Metal plasmonic nanoarrays for surface-enhanced Raman spectroscopy and applications of atomic layer deposition

Li, Xianglin

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**METAL PLASMONIC NANOARRAYS FOR SURFACE-
ENHANCED RAMAN SPECTROSCOPY AND
APPLICATIONS OF ATOMIC LAYER DEPOSITION**

LI XIANGLIN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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LI XIANGLIN

School of Physical and Mathematical Sciences

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Summary

As a powerful spectroscopic technique, surface-enhanced Raman spectroscopy (SERS) has attracted much attention in the past decade due to its wide applications in biological sensing and diagnostics. One major challenge to make SERS as a general analytical tool lies in design and fabrication noble metal nanostructure substrates with large and reproducible Raman enhancements over wide area, ideally using inexpensive, easily handled, high-throughput method. As a reliable and inexpensive fabrication method, nanosphere lithography (NSL) has been widely used for producing of large-area ordered nanostructures for SERS substrates. Atomic layer deposition (ALD) is a powerful thin film deposition technique, which can provide thin films with perfect thickness control at atomic level and excellent conformality to various substrates. Now, ALD is finding more applications in plasmonics. In this thesis, we were trying to design and fabricate metallic nanostructures arrays for SERS applications based on the combination of NSL and ALD.

Firstly, a recyclable SERS-active substrate was demonstrated based on 2-D ordered arrays of Au semishells on TiO_2 spheres. The Raman enhancement originates from the ordered gold nanogaps, and the recyclability stems from the UV-photocatalytic degradation of the target molecules by the exposed surfaces of the TiO_2 spheres (i.e., self-cleaning). Sensitivity, reproducibility, and recyclability are demonstrated by Raman detection typical molecules.

Secondly, to further improve the SERS enhancement of the metal semishell arrays, metal particles on semishell (PoSS) structure array was designed and fabricated. The

metal particles are formed via a simple thermal-induced dewetting of thin film. The local field enhancement of the PoSS structure is verified by both simulation and SERS measurements. This subtle designed PoSS array generates further SERS enhancement up to 10 times that of conventional metal semishell arrays.

Thirdly, a highly-ordered particle-in-bowl (PIB) nanostructure array is designed and fabricated to achieve large field enhancement for SERS application. This new type of PIB structure is composed of an Ag particle located at the bottom of an Au bowl and the two are separated by a precise-controlled nanoscale dielectric layer. Numerical simulation reveals a high enhancement of the local field at the nanogaps. The SERS performance of the PIB arrays, and the effects of the Ag particle size and the ALD dielectric layer thickness are characterized, results of which are in reasonable agreement with simulation. The spatially averaged SERS enhancement factor is on the order of 3.8×10^7 and the local field enhancement from simulation can be up to 10^8 .

I have also conducted some other research on ALD in nanofabrication. We have demonstrated that the ALD ZnO film can be used as seed layer for hydrothermal growth ZnO nanorod arrays. With this technique, we have successfully fabricated various 3-D hybrid nanostructures, including Si-ZnO nanotrees, urchin ZnO structure, and CNT-ZnO heterostructures. Those 3-D nanostructures may find applications in SERS or energy-related applications. We have also demonstrated a micro-pulse process of ALD of Fe_2O_3 using ferrocene and ozone precursors and Ti-doping for photoelectrochemical water splitting.

Publications

- [1] **Xianglin Li**, Yongzhe Zhang, Ze Xiang Shen, and Hong Jin Fan. Highly Ordered Arrays of Particle-in-Bowl Plasmonic Nanostructures for Surface-Enhanced Raman Scattering, *Small* **2012**, 8, (16), 2548-2554.
- [2] **Xianglin Li**, Hailong Hu, Dehui Li, Zexiang Shen, Qihua Xiong, Shuzhou Li, and Hong Jin Fan. Ordered Array of Gold Semishells on TiO₂ Spheres: An Ultrasensitive and Recyclable SERS Substrate, *ACS Appl. Mater. Interfaces* **2012**, 4, (4), 2180-2185.
- [3] **Xianglin Li**; C. Li; Y. Zhang; D. P. Chu; W. I. Milne; Hong Jin Fan. Atomic Layer Deposition of ZnO on Multi-walled Carbon Nanotubes and Its Use for Synthesis of CNT-ZnO Heterostructures *Nanoscale Res. Lett.* **2010**, 5, (11), 1836-1840.
- [4] **Xianglin Li**, Ng Chin Fan, and Hong Jin Fan. A micro-pulse process of atomic layer deposition iron oxide using ferrocene and ozone precursors, and Ti doping, *Chem Vapor Deposition* **2013** 19 (4-6), 104-110. (Invited article)
- [5] **Xianglin Li**; Chuanwei Cheng; Hong Jin Fan. Atomic layer deposition ZnO film as seed layer for hydrothermal growth of ZnO nanorods, *Mater. Res. Soc. Symp. Proc.* **2010**, Vol. 1258.
- [6] Cao Guan, **Xianglin Li**, Zilong Wang, Xiehong Cao, Cesare Soci, Hua Zhang, Hong Jin Fan. Nanoporous Walls on Macroporous Foam: Rational Design of Electrode to Push Areal Pseudocapacitance, *Adv. Mater.* **2012**, 24, (30), 4186-4190.
- [7] Monan Liu, **Xianglin Li**, Siva Krishna Karuturi, Alfred Iing Yoong Tok,

Hong Jin Fan, Atomic layer deposition for nanofabrication and interface engineering.

Nanoscale **2012**, 4 (5), 1522-1528.

[8] Hongxing Li, Chuanwei Cheng, **Xianglin Li**, Jinping Liu, Cao Guan, Yee Yan Tay, and Hong Jin Fan. Composition-graded $\text{Zn}_x\text{Cd}_{1-x}\text{Se}@\text{ZnO}$ Core-shell Nanowire Array Electrodes for Photoelectrochemical Hydrogen Generation, *J. Phys. Chem. C* **2011**, 116, (5), 3802-3807.

[9] Bo Wu , Than Zaw Oo, **Xianglin Li**, Xinfeng Liu, Xiangyang Wu , Edwin Kok Lee Yeow , Hong Jin Fan, Nripan Mathews, and Tze Chien Sum. Efficiency Enhancement in Bulk-Heterojunction Solar Cells Integrated with Large-Area Ag Nanotriangle Arrays, *J. Phys. Chem. C* **2012**, 116 (28), 14820-14825.

[10] Cao Guan, Jinping Liu, Chuanwei Cheng, Hongxing Li, **Xianglin Li**, Weiwei Zhou, Hua Zhang and Hong Jin Fan. Hybrid Structure of Cobalt Monoxide Nanowire @ Nickel Hydroxidenitrate Nanoflake Aligned on Nickel Foam for High-Rate Supercapacitor, *Energy Environ. Sci.* **2011**, 4, (11), 4496-4499.

[11] Chuanwei Cheng, Bin Yan, She Mein Wong, **Xianglin Li**, Weiwei Zhou, Ting Yu, Zexiang Shen, Hongyu Yu and Hong Jin Fan. Fabrication and SERS Performance of Silver Nanoparticles-Decorated Si/ZnO Nanotrees in Ordered Arrays, *Acs Applied Mate. Interfaces* **2010**, 2, (7), 1824-1828.

[12] Xinhui Xia, Zhiyuan Zeng, **Xianglin Li**, Yongqi Zhang, Jiangping Tu, Chin Fan Ng, Hua Zhang, and Hong Jin Fan. Fabrication of Metal Oxide Nanobranches on Atomic-layer-deposited TiO_2 Nanotube Arrays and Their Application in Energy Storage, *Nanoscale* **2013**, 5, 6040-6047.

Chapter 1

Introduction

1.1 Introduction of surface plasmon resonance (SPR)

The coherent electron oscillations exist at an interface between metal and dielectric materials, such as metal thin film in air, which are the so called surface plasmons (SPs).¹ When SPs couple with an incident photon, it will result in a hybridised excitation. The subject of studying such particular light-matter interactions is called plasmonics, which have enabled various applications, including surface-enhanced Raman spectroscopy (SERS),²⁻⁷ biological and chemical sensing.⁸⁻¹¹ Plasmonic materials have been used in some commercial instruments, such as the BIA-core used for bio-molecular detection and characterization,¹²⁻¹⁴ in which the propagating plasmons from thin metal films are used.^{12, 15} However, benefiting from the recent advances in nanofabrication techniques which allows the manipulation and fabrication of plasmonic structures down to nanoscale range with well control, various new applications that take the advantages of the localized surface plasmon resonance (LSPR) have been demonstrated.

1.1.1 Introduction to surface plasmon polaritons (SPPs)

In 1957, Ritchie described the existence of quantized surface waves of the degenerate electron gas in thin films corresponding to longitudinal surface plasma oscillations propagating along a metal and dielectric interface, which is the first prediction of

surface plasmons.¹⁶ Figure 1.1 shows the simplest geometry sustaining SPPs, which is a single, flat interface between a dielectric material and metal material. The condition for existence of a SPP mode of this simple geometry can be derived from Maxwell's equations, which is

$$k_{spp}^2 = k_0^2 \epsilon_d \frac{\epsilon(\omega) + 1}{\epsilon(\omega)} \quad (1-1)$$

where k_0 is the wave vector of the propagating wave in vacuum and $k_0 = \omega/c$ (c is the speed of light in vacuum), $\epsilon(\omega)$ is the dielectric function of the metal, and ϵ_d is the dielectric constant of the upper dielectric material. The SPP at such an interface can only be excited with transverse electromagnetic radiation (TM, or p-polarized). See the detailed derivative in reference.¹⁷ The SPP electric field (E_z) is normal to the interface and exponentially decreases away from the surface, as shown in Figure 1.1 (right side). The resulting dispersion relationship of the SPP is as below.

$$k_{spp} = k_0 \left(\frac{\epsilon(\omega) \epsilon_d}{\epsilon(\omega) + \epsilon_d} \right)^{1/2} \quad (1-2)$$

Figure 1.1 Schematic of the charges and electromagnetic fields of planar SPP at a metal and dielectric interface. The exponential dependence of the field E_z is seen on the right, H_y show then magnetic field in the y direction of this p-polarized wave.

Figure 1.2 shows the dispersion relation of the SPP travelling waves at a flat interface between air and a Drude metal with negligible collision frequency. The gray region to the left of the light-line represents the dispersion of the photons for $k_0 > k_{spp}$. Since the SPP dispersion curve (red solid line) lies to the right of the light line (white region) of the dielectric. Thus the excitation of SPPs requires increasing the momentum of light. One method to compensate this momentum mismatch is using a grating coupling, in which the incident light impinges on a metal surface with shallow grating of holes or grooves. More generally, the propagating SPPs can be excited on all of the metal surfaces with random roughness and the patterned metal surface.¹⁸ Another way to excite the SPPs is using a prism coupling, in which the incident light illuminates on a metal surface through a prism in an attenuated total internal reflection (ATIR) mode.¹⁸

Figure 1.2 Dispersion relations of the SPPs at a metal and air interface. The frequency ω is normalized to the plasma frequency ω_P .

