods, negatively charged PS nanospheres in a fluid experience an attractive electrostatic force with a positively charged substrate. [132-134] As the nanospheres electrostatically adsorb onto the

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surface of a substrate, they stack upon one another, creating multi-layers as shown in **Table 2.2.** In order to create a monolayer, several strategies are used to remove the higher layers of nanospheres. For instance, Zhang *et al.* introduced a self-assembly method where PS nanospheres in an ethanol suspension aggregated and dried onto a positively charged polymer. [134] They showed that by generating a relatively weak electrostatic field between the PS nanospheres and substrate, and all layers except the first could be removed by rinsing the substrate in water, but the electrostatic force was strong enough to retain the first nanosphere layer. Trau *et al.* employed an alternating current (AC) across a substrate to assemble PS monolayers.[133] By changing the charge of the substrate, PS nanospheres could cycle between multilayers and single layers, as shown in **Table 2.2**. This method is optimized to assemble nanoparticles into a monolayer. [133]

The electric field induced assembly technique is a simple and quick method to fabricate close packed monolayers. These methods have quick assembly times and can deposit monolayers onto curved or jagged surfaces. However, this technique suffers from low surface coverage, low throughput, and limited substrate variety (only conductive substrates).

2.3 SNSL: Colloid Assembly, Mask Modification, and Deposition Set-up

2.3.1 Self-assembly by air/water interface

Among all the assembly methods described in **Section 2.2.2**, the air/water interface method is a scalable and high throughput method, and can be used to deposit nanosphere monolayers on a variety of surfaces. For these reasons, we adopt this method to form monolayers for all my thesis



Figure 2.3.1. An illustration the air-water interface self-assembly method.

work. However, since the air/water method needs a long processing time, we have developed a semi-automatic procedure to prepare high quality monolayers.

Our method can be divided into several steps as outlined in **Figure 2.3.1**. A detailed description of the assembly procedure is given in **Appendix 1**. Briefly, as shown in **Figure 2.3.1**, Step 1 is the preparation of the colloid monolayers at the air/water interface inside a glass Petri dish. Commercially purchased PS nanospheres are first sonicated in their original container to ensure the PS nanospheres are well dispersed. Then a specific volume of PS suspension is "washed" using a centrifugation method (see **Appendix 1**). This washing procedure is necessary to remove surfactants used in the original suspension to improve PS dispersion. We find that the washing procedure is an effective method to improve the packing density of the PS nanospheres at the air/water interface. After the washing, the suspension is dispersed in ethanol. During this time the glassware used is cleaned using a boiling Piranha solution.

In step 2, the cleaned suspension is withdrawn into a 20-gauge syringe with the needle bent at a 90° angle towards a 15 cm diameter glass Petri dish which is partially filled with water. A



Figure 2.3.2 (a) A photo of the air/water interface experimental set-up showing the colloid monolayer film floating on water surface in a 15 cm-diameter Petri dish. (b) A SEM image of single domain area of a colloid monolayer on a silicon substrate

syringe pump is slowly pushing the suspension in the syringe to drip at a rate of 0.015 μ L/ minute. When a droplet of the PS nanosphere suspension hits the water surface, the ethanol in the droplet lowers the local surface tension, causes the water to flow away radially from the droplet (needle) location, then carry and compress the PS nanospheres floated on the water surface. Thus, the ethanol acts as a chemical dispersion and compression mechanism to help the formation of the monolayer. In order for this dispersion method to occur, the original water level in the Petri dish must be shallow. In our studies, we initially put about 24 *m*L water inside the Petri dish, which is just enough to cover the bottom of the Petri dish. In addition, during the monolayer assembly, the Petri dish is tilted 7° to further help the dispersion and nanosphere compression. **Figure 2.3.2 (a)** shows a photo of the experimental set-up. After a monolayer film is formed, a Teflon ring is placed around the perimeter of the Petri dish to prevent the monolayer depositing on the side wall of the Petri dish. More water is pumped into the Petri dish and raises water level. Then substrates are slid slowly and gently below the monolayer film.

In step 3, water is pumped out from the Petri dish. As the water level is lowered, the floating monolayer film will eventually deposit onto the substrates. The newly coated substrates are left on the Petri dish to dry overnight (typically 8-12 hours). After dried, the substrates are removed from the Petri dish, and are stored in plastic Petri dishes for future use. **Figure 2.3.2** (b) shows a typical SEM image of a colloid monolayer with 500 nm diameter PS nanospheres.

2.3.2 Etching of nanosphere mask

A nanosphere monolayer provides an excellent mask for lithography-based nanofabrication. However, the variety of nanopatterns can be formed via SNSL are limited due to fixed arrangement of the nanospheres. One common method to change the spacing among

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Figure 2.3.3 (a) SEM image of 500 nm-diameter nanospheres. (b-d) SEM images of 500 nm-diameter nanospheres after RIE for time of (b) 3min., (c) 5 min. and (d) 8 min.

nanospheres is to reduce their diameter by RIE. [136-138] RIE is a plasma-based etching technique where free ion radicals can chemically etch or physically ablate the targeted materials.

The change in diameter of the nanosphere, or etch rate, is an essential parameter for utilizing RIE. Etch rates will vary significantly with the brand of machine, gas used, power applied, and background pressure retained. In this section, systematical study was performed on the etching of select PS monolayers with an inductively coupled plasma (RIE/ICP) system (Trion®) under oxygen plasma. **Figure 2.3.3** shows an example of the controlled etching of 500 nm PS nanospheres. The etching was performed with a background pressure of about 8 mTorr, a RIE power of 25 mW, and an ICP power of 50 mW. The flow rate of oxygen was 40 SCCM. Similar etching conditions were performed for nanospheres ranging from 200 nm to 2000 nm.

The profile of the etched nanospheres were also determined from cross section SEM images as shown in **Figure 2.3.4 (a-b)**. The SEM images show nanospheres etched for 3.3 minutes. Close inspection of nanospheres shows small "protrusions" on the sides. These protrusions are known as nanolinks [139]. During the initial etching of the PS nanospheres, the surface of the sphere melt slightly and are linked to their nearest neighbors. As etching continues, the links eventually become disconnected. This effect does not impact the overall morphology of the nanospheres. To quantify the morphology of the nanospheres, we carefully measure the outline of the nanospheres from the cross-sectional SEM images using the "edge find" function in Image-J software as shown in **Figures 2.3.4 (c-d)**. The outline is then split into the upper and lower hemispheres shown in **Figures 2.3.4 (e)** and (**f**). The outlines were digitized and fitted with an ellipse defined as $\frac{(x-x_0)^2}{a^2} + \frac{(y-y_0)^2}{b^2} = 1$, where *a* and *b* represent the major/minor axis of the nanosphere, x_0 and y_0 are defined as the center coordinates of the ellipse. Based upon the fitting results, the eccentricity η of the upper and lower ellipsoid is,



Figure 2.3.4 (a-b) The cross-section SEM images of 500 nm-diameter nanospheres etched for3 min. (c) Modified SEM image of an etched nanosphere. (d) The outline of an etched nanosphere. (e-f) The upper and lower hemisphere of the nanosphere. (g) Plot of eccentricity of etched nanospheres versus time

$$\eta = \sqrt{1 - \frac{b^2}{a^2}} \text{ if } a > b, \text{ or } \eta = \sqrt{1 - \frac{a^2}{b^2}} \text{ if } b > a.$$
(2.3)

Figure 2.3.4 (g) shows how η changes as a function of etching time *t*. When *t* is small ($\leq 1 \text{ min}$), η is close to 0, and both the η of the lower and upper hemispheres overlap, meaning that the etched nanospheres still maintain the spherical shape. When the *t* increases, the η of the lower hemisphere does not change significantly, while the η of the upper hemisphere increases monotonically. Thus, the upper hemisphere becomes more elliptical while the bottom half of the nanosphere remains circular. Therefore, we can infer that the nanospheres are etches anisotropically. This trend can be seen clearly by plotting the average profiles of etched PS nanospheres taken from SEM images as shown in **Figure 2.3.5**. The profiles in the figure are aligned so that the center of each profile occurs along *x* = 0, and the minimum value of the profile is centered at *y* = 0. As the etch time increases, the upper half of the nanosphere is clearly etched more than the bottom half.

Based upon the profiles observed in **Figure 2.3.5**, the shape of the etched nanosphere can be modeled by the relative motion of two overlapping spheres. **Figure 2.4.6** (a) illustrates that at time t = 0, two nanospheres located at the origin overlap completely. This shape represents an



Figure 2.3.5 Outline of PS nanosphere etched at t = 0, 1, 2.2, 3.3, and 4 min.



Figure 2.3.6 An illustration of the 2D projection of two overlapping nanospheres. (*a*) The unetched nanosphere and (*b*) nanosphere etched to a time t.

unetched nanosphere with diameter D_0 . At time t, one sphere (blue) moves downward at a constant speed k as shown in **Figure 2.4.6** (b), i.e., its center becomes (0, -kt, 0), and the shaded region between the overlapping nanospheres is the new etched nanosphere front with diameter D(t). Based on the geometric equations for the two spheres, D(t) is given as,

$$D(t) = \sqrt{D_0^2 - (kt)^2} .$$
(2.4)

To validate this model (**Equation (2.4**)), we use it to fit the experimental data as shown in **Figure 2.3.7**. Etching was performed under a background pressure of about 8 mTorr, a RIE power of 25 mW, an ICP power of 50 mW, and an oxygen flow of 40 sccm. For the three sets of data, the initial diameters of the nanospheres measured from SEM images are $D_0 = 750$ nm, 500 nm, and 200 nm, and the obtained etching rates are k = 0.103, 0.081, and 0.09 μ m/min, respectively. Within the error bar, the three values are about the same. Overall, the SI model fits well with experimental values. Therefore it is an accurate model to predict the shape change of nanospheres etched by RIE.



Figure 2.3.7 The measured diameter of nanospheres etched over time for nanospheres with initial diameters of 750 nm, 500 nm, and 200 nm. The solid curve is the fitting of the SI model to the etched nanosphere diameter

2.3.3 Deposition setup

In this dissertation, an electron beam (e-beam) PVD system is used to coat material onto the nanosphere covered substrates. E-beam PVD is a process in which a focused beam of electrons melts a material (*i.e.* Ag pellets) inside of a vacuum chamber. Once the material vaporizes, the vapor can condense onto the surface of the substrates at a relatively low temperature. The angle of the vapor flux with respect to the substrate normal θ as well as the position of the substrate can be tuned during the deposition so that the amount of vapor accumulated onto the substrate will vary due to the shadowing effect of the nanospheres as discussed in **Section 1.4.3**.

Figure 2.3.8 shows the components of an e-beam PVD system. A vacuum pump, connected to the chamber, is used to lower the chamber pressure to below 10^{-6} Torr. A tungsten filament is used to generate an electron beam. When a voltage and current are applied across the filament, electrons are extracted and accelerated from the filament, and are deflected 270° by a magnet. The defected electrons are focused onto the deposition material contained inside a


Figure 2.3.8 A diagram of an e-beam PVD system.

crucible. The crucible is housed inside a water-cooled jacket. There is a quartz crystal microbalance (QCM) mounted above the crucible to measure the rate and monitor the thickness of the evaporating material. A shutter is used to block the vapor until a desired deposition rate is achieved. Most important, for the OAD or GLAD system, the substrate holder is coupled to two stepper motors to control the incident angle θ and azimuthal orientation φ .

Two different e-beam PVD chambers are used to fabricate SNSL nanopatterns. One chamber is only capable of evaporating one source material, as shown in **Figure 2.3.9** (a). This single source deposition system contains a substrate holder located approximately 20" vertically above the crucible. The deposition rate is monitored by a single QCM above the crucible. The substrate holder shown in **Figure 2.3.9** (a) is coupled to two stepper motors to control both θ and



Figure 2.3.9 Photos of e-beam PVD systems: (a) a single source deposition system, and (b) a dual source deposition system.

 φ rotations. The other deposition system is a dual source system shown in **Figure 2.3.9** (b). This system contains two e-beam and is capable of simultaneously melting two separated materials. The two crucibles have a center-to-center horizontal separation distance of 7". Two QCMs are used to monitor the deposition rate and thickness of each source independently. A substrate holder similar to that of the single deposition system is mounted approximately 21" above sources. Additionally, another holder contains 6 smaller rotary assembly capable to rotate at different speeds is shown in **Figure 2.3.9** (b). Details regarding the deposition system type, deposition rate, thickness, and substrate orientation that are used to fabricate the SNSL nanopatterns are specified in the experimental method sections in each of the following chapters.

2.4 SNSL Nanopattern Characterization

2.4.1 Morphology characterization

Scanning electron microscopy (SEM) images and energy dispersive X-ray measurements (EDS) of the SNSL nanopatterns are taken by a field emission scanning electron microscope (SEM, FEI Inspect F). The topography of the nanopatterns are measured by an atomic force

microscopy (AFM, Bruker, Multimode 8). SEM images are analyzed by ImageJ software (NIH), and AFM measurements are investigated by the software Nanoscope Analysis. The crystal structure of the nanopatterns is characterized by a PANalytical X'Pert PRO MRD X-ray diffractometer (XRD) with a fixed incident angle of 0.5°. The XRD scans of the thin films are recorded with a Cu K α 1 radiation ($\lambda = 1.541$ Å) in the 2 α range from 20° - 80° with a step size of 0.010°.

The morphology of nanopatterns can be predicted by numerical calculation using an inhouse Matlab code. [103] Briefly, this algorithm is based upon three assumptions. First, this model only considers the shadowing effect of the 36 nearest neighbor nanospheres. Other effects such as surface diffusion are ignored. Second, depositions onto the entire surface will occur simultaneously. Lastly, the thickness of the coating uniformly decreases with incident angle according to a cosine rule. [140] **Figure 2.4.1** shows the predicted nanopatterns and graphic



Figure 2.4.1 An image of the graphic user interface of the Matlab program to predict nanopatterns.

interface of the Matlab simulation code. The code can be used to predict nanopatterns on the substrate surface and on the nanosphere.

A Monte Carlo simulation is also used to predict the surface of the nanopattern. [141] In this code, the vapor flux consists of discrete atoms that are generated at random positions around the nanosphere template and allowed to move along a straight trajectory at an incident angle θ .

2.4.2 Optical characterization

The optical transmission spectra of the Ag-Cu nanopatterns are measured by an ultravioletvisible spectrophotometer (UV-Vis, Jasco-750). Reflection measurements of the nanopatterns are taken at an incident angle of 0° by a custom-built set-up reported in Ref.[142]. The samples used for both optical transmission and reflection measurements are deposited on glass substrates. To reduce the effect of oxidation, all UV-Vis measurements are taken immediately after deposition.

Spectral ellipsometry (SE) measurements of nanopattern on glass substrates are taken by a spectroscopic ellipsometer (M-2000, J.A Woollam Co., Inc.) at an incident angle of 65° , 70° , 75° , and 80° , respectively, over a wavelength rage of 370 - 1000 nm.

SERS measurements used in this work are either taken with a portable Raman spectrometer (Enwave Optronics, Pro-L) with an excitation wavelength of 785 nm or a confocal Raman microscope (Renishaw inVia) with an excitation wavelength of 633 nm.

CHAPTER 3

AG FILMS ON NANOSPHERES

3.1 Introduction

Metal film on nanospheres (FONs), also referred to as metal-capped nanospheres, are a simple nanostructure fabricated using polystyrene (PS) or silica nanospheres as a cost-effective SERS substrate. [143-147] These structures have been used for SERS detection of anthrax, glucose, biotin, and DNAs. [148-153] In addition to their sensing applications, metal FONs can possess tunable plasmonic properties by modifying nanosphere's size, separation, and coating material. For instance, Zhu et al. reported the fabrication and study of stretchable Ag FONs on PDMS. [147] Their results showed that the structure could be used to produce tunable plasmonic nanostructures. Wang et al. varied the ratio of Ag and Au FON bi-layers with a constant thickness, and identified optimum conditions to produce strong SERS signals.[154] Greeneltch et al. reported to tune the LSPR wavelength by using silica nanosphere monolayers, with diameters ranging from 310 nm to 780 nm. [155] They demonstrated that by varying colloid size while keeping the Ag film thickness constant, the LSPR wavelength would shift broadly, ranging from 400 nm to 1200 nm. While these methods demonstrate the tunability of the LSPR wavelength for metal FONS, it would be advantageous to tune and understand the shift of LSPR wavelength using Ag films on a single sized nanosphere template.

One disadvantage to using metal FONs for SERS substrates is the lack of reproducibility, which can limit quantitative assessments of analyte's concentration. For metal FONs, defects on the substrate can cause the SERS signal to vary. These defects may be cracks, unfilled areas in the monolayer, multilayers, or uneven coverage of metal, and result in an ununiformed signal enhancement at different locations on the same substrate. While the Raman signal is expected to be changed monotonically with the analyte's concentration, variations in the surface enhancement on the substrate make it difficult to determine the absolute intensity of a signal that is needed to consistently predict analyte's concentration. [156,157] Signal degradation due to prolonged laser exposure is another factor that affects reproducibility, and would significantly decrease signal intensity over time if measured on the same location. [156-160] To overcome these limitations, an internal standard is typically applied for SERS quantitative analysis. An internal standard is a chemically inert substance added to a bulk analyte solution. It should produce vibrational modes that do not interfere with the characteristic peaks of the target analyte, and can still be detected within a broad range of concentrations of the target analyte.[161] Normalization of the analyte peak intensity with the internal standard negates several factors that affect variations in signal intensity. Commonly used internal standards include glutaric acid, pyridine, acetonitrile, and pthiocresol.[162-164] One of the most accurate quantitative methods to predict analyte concentration is the use of isotope-edited compounds added to the solution of the original analyte.[165,166] Their results show that the ratio of the analyte to be predicted with errors of less than 8%. Internal standards added to bulk solutions can provide good quantitative results, but this type of internal standard typically requires high concentration when added to the bulk solution, and could compete with the target analytes for hot-spot adsorption. [161]Another method to apply an internal standard is to utilize the vibrational modes from the SERS substrate. These vibrational

modes can include those generated from polystyrene, silicon, PDMS, nitrocellose membranes, or the photon/phonon interface vibrational mode of metals. [167-171] In this case, the internal standard will not compete with the analyte for potential hot-spot locations. For instance, Kim *et al.* demonstrated the application of a novel microfluidic SERS device for the detection of trans-1, 2 bis(4-pyridyl) ethylene (BPE). [170] In their study, they took advantage of PDMS's strong vibrational peaks as an internal standard, and drew a linear correlation between BPE concentration and spectral intensity. In another study by Péron *et al.*, gold coated PS nanospheres were used for the SERS detection of trace amounts of naphthalene. [172] In their work, Au coated, 800 nm PS nanospheres were deposited on the surface of a functionalized quartz substrate and produced peak at Raman shift of $\Delta v = 1004$ cm⁻¹. This peak was utilized as an internal standard and was used to derive a linear relationship between predicted naphthalene peak intensity and concentration.

The aim of this work is to optimize Ag FONs based upon a single-sized polystyrene nanosphere template and demonstrate its use as an internal standard for quantitative SERS analysis.

3.2 Experimental Methods

Colloid Monolayers

150 nm-diameter PS nanospheres were to make the colloid monolayer used for of Ag FONs. Monolayer preparation method for 150-nm PS beads is given in Appendix 1.

Deposition Configuration

Ag FONs nanopatterns were prepared using a single-source deposition system, discussed in **Section 2.3.3.** The deposition configuration of Ag FONs is illustrated in **Figure 3.2.1.** The PS nanosphere coated substrates were mounted on pre-machined wedges to simultaneously form

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Figure 3.2.1 The deposition configuration of Ag FONs nanopatterns.

different incident angles, θ , between the substrate surface normal and the vapor deposition direction during a single deposition. The substrates were mounted at angles $\theta = 0^{\circ}$, 15° , 25° , 35° , 45° , 55° , 65° , 75° and 85° , and were placed about 50 cm away from the Ag source. All the coatings were carried out in a single deposition at a rate of 0.5 Å/s until a final thickness of 20 nm was reached. After the Ag was deposited, the substrates were allowed to cool in vacuum before removal from the chamber

Morphological and Optical Characterization

The optical extinction spectra of Ag FONs were characterized by a UV-Vis-NIR spectrophotometer. The morphology of the SERS substrate was examined using scanning electron microscopy (SEM). The height profile and morphology were also determined by atomic force microscopy (AFM). SERS measurements were taken with a portable Raman spectrometer with an excitation wavelength of 785 nm, a laser power of 30 mW, and an integration time of 10 s. The

average SERS spectra were obtained from nine different locations on the substrate. Refer to **Section 2.4.2** for the equipment model of the listed equipment. (Note discuss chemicals)

Concentration Dependent and Dynamic SERS Study

R6G solutions with concentrations ranging from 5×10^{-6} M to 1×10^{-2} M in methanol were used for concentration dependent SERS measurements. The SERS substrates used in this study were Ag FONs deposited at incident angles of $\theta = 0^{\circ}$, 25°, and 55°, respectively. Two microliters of the solution were dispensed on the center of the Ag FON substrate. The droplet spreads out radially to a circular area of an approximate diameter of 2 cm.

For R6G and MPH adsorption dynamics measurements, the SERS substrate was first placed in a cleaned glass Petri dish filled with 5 mL of ultra-pure water. Then, 1 mL of R6G, diluted in ultra-pure water to a concentration of 0.66 mM, was dispensed below the water surface to achieve a net concentration of 0.1 mM. The study of MPH was performed in a similar manner, but the stock solution was 200 μ L of 5.6 μ M MPH. While the Ag FON substrates were submerged in the solution, time-dependent SERS measurements were taken automatically every 0.5 minutes for the first 60 minutes, then the time-interval increased to 1 minute for the next hour. During all dynamic measurements the location of the excitation beam was not altered, and the evaporation of water would be negligible within the time frame of the experiment.

All the SERS spectra were analyzed using the spectroscopic software GRAMS AI and Origin Pro 9.0 to determine the peak locations and strengths.

Numerical Calculations and FDTD Simulations

The coverage of the Ag on the colloid nanosphere was simulated by an in-house Matlab reported in **Section 2.4.2**. This simulation predicted the thickness distribution of the Ag coating on nanospheres at different incident angles by considering the shadowing effects of the thirty-six

nearest neighboring nanospheres. The optical properties of Ag FONs deposited at different θ were simulated by the FDTD method using FDTD Solutions software. In the calculations, the shape and coverage of Ag FONs were modeled using a shadowing mechanism based on the parameters obtained from both SEM and AFM measurements and ta detailed simulation configurations and boundary conditions were elaborated in the **Appendix 1**.

3.3 Morphology

Figures 3.3.1 (a-e) and (a'-e') show the corresponding AFM and SEM images of PS monolayers and Ag FONs of $\theta = 0^{\circ}$, 25°, 40°, and 65°, respectively. For $\theta > 0^{\circ}$, the arrows shown in the AFM images indicate the projected direction of the Ag vapor on the substrate plane. In Figure 3.3.1 (a)/(a'), the shape of the bare PS nanospheres were very similar to that of Ag FONs at $\theta = 0^{\circ}$ shown in Figure 3.3.1 (b)/(b'). However, the surface of each nanosphere in Figure 3.3.1 (b) is rougher compared to the uncoated nanosphere, indicating material deposition. Also, in some regions, the Ag coating connects nearby nanospheres. When θ increases to 25° (Figure 3.3.1 (c)/(c')), AFM shows that the nanosphere surface becomes rougher, but there are no connected nanospheres. The SEM image demonstrates large area, near circular shaped Ag patch on each nanosphere. When θ increases to 40°, the AFM image shows similar features as that of $\theta = 25^{\circ}$ (Figure 3.3.1 (d)). However, the SEM image clearly shows half-circle like Ag patch. When θ further changes to 65°, both AFM and SEM images show clear patches (Figures 3.3.1 (e)/(e')), especially in **Figure 3.3.1** (e'), and the Ag patch becomes an elongated band on the nanosphere. It appears that with increased θ the area of the Ag coating becomes smaller and the shape becomes more anisotropic. To better illustrate the change in Ag coating on PS nanospheres with respect

, to θ , Figure 3.3.2 shows the average height profiles of Ag FONs scanned across the center of the nanospheres along the incident vapor direction. The average height profiles are taken from at



Figure 3.3.1 (a-e) $1 \ \mu m \ \times 1 \ \mu m \ AFM$ scans and (a'-e') the corresponding SEM top view images of uncoated and Ag coated PS nanospheres at $\theta = 0^{\circ}, 25^{\circ}, 40^{\circ}, and 65^{\circ},$ respectively. All the AFM images were took by aligned the deposition direction upward indicated by the arrows in AFM images. The dashed red circles and green patches in SEM images outlined bead and Ag patchy perimeters.

least five different nanospheres, and are offset and aligned along the curvature of the nanospheres in the region opposing vapor direction (right region of **Figure 3.3.2**). We observe from **Figure 3.3.2**, that the height protrusion in the vapor direction becomes more and more pronounced with increased θ , which is a clear indication of the shadowing growth effect. Therefore, a general trend can be found; as θ increases, the area of the Ag coating becomes more anisotropic and localized in the direction of the incident vapor.

We have performed computer simulations of the Ag thickness distribution on PS nanospheres at different θ . This simulation considers the shadowing effect from neighboring nanospheres, and the resulting simulated film is assumed to be non-porous. The shape and coverage of the Ag coating on a nanosphere is determined by both θ and the relative orientation of the nanosphere monolayer domain φ . As shown in **Figure 3.3.3** (a), φ is the angle between the projected vapor direction and the centers of the two adjacent nanospheres. This angle represents the direction of the incident vapor with respect to the colloid monolayer domain. **Figure 3.3.3** (b)



Figure 3.3.2 The average height profiles of Ag FONs measured along vapor incident direction and across the center of the nanosphere for uncoated and Ag coated PS nanospheres at different θ . The profiles are aligned along the curvature of nanospheres in the opposite direction of the incident vapor.

shows the thickness distribution on a nanosphere for $\theta = 25^{\circ}$, 40°, 65°, and 85°, respectively, for $\varphi = 0^{\circ}$. The resulting images reveal that the Ag layer coverage becomes smaller and more anisotropic. The overall long-axis of the Ag coating shape for large θ is perpendicular to the vapor direction. Although we had difficulty to determine φ from each AFM image, the shape of the Ag coating in **Figure 3.3.1** follows the same trend as predicted by the simulation. It is known from literature that the PS monolayer templates can contain multi-oriented domains. [103,131] Multiple domains could also affect the Ag coverage even when θ is fixed. For example, **Figure 3.3.3** (c) shows when φ varies from 5° to 60°, for fixed $\theta = 55^{\circ}$, the shape of the Ag coating changes slightly. Such a shape change could induce broader optical response, which we will pay particular attention to.

3.4 Optical Properties

Since the shape and coverage of Ag FONs are different for each incident angles, it is



Figure 3.3.3 (a) Representation of φ angle orientation. (b) Simulation results of Ag coating on PS nanospheres for $\theta = 25^{\circ}$ to $\theta = 85^{\circ}$ at fixed $\varphi = 0^{\circ}$. (c) Simulation results of Ag coating on PS nanospheres for $\varphi = 5^{\circ}$, 25° , 40° , and 60° , respectively, at fixed $\theta = 55^{\circ}$.

expected that their optical properties will also vary. **Figure 3.4.1(a)** shows the extinction spectra of Ag FONs at different incident angles, from $\theta = 0^{\circ}$ to $\theta = 85^{\circ}$. At $\theta = 0^{\circ}$ a broad extinction peak centered at $\lambda = 863$ nm dominates the spectrum. The samples at $\theta = 15^{\circ}$ to $\theta = 55^{\circ}$ have a similar dominant extinction peak, but the peak location blueshift consistently, beginning with $\lambda = 874$ nm, and then $\lambda = 844$ nm, $\lambda = 808$ nm, $\lambda = 781$ nm, and $\lambda = 773$ nm, while the extinction amplitude becomes smaller and smaller for $\theta > 15^{\circ}$. The peak shift as a function of θ is plotted in **Figure 3.4.1 (c)**. When $\theta > 55^{\circ}$, the extinction spectra change dramatically. Each spectrum becomes relatively flat over a large spectral range, while the extinction strength decreases significantly. The extinction strength also follows a general trend: as θ increases further the extinction strength decreases while the spectra becomes broader. The change of the optical property as a function of θ is determined by the shape and coverage variation of the Ag coating.



Figure 3.4.1 Experimental (a) and FDTD simulation (b) results of Ag FONs coated at different θ . (c) Plot of the LSPR wavelengths versus θ for the simulation and experiment.

To understand the optical properties of Ag FONs at different θ , we have carried out FDTD simulations on the Ag FONs. Because the Ag FONs contain multiple domains, we expect that the experimentally measured spectra in Figure 3.4.1 (a) are the average extinction spectra from different monolayer domains, i.e., domains with different φ . To accommodate such an effect in simulation, we use the average extinction spectra of Ag FONs oriented at $\varphi = 0^{\circ}$, 10° , and 20° for different θ , and the result of the simulations are shown in **Figure 3.4.1** (b). Overall, the FDTD results show similar trends to those observed in experiments. An intense and relatively narrow extinction peak in near IR region ($\lambda = 800 - 900$ nm) for small θ is observed; then for larger θ , the spectra becomes very broad. When θ increases from $\theta = 0^{\circ}$ to 35 °, the peak wavelength decrease monotonically with θ , where $\lambda = 852$ nm, 837 nm, 836 nm, 808 nm, respectively. The extinction strength also decreases monotonically within this range. At $\theta = 40^{\circ}$, the peak redshifts slightly to λ = 812 nm. At $\theta > 40^{\circ}$ the peaks become much broader and the extinction intensity decreases significantly. Figure 3.4.1 (c) shows the comparison of LSPR wavelength as a function of θ from both the FDTD and experiment results. The overall trend matches very well. Clearly θ can be used to finely tune the LSPR wavelength of Ag FONs.

The optical response of the Ag FONs originates from two Ag nanopatterns for small θ . One is the Ag coating on the nanospheres as demonstrated by AFM and SEM images in **Fig.3.3.1**, and the other is the underlying Ag nanotriangles deposited onto the substrate. However, not all the Ag FONs have the nanotriangle patterns. There is a critical θ_c that when $\theta > \theta_c$, no nanotrianges will be formed on the substrate due to the shadowing effect. Such a θ_c , also depends on φ . When $\varphi = 0^\circ$, $\theta_c = 40^\circ$; but when $\varphi = 30^\circ$, θ_c can be as high as 60° . Experimentally we find that the overall θ_c is around 55°, which is reasonable. Nevertheless, even with the nanotriangle layer, the contribution of the nanotriangle extinction is very small compared to the overall optical



Figure 3.4.2 (a) The experimental extinction spectrum of nanotriangle patterns at $\theta = 0^{\circ}$ and (b) the simulated extinction spectra of simulation extinction spectrum Ag FONs and nanotriangles, Ag FONs and nanotriangles modeled separately, and the sum of the separately modeled Ag FON and nanotriangle.

extinction spectra as shown in **Figure 3.4.2** (a). In fact, the FDTD simulation has confirmed this assessment as shown in **Figure 3.4.2** (b). From the simulation results, there is no optical coupling between the triangle layer and the Ag on sphere layer, and the optical properties of Ag FONs are dominated by the Ag coating on the nanospheres.

It is very interesting to notice the sudden change of the extinction spectra above θ_c from both simulation and experiment. This extinction shifts occurs when $\theta > 55^\circ$ in the experiment, and $\theta > 40^\circ$ in the simulation. To determine the cause of this broadening, we examine carefully two cases, $\theta = 25^\circ$ and $\theta = 75^\circ$, by FDTD simulation. **Figure 3.4.3** shows the polarized extinction spectra at different φ for these two θ angles, one is the polarization parallel to the vapor direction



Figure 3.4.3 The polarized extinction spectrum of Ag FONs at $\theta = 25^{\circ}$ (a_1 - a_3) and $\theta = 75^{\circ}$ (b_1 - b_3) for $\varphi = 0^{\circ}$, 10°, and 20°, respectively. Inset shows the corresponding top view of the simulation model in the specified polarization directions.

, the y-axis, and the other is perpendicular, the x-axis. A diagram of the direction of each polarization is shown in **Figure 3.4.3**. The insert in each plot shows the top view of modeled Ag coating at corresponding φ . For $\theta = 25^{\circ}$, the shape and coverage of the Ag coating at different φ are similar. Thus, the *x*-polarized and *y*-polarized extinction spectra are similar, both show a sharp peak at $\lambda \approx 833$ nm. Even for different φ , the peak location variation is small, with a standard deviation of ± 17 nm. Therefore the average spectrum is a predominant peak as shown in **Figure 3.3.3**. For $\theta = 75^{\circ}$, however, the shape and coverage of the Ag coating at different φ are very different. At $\varphi = 0^{\circ}$, the coating looks like a stripe along the edge of the nanosphere; at $\varphi = 10^{\circ}$, the coating shape becomes an elongated triangle; while the coating at $\varphi = 20^{\circ}$ appears to be a small

triangle. The highly anisotropic Ag coatings and different coverages significantly change the polarization extinction spectra. For $\varphi = 0^{\circ}$, the y-polarized extinction has a broad spectrum in the wavelength range of $\lambda = 350$ nm to $\lambda = 600$ nm, with low extinction intensity; but x-polarized spectrum shows a strong extinction peak at $\lambda = 1419$ nm and two smaller peaks at $\lambda = 940$ nm and $\lambda = 1043$ nm. For $\varphi = 10^{\circ}$, the extinction of both polarizations are small (< 0.3). The y-polarized extinction shows a double peaks at $\lambda = 665$ nm and $\lambda = 733$ nm, while the x-polarized extinction shows two distinguished broad peaks at $\lambda = 1036$ nm and $\lambda = 781$ nm. For $\varphi = 20^{\circ}$, the polarized extinction spectra are very different. The y-polarized spectrum appears very similar to that of $\varphi = 0^{\circ}$ case, both in shape and amplitude, while the x-polarized spectrum possesses a narrow and strong peak at $\lambda = 1143$ nm. Because of the large variations in extinction spectrum due to domain orientation, the average extinction spectrum over different domains becomes very broad, as shown in **Figure 3.3.3**. Therefore the orientation of the domain plays a much more significant role at higher incident angle θ in the determination of the optical extinction property.

3.5 Applications

3.5.1 SERS response of Ag FONs

Since the optical extinction spectra of Ag FONs for small θ show a significant LSPR extinction peak and these peaks are close to the Raman excitation wavelength, $\lambda = 785$ nm, we have carried out SERS measurements on those samples. The SERS spectra of different concentrations *C* of R6G where $C = 5 \times 10^{-6}$, 1×10^{-5} , 1×10^{-4} , 5×10^{-4} , 1×10^{-3} , and 1×10^{-2} M, are acquired on different Ag FON substrates of $\theta = 0^{\circ}$, 25° , and 55° . Figure 3.5.1 shows the representative R6G SERS spectra for Ag FON substrates at $\theta = 25^{\circ}$. The spectrum labeled "control" in the figure shows the SERS response of the bare Ag FON substrates, and possesses characteristic of vibrational modes of polystyrene, with an intense peak at $\Delta v = 1004$ cm⁻¹ and



Figure 3.5.1 The SERS spectra of R6G at different concentration C on Ag FON substrate for θ = 25°.

other weak peaks at $\Delta v = 1033$ cm⁻¹ and 1601 cm⁻¹ [173,174]. According to Refs. 120 and 121, the $\Delta v = 1004$ cm⁻¹ peak corresponds to the phenol ring breathing mode for PS. When R6G is added, the R6G characteristic peaks at $\Delta v = 614$, 776, 1186, 1312, 1363, and 1510 cm⁻¹ start to appear and become stronger and stronger with increased *C*. [175-177] Two predominant peaks of R6G at $\Delta v = 614$ cm⁻¹, which corresponds to the C-C-C bending mode, and $\Delta v = 1510$ cm⁻¹, which is the C-C aromatic stretching mode, are highlighted in **Figure 3.5.1**. It appears that as *C* increases, both the peak intensities at $\Delta v = 614$ cm⁻¹ and $\Delta v = 1510$ cm⁻¹ increase monotonically. Although the PS at $\Delta v = 1004$ cm⁻¹ is still detectable, its strength has been significantly reduced with *C*.

To quantify how the SERS signals of PS and R6G change as a function of *C* on Ag FON substrates we analyze the peak intensities at $\Delta v = 1004$ cm⁻¹, I_{1004} , and $\Delta v = 614$ cm⁻¹, I_{614} , **Figures**



Figure 3.5.2 The SERS peak intensity versus R6G at concentration C for (a) I_{614} and (b) I_{1004} , and (c) the normalized peak ratio $\delta_{614/1004}$ as a function of C.

3.5.2 (a) and (b) show the log-log plots of I_{614} and I_{1004} as a function of *C* for different Ag FON substrates. We observe that the I_{614} -*C* and I_{1004} -*C* relationships follow the same trend for different Ag FON substrates: I_{614} increases monotonically with *C* when $C \leq 10^{-3}$ M, and then saturates at higher *C*; while I_{1004} decreases monotonically with *C*. The data are scattered for different substrates, which is a reflection of the non-reproducibility and ultimately lack of quantification of SERS measurements for these substrates. However, at the same *C*, both I_{614} and I_{1004} values show similar trend for different Ag FONs. For example, at $C = 10^{-5}$ M, I_{614} is the minimum at $\theta = 25^{\circ}$ and the maximum at $\theta = 0^{\circ}$, and the same trend occurs for I_{1004} . Thus it is expected that the ratio, $\delta_{614/1004}$, $= I_{614}/I_{1004}$ may not depend on θ . **Figure 3.5.2 (c)** shows the plot of $\delta_{614/1004}$ versus R6G concentration *C*. As expected, regardless of the Ag FON substrates, all the three sets of data

collapse together. The log-log relationship of the normalized peak intensities can be expressed as $\delta_{614/1004} = 10^{3.9}C^{1.03\pm0.01}$ for $C \leq 10^{-3}$ M. Therefore, the normalized value $\delta_{614/1004}$ is only dependent on the R6G concentration, and different substrate fabrication conditions have very little effect. Such a fabrication condition invariance may be due to the following reason: for the Ag patches covered PS spheres, in principle, the SERS signal generated from the PS (I_{1004}) shall be proportional to the total number of hot spots (N_0) on the Ag patches, $I_{1004} \propto N_0$, while the target molecules (R6G) shall occupy fraction of the hot spots, and its SERS intensity $I_{614} \propto CN_0$. Then the intensity ratio, $I_{614}/I_{1004} \propto C$, is only a function of the concentration of the targeted molecules. Thus, even though at different vapor incident angle, the surface coverage of Ag on PS beads is different, and the total number of hot spots may be different, the intensity ratio is only a function of R6G concentration, not the Ag surface coverage. Thus, the PS peak at $\Delta v = 1004$ cm⁻¹ can be used potentially as an internal standard for quantitative SERS measurements.

In fact, the PS peak at $\Delta v = 1004 \text{ cm}^{-1}$ do meet the requirements for an internal standard. It does not interfere with the presence of R6G since it is originated from the Ag/PS interfaces, and its signal is identifiable within the presence of different concentrations of R6G. Unlike internal standards added to a solution as mentioned earlier, the analyte and the PS coating are separated by the two surfaces of the silver layer. Due to the interfacial separation, target analytes and internal standard are not competing for surface adsorption. In fact, Péron *et al.*'s study was the first to apply PS as an internal standard for SERS detection. [172]Their SERS substrate consisted of sparsely coated Au nanoparticles on the PS nanospheres chemically bonded to a quartz surface in a random arrangement. Although they demonstrate the PS peak could be used to quantitatively determine the target analyte, naphthalene, the PS peak could not be identified directly when coated with the analyte. Rinsing in 10 mL of ethanol for 10 minutes was required to eliminate surplus analyte and

recover the PS peak, which also significantly reduced the signal of the target analyte. To our knowledge, no other work has been reported with PS as an internal standard. And, by comparison to Peron's work, the Ag FON substrates can be utilized as a direct method to quantitatively detect an analyte without any alteration of the substrate.

It also comes to our attention that when the Ag FON substrates are excited by 514 nm laser, the SERS spectrum does not have the PS peak $\Delta v = 1004$ cm⁻¹, see **Figure 3.5.3**, which means this internal standard is excitation wavelength dependent. The reason for such a spectral change is not clear yet.