1.1.2 Localized surface plasmons resonance (LSPR)

In the previous section, the propagating SPPs behaviour and the dispersion relation were described at an interface between a metal and dielectric. Compared to SPPs, we are much more interested in LSPR that exists on metal nanoparticles or composite plasmonic nanostructures in this thesis. So what is LSPR? When the dimensions of a metal nanostructure is comparable or smaller than the wavelength of the incident light, the nature of the SPR generated on such structure is highly modified and exists for a discrete value of resonance frequency (ω).¹⁹ For example, when the SPs are confined to a metal sphere with diameter smaller than the wavelength of the incident light, the free electrons will participate in a collective oscillation, that is the so called LSPR. Figure 1.3 schematically shows the dipolar LSP optical response of a metal nanosphere under a polarized excitation condition.²⁰

Figure 1.3 Schematic of a dipolar LSP excited by polarized electric field.¹⁵

The positive ionic charges of the metal nanosphere can be assumed immobile, while the free electrons of the metal sphere oscillate under the incident external field, which will result in a displacement between the negative free electrons and the positive ions

in the metal sphere. In order to show how the local electromagnetic fields at the metallic surface can be affected by the LSPR, a single metal nanosphere can be used as the typically model for analyzing. Applying the electrostatic approximation (quasi-static regime) and a uniform plane-wave excitation electric field (E_0), inside the metal nanosphere, the electric field (E_{in}) is given as,¹⁸

$$E_{in} = \frac{3\varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d} E_0 \quad (1-3)$$

In order to obtain a maximum E_{in} , which requires $\varepsilon(\omega) \approx -2\varepsilon_d$, however, this is not possible for most dielectric materials since the dielectric constant is positive. Compared to the propagating SPPs on flat metal-dielectric interface, the LSPR frequency is $\omega_{lsp} = \omega_p/\sqrt{3}$.¹⁸ The displacement of the free electrons on the metal nanosphere surface will result in polarized charges and such polarized charges result in a linear restoring force, which determines the resonance frequency of the system. Thus, the free electrons on a metal nanosphere behave like a classical spring oscillator system, while the free electrons in bulk material act like a classical relaxator system, in which the Drude plasmon frequency ω_p is not excited by light.²⁰ For some metals they have negative $Re[\varepsilon(\omega)]$ over a certain frequency (wavelength) range. When the absorption ($Im[\varepsilon(\omega)]$) is small at a particular wavelength and on the same time the real part of the optical constant $\varepsilon(\omega) \approx -2\varepsilon_m$, a SPR is established. Therefore, the dielectric function $\varepsilon(\omega)$ of the metal plays a very important role in LSPR. The real part of the optical constant, $Re[\varepsilon(\omega)]$, responses for the resonance wavelength of the plasmon and imaginary part of the optical constant, $Im[\varepsilon(\omega)]$, responses for the absorption in a metal material. From equation 1-3, we know that in order to have large E_{in} , $Re[\varepsilon(\omega)]$

should be negative and $Im[\epsilon(\omega)]$ should be small at the same wavelength to minimize losses in the metal. Here we have discussed the LSPR on a metal nanosphere. The LSPR is a sensitive function to the geometry (including size and shape) of the nanostructure, the optical constant of the material, the surface roughness and the surrounding medium etc. For example, Figure 1.4 shows the shape dependence of the LSPR properties of the gold nanoparticle. It can be clearly seen that under a dark-field microscope the gold nanoparticles with different shapes show different colours. Their dark-field spectra show different characteristic peaks. These characteristic peaks correspond to different LSPR modes of the gold nanoparticles.²¹

Figure 1.4 Scanning electron images, dark-field images, and dark-field spectra of different shaped gold nanoparticles. The height of the above particles were 30 nm.²¹

Among the various noble metals, the most commonly metals used for plasmonic applications are silver (Ag) and gold (Au). The excitation wavelength for Au is

limited to wavelengths longer than 600 nm, due to the strong absorption near the first inter-band transition. Therefore, Au is the best choice for applications in the wavelength regimes larger than 600 nm while Ag is the best for the applications requiring wavelengths shorter than 600 nm.

Aside from the resonance energy, another important plasmonic feature is the enhanced local electromagnetic field at the metal surface. This enhancement will dramatically increase especially when the corresponding LSPR modes are excited on a nano size metallic gap. For example, when two metal nanoparticles are in close proximity at distances less than $d \sim 5$ nm forms a nanogap structure, which is the so called nanodimmer. The electromagnetic field magnitude in the nanogap is dramatically increased when the excitation radiation polarization is aligned along the inter-particle axis (seen Figure 1.5). With a reduced inter particle distance, their transition dipoles composed of oscillation conduction electrons couple with each other and the classical electromagnetism predicts that such enhanced local electromagnetic fields around each sphere coherently interfere.²²

Figure 1.5 The plasmonic response at a nanogap between two metal nanospheres excited by electric field polarized along the inter-particle axis.

With decreasing the inter-particle distance, the coupling of the electron oscillation will become much stronger and the corresponding plasmon resonance wavelength will red shift. This local field enhancement between the metal nanogap can be further improved through reducing the inter-particle distance till that the conduction electrons can tunnel from one to the other. The LSPR modes of each metal nanosphere form hybridized modes and it is believed that all single-molecule SERS reports are based on the largest local field enhancement from metallic nanogaps.^{23, 24}

1.2 Introduction of SERS

1.2.1 Raman scattering

The conception of a scattered photon, when the electromagnetic radiation hits the atom or molecule under study, actualizes the Raman phenomenon. The difference in the energies of the scattered and incident photons, helps categorize the phenomenon as either Raman or Rayleigh scattering. If the energies of these two photons are identical, the scattering is called Rayleigh scattering whereas a difference in energies results in Raman scattering, as shown in Figure 1.6. Raman scattering of the incident laser forms backbone of Raman spectroscopy. Since the weak Raman scattering is always accompanied by an aggressive Rayleigh scattering, the results of Raman spectroscopy can be equivocal.

Figure 1.6 Schematics of the Raman and Rayleigh scattering processes.

1.2.2 SERS

In 1974, Fleischmann et al. observed a strong Raman signal enhancement of pyridine molecules adsorbed on a roughened silver electrode, which is the first report of SERS phenomenon.²⁵ However, SERS was not identified until 1977.² In the early experiments, researchers have demonstrated that Raman signal from the molecules adsorbed on roughened metallic electrodes is significantly stronger per molecule than those observed in normal solution-phase. The enhancement factors of the Raman signal in these experiments were very large, up to 10^6 magnitudes. In the following 30 years considerable progress has been made in understanding the mechanism of the SERS enhancement and in developing SERS substrates to maximize enhancement factor.¹⁹ The origin of SERS is typically broken down into two factors: electromagnetic and chemical. The origin of the chemical enhancement has not been conclusively demonstrated, but it is believed to be a result of mixing of the electronic and vibration wave functions of the molecule and metal, which can result in charge transfer between the metal substrate and adsorbed molecules.²⁶ The electromagnetic

mechanism is attributed to surface plasmons and is entirely a very sensitive function of the metallic nanostructure's geometry and dielectric function. Between these two enhancement mechanisms, electromagnetic is dominant as chemical enhancement only contributes the enhancement on one or two orders of magnitudes.

1.2.3 Electromagnetic mechanism for SERS

As a fundamental theory for numerical simulation the SERS enhancement, the electromagnetic mechanism has been thoroughly reviewed in literatures.²⁷⁻³² Some concepts in the electromagnetic mechanism of SERS are still being revised and developed, such as the cascade field enhancement and the 'hot spots' concept.^{30, 33, 34} Moskovits and Vo-Dinh have summarized several electromagnetic modes for mechanism of SERS phenomenon in their reviews, including models for metallic nanoparticles with spherical or nonspherical shapes, and flat or roughened metallic surfaces.^{28, 29}

Figure 1.7 shows a simplified and typical schematic diagram for understanding the electromagnetic mechanism of SERS. Such a simplified mode is based on a metallic nanosphere in a surrounding medium as we introduced previously (section 1.1.2). The size of the metal nanosphere ($2r$) is chosen to smaller than the incident wavelength. The distance between the target molecule and the metal nanosphere surface is d .

Figure 1.7 Schematic diagram of the electromagnetic mechanism for SERS.²⁹

The molecule is exposed to an electromagnetic field (E_M). Both of the incident field (E_0) and the electromagnetic field induced by the LSPR of the metal nanosphere (E_{SP}) will contribute to the exposure field of the target molecule. Thus, the total field enhancement factor $A(\omega)$, the ratio of E_M ($E_M = E_{SP} + E_0$) to E_0 , can be written as:

$$A(\omega) = \frac{E_M(\omega)}{E_0(\omega)} \sim \frac{\epsilon(\omega) - \epsilon_0}{\epsilon(\omega) + 2\epsilon_0} \left(\frac{r}{r+d} \right)^3 \quad (1-4)$$

It can be clearly seen in equation 1-4, when the real part of the optical constant of the metal nanosphere $\epsilon(\omega) = -2\epsilon_0$, the field enhancement factor is particularly strong. Additionally, to achieve a strong field enhancement, the imaginary part of the optical constant of the metal sphere needs to be small. These conditions are exactly the same to the conditions for the resonant excitation of the LSPR of a metal nanosphere as we described in the previous section (1.1.2). Analogously, if the scattered Stokes or anti-Stokes field is in resonance with the LSPR of the metal nanosphere, it will be enhanced. Taking both of the enhancing effects from the incident laser field and the scattered field into account, the field enhancement factor for a scattered stokes signal power $G(\omega_S)$ is described by the following equation,

$$G_{em}(\omega_S) = |A(\omega_L)|^2 |A(\omega_S)|^2 \sim \left| \frac{\epsilon(\omega_L) - \epsilon_0}{\epsilon(\omega_L) + 2\epsilon_0} \right|^2 \left| \frac{\epsilon(\omega_S) - \epsilon_0}{\epsilon(\omega_S) + 2\epsilon_0} \right|^2 \left(\frac{r}{r+d} \right)^{12} \quad (1-5)$$

where $A(\omega_L)$ and $A(\omega_S)$ are the incident laser field enhancement factor and the scattered Stokes field enhancement factor, respectively. Although equation (1-5) is based on the simplest spherical model, it describes the important properties of the electromagnetic mechanism for SERS. In equation (1-5), one can see that there exists a fourth power relationship between the local field enhancements and the electromagnetic SERS enhancement, which means that for a local electric field enhancement of $100\times$ the SERS signal will be enhanced by 10^8 . The SERS enhancement will be particularly strong if the incident and scattered fields are in resonance with the LSPR of a metal nanostructure.

One can also see that electromagnetic SERS enhancement have a long range feature from equation 1-5, which means that the detected molecules are not required to contact with metallic SERS substrate directly. However, the electromagnetic SERS enhancement decreases dramatically with increasing d . As described in equation (1-4) the decay of E_{SP} over the distance is proportionate to $[1/d]^3$, as a result the electromagnetic SERS enhancement is proportionate to $[1/d]^{12}$ as described in equation (1-5).

The important features of the electromagnetic enhancement mechanism can be summarized as bellow.^{29, 30}

Firstly, as LSPR can be excited in metallic nanostructures, including isolated nanoparticle, nanoparticle aggregates, nanovoid, and roughened metallic surface, the electromagnetic SERS enhancement can be observed on these metallic nanostructures. Similar to the LSPR, electromagnetic SERS enhancement is very sensitive to the

geometry (including size and shape) of the nanostructure, the optical constant of the material, the surface roughness of the structure and other variables as we described in the previous section.

Secondly, there exists a first layer effect in electromagnetic SERS enhancement because the local field enhancement reaches a maximum when the detected molecule directly attached to the substrate surface. There also exists a long range component which can extend to ~10 nm away from the substrate surface.

Lastly, as the local field enhancement is independent to molecules, the electromagnetic SERS enhancement is also independent to molecules.

1.2.4 SERS applications

As a powerful spectroscopy technique that Raman spectroscopy can be used for detection and characterization of chemical and biological molecules. However, the broad application of this technique is limited by the weak signal from normal Raman spectroscopy, as the normal Raman scattering cross sections of molecules are extremely small, typically in the range of 10^{-30} ~ 10^{-25} cm². SERS really boosted the field because the Raman signal can be strongly enhanced with enhancement factor on the order of 10^6 . In the past few decades, SERS has been applied to chemical and biological molecular identification, new drugs innovation and cell research. Based on this, numerous Raman spectra were recorded based on different molecules under different environment.³⁵⁻⁴¹ Highly related to the chemical identification, pharmacists are also interested to know the chemical structure and identify the molecules. SERS has also found wide applications in the field of biology, such as the identification of

DNA,⁴²⁻⁴⁴ protein^{45, 46} and bacteria.⁴⁷⁻⁴⁹ All these applications have been reported for in vitro measurement as well as in vivo measurement.⁵⁰

1.2.5 Recent progress in SERS study

Since the discovery of SERS in 1970s, a vast array of SERS-active substrates have been reported, such as colloidal metal particles,⁵¹ roughened metal films,⁵² nanoparticles and particle aggregates.^{23, 53-56} Benefiting from the recent advances in nanofabrication techniques, many other non-conventional nanostructures like nanowires,^{57, 58} nanotips,⁵⁹ nanorings,⁶⁰ nanobowls,^{61, 62} and nanocrescent moons have been reported for SERS application.^{63, 64} Recently, more research interests lie in designing and fabricating the composite metallic nanostructures to achieve strong field enhancement for SERS application. For example, a particle-in-cavity structure has been demonstrated to produce extremely high local field enhancements because of the cascaded focusing of the optical cross sections into small gaps, as shown in Figure 1.8 (a).⁶⁵ Negro *et al.* studied the genetically optimization of metallic nanoparticle array to maximize the field enhancement for SERS application (Figure 1.8 b).⁶⁶ Figure 1.8 (c) schematically shows a self-similar composite structure designed to achieve a cascade field enhancement for SERS application.³³ Gordon *et al.* reported a single molecule directivity enhanced Raman scattering based on a nanoantenna coupled with a resonant ring-reflector, as shown in Figure 1.8 (d).⁶⁷

Figure 1.8 Various composite metallic nanostructures designed to achieve strong field enhancement for SERS. (a) Schematically shows a particle-in-cavity architecture for further field enhancement;⁶⁵ (b) Genetically optimization of particle array to maximize the field enhancement: simulated field distribution of a genetically optimized array (b1), dimmers (b2) and a periodic array (b3) (scale bar 300 nm), and (b4) SEM image of the genetically optimized array;⁶⁶ (c) Schematics of a self-similar composite structure for cascade field enhancement;³³ (d) Schematically shows a nanoantenna coupled with resonant ring-reflector for directive single molecule detection.⁶⁷

1.2.6 Scientific standards of SERS substrates in real application

One of the paramount issues with SERS has been the inability to reach consensus on what comprises a good substrate. The scientific standards of a good SERS substrate with respect to the enhancement factor, reproducibility, stability and cost of fabrication are essential for practical technology adoption. M. J. Natan proposed several scientific standards in 2006: ⁶⁸

1. Spot-to-spot reproducibility: $< 20\%$ (over 10 mm^2);
2. Substrate-to-substrate reproducibility: $< 20\%$ (over 10 substrates);
3. Determination of the SERS enhancement factor: three kinds of non-resonant analytes are recommended for the enhancement factor estimation;
4. Stability: signal variation $< 20\%$ (measured weekly over one month);

1.3 Atomic layer deposition (ALD) in plasmonics and SERS

ALD is a thin film coating method which is capable of applying conformal thin films with excellent thickness control in nanoscale range to various substrates. Now this technique is finding more applications in plasmonics, an emerging subject of studying the light-matter interactions. In particular, the ALD thin films can be used to tune the optical properties of a plasmonic nanostructure, to protect the plasmonic structure surfaces, or as a sacrificing layer to create nanogap based plasmonic nanostructures etc.

1.3.1 Introduction of ALD

ALD was invented by Suntola and Antson in the 1970s, and originally it was named atomic layer epitaxy (ALE). ALD is based on fully surface-controlled chemical reactions from gas phase to produce thin films with thickness at atomic level and with excellent conformality to various substrates. The principle of ALD is similar to chemical vapour deposition (CVD). The difference is that the precursors are introduced to the reaction chamber separately in ALD, which breaks the CVD reaction into two half reactions. Figure 1.9 schematically shows a typical ALD process. The ALD film thickness is precisely controlled by the cycle numbers, and the growth rate per-cycle depends on the reaction parameters, i.e. the two reactants, substrates and reaction temperature.

At first ALD was used for producing large-area, high-quality thin films for electroluminescence based flat panel displays.⁶⁹ With the semiconductor device dimensions scaling down, the requirement of thin films in nanoscale range has grown enormously. Thus, ALD has found new applications in manufacturing of metal oxide semiconductor field effect transistors (MOSFETs) and integrated memory devices.⁷⁰ Currently, ALD is considered as an important thin film deposition technique for industrial manufacturing of nanoscale devices.⁷¹

Figure 1.9 Schematic of an ALD process. There are four separate steps in one ALD cycle. Step 1: the substrate is exposed to precursor 1, and the precursor molecules adsorb on the substrate surface as a monolayer. Step 2: the excess precursor molecules and the by-products in step 1 are removed using inert gas purging. Step 3: the second reactant molecules is introduced to react with the adsorbed precursor one. Step 4: the excess of precursors and the reaction by-products are removed using inert gas purging.⁷²

Aside from the perfect thickness control and excellent conformality, ALD shows some other advantages compared to other thin film deposition techniques. For example, ALD has the ability to coat 3D-nanostructures with high aspect ratios such as wires, gaps, pores, and deep trenches.^{72, 73} In addition, ALD can take place at low temperatures (e.g., below 100 °C). Therefore, ALD has tremendous potential applications in soft materials and biotechnology. ALD thin films have been used to

functionalize, or to protect a vast array of substrates such as polymers, glasses, semiconductors, metals, carbon nanotubes, and graphene.^{72, 73} In particular, the ALD dielectric thin films deposited at low temperatures ($< 100\text{ }^{\circ}\text{C}$) on nanostructured metal surfaces with a high density and uniformity is essential for the plasmonic properties and SERS applications.⁷⁴

1.3.2 ALD for tuning of optical properties of plasmonic nanostructures

As described in the previous section, the SP is very sensitive to the geometry and the surrounding medium of the metallic nanostructures. The changing of surrounding environmental refractive index will change the plasmonic properties of a metallic nanostructure, e.g. the resonance wavelength and the resonance excitation angle. Based on these changes, SPs have found their applications in biosensing. For example, the SPs based biosensors have been successfully commercialized in fact, and it has been widely used in detection and characterization of chemical and biological molecular interactions.^{75, 76} The SPs based biosensors are measuring the SPR wavelength shift caused by the changing of the refractive index of the surrounding mediums, the adsorbed molecule layers. Also the plasmonic properties of a given metallic nanostructure can be tuned through a conformal dielectric layer coating. For example, it has been reported that the ALD-grown Al_2O_3 films can be used for studying the distance-dependent a nanohole-based plasmonic sensors and nanoparticle-based LSPR sensors.^{77, 78} The transmission spectrum of the plasmonic nanohole array has its characteristic peaks, which determined by the periodicity, size, and other geometrical parameters of the nanohole array. Through ALD dielectric layer

coating the probing ranges of the metallic nanohole arrays can be tuned, as shown in Figure 1.10.

Figure 1.10 SEM images of 40 nm Al_2O_3 layer coated gold nanohole arrays, (a) top view and (b) cross-section view. (c) Transmission spectra from a nanohole-based SPR sensor as ALD Al_2O_3 layer thickness increases from 0 to 42 nm with a step of 6 nm.⁷⁸

1.3.3 ALD in SERS applications

ALD dielectric spacer on plasmonic nanostructures:

As described in the previous section 1.2.3, the dominate SERS enhancement of a metallic nanostructure comes from the electromagnetic enhancement. The SERS enhancement decrease dramatically with increasing the distance (d) between the adsorbed molecules and the metallic nanostructure surface, as seen from the equation (1-5) in the previous section 1.2.3. Although the electromagnetic SERS enhancement is a long range effect, it can only extend to ~ 10 nm away from the metal surface. For

example, Dieringer *et al.* studied the SERS signal intensity from an ALD Al_2O_3 coated Ag surface sample. A 10-fold decrease of the SERS intensity for every 2.8 nm increase of the Al_2O_3 spacer layer was observed.⁷⁹ Therefore, to function as a SERS spacer, the dielectric layer needs to be precisely controlled in sub-10 nm range. Among various thin film deposition techniques, only ALD can provide thin dielectric layer with precisely thickness control down to ~ 1 nm. Therefore the ALD thin film can still be used as a buffer layer between the attached molecules and the metallic nanostructure without sacrificing the SERS enhancement. For example, a new technique of SERS was reported by Tian *et al.* in 2010. In their experiment the Raman signal enhancement is provided by the dielectric shell isolated gold nanoparticles. The ultrathin dielectric shell was produced by ALD method. The ultrathin ALD dielectric layers have dual functions: to keep the nanoparticles against from agglomerating, separate the probed material from direct contact with the nanoparticles. The thickness of the dielectric shell plays a very important role to the Raman enhancement of such a structure. As shown in Figure 1.11 (e), the evident Pt-H band Raman signal was observed based on Au/ SiO_2 or Au/ Al_2O_3 nanoparticles with the shell thickness 2 nm, while the thickness increased to 20 nm, the surface Raman signal at that range was disappeared. This new technique was named as shell-isolated nanoparticle enhanced Raman spectroscopy (SINERS), which could be used to detect the molecules adsorbed on any substrate.⁸⁰ Xu *et al.* also observed a strong SERS enhancement based on Au nanoparticles on film structures with an ultrathin ALD oxide spacer layer (Figure 1.12). They have found that the dielectric constant of the ALD spacer layer

plays a important role to the SERS intensity and the most intense SERS signals was obtained from the sample with a low dielectric constant spacer layer (SiO_2).⁸¹

Figure 1.11 (a) Schematics of shell-isolated nanoparticle array for SINERS. (b) SEM image, (c) TEM images and (d) HRTEM images of the shell-isolated nanoparticles. (e) SINERS spectra of the hydrogen adsorbed on Pt (111) surface under different potential. Curve I ~ III: -1.2, -1.6, -1.9 V based on Au/SiO₂ or Au/Al₂O₃ nanoparticles with shell thickness 2 nm. Curve V: with 20 nm thick shell-isolated nanoparticles.⁸⁰

Figure 1.12 (a) Shows the 3-D schematic of the Au nanoparticles on gold film with a 2 nm SiO₂ separation layer and (b) shows the TEM image of such structure with an individual Au particle. (c) Comparison Raman maps of the particles on film structure, “A” and “B” correspond to the structure with or without the 2 nm SiO₂ spacer, respectively. The corresponding SERS spectra of “A” and “B” are shown in the right. The strong peak at $\sim 520\text{ cm}^{-1}$ is from the Si substrate.⁸¹

ALD-grown films as a protection layer for SERS substrate:

To build plasmonic devices operating in the visible or infrared regime, Au and Ag are the commonly used materials. Compared these two, Ag exhibits lower SP damping and ohmic losses than Au at wavelengths below $\sim 600\text{ nm}$, and also Ag is much cheaper. However, Ag has a poor chemical and thermal stability and because of that it is readily oxidized in the air. Fortunately, the stability of Ag can be improved with a

thin dielectric protective layer. As we mentioned above, the thickness of the protective layer should be less than ~10 nm, otherwise the strong enhanced electromagnetic field will be buried in the dielectric protect layer. On the other hand, to function as a barrier, ultra-thin protective layer must be very dense and with excellent conformality. Furthermore, the deposition of the protective layer should be carried out at a low temperature ($< 100\text{ }^{\circ}\text{C}$) to avoid oxidizing or degrading the Ag nanostructure during the deposition process. Among various thin film deposition methods, only ALD can meet these demands. Indeed, the ALD Al_2O_3 thin films have been used to improve the stability of Ag-based nanostructures for SERS applications.^{82, 83} For example, Dai *et al.* demonstrated that Ag nanowires coated with an ultrathin Al_2O_3 capping layer via ALD showed significant SERS enhancement even after annealing the substrate in air at $400\text{ }^{\circ}\text{C}$ for 24 h, while the same nanowires without ALD Al_2O_3 protective layer were melted and showed no SERS signal.⁸⁴ It also has been demonstrated that the ALD Al_2O_3 thin film coated Ag nanostructures based SERS substrate can survive from oxidation stored in ambient conditions for 9 months with no appreciable decrease of the SERS enhancement. These experiments suggest that ALD thin film coated Ag nanostructures may be suitable for long-term SERS and sensing applications.⁸⁵