3.5.2 Real-time, in-situ SERS measurements

With an internal standard, one can perform better quantitative dynamic measurements using SERS. It has been well documented that the SERS intensity will decrease over time when illuminated at the same location. Such an effect could be due to analyte decomposition or fragmentation under continuous laser irradiation, or diffuse away molecules from the lase spot. In addition, localized elevated temperatures from prolonged laser exposure can change the optical



Figure 3.5.3 The normalized SERS spectra R6G on Ag FON substrates obtained by 514 nm and 785 nm excitation wavelength.

properties of metal nanostructures and can reduce SERS signal intensity. [156-159] Normalization by an internal standard could factor out the spectral decay caused by above mentioned external changes when taking prolonged stationary measurements. We verify this concept by investigating molecular adsorbance kinetics using Ag FON at $\theta = 0^{\circ}$. Figure 3.5.4 (a) shows the time-dependent SERS spectra after the Ag FON has been immersed in 0.1 mM R6G. In the figure, the R6G peaks of $\Delta v = 614$ cm⁻¹ and $\Delta v = 1510$ cm⁻¹, and the PS peak at $\Delta v = 1004$ cm⁻¹ are labeled. We observe that the R6G and PS peak values appear to all decrease over time t. To be quantitative, Figure **3.5.4** (b) plots I_{614} , I_{1510} , and, I_{1004} as a function of t. I_{1004} decays almost exponentially over time, while both I_{614} and I_{1510} stay relatively constant for t < 4 min, then decay exponentially. Such decays do not match with the known surface adsorption kinetics; we expect that as more and more R6G molecules adsorb on the surface, both the I_{614} and I_{1510} should increase with t until a saturation occurs. However, by taking the PS internal standard into account, the observed kinetics has changed. Figure 3.5.4 (b) plots the normalized peak intensities, $\delta_{1510/1004}$ and $\delta_{614/1004}$, as a function of t. Both plots show a similar trend: when t < 20 min, both $\delta_{1510/1004}$ and $\delta_{614/1004}$ increase monotonically with t; then at $t \ge 20$ min, these ratios reach a saturation value. Such a trend is consistent with molecular adsorption kinetics on a surface, and can be described by the following kinetic equation,

$$\delta = \delta_0 \left[1 - e^{-k(t - t_0)} \right] \,, \tag{3.1}$$

where δ is the normalized SERS peak value, *k* is the adsorption rate constant, δ_0 is a constant proportional to initial molecule concentration, and t_0 is the initial time of adsorption.

By fitting the equation to the experimental data shown in **Figure 3.5.4** (b), the adsorption rate constants are found to be $k_{614} = 0.36 \pm 0.04 \text{ min}^{-1}$ for $\Delta \nu = 614 \text{ cm}^{-1}$ and $k_{1510} = 0.40 \pm 0.05$



Figure 3.5.4 (a) The time-dependent SERS spectra of R6G adsorbing onto the Ag FON substrate. (b) The solid lines are I_{614} , I_{1510} , and I_{1004} plots and the scattered points are the normalized intensities of $\delta_{614/1004}$, $\delta_{1510/1004}$ and $\delta_{614/1510}$ plotted against time.

min⁻¹ for $\Delta \nu = 1510$ cm⁻¹. Clearly, $k_{614} \approx k_{1510}$, which demonstrates that in the adsorption process, both the C-C-C bending and C-C aromatic stretching can be probed with equal probabilities. This result means R6G tends to randomly adsorb on the Ag surface. In fact, the ratio of the two R6G

peaks, $\delta_{1510/614}$ versus *t*, is kept almost constant through the entire duration (**Figure 3.5.4 (b**)), which further demonstrates this claim.

A similar study has been performed with 4-mercaptophenol (MPH). Figure 3.5.5 (a) displays the results of the time-dependent SERS spectra of Ag FONs after immersion in 1 µM of MPH. Besides the $\Delta v = 1004$ cm⁻¹ peak for PS, each SERS spectrum has two additional MPH vibrational peaks at $\Delta v = 1075$ cm⁻¹ and $\Delta v = 400$ cm⁻¹. There is a difference in the literature to the assignment of these two peaks. According to Li *et al.*, the $\Delta v = 1075$ cm⁻¹ peak is attributed to C-S stretching and in-plane ring vibration (9b in Wilson notation), while the $\Delta v = 400 \text{ cm}^{-1}$ peak corresponds to C-S bending or stretching. [178] However, Lee *et al.* attributes the $\Delta v = 1075$ cm⁻¹ peak to in plane ring vibrational of mode of 1 (Wilson notation), and $\Delta v = 400$ cm⁻¹ to a ring vibration of 7a (Wilson notation). [179] Figure 3.5.5 (b) shows quantitative plots of MPH peak intensities of I_{400} , I_{1075} , and I_{1004} , versus t. For both I_{1004} and I_{400} , the trend is similar to R6G, *i.e.*, I_{1004} decays exponentially with t while I_{400} increases initially, then decays monotonically. However, I_{1075} shows a different trend. It continues to increase as a function of t for $t \le 100$ min and reaches a maximum around t = 150 min, and then decreasing slightly. By normalizing with the internal standard I_{1004} , the $\delta_{1075/1004}$ and $\delta_{400/1004}$ show different absorption kinetics as shown in Figure 3.5.5 (b). The $\delta_{400/1004}$ increases rapidly for $t \leq 8$ minutes and then begins to saturate towards a constant value, while $\delta_{1075/1004}$ raises slowly, and it does not reach saturation even after t = 100 min. Using Equation (3.1) to fit the data, we obtain that $k_{400} = 0.21 \pm 0.1$ min⁻¹ for $\Delta v =$ 400 cm⁻¹ and $k_{1075} = 0.0234 \pm 0.0004 \text{ min}^{-1}$ for $\Delta v = 1075 \text{ cm}^{-1}$. The difference in absorption kinetics for different SERS vibrational modes of MPH reflects that during adsorption, the adsorbed MPH molecular orientation is dynamically changing, and is a property observed in self-assembled monolayers (SAMs) and DNAs. [180-183] When MPH coverage is small, the MPH molecules lie



Figure 3.5.5 (a) The time-dependent SERS spectra of MPH adsorbing onto the Ag FON substrate. (b) The solid lines are I₄₀₀, I₁₀₇₅, and I₁₀₀₄ and the scattered points are the normalized intensities of δ_{400/1004}, δ_{1075/1004} and δ_{1075/400} plotted against time.

flat on the Ag surface as shown in **Figure 3.5.6** (a). When the incident Raman laser beam is exciting the MPH molecules, both the C-S stretching modes and ring modes are excited, but the ring vibrations form an angle with respect to the E-field of the laser. When MPH coverage increases over time, the MPH molecules start to reorient and stand on the surface as shown in **Figure 3.5.6** (b), the contribution of the C-S stretching mode becomes less since its vibration



Figure 3.5.6 A diagram of MPH orientations on Ag surfaces: (a) small coverage case and (b) near unity covered case

direction is perpendicular to the E-field direction of the laser, while the ring mode can be fully excited by the E-field. Since our surface is curved and has roughness, when more and more MPH molecules are adsorbed onto the surface over time, the C-S mode intensity does not go to zero; rather, it reaches a saturation while the ring mode can still reorient. It is expected that as *t* increases, the ring mode intensity increases while the stretching mode intensity deceases. In fact, from **Figure** (**3.5.5**) we also plot $\delta_{1075/400}$ versus *t*, and we see that this ratio increases with *t*. Therefore our results suggest that the $\Delta v = 400$ cm⁻¹ may be primarily due to the C-S stretching mode, while the $\Delta v = 1075$ cm⁻¹ is due to the ring vibration. The different adsorption time is caused mainly by the reorientation of MPH molecules.

3.6 Conclusions

In conclusion, Ag FONs were fabricated using SNSL, and its LSPR wavelength was tuned by varying θ , while fixing the Ag deposition thickness. The shift of the LSPR quantitatively agrees with that predicted by FDTD simulations. Although the Ag FON pattern consists of the Ag coating on the nanospheres and underlying nanotriangles, the simulation results show that the major contribution to the LSPR peak comes from the Ag coating on the nanospheres. Additionally, simulations also demonstrate that domain effects, which can change the shape of the Ag coating, broaden and shift the LSPR wavelength. The SERS spectrum peak of polystyrene is used as an internal standard. The normalized SERS peak intensity versus rhodamine 6G (R6G) concentration is independent of substrate's deposition conditions. In addition, using the internal standard, the SERS can be used to quantitatively study the dynamic adsorption process of R6G and 4mercaptophenol (MPH) on Ag FON substrate. This work highlights the significance of utilizing Ag FONs as an internal standard and its benefits for real-time, in-situ measurements.

CHAPTER 4

AG TRIANGULAR NETWORKS

4.1 Introduction

In previous chapter, a SNSL method is used to fabricate and systematically tune Ag FONs by changing θ . However, our experimental results showed that as θ increased, the dependence of LSPR on the domain quality of the monolayer became more severe. This domain effect can also be seen in other SNSL methods where the nanospheres were removed after deposition. For instance, **Figure 4.1.1** shows triangular nanopatterns fabricated at a fixed deposition angle $\theta = 20^{\circ}$ with varying domain orientations $\varphi = 0^{\circ}$, 10° , 20° , and 30° (see **Figure 3.2.1** for the definition of the orientation angle). The figure shows that for different orientations, the shape of the triangular



Figure 4.1.1 The simulated triangular nanopatterns deposited at $\theta = 20^\circ$, and $\varphi = 0^\circ$, 10° , 20° , and 30° .

nanopatterns will change. This means that for different domains on the substrate, the LSPR will have a slightly different peak. The combined contribution of each domain will broaden the LSPR wavelength, which reduce its sensitivity for LSPR sensor and SERS

. One possible method to overcome the domain effect is to rotate the substrate during the deposition. In doing so, the resulting patterns are no longer domain dependent. Therefore, in this chapter we introduce a rotation-based SNSL strategy to fabricate nanopatterns called triangular networks (TN), and demonstrate that this strategy can also be used to tune the LSPR of the TN nanopatterns.

4.2. Experimental Methods

Colloid Monolayers

500 nm-diameter PS nanospheres were obtained to form the colloid monolayers.



Figure 4.2.1 A schematic diagram of shadow nanosphere lithography.

Monolayer preparation method for 500-nm PS beads is given in Appendix 1. Deposition Strategy

Ag TN nanopatterns were prepared using a single-source electron beam deposition system (see Section 2.3.3), with a deposition configuration shown in Figure 4.2.1. Monolayer coated substrates were mounted on a holder placed 50.8 cm above the crucible. As shown in Figure 4.2.1, the monolayer coated substrates were positioned at a fixed θ , and were rotated azimuthally at a speed of 20 rpm for the duration of the deposition. For each deposition, θ was set to 0°, 5°, 7°, 10°, 12°, 15°, 17°, and 20°, respectively, with an accuracy of ±1°. For different θ , the deposited Ag thickness were initially varied to ensure that the final thickness of the Ag patterns was ~ 50 nm, which was determined by atomic force microscope (AFM) measurements. However, as θ increased, the deposition made the shadowing effect of the opening among nanospheres smaller and smaller which minimized the actual Ag film thickness. Therefore, the Ag nanopatterns possess decreasing thickness with increasing θ . After the Ag deposition, the monolayer template was removed using Scotch tape, and then the substrates were rinsed in toluene, acetone, and 2-propanol successively to remove PS residual.

Morphological and Optical Characterization

Optical measurements were taken using the equipment specified in Section 2.3.3. The optical transmission spectra of the Ag nanopatterns were measured by an ultraviolet-visible spectrophotometer. The resulting transmission spectra were converted into extinction spectra. The morphology of the samples was characterized by AFM and SEM. The resulting SEM images were analyzed by Image J software (NIH), while AFM images were analyzed using NanoScope Analysis software. SERS spectra of the Ag nanopatterns were measured using a confocal Raman microscope (Renishaw inVia), with an excitation wavelength of 633 nm. A 2 μ L droplet of BPE (10⁻⁴ M) in methanol was dispensed onto the Ag nanopattern substrate. The nine SERS spectra measured from randomly chosen positions on each substrate were obtained. All quantitative

analysis of the average SERS spectra, such as peak positon and amplitude, were processed using the spectroscopic software GRAMS AI (Thermo Scientific).

Numerical Calculation and Simulations

Ag nanopatterns were simulated using the numerical calculation method mentioned in **Section 2.4.2**. The formation of Ag nanopatterns was also simulated by a kinetic, threedimensional Monte Carlo (MC) simulation discussed in **Section 2.4.2**. In short, In the MC ballistic deposition model, the incident particles approached the surface in a straight trajectory at an angle of θ . When the particle arrived on the surface or passed by the nearest-neighbor site of a previously deposited particle, it would deposit and become part of the surface. In order to simulate the surface diffusion after the incoming particle settled on the surface, one particle on the surface would be randomly chosen to perform the diffusion. The diffusion was a random walk on the surface with a diffusion length of one unit. There was a predetermined number *D* of particles selected to perform diffusion, which represented the strength of diffusivity of a particular material such as Ag. Preoccupied sites above a planar surface were formed according to the hexagonal pattern of nanospheres to mimic the templates used in experiments. The substrate rotation was included in the MC simulation. After the deposition is done, the templates and the deposition above the top surface of the templates were digitally removed.

The optical properties of selected Ag nanopatterns deposited at $\theta = 0^{\circ}$, 10° , 12° , 17° , and 20° were simulated using the finite-difference time-domain (FDTD) method The Ag nanopattern simulation models were based upon AFM data and SEM images.

4.3 Morphology

Figures 4.3.1(a-c) show representative Ag nanopatterns predicted by numerical calculations, experimentally obtained *via* SEM, and generated by MC simulation for $\theta = 0^{\circ}$, 10° , 15° , and 20° , respectively. As predicted by the numerical calculations **Figure 4.3.1** (a), when $\theta = 0^{\circ}$, individual and disconnected nanotriangles were formed on the substrates. When θ was increased from 0° to 10° , the characteristic pattern changed to a hexagonal shape with a thick central triangle (the red colored areas), while the neighboring patterns remained unattached. As θ changed to 15° and 20° , each individual pattern started to join with the adjacent patterns, and individual pattern became a cup-like triangular shape, *i.e.*, there was a triangular hole in the middle of each pattern. When θ increased, the hole became larger, and the entire pattern grew larger as well. But the overall arrangement for all the patterns still followed close-packed symmetry



Figure 4.3.1. Representative nanopatterns formed by SNSL: (*a*) numerical calculations, (*b*) experimental SEM images, and (*c*) Monte Carlo (MC) simulation at $\theta = 0^{\circ}$, 10° , 15° , and 20° , respectively.

regardless of the θ value. Notice that for $\theta \ge 40^\circ$, therewere no patterns formed on the substrate due to the shadowing effect. These predictions matched well with the experimental results, as shown in **Figure 4.3.1(b)**. At $\theta = 0^\circ$, well separated nanotriangles with concave sides were formed. When θ increased to 10°, the nanopattern became separated, larger equilateral triangle. The highmagnification SEM images showed that the Ag nanopatterns also contain small Ag nanoparticles (NPs) formed around each apex of the triangle, with a solid hexagon-like pattern in the middle. For $\theta = 15^\circ$, the resulting pattern emerged as an elongated triangle with a slight depression at its center, filled randomly with NPs. The neighboring nanopatterns were connected to one another at the respective apex of each triangle. When θ increased to 20°, the triangular nanopattern appeared wider, and consisted of different sized Ag NPs. The middle of each pattern had smaller and less dense Ag NPs compared to the edges of the triangle.

Though the experimental results match well with the numerical calculations, there are morphology differences at $\theta > 0^\circ$. The individual unit cell consisted of multiple Ag NPs, rather than the smooth, singular Ag patterns predicted in **Figure 4.3.1(a)**. The reason is that the numerical calculation used a continuous mathematical model, while during deposition, other growth related phenomenon such as adatom surface dynamics can take place. In particular, for low melting point



Figure 4.3.2 $4\mu m \times 4 \mu m AFM$ scans of 500 nm -nanospheres for $\theta = 15$. (a) Ti and (b) Ag. The inset shows an enlarged nanoparticle array

 (T_m) metals, like Ag, not only is surface diffusion important, but the sticking coefficient during the initial nucleation of the vapor can also play a dominant role. For example, Kosiorek *et al.* can match their experimental Ni and Cr TN nanopattern with their numerical calculation since both Ni and Cr have $T_m = 1,453^{\circ}$ C and $1,857^{\circ}$ C, respectively. [184] We have also deposited Ti nanopatterns with $T_m = 1,660^{\circ}$ C at $\theta = 15^{\circ}$ for comparison with those from Ag with $T_m = 961^{\circ}$ C, as shown in **Figure 4.3.2 (a-b).** The resulting Ti nanopattern was smooth with no NPs in the unit cell as compared to those formed by Ag. Thus, to better reflect the formation of Ag nanopatterns, one has to consider the effect of surface diffusion and reemission.

The effects can only be accounted for in MC simulations. Figure 4.3.1(c) shows the simulated results using our MC deposition model. The overall patterns matched well with both the numerical calculation and experimental results. However, when $\theta \ge 10^\circ$, Ag NPs started to form within and around the patterns, especially when $\theta \ge 15^\circ$, the simulated results resembled more



Figure 4.3.3 The shape parameter ratio η as a function of θ obtained from the numerical calculations, SEM images, and MC simulations.

like the experimental results, which demonstrated that adatom surface dynamics did play an important role in SNSL pattern formation.

To gain a quantitative comparison, we define a geometric factor η , which is the ratio of the length *d* to the height *a* of nanopatterns, and plot η versus θ in **Figure 4.3.3** for all nanopatterns deposited. We notice that, for $\theta = 0^\circ$ the η values for NC simulation and SEM matched more closely than that from numerical calculation. This is because the nanopatterns of both the MC and experiment had slightly rounded apex due to the shadowing effect of the PS nanosphere, therefore the *a* value was slightly shorter than that of the numerical calculation. When $\theta = 12^\circ$, the results from SEM and numerical calculation agreed more closely, and the thickness distribution of the pattern was greater towards the center of the unit cell for the numerical calculation and SEM, while the MC predicted a more uniform distribution of Ag. For $\theta \ge 15^\circ$, the MC, SEM, and numerical calculation both show that they can predict the shape of the Ag nanopatterns.

4.4 Optical properties

The extinction spectra of the Ag nanopatterns shown in **Figure 4.4.1(a)** all exhibited multiple resonance peaks within the 300 - 1500 nm wavelength range. When $\theta < 12^{\circ}$, all the samples had three resonant peaks, while when $\theta \ge 12^{\circ}$, there were only two peaks. The strongest extinction peak red shifted with θ . **Figure 4.4.1(b)** plots resonance peak wavelengths λ_0 as a function of θ . For $\theta = 0^{\circ}$, three resonances occurred at $\lambda_0 = 363$ nm, 423 nm, and 689 nm, respectively. These spectra features are typical for Ag nanotriangle arrays obtained from NSL. [185,186] The strong $\lambda_0 = 689$ nm peak is due to a strong dipole resonance; the peak at $\lambda_0 = 423$ nm is a weak in-plane quadrupole resonance, while the peak at $\lambda_0 = 325$ nm is due to the out-ofplane quadrupole extinction. [185,186] When θ was increased to 5° and 7°, the nanopatterns were
still disconnected nanotriangles, and it was expected that the spectral features were similar to those of $\theta = 0^{\circ}$ sample: the strongest resonant peak located at $\lambda_0 = 678 - 685$ nm, and two other peaks at ~ 477 nm and ~ 347 nm, which may all correspond to the dipole and quadrupole resonances as discussed for $\theta = 0^{\circ}$ sample. However, the extinction peak became stronger, especially at $\lambda_0 = 678$ - 685 nm region, and the corresponding peak width was smaller compared to that of $\theta = 0^{\circ}$ sample. Such a narrow extinction peak is preferred for high sensitive LSPR sensors. When $\theta = 10^{\circ}$, there were still three peaks observed and the peak at $\lambda_0 = 677$ nm became even stronger. However, when θ was increased to 12°, the spectrum became very different: only two peaks were observed, with the strongest peak suddenly shifted to $\lambda_0 = 833$ nm, while the second peak ($\lambda_0 = 471$ nm) stayed almost unchanged. With the further increase of θ , the second peak location almost did not change while the largest peak kept on red shifting almost linearly with respect to θ until $\theta = 20^{\circ}$. Such a change in the extinction spectra at $\theta \ge 12^{\circ}$ is consistent with the changes in nanopatterns. As shown in **Figure 4.3.1(b**), when $\theta < 12^{\circ}$, the nanopatterns were essentially a separated, solid triangle array. Only at slightly larger θ , there were small NPs appeared around the solid triangles.



Figure 4.4.1 (a) The extinction spectra of Ag TNs at different incident angle θ and (b) the extinction peak wavelength versus θ .