ALD used in fabrication of sub-10 nm nanogaps for SERS:

Figure 1.13 (a) Schematically shows of the fabrication process of vertical aligned nanogap arrays based on ALD. Starting from a patterned metallic nanoarray, the secondary metal film is separated from the pre-patterned array by a thin Al_2O_3 layer. The gap width is determined by the ALD Al_2O_3 sacrificing layer thickness. (b) SEM images of the fabricated nanogap structures. (c) Comparison of SERS spectra of benzethiol molecule from nanogap areas (red curve) and non-nanogap areas (blue and black curves).⁸⁶

It is well known that the strong electromagnetic fields between metallic nanogaps under illumination can serve as SERS “hot spots”. However, the production of nanogaps in sub-10 nm range with precise control of the gap width, position, geometry and orientation using a reproducible fabrication method remains a significant challenge. ALD can provide thin films with thickness control down to atomic level. Thus, it is desirable to create a fabrication strategy wherein the nanoscale thin films can be converted into nanogaps with critical size. For example, Im H. *et al.* have demonstrated a method for producing large area vertical aligned sub-10 nm gap arrays based on ALD Al_2O_3 sacrificing layer for SERS applications. The fabrication process

is schematically shows in Figure 1.13.⁸⁶ Using this strategy, various shapes and sizes nanogap based structures can be fabricated, while the ALD sacrificing layer film determines the size of gap with precise control.

1.4 Motivation and objectives

My Ph. D project is mainly on the design and fabrication of noble metal nanostructures for SERS application. Not only the strong enhancement factors but also excellent reproducibility and stability are required for an SERS substrate in practical applications. Furthermore, to make SERS as a general analytical tool, the fabrication method of the SERS substrates should be inexpensive and easy-handled. NSL as a inexpensive, facile, and reproducible method, it has been adopted by many researchers for fabrication of large-area ordered nanostructure arrays for SERS application. In particular, the metal semishell array fabricated by the NSL has been reported with a strong SERS enhancement and a high reproducibility. As ALD is capable of applying conformal and uniform thin films with thickness control at atomic level to various nanostructures, which is finding more applications in the plasmonics - an emerging subject of studying the particular light-matter interactions. My Ph. D project is trying to fabricate SERS substrates with high enhancement factor and good reproducibility by combining ALD and NSL.

Most of the traditional metal-based SERS substrates cannot be easily reused, which is a serious drawback when considering the preciousness of transition metals. It is more desirable to fabricate recyclable SERS substrates in a large-scale ordering,

which allows a better control in enhancement and reproducibility. In the first work (Chapter 3), we use all-scalable techniques including NSL, ALD, and metal evaporation to fabricate a 2-D ordered arrays of Au semishells on TiO₂ spheres as a recyclable SERS substrate.

The SERS enhancement factor of the metal semishell array substrates in previous studies is only round $10^4 \sim 10^5$ due to a limited density of SERS ‘hot spots’ contributing to the overall SERS signal and relatively large gap size. Thus it is desirable to further increase the SERS enhancement through increasing the density or the field enhancement of the hot spots. In the second work (Chapter 4), we attempt to fabricate a SERS active substrate based on Ag particles on Ag semishell array with an ultra thin ALD TiO₂ spacer. The results show that the additional Ag nanoparticle improves the SERS enhancement factor by almost an order of magnitude compared to the conventional Ag semishell arrays substrate.

Recently it is reported that the composite plasmonic nanostructure can provide further electromagnetic field enhancement in SERS application. For example, a “particle-in-cavity” plasmonic architecture has been demonstrated to provide extremely high local field enhancements for SERS application. The further field enhancement is due to the cascaded focusing of the optical cross sections into small gaps. Inspired by this we try to fabricate a highly-ordered particle-in-bowl (PIB) nanostructure array also based on ALD and NSL to further improve the field enhancement of nanosphere-based SERS substrates. Results are presented in Chapter 5.

In addition, during my Ph. D study I have also done some works on application of ALD in nanofabrication. I am very grateful that Dr. Fan, my supervisor lets me to take in charge of the ALD system in our group, which provides me a lot of opportunities to widen my knowledge scope by collaborating with others. During the last four years I have taken the responsibility of training others to use the ALD system, maintenance of the system and developing recipes for new precursors. Chapter 6 presents a few selected works related to ALD. Although I cannot include all of the efforts and results, the experience I gained in the last four years will benefit me in long term.

Chapter 2

Experimental Techniques and Numerical Simulation

2.1 Nanosphere lithography (NSL)

NSL, also named as “colloidal lithography”, is a method used for fabrication of large-area ordered nanostructure arrays, which is based on the combination of colloidal self-assembly with other nanofabrication techniques, such as thermal or e-beam evaporation, reactive ion etching (RIE), thin film deposition (CVD, ALD), and imprinting etc. The function of the self-assembled two-dimensional (2D) ordered array is used as a template or mask. Various ordered nanostructure arrays have been reported based on the NSL method.¹⁸ Now NSL is recognized as an inexpensive, facile and reproducible fabrication method of ordered nanostructure array in large area. Also it has been demonstrated as a power tool to create noble metal nanostructures for SERS and plasmonic sensing applications.⁸⁷⁻⁹³

A typical self assembly process used in this thesis is described as below. First, the monodispersed polystyrene (PS) spheres suspension was diluted by mixing with an equal volume of ethanol and then the mixed suspension was applied to an ultrasonic treatment for several seconds. The PS spheres used in this thesis were purchased from Polysciences Inc with concentration ~2.6 wt% in water and the size of the PS spheres ranged from 200 to 700 nm. Second, a Si (without SiO₂ over layer) substrate with size about 5 × 5 cm was cleaned using ultrasonic bath in acetone, then

in ethanol, and at last in deionized water at room temperature. After that it was rinsed using deionized water and dried with N₂ blow. In the third step, the cleaned and dried Si substrate was kept in a dodecylsodiumsulfate solution with concentration of ~10% in weight for more than 24 hours. In the fourth step, the ordered PS monolayer spheres was first self-assembled on a water surface similar to the technique reported by Rybczynski et al.⁹⁴ The dodecylsodiumsulfate solution treated Si substrate were rinsed with water to remove the excess dodecylsodiumsulfate and dried with N₂ blow. Then several drops of the prepared PS solutions were dropped onto the Si substrate. After the whole Si substrate surface was covered by PS solution, it was gradually immersed in a plastic or glass vessel filled with deionized water. During the immersing process the PS spheres the PS monolayer was formed on the water surface. In the last step, the as formed PS monolayer on water surface was transformed to another cleaned substrate and dried at 60 °C in air. The size of the PS monolayer on the water surface is mainly determined by the size of the Si substrate used in the second step.

2.2 Beneq TFS 200 ALD system

The ALD in this thesis is conducted on a Beneq TFS 200 ALD system, which is capable of coating planar objects, nanoparticles, and complex 3D structures with high aspect ratio. The deposition temperature can up to 500 °C. Figure 2.1 shows a photo of the ALD system in our lab. Three kinds of reaction chambers are designed for deposition of thin film on different substrate. The precursor capabilities of our TFS

200 are unique, including 4 liquid source lines, one hot source line up to 200 °C, plasma line and one ozone line.

Figure 2.1 Photo of Beneq TFS 200.

2.3 Confocal Raman spectroscopy

A Renishaw inVia confocal Raman system has been used for SERS measurement in this project. Figure 2.2 shows the schematic diagram of the Renishaw Raman system. The coupled laser first undergoes a beam expanding. After reflected twice, the laser beam is split into two beams with one of that directed to the microscope and the other goes to the slit. A $\times 50$ objective lens is used in our SERS measurement, which corresponds to a spot size round $1\mu\text{m}$ at the focus point. The prepared SERS substrates are located on a XYZ stage. The Raman signal is collected via a backscattering mode. Two lasers are used as the excitation wavelength in this thesis, one is 532 nm and the other is 785 nm.

Figure 2.2 Schematic of a confocal Raman system.

2.4 Numerical simulation

The problem of electromagnetic analysis can be considered as solving Maxwell's equations under some given boundary conditions. For the simplest sphere structure with boundary conditions of continuity at the interface between the sphere surface and the surrounding medium, the well known Mie scattering theory provides the rigorous solution, and it describes the optical properties of the sphere very well.¹⁸ However, for nonspherical geometries, i.e. arbitrarily shaped particles, the Mie theory is no longer exact to account of the retardation effects induced by factors like geometry, size and orientation of arbitrarily shaped particles. Hence, determination of the plasmonic properties of a subject with arbitrary shape is to find the exact solutions to Maxwell's equations. The commonly used computational methods reported in literatures include discrete dipole approximation (DDA),⁹⁵ finite element method (FEM),⁹⁶ and finite-difference time domain (FDTD).^{97, 98}

FDTD is a popular computational method for electromagnetic modelling system and it is based on numerically evaluating the temporal evolution of the electromagnetic fields. The time-dependent Maxwell's equations are discretized to space and time partial derivatives. Based on that, the resulting finite-difference equations are solved through repeating the calculations on electric field vector components in a volume of space at a given instant in time and magnetic field vector components in the same spatial volume at the next instant in time until the desired steady-state electromagnetic field is fully established. During the FDTD simulation the electromagnetic field values for both of the near and far fields at any time can be observed. In this thesis, we used the commercial software package, Lumerical FDTD Solution 7.1, Inc. Canada, for the FDTD simulation.

2.5 Sample characterization

The morphology of all the samples studied in this thesis was characterized using a JEOLJSM-6700F field emission scanning electron microscope (FE-SEM). A Zolix Solar Cell QE/IPCE measurement system was used for the reflectance spectra measurement. The ALD thin film thickness on flat Si substrate was measured using a SE (α -SE, J. A. Woollam). The fitting modes and the optical constant used for fitting were provided by J. A. Woollam. The UV- vis absorption spectra of all the samples were recorded using a microspectrophotometer (Craic 2000).

Chapter 3

Ordered Array of Gold Semishells on TiO₂ Spheres as a Recyclable SERS Substrate

3.1 Introduction

SERS as a powerful spectroscopic technique, it has attracted much attention in the past decade due to its wide applications in various fields, including analytical chemistry, life science, and medical science.⁹⁹⁻¹⁰⁴ Not only strong enhancement factors but also good stability and reproducibility are required for an efficient SERS substrate in practical application.^{105, 106} Furthermore, to make SERS as a general analytical tool, the fabrication process of SERS substrates should become much cheaper and easier handled.