However, when $\theta \ge 12^\circ$, the main solid triangles changed into small Ag particles, and the adjacent Ag patterns started to connect together to form a network structure. Since some Ag NPs were very closely spaced, it was expected that the electromagnetic coupling between small Ag NPs would play an important role for the optical properties. Since some Ag NPs were very closely spaced, it was expected that the electromagnetic coupling between small Ag network at the electromagnetic coupling between small Ag nelectromagnetic coupling between small Ag network at

To gain a better understanding of the optical properties, FDTD calculations were carried out based on the nanopatterns at $\theta = 0^{\circ}$, 10° , 12° , 17° , and 20° , respectively, and the resulting numerical extinction spectra, the experimental spectra, and an inset of the simulated unit cell of the nanopattern array were plotted together in Figure 4.4.2. For all of the calculations, the thickness of the Ag particles was fixed at 100 nm, 43 nm, 24 nm, and 6 nm, respectively. These height values were based upon AFM average height measurements. For $\theta = 0^{\circ}$, the calculated extinction spectrum showed a prominent and sharp LSPR peak at $\lambda_0 = 664$ nm, and a secondary peak at $\lambda_0 = 493$ nm. Two weaker peaks at $\lambda_0 = 416$ nm and 374 nm were also visible. These peak locations were close in value to the experimental peaks at $\lambda_0 = 688$ nm, 433 nm, and 339 nm. However, compared to the experimental peak at $\lambda_0 = 688$ nm, the calculated peak was narrower, and had a higher extinction. These deviations are due to the statistic variation in the shape, size, and thickness of the triangles obtained experimentally. For $\theta = 10^{\circ}$, the calculated extinction spectrum showed a similar, but broader peak at $\lambda_0 = 786$ nm, and secondary peaks at $\lambda_0 = 664$ nm and 436 nm. By comparison, the experimental LSPR peak at $\lambda_0 = 677$ nm was also much narrower and blue-shifted compared to that of simulation which, may be caused by broad deviations in the experimental nanopatterns. The experiment and simulation spectra show much broader extinction when $\theta = 12^{\circ}$. The simulated spectrum showed a broad extinction ranging



Figure 4.4.2 The comparison of the extinction spectra from finite-difference time-domain simulations and experimental results for selected θ . The unit cell for FDTD simulation for each θ is shown as the insert image.

between 350 to 1050 nm, with the highest extinction value at $\lambda_0 \sim 863$ nm. The experimental spectrum also showed a broad spectrum with $\lambda_0 = 794$ nm. For $\theta = 17^\circ$ the calculated spectrum was broad, covering the 450 nm to 1400 nm wavelength region, which was qualitatively consistent with the experimental spectrum. For $\theta = 20^\circ$, the simulated spectrum show a broad extinction value between 300 nm to 1500 nm, with a maximum extinction value at $\lambda_0 = 410$ nm. Similarly, the experiment extinction spectrum also shows a broad peak, with $\lambda_0 = 452$ nm. Clearly, the simulated spectra qualitatively matched well with the experimental spectra.

The broadening of the extinction spectra at $\theta > 10^{\circ}$ are due to the appearance of smaller Ag NPs of different sizes and orientations as well as the electromagnetic coupling among the

particle assembles. [187] This can be clearly demonstrated by investigating the polarization dependent extinction spectra as well as the local electric field distributions at the extinction resonant wavelengths. **Figure 4.4.3** shows an example for the Ag nanopatterns at $\theta = 17^{\circ}$. The two orthogonal polarized extinction spectra, one excited by the horizontal (*x*-) polarization, and the other by vertical (*y*-) polarization, show distinguished different features: for *x*-polarization excitation, two strong resonances appeared at $\lambda_0 = 850$ nm and 1005 nm, while under *y*-polarization, a different resonant peak at $\lambda_0 = 684$ nm appeared, though a relatively small resonant peak at $\lambda_0 = 1005$ nm was still present. Such a difference originated from the orientation of the Ag NPs on the substrates, which means that the NPs are highly anisotropic. The multiple resonance



Figure 4.4.3 (a) Polarized extinction spectra of Ag TNs at $\theta = 17^{\circ}$; and the local electric field distributions of the $\theta = 17^{\circ}$ nanopatterns excited by x-polarized light at (b) $\lambda_0 = 825$ nm and (c) $\lambda_0 = 1005$ nm, as well as (d) $\lambda_0 = 684$ nm excited by y-polarized light.

features in both *x*- and *y*- polarization excitations resulted from the size distribution of the Ag NPs. In addition, the local electric field distributions at the resonant wavelength shown in **Figure 4.4.3(b-c)** demonstrated strong coupling among adjacent Ag NPs, especially large Ag NPs. For the *x*-polarization excitations at $\lambda_0 = 825$ nm and 1005 nm, hot spots with strongest local electric field occurred only around largest Ag NPs due to their larger wavelengths; however, for the *y*-polarization excitation at $\lambda_0 = 684$ nm, hot spots occurred at multiple gaps among Ag NPs. Those high electric field hot spots were evidence of plasmonic coupling effect which would not occur for isolated nanopatterns formed at $\theta < 10^\circ$. In addition, the high density of hot spots presented in **Figure 4.4.3(d)** infer that those nanopatterns could be potentially used for SERS substrates.

4.5 Applications

Since the optical extinction of the Ag nanopatterns had a strong resonant peak at $\lambda_0 = 633$ nm for samples at $\theta < 12^\circ$, while for samples at $\theta \ge 12^\circ$, there were multiple hotspots available on the substrate due to the statistic arrangement of NPs in the pattern; it was expected that those patterned substrates were good SERS substrates for excitation at $\lambda = 633$ nm. Figure 4.5.1 (a) shows the average BPE SERS spectra of different substrates. The characteristic peaks of BPE at $\Delta v = 1200$ cm⁻¹, 1606 cm⁻¹, and 1636 cm⁻¹ are indicated in the figure, which correspond to ethylenic C = C stretching mode, pyridine ring C = C stretching, and whole ring C = C stretching mode respectively [188,189]. For $\theta = 0^\circ$, there was no discernable BPE signal. For $\theta = 5^\circ$, BPE peaks started to emerge, became stronger with the increase of θ , and reached a maximum when $\theta = 10^\circ$. With the further increase in θ , all the BPE peaks decreased. In fact, the baseline corrected peak height as a function of wavelength, shown in 4.5.1 (b), show quantitatively that for peak intensities at $\Delta v = 1200$ cm⁻¹, 1606 cm⁻¹, and 1636 cm⁻¹, the greatest SERS intensity occurs at $\theta = 10^\circ$.



Figure 4.5.1 (a) A plot of the SERS spectra of BPE measured on each nanopattern for different θ . (b) Characteristic peak intensities of BPE at 1606 cm⁻¹, 1636 cm⁻¹, and 1200 cm⁻¹ as a function of deposition angle



Figure 4.5.2 (a) The shapes of triangular prism, circular and concentric disk, and sphere that were used in the calculation of the average surface area of Ag TNs. (b) Plot of the deposition angle as a function of the average surface area per unit cell.

However, since the nanopatterns were different at different incident angle θ , the effective Ag surface area exposed to BPE was also different. If one assumes that the BPE were uniformly coated on the Ag surface, then different patterns would have different amount of BPE molecules coated on Ag surface, which could potentially give different strength of SERS signal. Therefore, to fairly compare the SERS response of different nanopatterns, the SERS intensity per unit Ag area needs to be considered. Based upon SEM and AFM images, the surface area of the Ag nanopatterns were calculated as either triangular prisms, circular disks, concentric disks or spheres. **4.5.2** (a) below shows dimensions and measured parameters for each shape. For $\theta = 0^\circ$, Ag nanopatterns were measured as triangular prisms or circular disks, while smaller particles were assumed to be spheres. Lastly, for $\theta = 20^\circ$, all particles were assumed to be spherical. With the exception of *h*, height derived from the AFM images, all parameters were



Figure 4.5.3 The surface area of Ag TNs normalized SERS peak intensity at $\Delta v = 1200 \text{ cm}^{-1}$ versus extinction (E) at $\lambda = 633$.

measured using image analysis software from the SEM images. The average of one unit is plotted as a function of deposition angle as shown in **Figure 4.5.2** (b). As expected, as the deposition angle increases the surface area increases exponentially. These results then normalized with the SERS peak intensity of BPE to normalize the effect of surface area. **Figure 4.5.3** shows the result of the area normalized BPE peak intensity at $\Delta v = 1200$ cm⁻¹ as a function of the optical extinction at $\lambda = 633$ nm. The normalized SERS intensity increased almost linearly with the extinction magnitude, which is consistent with other studies. [20,190]The substrate gives the highest SERS intensity is the nanopattern deposited at $\theta = 10^{\circ}$. This result shows that using the SNSL one can tune the LSPR response and optimize SERS substrates.

4.6 Conclusions

In this chapter, we have investigated the morphological and optical properties of Ag TN nanopatterns prepared by a rotation-based SNSL method. By changing the θ , we show that a diverse variety of nanopatterns can be prepared. These patterns can be predicted by a numerical model as well as a Monte Carlo simulation. Due to the variations on the size, shape, and arrangement of Ag NPs in the pattern, the optical properties of these nanopatterns can be tuned systematically, especially the LSPR wavelengths, and the results are confirmed by FDTD simulation. This is a relatively simple strategy to tune the LSPR based on NSL. Therefore, we have demonstrated that the tuning of LSPR using SNSL nanopatterns can optimize the SERS response for chemical and biological applications.

CHAPTER 5

DOUBLE TRIANGLE NANOPATTERNS

5.1 Introduction

Chapters 3 and **4** describe SNSL methods that can tune the LSPR wavelength of nanopatterns by systematically changing their size and shape. As discussed in **Section 1.2.1**, another strategy to tune the LSPR wavelength is to change the relative distance between individual nanopatterns. Though most studies on the effect of the gap between nanopatterns have heavily relied on EBL, SNSL can also produce nanopatterns with changing separation between nanopatterns and can shift the LSPR wavelength. As shown in previous chapters, a single deposition at a specific angle θ through the nanosphere monolayer can generate nanotriangle



Figure 5.1.1 Example of DT nanotriangle nanopatterns using 1000 nm diameter nanosphere monolayers deposited at $\theta = 15^{\circ}$. Parameters listed in the diagram are the center to center separation distance, s, side length of nanotriangle, a, and base length, l. [191]

patterns with different size, shape and location. Thus, if two depositions are carried out at the same θ but different azimuthal angle with respect to the monolayer domains, two nanotriangles can be formed at different locations on the substrate. Figure 5.1.1 shows an example of such a structure deposited at $\theta = 15^{\circ}$ using two opposite azimuthal angles, $\varphi = 0^{\circ}$ and 180°, respectively. These nanopatterns are known as overlapping or double triangle (DT) nanopatterns. The relative center-to-center separation distance, *s*, between each nanotriangle (defined in **Figure 5.1.1**) can be controlled systematically during fabrication.

DT nanopatterns exhibit optical properties not observed in their single pattern counterpart. For instance, the extinction spectra of single nanotriangles exhibit typically a single, strong resonance peak that attributes from the dipole resonance. [192] DT nanopatterns, however, have the combined shape of two overlapping triangles, and thus have a much larger size compared to single nanotriangles. Therefore, higher order resonance modes are observed in their optical spectrum. Zhao *et al.*, for instance, performed simulational and experimental studies of Au DT nanopatterns templated from 500 nm-diameter nanospheres. [108] They showed that the transmission spectra of DT nanopatterns possessed multiple resonance peaks (or LSPR wavelengths) due to the dipole and quadrupole resonances. Another optical phenomena DT nanopatterns can exhibit is Fano resonance, which is the constructive or destructive interference between lower and higher order resonance modes. [193]Yan et al. detected Fano resonance in DT nanopatterns both theoretically and experimentally on separation-dependent Au DT nanopatterns. [191] For certain s, they demonstrated that the dipole and quadrupole resonances of the DT nanopatterns could destructively interfere to create a Fano resonance peak. Yan et al. also compared the LSPR sensitivities of the Fano resonance peak of DT patterns and the dipole resonance peak of single nanotriangle patterns, and showed the DT nanopattern with a FOM of 3.5 is much more sensitive than the single nanopattern with FOM = 0.9. Lastly, when *s* of the DT nanopattern is large enough to form a gap between the two individual triangle (*i.e.* they are no longer overlapping), the localized electric field in the gap can become enhanced, as discussed in **Section 1.2.1**. Sundaramurthy *et al.* performed a simulation on gap-dependent Au DT nanopatterns, and verified that as the gap between the nanopatterns decreased the localized electric field located between the nanotriangles was enhanced significantly. [194]

The fabrication of all DT nanopatterns reported thus far uses a single source deposition system. Although this method is simple, it requires multiple deposition steps. For instance, Haynes et al. used a multi-step SNSL procedure to tune the separation distance between the nanotriangles. [195] First, they mounted their substrates on an aluminum bracket with a fixed θ . Then after one deposition, the substrate was removed and remounted with a different angled bracket. This and other similar multi-step SNSL methods present several problems: they are time-consuming and complex, which make the fabrication method difficult to scale up; the interruption during consequent deposition introduces unnecessary oxidation for metals like Ag or Cu; additionally, since the size of the triangular opening among nanospheres is very small, during the deposition, such an opening will become smaller and change the shape of later deposited pattern. For instance, Kandulski et al. showed that for 540 nm-diameter nanosphere monolayer the opening was filled when a 123 nm thick Ag was deposited. [196] For smaller nanospheres, this effect will become more severe. Finally, the nanopattern in early deposition will also introduce an additional shadowing effect for patterns deposited later. To resolve some of these shortcomings, one strategy is to simultaneously deposit two or more materials using multiple sources with the right deposition configurations.

In this Chapter, we introduce a strategy to fabricate DT nanopatterns with tunable LSPR properties using a dual source deposition system. By placing colloidal monolayer substrates on different locations, DT nanopatterns with different separation and shape can be fabricated simultaneously. As a result, each sample has a different LSPR wavelength. Such a method can be used to perform a high throughput screening of DT patterns for different plasmonic applications.

5.2 Experimental Methods

Colloid Monolayer

500 nm-diameter PS nanospheres were used to form the colloid monolayers according to Appendix 1.

Deposition Strategy

Ag DT nanopatterns were prepared using a dual source electron beam deposition system with a deposition configuration shown in **Figure 5.2.1**. The chamber contains two Ag sources with a center to center distance of 7". A 21"-long aluminum substrate holder was mounted 20" above and parallel to the center-to-center direction of the two sources. If the substrate was placed at different location of the holder, the vapor incident angles from Source 1 (θ_1) and Source 2 (θ_2) could be different. In the experiment, substrates were placed at three different locations as illustrated in **Figure 5.2.1** (a) in order to obtain three different DT patterns: Location A1 was directly above Source 1 and horizontally 7" away from Source 2, with $\theta_1 = 0^\circ$ and $\theta_2 = 18^\circ$; Location A2 was 3" away from Source 1 and 10" away from Source 2 with $\theta_1 = 8^\circ$ and $\theta_2 = 25^\circ$; and Location A3 was 6" away from Source 1, and 13" away from Source 2 with $\theta_1 = 15^\circ$ and $\theta_2 = 32^\circ$. We also denote the DT nanopatterns resulted from these three locations as Samples A1, A2,



Figure 5.2.1 (a) Deposition configuration of substrates relative to the two substrate sources (b) Up-side down view of substrate relative to sources.

and A3. Additional substrates could not be placed further on the holder since the shadowing effect would prevent the deposition of Source 2 through the gaps in the nanosphere monolayer when $\theta_2 \ge 40^\circ$. [141] Depositions were performed when the pressure of the chamber reached 10^{-6} Torr. The Ag deposition rate of each source was controlled to be 0.5 nm/s, which was monitored by a separated QCM facing each source. After the depositions, the colloidal monolayers were removed using Scotch tapes, and the substrates were rinsed in toluene, acetone, and 2-propanol successively to remove PS residual.

5.3 Morphology

Figures 5.3.1 (a₁) - (a₃) show the predicted DT nanopatterns by numerical simulation (NS) at the A1, A2, and A2 locations, respectively. Each pattern is consisted of two overlapped nanotriangles, a large triangle and a small triangle, where the large triangle is formed by Source 1 with a relative small θ_1 while the small triangle is formed by Source 2 at a large θ_2 . The relative position and size of the two triangles also change with the positions: From Location A1 to A3. The

separation between the two triangles becomes larger and larger while the sizes of both triangles become smaller, especially for the smaller triangle, the change is significant. This change is due to the increasing θ_1 and θ_2 when substrate location varies from A1 to A3. These results match well with the SEM images of experimentally obtained DTs as shown in **Figure 5.3.1** (a1') – (a3'). The SEM images show that as the substrate positions move from A1 to A3, the double triangle nanopatterns become smaller and more separated. However, for the sample fabricated at Location A3, the SEM image of the nanopattern shows that the large and small triangles become well separated, which is different from that predicted in **Fig. 5.3.1** (a3).



Figure 5.3.1 (a₁-a₃) The numerical calculation (NC) and the (*a₁'-a₃')* SEM images of Ag DTs for samples A1, A2 and A3. The scale bars represent 250 nm.

Label	$H_{ip}(\theta_1)$	$H_{ip}(\theta_2)$	Separation Distance (nm)	$H_{ip}(\theta_1)$ s $H_{ip}(\theta_2)$
A1 (NC)	142 ± 3	97±2	85±5	W W
A1 (Exp)	120±10	97 ± 2	87±5	A A A A A A A A A A A A A A A A A A A
A2 (NC)	129±5	73 ± 2	89± 5	
A2 (Exp)	105 ± 9	94 ± 10	100± 5	44
A3 (NC) A3 (Exp)	112 ± 4	50 ± 2	97±5	1
	94 ± 10	61 ± 10	116±7	

Table 5.3.1 Values of the in-plane height (H_{ip}) and separation distance of numerically calculatednanopatterns (NC) and experimentally measured (Exp) nanotriangles. SEM image illustrates themeasurement strategy for each parameter.

To quantitatively characterize the DT patterns, the size, shape, and separation distance of the predicted and experimental nanotriangles were measured. In the right figure of **Table 5.3.1**, the parameters of in-plane height and separation distance are defined: the in-plane height H_{ip} is a distance measure of the triangle from one vertex to its base; while the separation distance, *s* is the center to center separation distance of the nanotriangles. For the DT patterns, there are two $H_{ip}s$: $H_{ip}(\theta_1)$ corresponding to Source 1 and $H_{ip}(\theta_2)$ due to Source 2. **Table 5.3.1** summarizes the values of $H_{ip}s$ and *s* for the DT nanopatterns both predicted by NS and revealed from SEM images. Overall, the values in the table show that as the substrate position changes from A1 to A2, the size of the corresponding nanopatterns become smaller, and the separation distance between two triangles increases. Also, the trend predicted by the NC and measured from experiment is consistent with each other.

5.4 Optical Properties

The optical extinction spectra of the DT nanopatterns are shown in **Figure 5.4.1**, and reveal multiple resonances within the wavelength range of 350 nm to 1200 nm. For Sample A1, the spectrum shows a strong, dipole resonance peak at $\lambda_0 = 676$ nm. Similar resonance peaks were

observed in the study reported by Zhao *et al*, where DT nanotriangles were fabricated from 500 nm –diameter nanospheres and $\theta_1 = \theta_2 = 10.5^{\circ}[108]$ The spectrum of their DT nanopattern has a strong resonance peak around 750 nm. For Sample A2, the maximum resonance peak blue-shifts to $\lambda_0 = 656$ nm. The spectrum for Sample A3 consists of a single resonance peak at $\lambda_0 = 578$ nm. Overall, it is observed that the dipole resonance peak blue-shifts with increasing separation distance, which is also consistent with similar work reported by Zhao *et al.*[108]. Therefore, if one considers only the nanotriangle separation distance, the LSPR peak can be tuned by changing the nanotriangles' separation distance. However, other factors such as the size and thickness of each individual triangle can have an effect. However, additional work is needed to determine the influence of these parameters.

To better understand the multiple resonance behavior of the DT patterns, FDTD simulations of the DT nanopattern were performed. Because the substrates are stationary during the deposition, the relative orientation of the monolayer will change shape of the two nanotriangles, and thus influence the optical response of the nanopattern. This effect was taken into consideration in the simulation. **Figure 5.4.2** shows the simulated *x*-and *y*-polarized extinction spectra of Sample A1 at orientations $\varphi = 0^{\circ}$, 10° , 15° , and 20° , respectively. The insets in **Figure 5.4.2** are the nanopatterns predicted by numerical calculation. As the orientation of the nanostructures changes, the corresponding optical response also varies for each polarization direction. For the *y*-polarized extinction, the spectra at $\varphi = 0^{\circ}$ shows two strong peaks at $\lambda = 856$ nm and $\lambda = 1003$ nm; when φ changes from $\varphi = 10^{\circ}$ to $\varphi = 15^{\circ}$, these two peaks shift from $\lambda =$

861 nm and $\lambda = 981$ nm to $\lambda = 899$ nm and $\lambda = 950$ nm. When $\varphi = 20^{\circ}$, these two peaks merge into one strong resonant peak at $\lambda = 907$ nm. Similarly, for the *x*-polarized extinction, the spectra at $\varphi = 0^{\circ}$ shows two relative strong peaks at $\lambda = 1025$ nm and $\lambda = 870$ nm. When φ changes



Figure 5.4.1 The experimental extinction spectra for samples A1, A2, and A3.

to $\varphi = 10^{\circ}$, the stronger resonance peak redshifts, and the separation between these two peaks becomes larger ($\lambda = 1125$ nm and $\lambda = 912$ nm). When $\varphi = 15^{\circ}$, the larger resonance peak further redshifts (beyond the spectral range in our calculation), while the small resonance peak shifts to λ =830 nm. When $\varphi = 20^{\circ}$, the small resonance peak splits into two peaks, one at $\lambda = 841$ nm, and the other at $\lambda = 694$ nm. Clearly, these multiple resonance peaks should be the origins for the peaks observed in experiments (**Fig. 5.4.1**). In order to quantitatively compare the experimental results and FDTD spectra, we need more information regarding the orientation distribution and polarization state of the measurement system. Nevertheless, we demonstrate that using a twosource deposition system, one can finely tune DT nanopatterns, therefore to tune the LSPR property. Thus, by further changing the nanosphere size and deposition material, it is expected that the optical properties could be adjusted over a larger wavelength range to fit into specific applications.



Figure 5.4.2 The simulated extinction spectra for Samples A1, A2, and A3.

5.5 Conclusions

In this chapter, a single-step co-deposition SNSL strategy is used to fabricate Ag DT nanopatterns at with different size and separation distance, which can be used to tune the optical properties of the nanopattern. There patterns show multiple LSPR resonances which are due to the complicated DT configurations and orientation of the monolayer domains. In fact, our FDTD simulations demonstrate that DT nanopatterns fabricated at different domain orientations show different multiple resonance peaks which support the experimental results. Because this fabrication method is location dependent, it is best suited for high throughput combinatory studies of DT nanopatterns or similar structures where a large amount of samples can be deposited in one deposition and optical properties can be simultaneously measured.

CHAPTER 6

ALLOY SHADOW NANOSPHERE LITHOGRAPHY

6.1 Introduction

In **Chapter 5**, a co-deposition strategy is introduced. This strategy is a useful strategy to systematically prepare DT nanopatterns with different LSPR wavelengths by varying the locations of substrates. As discussed in **Section 1.2.1**, by varying the composition of the nanopatterns, one could also tune the LSPR wavelengths. Thus, if one of the sources is changing to a different materials, and by varying the relative deposition rates of the two sources, one is expecting to obtain mixed phase or alloy nanopatterns with different composition ratios and LSPR properties. However, due to the line-of-sight property of the deposition feature, if the substrate is stationary, the nanopatterns formed should be DT as demonstrated in **Chapter 4**, i.e., there will be two triangles with different materials. To ensure a uniform mixture of the two materials during the co-deposition, a fast azimuthal rotation can be introduced as demonstrated in **Chapter 3**. Such a rotation can also eliminate the domain effect as well.

In this chapter we introduce a new method to fabricate mixed-phase Ag-Cu nanopatterns and films by combining SNSL with a glancing angle co-deposition technique. The nanopatterns were prepared at different Ag compositions from 100% to 0% by changing the relative deposition rates of Ag and Cu. Characterizations by ellipsometry, energy dispersive X-ray spectroscopy, and X-ray diffraction revealed that the thin films and nanopatterns were composed of small, wellmixed Ag and Cu nano-grains with a diameter less than 20 nm, and their optical properties could be described by an effective medium theory. All the nanopattern had the same shape, but showed tunable LSPR properties. In general, the LSPR wavelengths redshifted with decreasing Ag composition. Such a relation could be fitted by an empirical model based on the bulk theory of alloy plasmonics.

6.2 Experimental Methods

Colloid Monolayers

500 nm- and 750-diameter PS nanospheres were obtained to form the colloid monolayers. The monolayer preparation method for 500 and 750 nm PS beads is given in Appendix 1.

Deposition Strategy

The Ag-Cu nanopatterns and thin films were fabricated using the dual source electron deposition system discussed in **Section 2.3.3**. Based upon the substrates position, the incident angle relative to the Ag and Cu crucibles were, $\theta = 10^{\circ}$ and -10° , respectively. **Figure 6.2.1** illustrates the deposition configuration relative to the substrate. After loading the samples, the deposition chamber was pumped down to a base pressure of $< 1 \times 10^{-6}$ Torr. The rate and total thickness of each deposition source were monitored by two quartz crystal microbalances (QCMs) independently, such that the total deposition rates of Ag and Cu were varied to achieve the atomic composition of Ag, $C_{Ag} = 0, 20, 40, 60, 80, and 100\%$. The individual deposition rate and thickness of Ag and Cu were determined according to their atomic mass % based upon to the following equation,

$$\frac{R_{Ag}}{R_{Cu}} = \frac{D_{Ag}}{D_{Cu}} = \frac{C_{Ag}}{(1 - C_{Ag})} \times \frac{(\rho_{cu} M_{Ag})}{(\rho_{Ag} M_{Cu})},$$
(6.1)

where R_{Ag} and R_{Cu} are the deposition rates (Å/sec) of Ag and Cu, respectively. D_{Ag} and D_{Cu} are the



Figure 6.2.1 Schematic diagram of SNSL and co-deposition with azimuthal substrate rotation.

thickness of Ag and Cu deposited throughout the deposition. ρ_{ag} and ρ_{cu} are the bulk densities and M_{Ag} and M_{Cu} are the molar mass of the corresponding materials. Based on this equation, the table below gives the deposition rates and thicknesses for each corresponding C_{Ag}^{Cal} . Table 6.2.1 summarizes the deposition rates for each concentration used in this study.

During the deposition, the chamber pressure was kept below 1×10^{-6} Torr, and the samples were rotated azimuthally at a speed of 10 rpm. After the co-deposition, the substrates were allowed to cool in the vacuum. Similar to the nanopatterns prepared in **Chapter 4**, once removed from the chamber, the colloid template was detached from the substrate using Scotch tape. Then, the substrates were rinsed in toluene, acetone, and 2-propanol successively to remove PS residual.

$C_{ m Ag}$	$D_{Ag}(nm)$	D _{Cu} (nm)	R_{Ag} (Å/s)	R _{Cu} (Å/s)	# of rotations
100	25 *	25*	0.7*	0.7*	59.5
80	42.6	7.4	1.2	0.2	61.3
60	34.2	15.75	0.9	0.4	65.7
40	25.5	25.4	0.7	0.7	60.5
20	13.2	36.7	0.4	1	61.2
0	25**	25**	0.7**	0.7**	59.5

 Table 6.2.1 Deposition conditions for alloy nanopatterns.

Morphological and Optical Characterizations

SEM images and energy dispersive X-ray measurements (EDS) of the nanopattered and thin films on silicon substrates were taken by SEM equipment. SEM images were analyzed by Image J software (NIH). The topographies of the nanopatterns on silicon substrates were measured by AFM.

Optical measurements were taken using the equipment specified in Section 2.4.2. The optical transmission spectra of the Ag-Cu nanopatterns were measured by a UV-Vis spectrophotometer. Reflection measurements of the nanopatterns were taken at incident angle of 0° by a custom-built set-up reported in ref. [142] Both optical transmission and reflection measurements were measured on glass substrates. To reduce the effect of oxidation, all UV-Vis measurements were taken immediately after deposition. The crystal structures of the thin films on glass substrates were characterized by a X-ray diffractometer (XRD) with a fixed incident angle of 0.5°. The XRD scans of the thin films were recorded with a Cu Ka1 radiation ($\lambda = 1.541$ Å) in the 2 α range from 20° - 80° with a step size of 0.010°. Spectral ellipsometry (SE) measurements of nanopattern on glass substrates were taken by a spectroscopic ellipsometer (M-2000, J.A Woollam Co., Inc.) at an angle of 65°, 70°, 75°, and 80°, respectively, over a wavelength rage of 370 - 1000 nm.

6.3 Composition and Morphology

6.3.1 Thin film composition

Due to the small size of the co-deposited nanopatterns, Ag-Cu thin films with different C_{Ag} were used to analyze the composition and crystal properties. These films were deposited simultaneously with the nanopatterns for each C_{Ag} . The composition of the thin films was verified by both EDS and SE. From EDS results, we ignored other composition data from the substrate and background, and assumed that the Ag and Cu compositions $C_{Ag} + C_{Cu} = 1$. For SE, the composition was estimated using a three layer model: a base layer of the Si wafer, a 1.3 nm-thick native oxide layer, and a composite Ag-Cu layer with optical property given by an effective medium approximation (EMA). The Bruggerman's formula for the EMA layer was used to estimate C_{Ag} . **Figure 6.3.1** shows the predicted C_{Ag}^{Cal} calculated from deposition rates *versus* the C_{Ag}^{Meas} measured/extracted by EDS and SE. The solid line was a guide to the eye where C_{Ag}^{Meas} equaled to C_{Ag}^{Cal} . For EDS C_{Ag}^{Meas} in **Figure 6.3.1** (a), and showed good agreement with C_{Ag}^{Cal} . For EDS C_{Ag}^{Meas} in **Figure 6.3.1** (a) we observed that these measured values were lower than those C_{Ag}^{Cal} predicted via deposition rates. As the C_{Ag} decreased, the incongruity



Figure 6.3.1 (a) The Ag composition ratio, C_{Ag}^{Meas} , measured by EDS and SE versus C_{Ag}^{Cal} calculated from the deposition rates. (b) XRD patterns of all thin film samples. with different C_{Ag}^{Cal} .

of the predicted and measured values increased until $C_{Ag}^{Cal} = 40\%$. This C_{Ag} inconsistency could be attributed to the difference in the sticking coefficients of Ag and Cu during the deposition. Because Ag has a lower melting point than Cu ($T_{Ag} = 962$ °C and $T_{Cu} = 1085$ °C, respectfully), it is expected that Ag would have a smaller sticking coefficient than Cu. And, even if the deposition fluxes were the same, less Ag would be deposited due to its lower sticking coefficient. This effect has been well studied in literature, and is a common problem in Ag based depositions. [197-199] Due to the consistency between predicted, ES, and EDS measurements, all C_{Ag} will now be referred to as C_{Ag}^{Cal} .

Because Cu and Ag are immiscible, the resulting mixed phase films were expected to have both Ag and Cu polycrystals or nanocrystals. [200] This assumption was confirmed by XRD. **Figure 6.3.1 (b)** shows the measured XRD patterns of the thin films. In general, the trend from **Figure 6.3.1(b)** indicated that as C_{Ag}^{Cal} decreased, the XRD peak intensities of Ag decreased, while the Cu peak intensities increased. For the pure Ag sample, four distinct peaks were present at 2α = 38, 44, 64, and 78°, respectively, which correspond to the (111), (200), (220), and (311) planes of cubic Ag (JCPDS Ref. No. 01-071-3762). With the introduction of Cu in C_{Ag}^{Cal} = 80% sample,



Figure 6.3.2 The Ag (111) crystal size for thin films plotted as a function of C_{Ag}^{Cal} .

the (200) peak of Ag vanished, and the (111), (220), and (311) peaks decreased significantly. As the C_{Ag}^{Cal} decreased further, all the remaining Ag peaks decreased as well. At $C_{Ag}^{Cal} = 60\%$, a broad peak from $2\alpha = 42 - 45^{\circ}$ appeared. This peak was consistent with both the (200) Ag plane and the (111) Cu plane of cubic Cu (JCPDS Ref. No. 01-071-4609). As the C_{Ag}^{Cal} decreased to $C_{Ag}^{Cal} = 40\%$, this broad peak shifted to the Cu (111) position ($2\alpha = 43.4^{\circ}$) and became sharper. At $C_{Ag}^{Cal} = 20\%$, only the (111) peak of Ag remained while the (200) peak of Cu, at $2\alpha = 50^{\circ}$, became distinguishable. The pure Cu spectra showed three peaks at $2\alpha = 43$, 50, and 74° , which corresponded to the (111), (200), and (220) planes of a cubic Cu. Within the limit of the XRD, no oxidation states of Cu or Ag were observed. This result was consistent with other studies of electron-beam deposited Ag [199] and Cu [142] thin films, and co-sputtered Ag-Cu thin films. [43] With the exception of the $C_{Ag}^{Cal} = 80\%$, very little peak shifting is present within the XRD patterns. From this result, composite films clearly did not follow Vegard's Law of a solid solution, which states that there is a linear dependence of the *d*-spacing vs. the atomic concentration. This law implies that the lattice parameter of a solid solution can be approximated by the mixtures of the two constituents' lattice parameters. Instead, our measurements showed two distinct cubic patterns. [201,202] Therefore, we confirmed that the deposited structure was not alloying, but was phase separated.

To better understand the crystallinity of the co-deposited samples, the crystal sizes, τ , of the (111) peaks of Cu and Ag were approximated using Scherrer's equation,

$$\tau = \frac{\kappa \lambda}{\Delta \cos \alpha},\tag{6.2}$$

where *K* is a shape factor, λ is the X-ray wavelength (1.541 Å), Δ is the full-width at half-maximum (FWHM) of the Ag/Cu (111) peak and α is the Bragg angle of each peak. Figure 6.3.2 show the crystal grain size of the Ag (111) peak as a function of C_{Ag}^{Cal} . The mixed phase nanopatterns

possessed crystal grain sizes less than 25 nm. The trend in **Figure 6.3.2** showed that as C_{Ag}^{Cal} decreases, so does the Ag crystal grain size. This occurrence may be caused by the increased interfacial stress between Cu and Ag as C_{Ag}^{Cal} decreases. [200,203]

6.3.2 Ag-Cu nanopattern morphology

Figure 6.3.3 (a-f) shows representative SEM micrographs of the Ag-Cu nanopatterns of different C_{Ag}^{Cal} . All the nanopatterns have a broad, quasi-triangular shape. This shape was also predicted by numerical simulations as shown in Figure 6.3.3. Clearly, all the nanopatterns possessed similar shape, which made the comparison of optical property easy. However, for nanopatterns at $C_{Ag}^{Cal} = 100\%$ and 0% smaller nanoparticles near apex were observed. This effect is related to the adatom diffusion properties of pure Ag and Cu and their low sticking coefficients, as discussed in the previous section. The shape of the Ag-Cu nanopatterns were measured and



Figure 6.3.3 The representative SEM images of Ag-Cu mixed phase nanopatterns at $C_{Ag}^{Cal} =$ (a) 0%, (b) 20%, (c) 40%, (d) 60%, (e) 80%, and (f) 100%.

C _{Ag %}	Average In-Plane	Average Hexagonal	Average	Average Height
	Height (h _p) (nm)	Diameter (d _h) (nm)	Maximum	h_{op} (nm)
			Height h _{ov} (nm)	
100	190 ± 10	410 ± 20	26 ± 6	13 ± 2
80	180 ± 10	410 ± 10	25 ± 3	14 ± 2
60	180 ± 10	400 ± 20	23 ± 3	12 ± 1
40	170 ± 10	410 ± 20	24 ± 3	14 ± 3
20	180 ± 10	410 ± 10	25 ± 3	12 ± 2
0	190 ± 10	410 ± 10	34 ± 5	13 ± 3

Table 6.3.1 The measured dimensions of triangular nanopatterns.

quantitatively compared. The in-plane height h_p and hexagonal diameter d_h shown in **Table 6.3.1** The table shows approximately that for all the samples, $h_p = 180 \pm 10$ nm and $d_h = 410 \pm 10$ nm.

Thus all the nanopatterns were consistent in size and shape. However, one may ask that since there was shadowing effect during pattern growth, as compared to the thin film, would the structures really poses the same properties. In particular, one can observe variations of the topography of the nanopatterns via SEM images in **Figure 6.3.1.** To address this question and ensure the patterns are a homogeneous mixture of Ag and Au, EDS mapping of the nanopatterns was used to determine their homogeneity. However, as the dimensions of the nanopatterns were too small, we could not obtain conclusive information. Instead a larger pattern was generated from the 20 µm colloid monolayer at $C_{Ag}^{Cal} = 40\%$ with a total QCM thickness of 500 nm (250 nm for each metal source). **Figure 6.3.4 (a)** shows a representative SEM image. This pattern was very similar to the $C_{Ag}^{Cal} = 40\%$ nanopattern shown in **Figure 6.3.1 (c)**. EDS mapping of the 20 µm templated nanopatterns, shown in **Figure 6.3.4 (b-e**), revealed that both the Ag and Cu across the entire triangular pattern, even in these high contrast regions, were well mixed. This result suggests that the brighter regions were topologically thicker local areas due to self-shadowing effect during the growth.



Figure 6.3.4. (a) SEM micrograph of original unit cell. A composition mapping of (b) Cu, (c) Ag, and (d) Si. (e) The combined element mapping of Cu and Ag.



Figure 6.3.5. The representative height profile of Ag-Cu nanopatterns for $C_{Ag}^{Cal} = (a)$ 40% and (b) 0%. AFM images of $C_{Ag}^{Cal} = 40\%$ Ag nanopatterns: (c) top view and (d) tilted view.

To estimate the thickness distribution of the nanopatterns, the topography of each nanopattern was characterized by AFM, and is summarized in **Table 6.4.1**. The measurements revealed that the nanopatterns possessed a non-uniform height distribution. The height profile of the Ag-Cu nanopatterns showed that the thickest areas of the pattern were localized to the center of the nanopatterns in **Figure 6.3.5 (a-b)** In addition, the three-dimensional AFM images of the $C_{Ag}^{Cal} = 40\%$ shown in **Figure 6.3.5 (c-d)** illustrated the height distribution of the triangular ridges near the center of the nanopattern. As inferred from SEM images, those ridges correspond to higher surface topological features. In fact, comparing all the AFM images from different samples, the nanopattern have similar topology. **Table 6.3.1** summarizes the measured height values for each nanopattern. Clearly, the average height measured across the center of the nanopattern was approximately 13 nm and the average maximum height was approximately 25 nm for all the samples.

6.4 Optical Properties

Because the shape of all the mixed Ag-Cu nanopatterns were consistent, it is expected that the change in their optical or LSPR properties shall be due only to the composition changes, no



Figure 6.4.1. (a) The transmission spectra of mixed phase Ag-Cu nanopatterns obtained from 500 nm-diameter nanosphere monolayers versus C_{Ag}^{Cal} . (b) The LSPR wavelengths λ_1, λ_2 , and λ_3 versus C_{Ag}^{Cal} . (c) The plot of FWHMs of different LSPR peaks versus C_{Ag}^{Cal} .



Figure 6.4.2. Optical properties of mixed phase nanopatterns. (a) The reflection spectra and (b) extinction spectra calculated from transmission and reflection.

the shape and size effect. **Figure 6.4.1** (a) shows the transmission spectra of the Ag-Cu nanopatterns obtained using a monolayer of 500 nm-diameter PS spheres as the template. Throughout this study the LSPR property was typically characterized by the extinction spectra,

E = 1 - R - T, where *R* is the reflection and *T* is the transmission. In previous chapters, *R* was negligible. However, from reflection measurements, we found that the effect of reflection cannot be ignored due to the limited wavelength range (450-1100nm) of our reflection measurements, extinction could not be evaluated for $\lambda > 1100$ nm. Based on both the transmission **Figure 6.4.2** (a) and extinction spectra **Figure 6.4.2** (b) we estimated the longest resonance wavelengths and summarized them in **Table 6.4.1** for different C_{Ag}^{Cal} . We found that the resonance wavelengths derived from extinction and transmission spectra showed little deviation. Therefore, for the sake of better comparison and discussion, we used the transmission spectra to identify the resonance wavelengths. As shown in **Figure 6.4.1** (a) most of the transmission spectra contained two or more resonances peaks within the 350 - 1500 nm wavelength range, and the corresponding resonance wavelengths as a function of C_{Ag}^{Cal} are plotted in **Figure 6.4.1** (b). These resonances were consistent with triangular nanopattern resonances reported in literature. [185,186] They

C _{Ag %}	Transmission	Extinction peak
	peak	(nm)
	(nm)	
100	717	717
80	914	912
60	1029	1024
40	1004	1005
20	1049	1045
0	967	989

Table 6.4.1 (a) Dipole resonance peaks for optical transmission and (b) extinctionresonance peaks.

correspond to a strong dipole resonance, the weaker in-plane and out-of-plane quadrupole resonances for triangular nanopatterns. These resonance wavelengths vary for Cu and Ag. Huang et al. prepared Ag nanotriangles templated from 450 nm PS nanospheres with $h_p = 99$ nm. [204] They reported with a strong in-plane dipole resonance peak at a wavelength of $\lambda_1 \sim 730$ nm and an in-plane quadrupole resonance, $\lambda_2 \sim 420$ nm. No other resonances were observed. However, according to discrete dipole approximation, these Ag nanotriangles should also have an out-ofplane resonance below 350 nm. [185] In our experiment for $C_{Ag}^{Cal} = 100\%$, we observe similar results as Ref. 48: an in-plane dipole resonance at $\lambda_1 = 717$ nm and a quadrupole resonance at λ_2 = 510 nm, respectively. No other peaks were observed within the measured wavelength range. Similarly, optical resonances of Cu nanotriangle patterns have also been reported in literature. Chan et al. fabricated oxide-removed Cu triangular nanopatterns using from 500 nm nanosphere monolayer template. They observed a strong dipole resonance wavelength at $\lambda_1 = 789$ nm and a broad quadrupole resonance around $\lambda_2 = 500$ nm. [31] For our measurements at $C_{Ag}^{Cal} = 0\%$ we observed a strong dipole resonance at $\lambda_1 = 967$ nm, a shoulder peak at $\lambda_2 = 690$ nm, and broad quadrupole resonance at $\lambda_3 = 440$ nm. Compared to the λ_1 values reported by Chan *et al.*, our measured values were redshifted. This difference may be resulted from a thin oxide layer on our Cu nanopatterns: Chan *et al.* demonstrated that λ_1 of the triangular nanopattern can be blue shifted



Figure 6.4.3. (a) The transmission spectra of mixed Ag-Cu phase nanopatterns obtained from 750 nm-diameter nanosphere monolayers versus C_{Ag}^{Cal} . (b) The LSPR wavelengths λ_1, λ_2 , and λ_3 versus C_{Ag}^{Cal} . (c) The plot of FWHMs of different LSPR peaks versus C_{Ag}^{Cal} .

by more than 100 nm when removing the oxide layer. [31] Another possibility for this difference may be due to the size of the nanopattern. Because we rotated the substrates during the deposition, the size of the nanopatterns will be larger than that of the patterns fabricated with stationary substrates reported by Chan *et al.* Overall, the $C_{Aq}^{Cal} = 100\%$ and 0% samples showed characteristic resonances for nanotriangle patterns compared to literature. However, when C_{Ag}^{Cal} changes, the three resonant wavelengths changed accordingly. When C_{Ag}^{Cal} decreased from 80% to 20%, the resonance wavelength λ_1 increased from 914 nm to 1029 nm, the decreased 1004 nm, and increased to 1049 nm, and a shoulder resonance peak, λ_2 , was observed for all C_{Ag}^{Cal} samples except for $C_{Ag}^{Cal} = 80\%$. When $C_{Ag}^{Cal} = 60\%$, $\lambda_2 = 716$ nm, then it blue-shifted to 712 nm, 710 nm, and 690 nm, as C_{Ag}^{Cal} decreased from 40% to 0%, respectively. The third resonance peak was also not observed for $C_{Ag}^{Cal} = 80\%$. When $C_{Ag}^{Cal} = 60\%$, $\lambda_3 = 450$ nm, and then it blueshifted to $\lambda_3 = 450$ nm, 447nm, and 440 nm for $C_{Aq}^{Cal} = 40\%$, 20%, and 0%, respectfully. Overall, the addition of Cu redshifted the dipole resonance, while the weaker quadrupole resonance wavelengths (λ_2 and λ_3) fluctuated or blueshifted within a narrow wavelength range. Figure 6.4.1 (c) shows FWHM of the Ag nanopatterns for the three different resonances. The FWHM of λ_1 for $C_{Ag}^{Cal} = 80\%$ to 20% were broader than those for $C_{Ag}^{Cal} = 100\%$ and 0%, while the FWHMs of λ_2 and λ_3 fluctuated in a narrow wavelength range. Generally, the FWHM of LSPR is correlated to fluctuations in nanopattern size, shape, thickness, and separation distance. [5] For instance, as shown by the AFM images and profiles shown in **Figure 6.3.4**, different triangular patterns could have different local thickness or height and shape fluctuations, which could be reasons to induce variations in FWHM.