The local electromagnetic field enhancement induced by the excitation of the SPs of the noble metal surface is the major mechanism for SERS.¹⁰⁰ While such a metallic nanostructure is illuminated it can create SERS “hot spots”.¹⁰⁶ At these “hot spots”, due to strong coupling of the plasmon-induced near field with vibration modes of the adsorbed molecules, the Raman scattering cross section of the adsorbates can be amplified by several orders of magnitude.¹⁰⁷⁻¹¹⁰ The SP response of a metallic nanoparticle is sensitive to its shape, size, and surrounding environment of the nanoparticle.^{111, 112} Various metallic nanostructures have been fabricated for SERS application, including nanoparticles, nanorods, nanocubes, nanotriangles, core-shell nanoparticles.¹¹³⁻¹¹⁸ In particular, since the report of the strong SERS enhancement

from semiconductor nanostructures recently,¹¹⁸ more semiconductor-noble metal nanocomposites were fabricated and shown strong SERS enhancement, such as TiO₂/Ag, ZnO/Ag, ZnO/Au, TiO₂/Au and Si/Ag composites.¹¹⁹⁻¹²³

Aside from the enhancement, the stability and reproducibility plays an important role in application of SERS as a general analytical tool. Thus, much effort has been put in fabrication of SERS substrates with better controllability, among which the periodic arrays of metallic nanoparticles is the most common type.^{80, 124} Particularly, the ordered array of metal semishells possesses favourable features for SERS applications: a controllable inter-particle distance, a precise control of the symmetry-broken geometry and uniform orientation of the created nanoapertures.¹²⁵⁻¹²⁷ The Ag semishell array fabricated through NSL has been reported with an evident SERS enhancement and good reproducibility.¹²⁸ However, considering the stability, Au is much more oxidation-resistant than Ag for SERS application.¹²⁹ Finally, most of the traditional metal-based SERS substrates cannot be easily reused, which is a serious drawback when considering the preciousness of transition metals. Thus, researchers have focused on developing renewable SERS substrates in recent years.^{130, 131} However, the so-far reported reusable SERS substrates are based on either random metal particles or particles supported by disordered arrays.¹³² It is more desirable to fabricate recyclable SERS substrates based on a uniform “Au semishell on TiO₂ structure arrays” in a large-scale ordering, which allows better control of the SERS enhancement and reproducibility.

In this scheme, we demonstrated a recyclable SERS-active substrate comprising

2-D ordered arrays of Au semishells on TiO₂ spheres in this chapter. The fabrication process includes NSL, ALD and metal evaporation, and all of those techniques are scalable techniques. The SERS enhancement originates from the ordered gold nanogaps and the recyclability stems from the UV-photocatalytic degradation of the target molecules by the exposed surfaces of the TiO₂ spheres (i.e., self-cleaning). The size of the nanogaps is controlled by the sphere size and ALD thickness (not by gold film thickness which would otherwise block the TiO₂ surface and weakens the self-cleaning function). Sensitivity, reproducibility and recyclability are demonstrated by Raman detection of two typical molecules. Such ordered structure could find applications in optical biosensing.

3.2. Experimental

3.2.1 Fabrication of Au semishell on TiO₂ sphere array

Figure 3.1 schematically shows the fabrication process for the ordered array of Au semishell on hollow TiO₂ sphere. First, a monolayer of polystyrene (PS) nanospheres (Polysciences, Inc.) was deposited on a glass substrate using the Langmuir-Blodgett technique as described in the literature.⁹⁴ The concentration of the PS we used here is 2.61% (w/w), and the size distribution of the PS is 465±10 nm. Second, the as-deposited PS monolayers were etched to a reduced size with a proper inter particle distance through a reactive ion etching (RIE) process. The RIE process was carried out on a March PX-250 plasma etching system with condition: pressure of 70 mtorr, a RF power of 100 W, and an O₂ flow rate of 50 sccm (cubic centimetre per minute),

and an etching time of 300 s. After RIE, about 20 nm TiO₂ were deposited on the PS monolayer through ALD on a Beneq TFS-200 system using TiCl₄ and deionized water as the Ti and oxygen precursor, respectively.¹³³ High purity N₂ was used as the process gas in our ALD system. The reaction chamber was maintained at 1.0 mbar with a steady N₂ steam at 200 standard-state cubic centimeter per minute sccm through the whole deposition process. Each half ALD cycle consisted of a 250 ms precursor pulse and 2 seconds purging time with N₂. The deposition temperature was set to 80 °C to avoid damage of the PS spheres. The ALD TiO₂ growth rate is ~0.06 nm/cycle. Subsequently, the substrates were annealed at 450 °C under air ambient to remove the PS sphere, and at the meantime to crystallize the TiO₂ layer. Finally, a ~30 nm thick Au layer was deposited on the as fabricated hollow TiO₂ sphere array using an Edward electron-beam evaporation system.

3.2.2 SERS experiments and self-cleaning cycles

The as fabricated ordered arrays of Au semishell on TiO₂ sphere were used as SERS-active substrates. Before SERS measurement, the substrates were first immersed in the prepared target molecular solutions for 30 min and then washed with deionized water and dried by N₂ flow. Rhodamine 6G (R6G) and brilliant cresyl blue (BCB) were chosen as the probe molecules. After the samples were studied for SERS under a 785 nm laser, they were immersed in deionized water and irradiated with a 4 W UV lamp (peak wavelength: 254 nm, 20 cm away from the lamp) at room temperature for a certain time (typically, 1.5 h for BCB, and 2 h for R6G. Note that the irradiation time could be shortened by using a higher power UV light source or decrease the

distance of the sample and the lamp). Then the samples were rinsed with deionized water several times to remove the residual ions and molecules and dried with N₂ flow. The “detection–cleaning” process was repeated five times for each sample for recyclability characterization.

Figure 3.1 Fabrication process schematic of the Au semishell on TiO₂ nanosphere array: (a) deposition of the monolayer PS sphere; (b) shrink of the PS sphere by using RIE; (c) deposition of TiO₂ by ALD and thermal annealing; (d) evaporation of Au on the hollow TiO₂ sphere array.

3.3 Results and discussion

The fabrication process of the ordered array of Au semishell on TiO₂ sphere SERS substrates mainly includes three main steps (see Figure 3.1): first, the deposition of large-area ordered monolayer of PS nanosphere on glass substrate; second, the reducing size of the PS sphere size by oxygen plasma in order to create enough

separation between the spheres for the subsequent ALD deposition; and last metal deposition. The size of the PS can be controlled in the RIE process by adjusting the etching time when other conditions are fixed. The thickness of the as deposited TiO₂ is precisely controlled by the ALD cycles. Here we used 340 ALD cycles to deposit about 20 nm thick TiO₂ film. After TiO₂ coating the substrates were annealed at 450 °C for one hour at ambient condition to remove the PS. Due to both of the RIE and ALD are controllable processes, the size of the hollow TiO₂ spheres, TiO₂ shell thickness, and the inter particle distance can be precisely controlled.

Figure. 3.2 SEM images: (a) PS sphere after the RIE etching; (b) hollow TiO₂ sphere array after ALD and thermal annealing; (c) Au semishell on TiO₂ hollow sphere array obtained by evaporation; (d) titled image of the structure in (c). The insets show the corresponding larger-magnification SEM images.

The etched PS sphere with the initial size 465 nm is shown in Figure 3.2 (a). The diameter of PS spheres is reduced to uniform 420 nm after RIE process. At the same time the inter particle distance is about 80 nm. Figure 3.2 (b) shows the hollow TiO₂ sphere array after ALD and thermal annealing processes. The hexagonal close-packed hollow TiO₂ spheres are with a uniform size about 440 nm. This demonstrates that a combination of nanosphere patterning, RIE and ALD provides a useful and powerful technique for preparing uniform micro/nano patterns with controlled particle size and tunable inter particle distance. Figure 3.2 (c) and (d) show the SEM image and the 20 degree tilted SEM image of the ordered array of Au semishells on hollow TiO₂ spheres. The as deposited Au films were 30 nm in thickness and homogeneous. After Au deposition, both of the interspaces between hollow TiO₂ spheres and the top surface of the hollow TiO₂ sphere were covered with Au. As the diameter of the etched PS sphere is identical, the size of the Au semishell is the same (~500 nm) and the inter particle distance is about 20 nm as indicated by the red marker in Figure 3.2(c). Figure 3.3 (a) shows the Raman spectrum of the initial ordered array of Au semishells on hollow TiO₂ spheres substrates. The Raman peaks can be assigned as the E_g (143 cm⁻¹), A_{1g} (395 cm⁻¹), or B_{1g} (515 cm⁻¹), and E_g (638 cm⁻¹) modes of the anatase TiO₂ phase, respectively.¹³⁴ Except the Raman peak at 143 cm⁻¹ all the other peaks are quite low, which means it has a clear background for SERS application.

Figure 3.3 (b) shows the UV-vis absorption spectra of the ordered array of hollow TiO₂ spheres array before and after Au deposition. The observed absorption edge at about 380 nm for both of the substrates corresponds to the bulk value (3.2 eV)

of the TiO₂ band gap. The ordered array of TiO₂ hollow spheres sample shows two main broad peaks at ~440 nm and ~560 nm, which are believed to originate from the hexagonal close packing of the spheres,¹³⁵ and there is no absorption peak in the range beyond 600 nm. The two peaks in the range of 400 to 600 nm blue shift slightly after Au deposition. That may be due to changes in the particle size and optical constant of the hexagonal packed monolayer.^{135, 136} Beyond 600 nm, a new broad plasmon band, centered at ~730 nm was observed, which corresponds to the transverse plasmon mode of the Au semishell. It is known that there are two kinds of plasmon modes exist for a single semishell, known as the axial mode and the transverse mode, and the excitation of those two kinds of plasmon modes depends on the excitation condition.^{126, 137} The resonance energy of the transverse mode is usually lower than the axial mode. Because of the overlapping we cannot observe the axial mode; whereas the transverse mode resonance peak appears clearly at ~730 nm.

Figure 3.3 (a) Raman spectrum and (b) UV-vis absorption spectra of the initial Au semishell on TiO₂ hollow sphere array substrates.

Figure 3.4 SERS spectra of BCB solutions at different concentrations. From top to bottom: 10^{-6} , 10^{-7} , 10^{-8} , 10^{-9} M. (b) Raman spectra of BCB solution (1×10^{-7} M) adsorbed on the Au semishell on hollow TiO₂ sphere array before and after UV-cleaning using 4 W UV lamp.

Figure 3.5 Raman spectra of five adsorption/UV-cleaning cycles of (a) BCB 10^{-7} M, and (b) R6G 10^{-6} M, respectively. Each cycle consists of adsorption of the target solution followed by UV irradiation. The graph shows the Raman spectra before and after cleaning.

The ordered arrays of Au semishells on hollow TiO₂ sphere samples are used as SERS-active substrates for detection of different molecular species. Figure 3.4 shows

the SERS spectra of BCB adsorbed on the substrates with the concentration ranging from 10^{-6} down to 10^{-9} M. Evident Raman detection was obtained from concentration from 10^{-9} M and above. A renewable substrate can be obtained for further detection after it fully cleans itself by TiO₂ photocatalytic degradation of the target molecules adsorbing on the substrates. For R6G and BCB molecules, their photocatalytic degradation in presence of TiO₂ has been studied by Baran et al.¹³⁸ The typical self-cleaning process is as follows: after Raman measurement, the substrates were immersed in deionized water with UV light for a certain time and then the sample was rinsed with deionized water to remove the residual ions and molecules and dried with N₂ flow. Figure 3.4 (b) shows the Raman spectra of BCB adsorbed on the substrate before and after cleaning. After 45 min UV irradiation the BCB signal is very weak and it completely vanishes after 90 min UV irradiation. The signal is fully recovered after subsequent soaking of the substrates into the BCB solution, indicating that the substrate preserves their functionality. Figure 3.5 (a) shows that the result is well reproduced after repeating the “detection–cleaning” procedure five times. In addition to BCB, other types of molecules can be detected repeatedly by the same substrate, for example, the R6G, as shown in Figure 3.5 (b). Remarkably, the characteristic vibration patterns can be clearly identified when the analyte is present but are completely eliminated after UV irradiation and washing. These results further demonstrate the general reversibility of such ordered array of Au-TiO₂ spheres for the detection of a variety of organic molecules.

To numerically estimate the electromagnetic field distribution of the structure, a

3D finite-difference time-domain (FDTD) simulation is carried out on a commercial software package (Lumerical FDTD Solution 7.1, Inc. Canada). The model of the structure is shown in Figure 3.6 (a), where the particle size is 500 nm and the inter particle distance is 20 nm. The grid is set to a 4.0 nm cubic in this calculation. The Au dielectric constant we used is from Johnson and Christy,¹³⁹ and for the TiO₂ we used is from Palik (supplied by Lumerical FDTD Solution 7.1, Inc. Canada). As our substrate is ordered array, a periodic boundary condition is used in the simulation. A 785 nm sinusoidal plane electromagnetic wave with normal incident from the top is chosen in our simulation, as shown in Figure 3.6(a). The simulation results show that the semishells array generates the localized plasmons and substantial electromagnetic field enhancement in the gaps between the semishells, as shown in Figure 3.6 (b, c), which is the boundary area of the uncovered TiO₂. Those nanogaps are vital hot spots for SERS. The field enhancement is dominated by those hot spots, and the residual molecules on the continuous Au semishell surfaces gives only negligible contribution to SERS. There should be some Au particles also deposited onto the surface of the substrate through the gaps. The corresponding resonance wavelength of these Au particle is ~640 nm,²¹ which is far away from our excitation wavelength (785 nm). Therefore the contribution by these Au particles to the overall SERS intensity is also rather small.

Figure 3.6 3D-FDTD simulation of a unit cell of the Au semishell arrays excited at 785 nm: (a) the simulation model; (b) top view of the simulation results; (c) side view of the simulation results. Significant electromagnetic field enhancement is seen in the gaps.

The sensitivity of a SERS substrate is characterized by the enhancement factor (EF). EF is defined by comparing the intensity of the SERS signal with that of the non-SERS signal,¹⁴⁰

$$EF = (I_{\text{SERS}}/N_{\text{SERS}})/(I_0/N_0) \quad (1)$$

where N_{SERS} and N_0 are the numbers of probe molecules contributing to the SERS signal and non-SERS signal, respectively; and I_{SERS} and I_0 are the intensities of the selected scattering bands in the SERS and non-SERS spectra, respectively (Figure 3.7 a). The probed molecules are assumed to distribute on the substrates uniformly. Since the specimens for SERS and non-SERS detection are prepared in the same way except for only the substrate (single crystal Au foil for non-SERS), the number of the detected molecule can be estimated by

$$N = (N_A M V_{\text{solution}}/S_{\text{sub}}) S_{\text{laser}} \quad (2)$$

where N_A is Avogadro constant, M is the molar concentration of the solution, V_{solution} is the volume of the droplet, S_{sub} is the size of the substrate, and S_{laser} is the size of the laser spot. To prepare the SERS sample, 2 μL of 10^{-6} M R6G solution is dropped on the Au semishells on TiO₂ spheres ordered array substrate with a diameter about 4 mm. For the reference, 2 μL of 10^{-3} M R6G solution is dropped on a single crystal gold foil for the non-SERS measurements with the diameter about 4 mm too. Result of the comparison measurement is shown in Figure 3.7(a), from which and by combining Eq. (1) and (2) the average EF of ordered array of Au semishells on TiO₂ spheres is estimated to be 1.4×10^5 , which is comparable with the Ag semishells arrays.¹²⁸ The characteristic band at 1360 cm^{-1} was chosen for the EF estimation.

In addition to the sensitivity, the reproducibility of SERS signal is also an important parameter. Usually, nanoparticle aggregates could produce large enhancement, but the signal reproducibility is poor due to the random field distribution. It is expected that the uniform nanostructure, and hence the uniform spatial distribution of the electric field, of an ordered array endow this substrate with improved reproducibility. To test the reproducibility of our sample, SERS spectra of R6G molecules with a concentration of 10^{-6} M from 20 random-selected places on the ordered array of Au semishells on hollow TiO₂ spheres substrate were collected under identical experimental conditions. Figure 3.7 (b) shows the SERS spectra. For the strongest peak at 1360 cm^{-1} , the relative standard deviation (RSD) of the SERS intensity is about 12%. This low RSD indicates the structure and surface property of our substrate is rather uniform.

Figure 3.7 (a) SERS spectra of R6G adsorbed on the ordered Au semishells (blue) on hollow TiO₂ spheres substrate and the single crystal gold foil (red) (excited at 785 nm). (b) SERS spectra of R6G on Au semishell on hollow TiO₂ sphere array substrate from randomly selected 20 places.

3.4 Conclusions

In this chapter, a facile and new strategy for the creation of recyclable SERS-active substrates has been presented based on the ordered array of Au semishells on hollow TiO₂ spheres. The whole structure is fabricated through all scalable techniques with good control, including NSL, ALD, and metal evaporation. SERS measurements reveal that the ordered array of Au-TiO₂ composite can indeed be a high-performance SERS platform which is rather sensitive (due to nanogaps between the Au semishells), stable, reproducible (uniform arrays) and recyclable (self-cleaning enabled by the UV photocatalytic characteristics of TiO₂). The unique recyclable capability provides a new opportunity in eliminating the single-use problem of traditional SERS substrates and creates promising applications as a functional component in surface-enhanced spectroscopy and quantitative analysis.

Chapter 4

Ordered Array of Metal Particles on Semishell Separated by Ultrathin Oxide

4.1 Introduction

As addressed in the previous chapter, the major challenge to make SERS as a general analytical tool lies in the fabrication of noble metal nanostructure substrates with large and reproducible Raman enhancements over a wide sampling area, using ideally less-costly and high-throughput method.^{68, 105, 106} Among various nanofabrication techniques for SERS substrates, NSL has been widely adopted as a inexpensive and reliable method for fabricating large-area ordered nanostructure arrays.⁸⁷⁻⁹³ In particular, metal semishell arrays have been widely employed in various SERS-based biosensing applications.^{141, 142} These semishell arrays consist of ordered nanogaps between the spheres, which create plasmonic features with good control and tunability compared to random metal structures. Nevertheless, the SERS enhancement factors in previous studies are only around $10^4 \sim 10^5$.¹²⁸ This is because in most of these conventional metal array nanostructures there are only limited number of SERS 'hot spots' contributing to the Raman signal enhancement, and the metal gap size is generally still very large compared to the desirable sub-10 nm regime.^{107, 143} It is therefore desirable to further increase the SERS enhancement through increasing the density of hot spots within the same sample surfaces and/or the local field by engineering the nanostructures.

Recently it was reported that the composite metallic nanostructures can provide further local field enhancement for SERS applications.¹⁴⁴ For example, it has been demonstrated that the SERS enhancement of Ag semishell array can be further improved by an order of magnitude by constructing a nanoring cavity on top forming sub-10 nm nanogaps.¹⁴⁵ In addition, the particle-in-cavity structures, such as particle-in-void and particle-in-bowl, have been also demonstrated to produce noticeably high field enhancement at the nanogaps between the metal particles and the metal surface.^{65, 146} Overall, a further increase of SERS enhancement factors relies essentially on the formation of sub-10 nm plasmonic nanogaps. To meet this challenge, ALD is a useful tool, as its capability to provide thin films with atomic level thickness control and excellent conformality to various substrates, and has been widely employed in nanofabrication and surface engineering of photonics, energy conversion and storage materials.¹⁴⁷ Recently ALD has been also proven useful in the fabrication of novel plasmonic structures, for example, an ultrathin dielectric layer on Au nanoparticles for SINERS,⁸⁰ nanogaps in plasmonic structures.^{81, 86}

In this chapter, we employ scalable techniques of NSL and ALD to achieve highly SERS active substrates consisting of metal particles on semishell (PoSS) array. The metal particles are formed via thermal-induced dewetting of thin films. The local field enhancement of the PoSS structure is verified by both simulation and SERS measurements. This subtle designed PoSS array generates further SERS enhancement up to 10 times that of conventional metal semishell arrays. Our results demonstrate

the usefulness of nanosphere self-assembly and ALD in fabricating plasmonic sensors towards application in biomedical science and food security.

4.2. Experimental

The fabrication process for the PoSS array started with hollow TiO₂ sphere array template. The fabrication of the hollow TiO₂ nanosphere array has been described in the previous section (Chapter 3). PS spheres with size distribution 505 ± 10 nm were used in this study. Then, a ~100 nm thick Ag layer was deposited using electro-beam evaporation. After that, a thin TiO₂ layer (~5 nm) was coated on the Ag film using ALD (See Chapter 3 for details). The deposition temperature was set to be low as 60 °C to avoid oxidation of the Ag film. Following the ALD, a thin Ag layer of various thickness was sputtered (JFC-1600, JEOL) followed by thermal annealing at 120 °C in an Ar atmosphere for 30 min. The coverage of Ag particles was controlled by sputtering time at a fixed current of 10 mA. To avoid oxidation of Ag, the samples were used fresh for SERS measurements. R6G was utilized as the standard probe molecule. The PoSS substrates were immersed in R6G solution with the concentration of 0.5 µM for 30 min and then washed with deionized water and dried by N₂ flow before SERS measurement.

3. Results and Discussion

The PoSS arrays are fabricated based on hollow TiO₂ array template using thin film sputtering and ALD. The Raman and UV-vis spectra of the initial hollow TiO₂

sphere array are shown in the previous chapter (Chapter 3 Figure 3.3). The process involves the following main steps (see Figure 4.1): deposition of ~ 100 nm thick Ag layer on the TiO_2 array to form semishells; deposition of a thin (5 nm) layer of TiO_2 using ALD; sputtering deposition of a top thin layer of Ag, followed by final thermal annealing. The final heating process converted the top Ag thin film to individual particles via dewetting. In our study, the TiO_2 layer covers the entire surface of the Ag semishell array, as well as the exposed surface of initial TiO_2 spheres, with a controllable thickness down to a few nanometers. The TiO_2 layer has two functions: first, it serves as a dielectric separation of the Ag particles from the Ag semishell. Second, it protects the Ag semishells from distortion during the final thermal annealing process. The size of the coated particles can be tuned by the sputtering time. Although the metal demonstrated herein is Ag, the fabrication and main conclusion are essentially the same for gold.

Figure 4.1 Schematics of the fabrication process of the metal PoSS array. The procedure includes the following steps: 100 nm Ag film deposited on TiO_2 hollow

sphere arrays; deposition of TiO_2 by ALD; Ag sputtering; and thermal annealing.

Figure 4.2 SEM images of the PoSS array. (a) A hexagonal close-packed monolayer of Ag semishells deposited atop TiO_2 hollow spheres. Inset: an enlarged and tilted view. (b,c) the PoSS array with 25 s Ag deposition time at different magnifications. (d) 20° -tilted view of (c).

Figure 4.2a shows a SEM image of the as fabricated monolayer array of Ag semishells with a PS size of 505 nm. The final Ag PoSS structures are shown in Figure 4.2 (b-d). The underneath Ag semishells are not destroyed by thermal annealing, because otherwise discontinuous islands would be clearly seen through the 5 nm thick TiO_2 film. The particles located at the valley region between adjacent spheres should be slightly smaller than those on the top due to shadowing effect.