The transmission spectra of triangular nanopatterns prepared using 750 nm diameter nanospheres Figure 6.4.3 also contained three resonance peaks for all C_{Aq}^{Cal} samples. The plot of these peak positions, λ_1 , λ_2 , and λ_3 , versus C_{Ag}^{Cal} is shown in Figure 6.4.3 (a) and they follow the same trend as those shown in **Figure 6.4.1** (a). As C_{Ag}^{Cal} decreased from 100% to 0%, the resonance peak λ_1 redshifted from 1053 nm to 1213 nm, 1310 nm, 1348 nm, 1373 nm, and then blueshifted to 1237 nm, respectively. The λ_2 peak also redshifted from 647 nm to 722 nm, 773 nm, 779 nm, 819 nm, and then blueshifted to 777 nm for $C_{Ag}^{Cal} = 100\%$ to $C_{Ag}^{Cal} = 0\%$, respectfully. Unlike the other two resonance peaks, λ_3 blueshifted with decreasing C_{Ag}^{Cal} from 448 nm to 430 nm, 410 nm, 394 nm, 382 nm, and 357 nm. Compared to 500 nm templated nanopatterns, λ_1 and λ_3 from the 750 nm template follow the same trend, while λ_2 does not. Therefore, for both the 500 nm and 750nm templated nanopatterns, the λ_1 was most responsive to changes in C_{Ag}^{Cal} , while the λ_2 and λ_3 shifted over a narrow wavelength range. The FWHMs of λ_1 of the mixed phase nanopatterns were broader than those of the pure Ag and Cu nanopatterns, and the FWHMs of λ_2 and λ_3 fluctuated within a narrow wavelength. Clearly LSPR wavelength increases with colloid template size. Thus, both the composition and the nanopattern size can be used to simultaneously to tune the LSPR wavelengths.

Currently, there are few theoretical models that can be used to predict the plasmonic properties of alloy or mixture nanostructures. For bi-layer or core-shell nanoparticles, Mie theory can be used to predict their optical absorption behavior. [205] The other widely used model to predict the optical properties of alloys is a composition-weighted averaging model. [206-208] However, both models cannot give accurate optical prediction for the truly mixed alloy nanomaterials [209]. More recently, Rioux et al. proposed an analytical model for the dielectric properties of alloys based on Drude-Lorentz model. [209] This model was used to build an empirical equation that accurately correlated the composition and plasma frequency within the dielectric function. Although this model was proposed to correlate bulk plasma frequency to the alloy composition, we suggest that the model could also be used to predict the relationship between composition of the alloy nanopatterns and their LSPR wavelengths, given the close relationship of bulk plasma frequency and LSPR wavelength. For example, according to a simplified Mie theory discussed in **Section 1.2.1**, the extinction cross section of a small spherical metal nanoparticle is given by (**Equation (1.29**)). According to Drude model, $\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau^2}{\omega^2 \tau^2 + 1}$ Thus, the resonance frequency ω_r can be expressed as $\omega_r = \frac{1}{\tau} \sqrt{\frac{\omega_p^2 \tau^2}{3} - 1}$. In the visible and near-infrared frequency range, $\frac{\omega_p^2 \tau^2}{3} \gg 1$, (this product is approximately 950 and 20,000 for Cu and Ag, respectively) ref. [210], $\omega_r \propto \omega_p$. Therefore, we can assume that $\omega_r \propto \omega_p$ and use the empirical model derived by

Rioux et al. to fit our experimental data [209],

$$\frac{1}{\lambda_0 \left(C_{Ag}^{Cal}\right)} = C_{Ag}^{Cal^2} \left(\frac{2}{\lambda_0 (100\%)} - \frac{4}{\lambda_0 (40\%)} + \frac{2}{\lambda_0 (0\%)}\right) + C_{Ag}^{Cal} \left(\frac{-1}{\lambda_0 (100\%)} + \frac{4}{\lambda_0 (40\%)} - \frac{3}{\lambda_0 (0\%)}\right) + \frac{1}{\lambda_1 (0\%)}$$
(6.3)



Figure 6.4.4. The plot of $1/\lambda_1$ as a function of C_{Ag}^{Cal} and their fitting curves using the empirical equation for samples fabricated from 500 nm and 750 nm-diameter nanosphere monolayers.

where $\lambda_1 \left(C_{Ag}^{Cal} \right)$ is the dipole resonance wavelength at C_{Ag}^{Cal} and $\lambda_1(100\%)$, $\lambda_1(40\%)$, and $\lambda_1(0\%)$ are the dipole resonance wavelengths for $C_{Ag}^{Cal} = 100\%$, 40%, and 0%, respectfully. Figure 6.4.4 shows the fittings of the LSPR wavenumber as a function of C_{Ag}^{Cal} by Equation (6.3) for nanopatterns obtained from both 500 nm template and 750 nm template. These no-parameter fittings shows that the experimental data agree very well with the prediction by Equation (6.3). Therefore Equation (6.3) can also be used to predict LSPR resonance of the mixed Cu and Ag nanopatterns.

6.5 Conclusions

In **Chapter 5**, a co-deposition strategy is introduced. This strategy is a useful strategy to systematically prepare DT nanopatterns with different LSPR wavelengths by varying the locations of substrates. As discussed in **Section 1.2.1**, by varying the composition of the nanopatterns, one could also tune the LSPR wavelengths. Thus, if one of the sources is changing to a different materials, and by varying the relative deposition rates of the two sources, one is expecting to obtain

mixed phase or alloy nanopatterns with different composition ratios and LSPR properties. However, due to the line-of-sight property of the deposition feature, if the substrate is stationary, the nanopatterns formed should be DT as demonstrated in **Chapter 4**, i.e., there will be two triangles with different materials. To ensure a uniform mixture of the two materials during the codeposition, a fast azimuthal rotation can be introduced as demonstrated in **Chapter 3**. Such a rotation can also eliminate the domain effect as well.

In this chapter we introduce a new method to fabricate mixed-phase Ag-Cu nanopatterns and films by combining SNSL with a glancing angle co-deposition technique. The nanopatterns were prepared at different Ag compositions from 100% to 0% by changing the relative deposition rates of Ag and Cu. Characterizations by ellipsometry, energy dispersive X-ray spectroscopy, and X-ray diffraction revealed that the thin films and nanopatterns were composed of small, wellmixed Ag and Cu nano-grains with a diameter less than 20 nm, and their optical properties could be described by an effective medium theory. All the nanopattern had the same shape, but showed tunable LSPR properties. In general, the LSPR wavelengths redshifted with decreasing Ag composition. Such a relation could be fitted by an empirical model based on the bulk theory of alloy plasmonics.
CHAPTER 7

CONCLUSIONS AND FUTURE OUTLOOK

In this dissertation, we have demonstrated that SNSL is a promising technique for preparing tunable plasmonic nanomaterials. Four different strategies have been introduced, which can systematically shift the LSPR wavelength of a specific nanopattern by changing its size, shape, separation distance, or composition. In Chapter 3, Ag FONs patterns were fabricated using a SNSL method where the vapor incident angle θ was changed systematically. This method changed the shape and size of the Ag coating on the PS nanospheres as predicted by numerical calculations. The morphology change caused the LSPR wavelength of each Ag FON to redshift with increasing θ . By controlling the LSPR wavelength of Ag FONs, these structures were optimized for SERS applications. Additionally, the SERS signal induced by the PS nanospheres could be used as an internal reference for quantitative SERS measurements. During this study, it was also observed that the quality of the monolayer can broaden the LSPR peak with increasing θ due to many differently oriented domains. Thus, to eliminate such an effect, in Chapter 4, Ag triangular networks were introduced. By continuously rotating the substrate azimuthally during the deposition and systematically changing θ , the resulting Ag nanopatterns fabricated on the substrates were independent of monolayer domain orientation. The variations in the size and shape of the nanopatterns, predicted by both numerical and Monte Carlo simulations, also induced shifts in the LSPR wavelength, which was used to optimize SERS response. To further increase the

variety of nanopatterns using SNSL method, a third fabrication strategy was introduced by combing SNSL with co-deposition. In **Chapter 5**, various Ag DT nanopatterns were fabricated. By changing the substrate locations, the size and the separation distance of the DTs could be tuned, so that the optical properties were varied. Finally, in **Chapter 6**, we expand upon the co-deposition method from **Chapter 5** to fabricate Cu-Ag alloy nanopatterns. The LSPR of the alloy nanopatterns were tuned by changing the relative composition of Cu (or Ag) and the size of the nanospheres. Such alloy plasmonic nanopatterns provide another means to create tunable plasmonic nanopatterns.

All the nanopatterns presented in this work demonstrate that NSL is a very powerful nanofabrication technique that can produce a variety of predictable plasmonic nanopatterns. We also demonstrate that these structures can be used to improve SERS performance. However, despite its numerous advantages, there are still several challenges associated with this technique.

The first challenge is the current monolayer self-assembly method. We use an air/water interface method to fabricate the colloid monolayer. While this method is potentially scalable, it takes a long assembly time (> 7 hours). To shorten the production time and improve the quality of the monolayer, we devised a semi-automatic procedure as describe in **Section 2.3.1**. However, to make this method more convenient, it must be fully automatic.

Another challenge arises from the quality of the colloid monolayer mask. As shown in **Chapters 3** and **5**, a large variation of the domain orientation causes a large variations of the nanopattern shape, thus induces a broader LSPR peak, which is not desirable for the applications. Thus, additional strategies are needed to either isolate single domains from the substrates or to improve the air-water interface method to consistently produce large area single domain monolayers.

The third challenge is the fixed lattice spacing of the monolayer. The size of the nanosphere determines the shadowing effect during the SNSL process. Therefore, with a fixed nanosphere, the lattice constant of the monolayer is fixed, so is the pattern. Therefore, if methods of varying the lattice constant can be introduced to SNSL, one will have more flexibility to create plasmonic nanomaterials. Few methods have been mentioned in the literature to achieve such a goal. For example, Yan *et al.* proposed that depositing monolayers onto a polymer substrate, then swelling that polymer at a controlled rate can be used to change the lattice spacing of the colloid monolayers.[211] Alternatively, to modify the PS monolayer by RIE, as discussed briefly in Chapter 2, can change the shape and size of the nanospheres, thus it can be used the alter the lattice. Lastly, not all materials evaporated will generate the same nanopattern. Due to the different diffusion and interfacial properties between low and high melting temperature metals, the resulting nanopattern could be different. For instance, in **Chapter 4**, the shape of triangular network patterns made from Ti were different from that by Ag. To overcome possible variations due to diffusion effects, alloying methods could be used. For instance, Larson *et al.* demonstrated that alloying Ag with a small amount of Ti could be used to stop the diffusion effects of Ag to create helical nanostructures. [212] Similarly, the co-deposition method presented in **Chapter 6** could also be used to create alloy nanopatterns with more consistent patterns.

Despite its many challenges, SNSL is still an inherently scalable and cost-effective nanofabrication technique. While this study highlighted optical sensing applications, SNSL could also be used to generate plasmonic structures for other applications such as solar cells, metamaterials, hydrogen capture and storage, thermal therapy, etc. [213,214]. Overall, the fabrication strategies presented in this dissertation improve some of the practical challenges

associated with SNSL while demonstrating that SNSL is a viable method to fabricate tunable plasmonic nanopatterns.

REFERENCES

- [1] Chang K, Tiny is beautiful: Translating 'Nano' into practical, in: New York Times, The New York Times, 2005.
- [2] Hergert W and Wriedt T, The Mie Theory: basics and applications, Springer, 2012.
- [3] Mie G 1908 Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen Annalen der physik **330** 377-445
- [4] Petryayeva E and Krull U J 2011 Localized surface plasmon resonance: nanostructures, bioassays and biosensing--a review *Anal. Chim. Acta.* **706** 8-24
- [5] Willets K A and Van Duyne R P 2007 Localized surface plasmon resonance spectroscopy and sensing Annu. Rev. Phys. Chem. 58 267-297
- [6] Haes A J and Van Duyne R P 2004 A unified view of propagating and localized surface plasmon resonance biosensors *Anal Bioanal Chem* 379 920-930
- [7] Fleischmann M, Hendra P J and Mcquilla.Aj 1974 Raman-Spectra of Pyridine Adsorbed at a Silver Electrode *Chemical Physics Letters* **26** 163-166
- [8] Jeanmaire D L and Vanduyne R P 1977 Surface Raman Spectroelectrochemistry .1. Heterocyclic, Aromatic, and Aliphatic-Amines Adsorbed on Anodized Silver Electrode *Journal of Electroanalytical Chemistry* 84 1-20
- [9] Schlucker S 2014 Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications *Angew. Chem. Int. Edit.* **53** 4756-4795
- [10] Tsai Y-L, Chen T-G, Tsai M-A, Hsu C-W, Tseng P-C, Wang H-W, Han H-W, Jin L-H, Yu P and Shieh J-M, Patterned glass substrates for enhanced solar energy harvesting in thin film solar cells, in: Photovoltaic Specialists Conference (PVSC), IEEE, 2011, pp. 945-947.
- [11] Lu L, Luo Z, Xu T and Yu L 2012 Cooperative plasmonic effect of Ag and Au nanoparticles on enhancing performance of polymer solar cells *Nano letters* 13 59-64
- [12] Pillai S, Catchpole K, Trupke T and Green M 2007 Surface plasmon enhanced silicon solar cells *Journal of applied physics* 101 1-8

- [13] Turpin J P, Bossard J A, Morgan K L, Werner D H and Werner P L 2014 Reconfigurable and tunable metamaterials: a review of the theory and applications *Int. J. Antennas Propag.* 2014 1-19
- [14] Garcia-Vidal F, Martin-Moreno L and Pendry J 2005 Surfaces with holes in them: new plasmonic metamaterials *Journal of optics A: Pure and applied optics* **7** S97-S101
- [15] Viarbitskaya S, Cuche A I, Teulle A, Sharma J, Girard C, Arbouet A and Dujardin E 2015 Plasmonic hot printing in gold nanoprisms *ACS Photonics* **2** 744-751
- [16] Winkler P, Belitsch M, Tischler A, Häfele V, Ditlbacher H, Krenn J, Hohenau A, Nguyen M, Félidj N and Mangeney C 2015 Nanoplasmonic heating and sensing to reveal the dynamics of thermoresponsive polymer brushes *Applied Physics Letters* 107 141906-141901 141906-141904
- [17] Bozhevolnyi S I, Plasmonic nano-guides and circuits, in: Plasmonics and Metamaterials, Optical Society of America, 2008, pp. MWD3.
- [18] Schuller J A, Barnard E S, Cai W, Jun Y C, White J S and Brongersma M L 2010 Plasmonics for extreme light concentration and manipulation *Nature materials* 9 193-204
- [19] Zia R, Schuller J A, Chandran A and Brongersma M L 2006 Plasmonics: the next chip-scale technology *Materials today* 9 20-27
- [20] McFarland A D, Young M A, Dieringer J A and Van Duyne R P 2005 Wavelength-scanned surface-enhanced Raman excitation spectroscopy *J. Phys. Chem. B* **109** 11279-11285
- [21] Halperin W 1986 Quantum size effects in metal particles *Reviews of Modern Physics* 58 533-606
- [22] Blaber M G, Arnold M D and Ford M J 2010 A review of the optical properties of alloys and intermetallics for plasmonics *Journal of Physics: Condensed Matter* **22** 1-15
- [23] Ordal M A, Bell R J, Alexander R W, Long L L and Querry M R 1985 Optical properties of fourteen metals in the infrared and far infrared: Al, Co, Cu, Au, Fe, Pb, Mo, Ni, Pd, Pt, Ag, Ti, V, and W Applied optics 24 4493-4499
- [24] Zeman E J and Schatz G C 1987 An accurate electromagnetic theory study of surface enhancement factors for silver, gold, copper, lithium, sodium, aluminum, gallium, indium, zinc, and cadmium *Journal of Physical Chemistry* **91** 634-643
- [25] Pitarke J, Silkin V, Chulkov E and Echenique P 2006 Theory of surface plasmons and surface-plasmon polaritons *Reports on progress in physics* **70** 1-87
- [26] Maier S A, Plasmonics: fundamentals and applications, Springer Science & Business Media, 2007.