First of all, numerical estimation of the electromagnetic field distribution in the PoSS structure is carried out using a 3D FDTD simulation (Lumerical FDTD Solution

8.5, Inc. Canada). For simplicity the Ag particles are treated as a sphere. The outer diameter of the TiO₂ hollow sphere is chosen to be 490 nm and the thickness is 15 nm. The centre-to-centre distance of the two TiO₂ hollow spheres is set to be 505 nm. The ALD TiO₂ layer between the Ag particle and Ag semishell is set to be 5 nm. The Ag particle size is chosen to be 30 nm, and for close view simulation we set two different particles with diameters 30 and 16 nm. The Yee cell in our simulation is set to $1.0 \times 1.0 \times 1.0$ nm. These settings are sufficient to characterize the feature size of the given geometry. The dielectric constant of Ag is from Johnson and Christy,¹³⁹ and that for TiO₂ is provided by J. A. Woollam. Co. The particle in a uniform dielectric medium ($n = 1$) is illuminated from the top with a 532 nm linear polarized plane wave. Figure 4.3(a-b) shows the simulation result of the structure from the cross-sectional side view and top view, respectively. The simulation results show that the PoSS structure generates hybridized LSPs and substantial electromagnetic field enhancement between the Ag particle and the Ag film. The SERS enhancement has the fourth power relationship to the electromagnetic field enhancement as described in Chapter 1. In our PoSS structure, the simulated largest field enhancement ($|E/E_0|$) coming from the gaps is about 200, corresponding to a SERS enhancement of $\sim 10^9$. This justifies these gaps to be plasmonic hot spots, provided that they are accessible by analytic molecules. For the commonly-studied metal semishells, however, the hot spots locate merely at the edge of the shells between adjacent spheres (see Figure 4.3d). After the Ag particle coating each particle generates one more hot spot. This means the density of hot spots is significantly increased in the PoSS array structure. Another important

gap without particles; and (e) Ag particles positioned between two Ag semishells with a 5 nm TiO₂ dielectric gap. The Max in (c-e) denotes the maximum field enhancement ($|E/E_0|$) value. The red arrows in (e) mark the open hot spots that are accessible by analytic molecules in SERS measurements.

The overall field enhancement can be characterized by SERS measurement. Figure 4.4 shows the Raman spectra collected from Ag PoSS arrays obtained from 25 s Ag deposition (blue curve), and those from the bare Ag semishell array and from Ag particles directly on TiO₂ spheres without Ag semishells for comparison. One can see that the Raman signal from the Ag PoSS array shows the strongest SERS signal, which is nearly 10 times that from the bare Ag semishell array. For the Ag particles directly on TiO₂ hollow spheres, the signal intensity is drastically low. This can be explained by the small local field enhancement in the structure, as revealed by simulation in Figure 4.3c. In addition, the relatively large separation between individual Ag particles (as shown in SEM images) makes the coupling between LSP modes of the particles negligible. Hence, the coupling of additional Ag particles with the semishell gaps in our PoSS structure indeed can provide further Raman enhancement.

We note that the enhancement of Raman scattering of molecules adsorbed on semiconducting TiO₂ nanoparticles has been observed, and the origin of the enhancement was arbitrated to charge transfer contribution.¹⁴⁸ Charge transfer (CT) between the TiO₂ nanoparticles and adsorbed molecules is like that electrons of TiO₂ valance band (VB) are excited to surface state energy levels by the incident light with

the sub-band gap energy and then injected into the LUMO of the adsorbed molecules. Such a CT process requires an appropriate band match and good electrical conductivity. However, in our case the TiO_2 thin layer is an amorphous layer, and such a CT process is not expected to occur. The reported CT contribution comes from the crystalline TiO_2 nanoparticles annealed at 450 °C or above,¹⁴⁸ while in our experiment both of the ALD TiO_2 temperature (80 °C) and post annealing temperature (120 °C) are much lower, so that the TiO_2 thin layer are poorly conductive.

Figure 4.4 SERS spectra of Ag PoSS with 25 s Ag deposition (blue curve), Ag semishell array (red curve) and Ag particles directly on TiO_2 hollow spheres array (black curve).

The particle size and the subsequent SERS enhancement of the PoSS array can be tuned by the Ag sputtering time. Figure 4.5 shows the SEM images of the Ag PoSS structure fabricated using different Ag sputtering times. When the sputtering time is

elongated from 15 to 40 s, the as obtained Ag particle size increases from ~8 to 30 nm. Diffuse reflection spectra of the samples with different Ag deposition times are shown in Figure 4.5d. For comparison, the spectrum from the bare Ag semishells on TiO₂ hollow sphere arrays is also shown. The absorption edge at 380 nm observed for all the samples correspond to the bulk value (3.2 eV) of the TiO₂ band gap. The Ag semishell array substrate exhibits two broad LSPR, located at ~480 and ~630 nm, which correspond to the axial and transverse modes, respectively. This result is consistent with the previous reports on the Ag semishell array.^{128, 145} The minimum at ~560 nm (indicated by the red star) is due to the hexagonal close-packed structure.¹⁴³ The reflection spectrum of the final PoSS structure with 40 s sputtering time shows two plasmon bands at ~520 and ~620 nm. These two peaks may come from the plasmon coupling between the particle and the semishell. The PoSS structure can be regarded as the well-known ‘metal particle on metal film’ system, since the size of the Ag particles (< 50 nm) is much smaller than the size of the semishells (~500 nm). In such a particle-on-film system, it is known that there exist two plasmon modes, called horizontal and vertical modes as described in the previous report.^{149, 150} The vertical mode has lower resonance energy than the horizontal modes. The s- and p-polarized incident light excites the horizontal and vertical mode, respectively.¹⁴⁹ In our case, as the Ag particles are anchored on a curved semishell surface, both horizontal and vertical modes can be excited under a vertical incident condition. With decreasing the Ag sputtering time, both of the plasmon peaks blueshift, as a result of reduction of the Ag particle size (seen Figure 4.5a-c).

Figure 4.5 SEM images of the Ag PoSS array with different Ag deposition time: (a) 15 s, (b) 25 s and (c) 40 s. Scale bar: 200 nm. (d) Diffuse reflection spectra of the three PoSS samples, together with bare Ag semishell array sample. (e) SERS spectra of the PoSS array substrates with different Ag deposition times.

The SERS intensity is accordingly dependent on the Ag sputtering time. Figure 4.5e shows that the PoSS structures with 25 s and 40 s Ag depositions have similar SERS intensities, both significantly higher than that of the 15 s sample. The simulation result (Figure 4.3) suggests that the particles in the valley region give the dominating contribution to the SERS enhancement. Therefore, the difference in their SERS intensity in Figure 4.5e should be related to the Ag particles (both number and size) in the valley region. The size of particles will affect the strength of local field (a larger particle corresponds to a smaller size of the open hot spot), as well as the LSPR resonance frequency. The similarity between the 25 s and 40 s sample could be due to tradeoff between particle size and number of open hot spots within the valley region.

As for the 15 s sample, the drastically low Raman intensity could originate from the blueshift of the LSPR wavelength away from the excitation wavelength (532 nm), as seen from Figure 4.5d.

Finally, we estimate the SERS EF to characterize the sensitivity of a SERS substrate. EF is defined by comparing the intensity of the SERS signal with that of the non-SERS signal,¹⁴⁰ that is, $EF = (I_{\text{SERS}}/C_{\text{SERS}})/(I_0/C_0)$, for details see the previous chapter (Chapter 3.3). A typical comparison of the spectra is shown in Figure 4.6. The characteristic band at 1360 cm^{-1} was chosen for the EF estimation. In this way, the average EF can be as high as $\sim 2.7 \times 10^6$ for the PoSS structure (Ag sputtering time 25 s), which is nearly 10 times to the bare Ag semishell array ($\sim 2.5 \times 10^5$). Note that, in our previous work of Au semishells, a SERS EF of 1.5×10^5 was also obtained.

Figure 4.6 SERS spectrum of the Ag PoSS array substrate with Ag sputtering time of 25 s. The reference is a bulk Raman spectrum ($\times 10$ magnified) recorded from 10 mM R6G aqueous solution evaporated on a single crystal gold foil.

4.4 Conclusions

Assisted by the PS sphere self-assembly and ALD, we have demonstrated a controllable fabrication of novel ordered arrays of Ag particles on semishells (PoSS) with a high SERS effect. The particles are obtained via dewetting of sputtered Ag thin films and the particle size is tunable. The SERS signal from the PoSS array shows up to 10 times increase compared to the commonly-studied bare metal semishell arrays. The SERS enhancement depends on the size and number of the Ag particles, and the largest SERS enhancement factor is $\sim 2.7 \times 10^6$. The FDTD simulation reveals that the further SERS enhancement is attributed primarily to the increase of the local field and the density of plasmonic hot spots near the gap regions. The large SERS enhancement of such metal PoSS arrays suggests their potential application as functional components in chemical and biosensors.

Chapter 5

Highly-ordered arrays of particle-in-bowl composite plasmonic nanostructure for SERS

5.1 Introduction

Due to the unique specificity of Raman spectroscopy to molecules and the vibration peaks of chemical bonds, now it is one of the most promising molecule-detection techniques.^{5, 31, 151, 152} Because of the extremely small scattering cross section, Raman scattering of organic molecules is a weak process, typically in the range of $10^{-30} \sim 10^{-25} \text{ cm}^2$. SERS has been used to enhance the scattering intensity by tens of orders of magnitude.^{6, 153, 154} The chemical enhancement (CM) and electromagnetic enhancement (EM) are two mechanisms to SERS, as described in Chapter 1.^{155, 156} And the EM is considered as the predominant mechanism. It has been theoretically predicted and experimentally demonstrated that the nano gaps between sharp corners or edges of the nanostructured noble metals, are essential to exciting the LSP for SERS applications, and those nano gaps are so-called SERS “hot spots”.^{31, 32, 157-159} Due to huge enhancement of the EM field, the intensity of the Raman spectra of the molecules located at these hot spots are several orders magnitude higher than those in other places and provides the dominating contribution to the spatially averaged SERS enhancement factors (EF).⁸⁶

As described previously, a large variety of SERS-active substrates have been reported, such as metal colloidal solutions,⁵¹ fractal metal films,⁵² and nanoparticles.^{23,}

⁵³⁻⁵⁶ Benefiting from the recent advance in nanofabrication techniques, many other non-conventional nanostructures like nanotips,⁵⁹ nanobowls,^{61, 62} nanowires,^{57, 58} nanorings,⁶⁰ and nanocrescent moons have been reported for SERS application.^{63, 64} Recently people have discovered that the composite metallic nanostructure can provide further field enhancement for SERS application.^{33, 144} For example, very recently a “particle in cavity” structure has been demonstrated to produce extremely high local field enhancements because of the cascaded focusing of the optical cross sections into small gaps.⁶⁵ In such a particle in cavity structure, the local field enhancement is quite sensitive to the particle size, location and its separation from the cavity surface.⁶⁵ However, it is still remains a challenge for the production of such sub-10-nm metal gaps with precise control of the nanoscale structure, especially a uniform gap thickness. Due to the unique capability of ALD, it provides a convenient tool for the fabrication of nanogaps with precise control.^{73, 160} ALD has been recently applied for the fabrication of SERS-active nanostructure, for example, an ultrathin isolated dielectric layer on the Au particles used for SINERS,⁸⁰ and nanogap plasmonic structures.⁸⁶ Furthermore, considering the requirement of the reproducibility in practical SERS application, a large-scale ordered array is more desirable compared to individual nanoplasmonic composite structures.^{161, 162}

In this chapter, we present a simple approach for fabricating a highly-ordered Ag-particle-in-Au-bowl structure array by combining the NSL and ALD, and demonstrate the good control in the dimensional properties of the particle-in-bowl (PIB) structure array. The numerical simulation shows a prominent field enhancement at the ALD

Al_2O_3 nanogaps between Ag particle and Au bowl, which is proposed to serve as the hot spots for the high SERS EF. The measured SERS enhancement is found dependent on the Ag particle size and gap separation, which is in accordance with the simulation result. Our result provides a new approach towards ordered array of particle-in-cavity plasmonic structure and also a demonstration of the emergent application of ALD in plasmonics.