- [27] Mayer K M and Hafner J H 2011 Localized surface plasmon resonance sensors *Chem. Rev.* 111 3828-3857
- [28] Stockman M I 2011 Nanoplasmonics: past, present, and glimpse into future Optics express 19 22029-22106
- [29] Born M and Wolf E, Principles of optics: electromagnetic theory of propagation, interference and diffraction of light, CUP Archive, 2000.
- [30] Cortie M B and McDonagh A M 2011 Synthesis and optical properties of hybrid and alloy plasmonic nanoparticles *Chem. Rev.* **111** 3713-3735
- [31] Chan G H, Zhao J, Hicks E M, Schatz G C and Van Duyne R P 2007 Plasmonic properties of copper nanoparticles fabricated by nanosphere lithography *Nano Lett.* **7** 1947-1952
- [32] Kravets V, Jalil R, Kim Y-J, Ansell D, Aznakayeva D, Thackray B, Britnell L, Belle B, Withers F and Radko I 2014 Graphene-protected copper and silver plasmonics *Sci. Rep.* **4**
- [33] Susman M D, Feldman Y, Vaskevich A and Rubinstein I 2012 Chemical deposition and stabilization of plasmonic copper nanoparticle films on transparent substrates *Chem. Mater.* 24 2501-2508
- [34] Yamaguchi T, Kazuma E, Sakai N and Tatsuma T 2012 Photoelectrochemical responses from polymer-coated plasmonic copper nanoparticles on TiO 2 *Chem. Lett.* **41** 1340-1342
- [35] Li J, Mayer J and Colgan E 1991 Oxidation and protection in copper and copper alloy thin films *J. Appl. Phys.* **70** 2820-2827
- [36] Tsuji M, Hikino S, Sano Y and Horigome M 2009 Preparation of Cu@ Ag Core-Shell Nanoparticles Using a Two-step Polyol Process under Bubbling of N2 Gas Chem. Lett. 38 518-519
- [37] Andolina C M, Dewar A C, Smith A M, Marbella L E, Hartmann M J and Millstone J E 2013 Photoluminescent gold–copper nanoparticle alloys with composition-tunable near-infrared emission J. Am. Chem. Soc. 135 5266-5269
- [38] Collins G, McCarty E and Holmes J D 2015 Controlling alloy formation and optical properties by galvanic replacement of sub-20 nm silver nanoparticles in organic media *Cryst. Eng. Comm.* **17** 6999-7005
- [39] Evans P, Hendren W, Atkinson R and Pollard R 2008 Optical transmission measurements of silver, silver–gold alloy and silver–gold segmented nanorods in thin film alumina *Nanotechnology* 19 1-8
- [40] Liu S, Chen G, Prasad P N and Swihart M T 2011 Synthesis of monodisperse Au, Ag, and Au–Ag alloy nanoparticles with tunable size and surface plasmon resonance frequency *Chem. Mater.* 23 4098-4101

- [41] Singh M, Sinha I, Singh A and Mandal R 2011 LSPR and SAXS studies of starch stabilized Ag–Cu alloy nanoparticles *Colloid Surface A*. **384** 668-674
- [42] Zhang Q, Lee J Y, Yang J, Boothroyd C and Zhang J 2007 Size and composition tunable Ag–Au alloy nanoparticles by replacement reactions *Nanotechnology* **18** 1-8
- [43] Gong C and Leite M S 2016 Noble Metal Alloys for Plasmonics ACS Photonics 3 507-513
- [44] Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment *The Journal of Physical Chemistry B* 107 668-677
- [45] Bilankohi S M 2015 Optical Scattering and Absorption Characteristics of Silver and Silica/Silver Core/shell Nanoparticles Oriental Journal of Chemistry 31 2259-2263
- [46] Walsh G F, Forestiere C and Dal Negro L 2011 Plasmon-enhanced depolarization of reflected light from arrays of nanoparticle dimers *Optics express* 19 21081-21090
- [47] Ringe E, Langille M R, Sohn K, Zhang J, Huang J, Mirkin C A, Van Duyne R P and Marks L D 2012 Plasmon length: a universal parameter to describe size effects in gold nanoparticles *The journal of physical chemistry letters* **3** 1479-1483
- [48] Ringe E, Zhang J, Langille M R, Sohn K, Cobley C, Au L, Xia Y, Mirkin C A, Huang J and Marks L D, Effect of size, shape, composition, and support film on localized surface plasmon resonance frequency: a single particle approach applied to silver bipyramids and gold and silver nanocubes, in: MRS Proceedings, Cambridge Univ Press, 2009, pp. 1208-01210-1202.
- [49] Gans R v 1915 Form of ultramicroscopic particles of silver Ann. Phys 47 270-284
- [50] Papavassiliou G C 1979 Optical properties of small inorganic and organic metal particles Progress in Solid State Chemistry 12 185-271
- [51] Link S, Mohamed M and El-Sayed M 1999 Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant *The Journal of Physical Chemistry B* 103 3073-3077
- [52] Fuchs R 1975 Theory of the optical properties of ionic crystal cubes *Physical Review B* **11** 1732-1740
- [53] Clarkson J, Winans J and Fauchet P 2011 On the scaling behavior of dipole and quadrupole modes in coupled plasmonic nanoparticle pairs *Optical Materials Express* **1** 970-979
- [54] Chung T, Lee S-Y, Song E Y, Chun H and Lee B 2011 Plasmonic nanostructures for nanoscale bio-sensing *Sensors* **11** 10907-10929
- [55] Jensen T R, Duval M L, Kelly K L, Lazarides A A, Schatz G C and Van Duyne R P 1999 Nanosphere lithography: Effect of the external dielectric medium on the surface plasmon

resonance spectrum of a periodic array of sliver nanoparticles *Journal of Physical Chemistry B* **103** 9846-9853

- [56] Jeong H-H, Mark A G, Alarcón-Correa M, Kim I, Oswald P, Lee T-C and Fischer P 2016 Dispersion and shape engineered plasmonic nanosensors *Nature communications* **7** 1-7
- [57] McFarland A D and Van Duyne R P 2003 Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity *Nano letters* **3** 1057-1062
- [58] Kazuma E and Tatsuma T 2014 Localized surface plasmon resonance sensors based on wavelength-tunable spectral dips *Nanoscale* **6** 2397-2405
- [59] Endo T, Yanagida Y and Hatsuzawa T 2008 Quantitative determination of hydrogen peroxide using polymer coated Ag nanoparticles *Measurement* 41 1045-1053
- [60] Sepúlveda B, Angelomé P C, Lechuga L M and Liz-Marzán L M 2009 LSPR-based nanobiosensors Nano Today 4 244-251
- [61] Lee K-S and El-Sayed M A 2006 Gold and silver nanoparticles in sensing and imaging: sensitivity of plasmon response to size, shape, and metal composition *The Journal of Physical Chemistry B* **110** 19220-19225
- [62] Miller M M and Lazarides A A 2005 Sensitivity of metal nanoparticle surface plasmon resonance to the dielectric environment *The Journal of Physical Chemistry B* 109 21556-21565
- [63] Sekhon J S and Verma S 2015 Controlling the LSPR properties of Au triangular nanoprisms and nanoboxes by geometrical parameter: a numerical investigation *Journal of Modern Optics* 62 435-440
- [64] Le Ru E and Etchegoin P, Principles of Surface-Enhanced Raman Spectroscopy: and related plasmonic effects, Elsevier, 2008.
- [65] Kennedy D C, Hoop K A, Tay L-L and Pezacki J P 2010 Development of nanoparticle probes for multiplex SERS imaging of cell surface proteins *Nanoscale* 2 1413-1416
- [66] Kneipp K, Moskovits M and Kneipp H 2007 Surface-enhanced Raman scattering *Physics Today* **60** 40-46
- [67] Albrecht M G and Creighton J A 1977 Anomalously Intense Raman-Spectra of Pyridine at a Silver Electrode *Journal of the American Chemical Society* **99** 5215-5217
- [68] Moskovits M 1978 Surface-Roughness and Enhanced Intensity of Raman-Scattering by Molecules Adsorbed on Metals *Journal of Chemical Physics* **69** 4159-4161
- [69] Alvarez-Puebla R A and Liz-Marzán L M 2012 SERS detection of small inorganic molecules and ions *Angewandte Chemie International Edition* **51** 11214-11223

- [70] Braun G, Lee S J, Dante M, Nguyen T-Q, Moskovits M and Reich N 2007 Surface-enhanced Raman spectroscopy for DNA detection by nanoparticle assembly onto smooth metal films *Journal of the American Chemical Society* **129** 6378-6379
- [71] Esmaielzadeh Kandjani A, Sabri Y M, Mohammad-Taheri M, Bansal V and Bhargava S K 2014 Detect, remove and reuse: a new paradigm in sensing and removal of Hg (II) from wastewater via SERS-active ZnO/Ag nanoarrays *Environmental science & technology* 49 1578-1584
- [72] Vendrell M, Maiti K K, Dhaliwal K and Chang Y-T 2013 Surface-enhanced Raman scattering in cancer detection and imaging *Trends in biotechnology* **31** 249-257
- [73] Chou A, Jaatinen E, Buividas R, Seniutinas G, Juodkazis S, Izake E L and Fredericks P M 2012 SERS substrate for detection of explosives *Nanoscale* 4 7419-7424
- [74] Stiles P L, Dieringer J A, Shah N C and Van Duyne R P 2008 Surface-enhanced Raman spectroscopy *Annu. Rev. Anal. Chem.* **1** 601-626
- [75] Abell J L, Garren J M, Driskell J D, Tripp R A and Zhao Y 2012 Label-free detection of micro-RNA hybridization using surface-enhanced Raman spectroscopy and least-squares analysis *Journal of the American Chemical Society* 134 12889-12892
- [76] Doering W E and Nie S 2002 Single-molecule and single-nanoparticle SERS: examining the roles of surface active sites and chemical enhancement *The Journal of Physical Chemistry B* 106 311-317
- [77] Le Ru E, Blackie E, Meyer M and Etchegoin P G 2007 Surface enhanced Raman scattering enhancement factors: a comprehensive study *The Journal of Physical Chemistry C* 111 13794-13803
- [78] Biswas A, Bayer I S, Biris A S, Wang T, Dervishi E and Faupel F 2012 Advances in topdown and bottom-up surface nanofabrication: Techniques, applications & future prospects *Advances in colloid and interface science* 170 2-27
- [79] Pimpin A and Srituravanich W 2011 Review on micro-and nanolithography techniques and their applications *Engineering Journal* **16** 37-56
- [80] Vecchi G, Giannini V and Rivas J G 2009 Shaping the fluorescent emission by lattice resonances in plasmonic crystals of nanoantennas *Physical review letters* **102** 146807
- [81] Lee S-W, Lee K-S, Ahn J, Lee J-J, Kim M-G and Shin Y-B 2011 Highly sensitive biosensing using arrays of plasmonic Au nanodisks realized by nanoimprint lithography ACS nano 5 897-904
- [82] Sharma Y D, Jun Y C, Kim J O, Brener I and Krishna S 2014 Polarization-dependent photocurrent enhancement in metamaterial-coupled quantum dots-in-a-well infrared detectors *Optics Communications* **312** 31-34

- [83] Chen Y, Li Z, Xiang Q, Wang Y, Zhang Z and Duan H 2015 Reliable fabrication of plasmonic nanostructures without an adhesion layer using dry lift-off *Nanotechnology* 26 405301
- [84] Tan K S and Cheong K Y 2013 Advances of Ag, Cu, and Ag–Cu alloy nanoparticles synthesized via chemical reduction route *J. Nanopart. Res.* **15** 1-29
- [85] Atwater H A and Polman A 2010 Plasmonics for improved photovoltaic devices *Nature materials* **9** 205-213
- [86] Wang A X and Kong X 2015 Review of recent progress of plasmonic materials and nanostructures for surface-enhanced Raman scattering *Materials* **8** 3024-3052
- [87] Wu Y, Yan H, Huang M, Messer B, Song J H and Yang P 2002 Inorganic semiconductor nanowires: rational growth, assembly, and novel properties *Chemistry–A European Journal* 8 1260-1268
- [88] Chen J, McLellan J M, Siekkinen A, Xiong Y, Li Z-Y and Xia Y 2006 Facile synthesis of gold-silver nanocages with controllable pores on the surface *Journal of the American Chemical Society* 128 14776-14777
- [89] Yang Y, Zhong X L, Zhang Q, Blackstad L G, Fu Z W, Li Z Y and Qin D 2014 The role of etching in the formation of Ag nanoplates with straight, curved and wavy edges and comparison of their SERS properties *Small* 10 1430-1437
- [90] Dhivya P, Prasad A K and Sridharan M 2016 Nanostructured perovskite CdTiO 3 films for methane sensing *Sensors and Actuators B: Chemical* **222** 987-993
- [91] Temple T L and Dligatch S 2015 Role of the spacer layer in plasmonic antireflection coatings comprised of gold or silver nanoparticles *Journal of Photonics for Energy* 5 053095-053095
- [92] Hawkeye M M and Brett M J 2007 Glancing angle deposition: fabrication, properties, and applications of micro-and nanostructured thin films *Journal of Vacuum Science & Technology A* 25 1317-1335
- [93] Zhao Y, Ye D, Wang G-C and Lu T-M, Designing nanostructures by glancing angle deposition, in: Optical Science and Technology, SPIE's 48th Annual Meeting, International Society for Optics and Photonics, 2003, pp. 59-73.
- [94] Taschuk M T, Hawkeye M M and Brett M J 2010 Glancing angle deposition *Handbook of* Deposition Technologies for Films and Coatings 621-678
- [95] Ye D, Karabacak T, Lim B, Wang G and Lu T 2004 Growth of uniformly aligned nanorod arrays by oblique angle deposition with two-phase substrate rotation *Nanotechnology* 15 817-821
- [96] Kesapragada S and Gall D 2006 Two-component nanopillar arrays grown by Glancing Angle Deposition *Thin Solid Films* 494 234-239

- [97] Hulteen J C and Van Duyne R P 1995 Nanosphere lithography: a materials general fabrication process for periodic particle array surfaces *Journal of Vacuum Science & Technology A* 13 1553-1558
- [98] Jensen T R, Malinsky M D, Haynes C L and Van Duyne R P 2000 Nanosphere lithography: Tunable localized surface plasmon resonance spectra of silver nanoparticles J. Phys. Chem. B 104 10549-10556
- [99] Hulteen J C, Treichel D A, Smith M T, Duval M L, Jensen T R and Van Duyne R P 1999 Nanosphere lithography: size-tunable silver nanoparticle and surface cluster arrays *The Journal of Physical Chemistry B* 103 3854-3863
- [100] Jensen T R, Schatz G C and Van Duyne R P 1999 Nanosphere lithography: Surface plasmon resonance spectrum of a periodic array of silver nanoparticles by ultraviolet-visible extinction spectroscopy and electrodynamic modeling *Journal of Physical Chemistry B* 103 2394-2401
- [101] Haynes C L, McFarland A D, Smith M T, Hulteen J C and Van Duyne R P 2002 Angleresolved nanosphere lithography: Manipulation of nanoparticle size, shape, and interparticle spacing *Journal of Physical Chemistry B* 106 1898-1902
- [102] Kosiorek A, Kandulski W, Chudzinski P, Kempa K and Giersig M 2004 Shadow nanosphere lithography: Simulation and experiment *Nano Letters* 4 1359-1363
- [103] Larsen G K, He Y Z, Ingram W and Zhao Y P 2013 Hidden Chirality in Superficially Racemic Patchy Silver Films *Nano Letters* 13 6228-6232
- [104] Pawar A B and Kretzschmar I 2008 Patchy particles by glancing angle deposition *Langmuir* 24 355-358
- [105] Zhang G, Wang D Y and Mohwald H 2005 Patterning microsphere surfaces by templating colloidal crystals *Nano Letters* 5 143-146
- [106] Kosiorek A, Kandulski W, Glaczynska H and Giersig M 2005 Fabrication of nanoscale rings, dots, and rods by combining shadow nanosphere lithography and annealed polystyrene nanosphere masks *Small* **1** 439-444
- [107] Nemiroski A, Gonidec M, Fox J M, Jean-Remy P, Turnage E and Whitesides G M 2014 Engineering Shadows to Fabricate Optical Metasurfaces ACS Nano 8 11061-11070
- [108] Zhao J, Frank B, Burger S and Giessen H 2011 Large-Area High-Quality Plasmonic Oligomers Fabricated by Angle-Controlled Colloidal Nanolithography Acs Nano 5 9009-9016
- [109] Santos A, Deen M J and Marsal L F 2015 Low-cost fabrication technologies for nanostructures: state-of-the-art and potential *Nanotechnology* **26** 1-20

- [110] Colson P, Henrist C and Cloots R 2013 Nanosphere Lithography: A Powerful Method for the Controlled Manufacturing of Nanomaterials J. Nanomater. 2013 1-20
- [111] Vogel N, Weiss C K and Landfester K 2012 From soft to hard: the generation of functional and complex colloidal monolayers for nanolithography *Soft Mater.* **8** 4044-4061
- [112] Zhang J, LBFGS Quasi-Newtonian Methods for Molecular Modeling Prion AGAAAAGA Amyloid Fibrils, in: Molecular Structures and Structural Dynamics of Prion Proteins and Prions, Springer, 2015, pp. 291-307.
- [113] Kralchevsky P A and Nagayama K 1994 Capillary forces between colloidal particles Langmuir 10 23-36
- [114] Kralchevsky P A and Denkov N D 2001 Capillary forces and structuring in layers of colloid particles *Current Opinion in Colloid & Interface Science* **6** 383-401
- [115] Micheletto R, Fukuda H and Ohtsu M 1995 A simple method for the production of a twodimensional, ordered array of small latex particles *Langmuir* 11 3333-3336
- [116] Denkov N, Velev O, Kralchevski P, Ivanov I, Yoshimura H and Nagayama K 1992 Mechanism of formation of two-dimensional crystals from latex particles on substrates *Langmuir* 8 3183-3190
- [117] Dimitrov A S, Dushkin C D, Yoshimura H and Nagayama K 1994 Observations of latex particle two-dimensional-crystal nucleation in wetting films on mercury, glass, and mica *Langmuir* 10 432-440
- [118] Yan Q, Zhou Z and Zhao X 2005 Inward-growing self-assembly of colloidal crystal films on horizontal substrates *Langmuir* 21 3158-3164
- [119] Yin Y, Lu Y, Gates B and Xia Y 2001 Template-assisted self-assembly: a practical route to complex aggregates of monodispersed colloids with well-defined sizes, shapes, and structures J. Am. Chem. Soc. 123 8718-8729
- [120] Kim M H, Im S H and Park O O 2005 Rapid Fabrication of Two-and Three-Dimensional Colloidal Crystal Films via Confined Convective Assembly Advanced functional materials 15 1329-1335
- [121] Malaquin L, Kraus T, Schmid H, Delamarche E and Wolf H 2007 Controlled particle placement through convective and capillary assembly *Langmuir* **23** 11513-11521
- [122] Ye J, Zentel R, Arpiainen S, Ahopelto J, Jonsson F, Romanov S G and Sotomayor Torres C M 2006 Integration of self-assembled three-dimensional photonic crystals onto structured silicon wafers *Langmuir* 22 7378-7383
- [123] Kim M H, Im S H and Park O O 2005 Fabrication and Structural Analysis of Binary Colloidal Crystals with Two-Dimensional Superlattices Advanced Materials 17 2501-2505

- [124] Chen J, Dong P, Di D, Wang C, Wang H, Wang J and Wu X 2013 Controllable fabrication of 2D colloidal-crystal films with polystyrene nanospheres of various diameters by spincoating *Applied Surface Science* 270 6-15
- [125] Colson P, Cloots R and Henrist C 2011 Experimental design applied to spin coating of 2D colloidal crystal masks: a relevant method? *Langmuir* 27 12800-12806
- [126] Jiang P and McFarland M J 2005 Wafer-scale periodic nanohole arrays templated from twodimensional nonclose-packed colloidal crystals *Journal of the American Chemical Society* 127 3710-3711
- [127] Marquez M and Grady B P 2004 The use of surface tension to predict the formation of 2D arrays of latex spheres formed via the Langmuir-Blodgett-like technique Langmuir 20 10998-11004
- [128] Meng X and Qiu D 2014 Gas-Flow-Induced Reorientation to Centimeter-Sized Two-Dimensional Colloidal Single Crystal of Polystyrene Particle Langmuir 30 3019-3023
- [129] Pan F, Zhang J, Cai C and Wang T 2006 Rapid fabrication of large-area colloidal crystal monolayers by a vortical surface method *Langmuir* 22 7101-7104
- [130] Rybczynski J, Ebels U and Giersig M 2003 Large-scale, 2D arrays of magnetic nanoparticles *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **219** 1-6
- [131] Sirotkin E, Apweiler J D and Ogrin F Y 2010 Macroscopic ordering of polystyrene carboxylate-modified nanospheres self-assembled at the water- air interface *Langmuir* 26 10677-10683
- [132] Lumsdon S O, Kaler E W and Velev O D 2004 Two-dimensional crystallization of microspheres by a coplanar AC electric field *Langmuir* **20** 2108-2116
- [133] Trau M, Saville D and Aksay I 1996 Field-induced layering of colloidal crystals Science 272 706
- [134] Zhang X, Zhang J, Zhu D, Li X, Zhang X, Wang T and Yang B 2010 A universal approach to fabricate ordered colloidal crystals arrays based on electrostatic self-assembly *Langmuir* 26 17936-17942
- [135] Reculusa S and Ravaine S 2003 Synthesis of colloidal crystals of controllable thickness through the Langmuir-Blodgett technique *Chem. Mater.* **15** 598-605
- [136] Plettl A, Enderle F, Saitner M, Manzke A, Pfahler C, Wiedemann S and Ziemann P 2009 Non-Close-Packed Crystals from Self-Assembled Polystyrene Spheres by Isotropic Plasma Etching: Adding Flexibility to Colloid Lithography Advanced Functional Materials 19 3279-3284
- [137] Vogel N, Goerres S, Landfester K and Weiss C K 2011 A Convenient Method to Produce Close-and Non-close-Packed Monolayers using Direct Assembly at the Air–Water

Interface and Subsequent Plasma-Induced Size Reduction *Macromolecular Chemistry and Physics* **212** 1719-1734

- [138] Yan L, Wang K, Wu J and Ye L 2006 Hydrophobicity of model surfaces with loosely packed polystyrene spheres after plasma etching *The Journal of Physical Chemistry B* 110 11241-11246
- [139] Cong C, Junus W, Shen Z and Yu T 2009 New colloidal lithographic nanopatterns fabricated by combining pre-heating and reactive ion etching *Nanoscale research letters* **4** 1324
- [140] Buzea C, Kaminska K, Beydaghyan G, Brown T, Elliott C, Dean C and Robbie K 2005 Thickness and density evaluation for nanostructured thin films by glancing angle deposition *Journal of Vacuum Science & Technology B* 23 2545-2552
- [141] Ingram W, He Y, Stone K, Dennis W M, Ye D and Zhao Y 2016 Tuning the plasmonic properties of silver nanopatterns fabricated by shadow nanosphere lithography *Nanotechnology* 27 1-9
- [142] Basnet P and Zhao Y 2016 Tuning the Cu x O nanorod composition for efficient visible light induced photocatalysis *Catal. Sci. Tech.* **6** 2228-2238
- [143] Dick L A, McFarland A D, Haynes C L and Van Duyne R P 2002 Metal film over nanosphere (MFON) electrodes for surface-enhanced Raman spectroscopy (SERS): Improvements in surface nanostructure stability and suppression of irreversible loss *Journal of Physical Chemistry B* 106 853-860
- [144] Kumar G V P 2012 Plasmonic nano-architectures for surface enhanced Raman scattering: a review *Journal of Nanophotonics* **6**
- [145] Stiles P L, Dieringer J A, Shah N C and Van Duyne R R 2008 Surface-Enhanced Raman Spectroscopy *Annual Review of Analytical Chemistry* **1** 601-626
- [146] Zhang X, Yonzon C R, Young M A, Stuart D A and Van Duyne R P 2005 Surface-enhanced Raman spectroscopy biosensors: excitation spectroscopy for optimisation of substrates fabricated by nanosphere lithography *IEE Proc.-Nanobiotechnol.* **152** 195-206
- [147] Zhu X L, Shi L, Liu X H, Zi J and Wang Z L 2010 A Mechanically Tunable Plasmonic Structure Composed of a Monolayer Array of Metal-Capped Colloidal Spheres on an Elastomeric Substrate Nano Research 3 807-812
- [148] Farcau C, Giloan M, Vinteler E and Astilean S 2012 Understanding plasmon resonances of metal-coated colloidal crystal monolayers *Applied Physics B-Lasers and Optics* 106 849-856
- [149] Himmelhaus M and Takei H 2000 Cap-shaped gold nanoparticles for an optical biosensor Sensors and Actuators B-Chemical 63 24-30

- [150] Lyandres O, Shah N C, Yonzon C R, Walsh J T, Glucksberg M R and Van Duyne R P 2005 Real-time glucose sensing by surface-enhanced Raman spectroscopy in bovine plasma facilitated by a mixed decanethiol/mercaptohexanol partition layer *Analytical Chemistry* 77 6134-6139
- [151] Ma K, Yuen J M, Shah N C, Walsh J T, Glucksberg M R and Van Duyne R P 2011 In Vivo, Transcutaneous Glucose Sensing Using Surface-Enhanced Spatially Offset Raman Spectroscopy: Multiple Rats, Improved Hypoglycemic Accuracy, Low Incident Power, and Continuous Monitoring for Greater than 17 Days Analytical Chemistry 83 9146-9152
- [152] Ngo H T, Wang H N, Fales A M and Vo-Dinh T 2013 Label-Free DNA Biosensor Based on SERS Molecular Sentinel on Nanowave Chip Analytical Chemistry 85 6378-6383
- [153] Zhang X Y, Young M A, Lyandres O and Van Duyne R P 2005 Rapid detection of an anthrax biomarker by surface-enhanced Raman spectroscopy *Journal of the American Chemical Society* **127** 4484-4489
- [154] Wang J J, Zhou F, Duan G T, Li Y, Liu G Q, Su F H and Cai W P 2014 A controlled Ag-Au bimetallic nanoshelled microsphere array and its improved surface-enhanced Raman scattering effect *Rsc Advances* 4 8758-8763
- [155] Greeneltch N G, Blaber M G, Schatz G C and Van Duyne R P 2013 Plasmon-Sampled Surface-Enhanced Raman Excitation Spectroscopy on Silver Immobilized Nanorod Assemblies and Optimization for Near Infrared (lambda(ex)=1064 nm) Studies *Journal of Physical Chemistry C* 117 2554-2558
- [156] Abell J L, Garren J M and Zhao Y P 2011 Dynamic Rastering Surface-Enhanced Raman Scattering (SERS) Measurements on Silver Nanorod Substrates Applied Spectroscopy 65 734-740
- [157] Viets C and Hill W 2001 Laser power effects in SERS spectroscopy at thin metal films *Journal of Physical Chemistry B* **105** 6330-6336
- [158] De Jesus M A, Giesfeldt K S and Sepaniak M J 2004 Improving the analytical figures of merit of SERS for the analysis of model environmental pollutants *Journal of Raman Spectroscopy* 35 895-904
- [159] De Jesus M A, Giesfeldt K S and Sepaniak M J 2004 Factors affecting the sorption of model environmental pollutants onto silver polydimethylsiloxane nanocomposite Raman substrates Applied Spectroscopy 58 1157-1164
- [160] Zheng X S, Hu P, Zhong J H, Zong C, Wang X, Liu B J and Ren B 2014 Laser Power Dependent Surface-Enhanced Raman Spectroscopic Study of 4-Mercaptopyridine on Uniform Gold Nanoparticle-Assembled Substrates *Journal of Physical Chemistry C* 118 3750-3757

- [161] Bell S E, Mackle J N and Sirimuthu N M 2005 Quantitative surface-enhanced Raman spectroscopy of dipicolinic acid--towards rapid anthrax endospore detection *Analyst* 130 545-549
- [162] Abbas A, Josefson M, Nylund G M, Pavia H and Abrahamsson K 2012 Chemical images of marine bio-active compounds by surface enhanced Raman spectroscopy and transposed orthogonal partial least squares (T-OPLS) Anal Chim Acta 737 37-44
- [163] Cowcher D P, Xu Y and Goodacre R 2013 Portable, quantitative detection of Bacillus bacterial spores using surface-enhanced Raman scattering *Anal Chem* **85** 3297-3302
- [164] Yu Z, Chen L, Wang Y, Wang X, Song W, Ruan W, Zhao B and Cong Q 2014 A SERSactive enzymatic product used for the quantification of disease-related molecules *Journal* of Raman Spectroscopy 45 75-81
- [165] Deb S K, Davis B, Ben-Amotz D and Davisson V J 2008 Accurate concentration measurements using surface-enhanced Raman and deuterium exchanged dye pairs *Applied Spectroscopy* 62 1001-1007
- [166] Deb S K, Davis B, Knudsen G M, Gudihal R, Ben-Amotz D and Davisson V J 2008 Detection and relative quantification of proteins by surface enhanced Raman using isotopic labels *Journal of the American Chemical Society* 130 9624-+
- [167] Bishnoi S W, Lin Y J, Tibudan M, Huang Y, Nakaema M, Swarup V and Keiderling T A 2011 SERS biodetection using gold-silica nanoshells and nitrocellulose membranes *Anal Chem* 83 4053-4060
- [168] Jiang X, Yang M, Meng Y, Jiang W and Zhan J 2013 Cysteamine-modified silver nanoparticle aggregates for quantitative SERS sensing of pentachlorophenol with a portable Raman spectrometer *ACS Appl Mater Interfaces* **5** 6902-6908
- [169] Kadam U S, Schulz B and Irudayaraj J 2014 Detection and quantification of alternative splice sites in Arabidopsis genes AtDCL2 and AtPTB2 with highly sensitive surface enhanced Raman spectroscopy (SERS) and gold nanoprobes *FEBS Lett* **588** 1637-1643
- [170] Kim D, Campos A R, Datt A, Gao Z, Rycenga M, Burrows N D, Greeneltch N G, Mirkin C A, Murphy C J, Van Duyne R P and Haynes C L 2014 Microfluidic-SERS devices for one shot limit-of-detection *Analyst* 139 3227-3234
- [171] Sun L, Yu C X and Irudayaraj J 2008 Raman multiplexers for alternative gene splicing Analytical Chemistry 80 3342-3349
- [172] Peron O, Rinnert E, Toury T, Lamy de la Chapelle M and Compere C 2011 Quantitative SERS sensors for environmental analysis of naphthalene *Analyst* 136 1018-1022
- [173] Anema J R, Brolo A G, Felten A and Bittencourt C 2010 Surface-enhanced Raman scattering from polystyrene on gold clusters *J. Raman Spectrosc.* **41** 745-751

- [174] Zhang D H, Qin J G, Shen J S, Wang Y and Liu W J 2000 Study on the concentration dependence of orientation of polystyrene on silver by the SERS technique *Chin. J. Polym. Sci.* 18 177-180
- [175] Hildebrandt P and Stockburger M 1984 Surface-Enhanced Resonance Raman-Spectroscopy of Rhodamine-6g Adsorbed on Colloidal Silver *J. Phys. Chem.* **88** 5935-5944
- [176] Vosgrone T and Meixner A J 2005 Surface- and resonance-enhanced micro-raman spectroscopy of xanthene dyes: From the ensemble to single molecules *Chem. Phys. Chem.* 6 154-163
- [177] Martinez V M, Arbeloa F L, Prieto J B and Arbeloa I L 2005 Characterization of rhodamine 6G aggregates intercalated in solid thin films of laponite clay. 2 - Fluorescence spectroscopy *Journal of Physical Chemistry B* 109 7443-7450
- [178] Li R, Ji W, Chen L, Lv H M, Cheng J B and Zhao B 2014 Vibrational spectroscopy and density functional theory study of 4-mercaptophenol Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy 122 698-703
- [179] Lee H M, Kim M S and Kim K 1994 Surface-Enhanced Raman-Scattering of Ortho-Mercaptophenol and Para-Mercaptophenol in Silver Sol Vibrational Spectroscopy 6 205-214
- [180] Barhoumi A, Zhang D M and Halas N J 2008 Correlation of Molecular Orientation and Packing Density in a dsDNA Self-Assembled Monolayer Observable with Surface-Enhanced-Raman Spectroscopy *Journal of the American Chemical Society* 130 14040-+
- [181] Calvente J J, Lopez-Perez G, Jurado J M, Andreu R, Molero M and Roldan E 2010 Reorientation of Thiols during 2D Self-Assembly: Interplay between Steric and Energetic Factors Langmuir 26 2914-2923
- [182] Moskovits M and Suh J S 1988 Surface Geometry Change in 2-Naphthoic Acid Adsorbed on Silver *Journal of Physical Chemistry* 92 6327-6329
- [183] Papadopoulou E and Bell S E J 2011 Surface-Enhanced Raman Evidence of Protonation, Reorientation, and Ag+ Complexation of Deoxyadenosine and Deoxyadenosine-5 '-Monophosphate (dAMP) on Ag and Au Surfaces *Journal of Physical Chemistry C* 115 14228-14235
- [184] Kosiorek A, Kandulski W, Glaczynska H and Giersig M 2005 Fabrication of nanoscale rings, dots, and rods by combining shadow nanosphere lithography and annealed polystyrene nanosphere masks *Small* **1** 439-444
- [185] Jin R C, Cao Y W, Mirkin C A, Kelly K L, Schatz G C and Zheng J G 2001 Photoinduced conversion of silver nanospheres to nanoprisms *Science* 294 1901-1903

- [186] Sherry L J, Jin R C, Mirkin C A, Schatz G C and Van Duyne R P 2006 Localized surface plasmon resonance spectroscopy of single silver triangular nanoprisms *Nano Letters* 6 2060-2065
- [187] Stranik O, Nooney R, McDonagh C and MacCraith B D 2007 Optimization of nanoparticle size for plasmonic enhancement of fluorescence *Plasmonics* **2** 15-22
- [188] Taylor C E, Garvey S D and Pemberton J E 1996 Carbon contamination at silver surfaces: surface preparation procedures evaluated by Raman spectroscopy and X-ray photoelectron spectroscopy *Analytical Chemistry* 68 2401-2408
- [189] Yang W h, Hulteen J, Schatz G C and Van Duyne R P 1996 A surface-enhanced hyper-Raman and surface-enhanced Raman scattering study of trans-1, 2-bis (4-pyridyl) ethylene adsorbed onto silver film over nanosphere electrodes. Vibrational assignments: Experiment and theory *The Journal of chemical physics* **104** 4313-4323
- [190] Haynes C L and Van Duyne R P 2003 Plasmon-sampled surface-enhanced Raman excitation spectroscopy *Journal of Physical Chemistry B* **107** 7426-7433
- [191] Yan Z, Gu P, Bao W, Du W, Chen Z, Xia X and Wang Z 2015 Robust Plasmonic Fano Resonances in π-Shaped Nanostructures *Plasmonics* 10 1159-1166
- [192] Sherry L J, Jin R C, Mirkin C A, Schatz G C and Van Duyne R P 2006 Localized surface plasmon resonance spectroscopy of single silver triangular nanoprisms *Nano Lett.* 6 2060-2065
- [193] Luk'yanchuk B, Zheludev N I, Maier S A, Halas N J, Nordlander P, Giessen H and Chong C T 2010 The Fano resonance in plasmonic nanostructures and metamaterials *Nature materials* 9 707-715
- [194] Sundaramurthy A, Crozier K, Kino G, Fromm D, Schuck P and Moerner W 2005 Field enhancement and gap-dependent resonance in a system of two opposing tip-to-tip Au nanotriangles *Physical Review B* **72** 165409
- [195] Haynes C L and Van Duyne R P 2003 Dichroic optical properties of extended nanostructures fabricated using angle-resolved nanosphere lithography *Nano Letters* **3** 939-943
- [196] Kandulski W 2007 Shadow nanosphere lithography University of Bonn Ph. D. thesis
- [197] Dick B, Brett M and Smy T 2003 Investigation of substrate rotation at glancing incidence on thin-film morphology *J. Vac. Sci. Tech. B* **21** 2569-2575
- [198] Flötotto D, Wang Z, Jeurgens L, Bischoff E and Mittemeijer E 2012 Effect of adatom surface diffusivity on microstructure and intrinsic stress evolutions during Ag film growth *J. Appl. Phys.* **112** 1-9

- [199] Larsen G K, He Y, Wang J and Zhao Y 2014 Scalable fabrication of composite Ti/Ag plasmonic helices: controlling morphology and optical activity by tailoring material properties *Adv. Opt. Mater.* **2** 245-249
- [200] Nag S, Mahdak K C, Devaraj A, Gohil S, Ayyub P and Banerjee R 2009 Phase separation in immiscible silver–copper alloy thin films *J. Mater. Sci.* **44** 3393-3401
- [201] Denton A R and Ashcroft N W 1991 Vegard's law Phys. Rev. A 43 3161-3164
- [202] Cordero Z C and Schuh C A 2015 Phase strength effects on chemical mixing in extensively deformed alloys *Acta. Mater.* **82** 123-136
- [203] Yang G, Fu X and Zhou J 2013 Dielectric properties of the silver–copper alloy films deposited by magnetron sputtering *J. Opt. Soc. Am.* **30** 282-287
- [204] Huang W Y, Qian W and El-Sayed M A 2005 The optically detected coherent lattice oscillations in silver and gold monolayer periodic nanoprism arrays: The effect of interparticle coupling *J. Phys. Chem. B* **109** 18881-18888
- [205] Ferrando R, Jellinek J and Johnston R L 2008 Nanoalloys: from theory to applications of alloy clusters and nanoparticles *Chem. Rev.* **108** 845-910
- [206] Gaudry M, Lermé J, Cottancin E, Pellarin M, Vialle J-L, Broyer M, Prével B, Treilleux M and Mélinon P 2001 Optical properties of (Au x Ag 1-x) n clusters embedded in alumina: evolution with size and stoichiometry *Phys. Rev. B* 64 1-7
- [207] Kim W-J, Kim S, Kim A R and Yoo D J 2013 Direct detection system for Escherichia coli using Au–Ag alloy microchips *Ind. Eng. Chem. Res.* 52 7282-7288
- [208] Lei D, Li J and Ong H 2007 Tunable surface plasmon mediated emission from semiconductors by using metal alloys *Appl. Phys. Lett.* **91** 1-7
- [209] Rioux D, Vallières S, Besner S, Muñoz P, Mazur E and Meunier M 2014 An analytic model for the dielectric function of Au, Ag, and their alloys *Adv. Opt. Mater.* **2** 176-182
- [210] Johnson P B and Christy R-W 1972 Optical constants of the noble metals *Phys. Rev. B.* **6** 4370
- [211] Yan X, Yao J, Lu G, Li X, Zhang J, Han K and Yang B 2005 Fabrication of non-closepacked arrays of colloidal spheres by soft lithography *Journal of the American Chemical Society* 127 7688-7689
- [212] Larsen G K, He Y, Wang J and Zhao Y 2014 Scalable fabrication of composite Ti/Ag plasmonic helices: controlling morphology and optical activity by tailoring material properties *Advanced Optical Materials* **2** 245-249

- [213] Bobb D, Zhu G, Mayy M, Gavrilenko A, Mead P, Gavrilenko V and Noginov M 2009 Engineering of low-loss metal for nanoplasmonic and metamaterials applications *Applied Physics Letters* **95** 151102
- [214] de Aberasturi D J, Serrano-Montes A B and Liz-Marzán L M 2015 Modern Applications of Plasmonic Nanoparticles: From Energy to Health *Advanced Optical Materials* **3** 602-617

APPENDIX A

COLLOID MONOLAYER SELF-ASSEMBLY: EXPERIMENTAL PROCEDURES

Preparation of substrates

Glass and silicon were cut into $1.2 \times 1.2 \text{ cm}^2$ pieces. Glass substrates and a 15 cm diameter Petri dish were cleaned in a boiling piranha solution (4:1 v/v of sulfuric acid: hydrogen peroxide) for at least 20 minutes. Silicon pieces were cleaned using the RCA-1 cleaning method (5:1:1 v/v/v of water: ammonium hydroxide: hydrogen peroxide) at ~ 70°C for at least 20 minutes. After chemical cleaning, all substrates were thoroughly rinsed in deionized (DI) water and dried with N₂ gas. Next, the solution of polystyrene nanospheres is prepared.

Preparation of colloid monolayers (Washing and Dilution)

The polystyrene nanospheres used in self-assembly method were purchased from Polysciences [®] or Bangs laboratories [®]. PS nanospheres were prepared by diluting the PS nanospheres and performing a "washing procedure". **Figure A1 (a-c)** illustrates the preparation procedures. First the solution is mixed with a vortexer, as shown in **Figure A1 (a)**. Then, the PS nanosphere suspension is diluted to specific concentration as specified in. **Table A1**. Next, the PS solutions are "washed". A washing procedure is as followed: The solution is diluted further by adding 600uL of water to the centrifuge tubes. Then the tubes are centrifuged at specific speed depending upon the nanosphere size. The centrifuge speeds are listed in **Table A1**. After

Bead Size	<i>Recipe</i> (v/v%)	Initial volume (µL)	Water (µL)	Ethanol (μL)	Centrifuge speed (rpm)/Time(min)
2000 nm	2.4%	480	40	260	5500/ 5
1000 nm	1.12%	230	300	320	7000/5
750 nm	0.9%	180	340	260	8500/5
500 nm	0.6%	120	400	260	9500/10
350 nm	0.15%	30	490	260	13500/10
200 nm	0.1%	20	520	260	15000/30
150 nm	0.09%	17	474	245	15000/30

Table A.1. Specific dilution concentration for specific PS nanosphere diameters, and typically used volumes of PS (based on concentrations from Polyscienes initial volume of 2 %), DI water, ethanol, and recommended centrifugation speed and time to use for when washing the PS nanosphere solution.

centrifugation, the PS nanospheres settle to the bottom of the centrifuge tube. The additional 600 uL solution is removed. This washing procedure is repeated two more times. After washing, the solution is diluted in ethanol using a 2:1 ratio of solution to ethanol.



Figure A.1 Photos of self-assembly method (*a-c*) *colloid monolayer preparation procedures.* (*d-f) Experimental procedures and mechanical set-up for air/water interface method.*

Monolayer Preparation: Air/Water Interface method

Figure A1 (d-f) illustrate the monolayer preparation method. Once washed, the suspension was loaded into a syringe with a 20G needle. The needle is bent, as shown in Figure **A1 (d)**, then the syringe is mounted onto a syringe pump (KD Scientific). A cleaned glass Petri dish (diameter of 10 cm), pre-filled with 24 mL of DI water, was tilted at an angle of $\sim 7^{\circ}$, and a needle attached to the syringe was bent towards the water within the Petri dish. Droplets of PS solution were dispensed onto the water surface at a rate of 0.015 ml/min. Each drop spread radially outward from the droplet location, and a monolayer of PS nanospheres was slowly formed on the water surface along the edge of the Petri dish. This process continues until the monolayer fills the entire dish.

A Teflon ring, with a diameter smaller than the diameter of the Petri dish, was placed gently on the water surface to protect the monolayer film against adhering to the side wall of the Petri dish. (As shown in **Figure A.2**). After the water level was raised, glass and silicon pieces were slid carefully under the water to the area below the monolayer film. Finally, the monolayer film was deposited onto the surface of the submerged substrates by slowly pumping water out from the Petri Dish.



Figure A.2 Photo of Teflon rings on the surface of the colloid monolayer film