5.2 Experimental Section

ALD process: The ALD deposition was carried out on a Beneq TFS-200 system using diethyl zinc ($\text{Zn}(\text{C}_2\text{H}_5)_2$, DEZ), trimethylaluminum (TMA) and water as the zinc, aluminum and oxygen sources, respectively. The reaction chamber was maintained at 1.0 mbar with a steady N_2 steam at 200 sccm through the whole deposition process. Each half ALD cycle consisted of a 250-ms precursor pulse and 1-s purging time with N_2 . The ALD film thickness was controlled by the numbers of the ALD cycles. ZnO was deposited at 80 °C to avoid the damage of the PS sphere, and 150 cycles was used to deposit about 20 nm thick ZnO. Al_2O_3 was deposited at 200 °C with a film growth rate of 0.13 nm per cycle.

Fabrication of the particle-in-bowl structure array: The detailed procedure includes the following six steps. (1) An ordered monolayer of PS spheres (465 nm) was deposited on a glass substrate. (2) The as-deposited PS monolayers were etched to a reduced size to a proper inter particle distance by RIE. (3) About 20 nm thick ZnO film was deposited on the PS mask using ALD followed by post annealing at 450 °C

in air for one hour. (4) A ~40 nm thick Au layer was deposited on the hollow ZnO array by an Edward electron-beam evaporation system. (5) Several drops of dilute HCl solution were dropped on the substrate in order to etch away the sacrificial ZnO layer. Then the substrate was gradually immersed into the deionized water, where the Au-coated monolayer of PS spheres detaches and remains as a free-standing membrane floating on the water surface. The floating membrane was then transferred to a new substrate by attaching the new substrate with the membrane and lifting up (note that uncoated ZnO spheres face upwards after this step). (6) A thin layer of Al_2O_3 (thickness from 5 – 15 nm) was deposited on the Au nanobowl array by ALD. (7) A layer of Ag was sputtered (JFC-1600, JEOL) and then annealed at 300 °C in vacuum ($\sim 4 \times 10^{-5}$ mbar) for one hour. The coverage of Ag particles was controlled by using different sputtering time at a fixed current of 10 mA.

SERS characterization: To prepare the SERS substrates, R6G solution (2 μL , 10^{-7} M) was dropped on the substrate. For the non-SERS reference substrate, R6G solution (2 μL , 10 m M) was dropped on an Au foil surface. The Raman spectra were recorded using Renishaw Raman system.

5.3 Results and Discussion

5.3.1 Fabrication of PIB structure array

The fabrication process of the PIB structure array is shown schematically in Figure 5.1 (a). First, Au nanobowl arrays are fabricated following five steps including self-assembly of monolayer PS spheres, oxygen plasma etching, ALD ZnO coating, Au

deposition and solution-etching assisted transformation. The ALD ZnO here serves as a sacrificial layer which retains the Au bowl array structure during the transformation, but can be readily etched away by a dilute HCl solution afterwards. The Au nanobowl array is then coated with a thin layer of Al_2O_3 using ALD. Finally, an Ag layer is deposited followed by vacuum annealing at 300 °C for one hour. The annealing converts the as-deposited Ag film into a major particle at the bottom of the Au bowl due to the dewetting effect, as shown in Figure 5.1 (b). The size of the major particle was adjusted by the second metal sputtering time. Due to the cyclic self-limiting reaction characteristics of ALD, the Al_2O_3 layer uniformly covers the entire surfaces of the Au nanobowls with desirable thicknesses down to several nanometers. This Al_2O_3 layer has two functions: 1) it protects the Au nanobowls from breaking during the annealing; 2) it serves as a dielectric layer separating the Ag particle from the Au bowl with a distance of 5–15 nm. Figure 5.1(c) shows a 3D model of the hexagonal-packed PIB structure array. This method is also applicable for fabricating the Au-in-Au PIB structure array.

Figure 5.1 (a) Schematics of the fabrication procedure of the Ag-particle-in-Au-bowl structure array. Step 1: self-assembly PS monolayer; step 2: oxygen RIE etching; step 3: ALD ZnO and thermal annealing to remove the PS; step 4: Au deposition; step 5: solution etching assistant transformation; step 6: ALD Al_2O_3 ; step 7: Ag deposition and vacuum annealing. (b) Cross-section schematic shows the formation of the Ag nanoparticle by vacuum annealing. (c) Oblique view of the 3D model of the hexagonal-packed PIB structure.

Figure 5.2 (a) SEM image of the hexagonal close-packed Au nanobowl array. (c) SEM image of the Au nanobowl array after ALD Al_2O_3 and Ag deposition. (e) SEM image of the Ag nanoparticle in Au nanobowl array after vacuum annealing at 300 °C for one hour. The right column (b, d, and f) shows the corresponding high magnification images.

Figure 5.2 (a) and (b) show SEM images of the as-fabricated hexagonal close-packed Au nanobowl array using the 465 nm PS spheres. The overall size and thickness of Au nanobowls are about 500 nm and 40 nm, respectively. Figure 5.2 (c)

and (d) show the structure after the deposition of a thin Ag layer. Figure 5.2 (e) and (f) shows typical SEM images of the final PIB structure array. It can be seen that after vacuum annealing, the Ag film transforms to individual Ag nanoparticles at the bottom of the Au bowls and a few tiny particles attached on the wall. Those small particles contribute little to the electric field enhancement (see discussion below). Figure 5.3 shows the SEM images of the PIB array fabricated using different Ag sputtering times. When the sputtering time increases from 30 to 80 s, the size of the main Ag particles increase from ~140 to ~210 nm, as indicated by the red makers. The size distributions of the main Ag nanoparticles are plotted and shown in the Figure 5.4.

Figure 5.3 SEM images of the Ag particles in Au bowl array with different Ag deposition time, (a) 30 s, (b) 40 s, (c) 60 s, (d) 80 s. The makers indicate the sizes of the Ag nanoparticles.

Figure 5.4 SEM images of the Ag particles in Au bowl array with different Ag deposition time, (a) 30 s, (b) 40 s, (c) 60 s. The right column shows the corresponding size distributions of the Ag nanoparticles.

5.3.2 Numerical Simulation

To numerically estimate the electromagnetic field distribution of the PIB structure, a 3D FDTD simulation is carried out using a commercial software package (Lumerical FDTD Solution 7.1, Inc. Canada). The model of the structure is shown in Figure 5.5 (a). For simplicity, only the main particle at the bottom has been considered and the tiny particles attached on the wall are neglected. Also, the Ag particles are treated as a sphere. The outer diameter of the Au nanobowl is chosen to be 500 nm and the thickness is chosen to be 40 nm. The Yee cell in our calculation is set to $2\text{ nm} \times 2\text{ nm} \times 2\text{ nm}$ and in the gap region it is set to $0.5\text{ nm} \times 0.5\text{ nm} \times 0.5\text{ nm}$, which is sufficient to characterize the feature size of the given geometry. The dielectric constant of Au is from Johnson and Christy,¹³⁹ and those for Ag and Al_2O_3 are from Palik (supplied by Lumerical FDTD Solution 7.1, Inc. Canada). The particle in a uniform dielectric medium ($n = 1$) is illuminated from the top with a 532 nm linear polarized plane wave, as shown in Figure 5.5 (a). Figure 5.5 (b-g) shows the simulation results of the structure with thicknesses of the Al_2O_3 separation layer ranging from 5 to 15 nm. Simulation results with different Ag nanoparticle sizes (from 140 to 210 nm) are shown in Figure 5.6. The simulation results show that the PIB structure generates LSP and substantial electromagnetic field enhancement. It is noted that under the normal incident condition, the strong field enhancement occurs in the area near to the contact point between the Ag sphere and the Al_2O_3 layers. These open areas are known as hot spots for SERS. The local field enhancement is sensitive to the gap size between the Ag particle and Au bowl, which lowers when the gap size

increases from 5 to 15 nm (see Figure. 5.6 b-d). In addition, with a fixed gap size of 5 nm, it is found that the structure with a 160 nm Ag particle gives the largest field enhancement (see Figure 5.7). To investigate the contribution of the small Ag particles attached on the wall, the field distribution of one 60 nm Ag particle attached on the side of Au bowl with a separation of 5 nm was simulated under the same condition (See Figure 5.6 e). The largest field enhancement from such structure is about 2706 ($|E/E_0|^2$), much smaller than that from the 160 nm particle located at the bottom of the bowl with a value of 14267 ($|E/E_0|^2$).

Figure 5.5 3D-FDTD simulations of a single Ag PIB nanostructure. (a) A view of the simulation model; (b-d) Cross-section views of the simulation results with different gap distances. (e-g) The corresponding enlarged view of the field distributions at the contact areas. The *Max* in (b-d) denotes the maximum field enhancement ($|E/E_0|^2$) value.

Figure 5.6 (a-d) Cross-section views of the simulated field distributions of the PIB structures with different Ag nanosphere size from 140 to 210 nm. (e-f) Simulated field distribution of the 60 nm Ag nanoparticle located at the side of the Au bowl.

5.3.3 SERS Characterization

In order to characterize the SERS performance of the PIB structure array, R6G is utilized as the probe molecule. The Ag particle size, as determined by the Ag sputtering time, is an important factor influencing the SERS EF. Figure 5.7 shows the Raman spectra collected from substrates with various Ag particle sizes but a constant Al_2O_3 gap distance of 5 nm. One can see that the substrate with 40 s Ag deposition

time (corresponding to an average Ag particle size ~ 160 nm) shows the strongest SERS signal. This is in good consistency with the numerical simulation.

Figure 5.7 Measured SERS spectra of the PIB nanostructure array treated by R6G at 10^{-7} M with the main variable of Ag deposition time.

In metal plasmonics, it is well known that the nanogap size affects drastically the electric field enhancement, and subsequently the SERS EF. Figure 5.8 shows the result from a control experiment where the Ag sputtering time was fixed to 40 s but the ALD Al_2O_3 layer thickness was varied. Obviously, the SERS intensity decreases dramatically upon the increase of the Al_2O_3 thickness from 5 to 15 nm. This is quite within expect, as the plasmon coupling between the local plasmons of the Ag particle and the Au bowl is most strong with a gap size down to sub 10 nm. It has been reported that an Ag film can be used to modify the Au nanocavity array and improve the SERS EF.¹⁶³ To check this, we conducted a comparison study of the SERS performance of the Ag film covered Au bowl array (i.e., without annealing). The

result (see Figure 5.8) shows that the SERS intensity of the Ag film substrate is significantly weaker than those of the PIB substrates. Hence, it is proven that the particles should be much more effective than a film in improving the local electric fields of the Au nanobowl array.

Figure 5.8 SERS spectra of PIB nanostructure array with different thicknesses of the ALD Al_2O_3 separation layers.

The sensitivity of a SERS substrate is characterized by the enhancement factor (EF). EF is defined by the following equation (see Chapter 3.3 for details),¹⁴⁰

$$\text{EF} = (I_{\text{SERS}}/C_{\text{SERS}})/(I_0/C_0)$$

where I_{SERS} and I_0 are the intensities of the selected scattering bands in the SERS and non-SERS spectra, respectively. C_{SERS} and C_0 are the molar concentration of R6G molecules in the aqueous solution used in the dipping step, and that of R6G for non-SERS spectra evaporated on a planar gold surface, respectively. Result of the comparison is shown in Figure 5.9. The characteristic band at 1360 cm^{-1} was chosen

for the EF estimation. In this way, the average EF can be as high as $\sim 3.8 \times 10^7$ for the PIB structure array with the Ag particle size of 160 nm and the Ag to Au gap size 5 nm. It should be noted that the SERS EF is spatially averaged over the entire laser focal spot. However, since molecules located in the non-Ag-Au approximate areas contribute little to the overall enhancement, the estimated SERS EF originates dominantly from the hot spots. Figure 5.10 shows the comparison of the estimated SERS EF from experiment and the simulated electromagnetic field enhancement of the PIB structure array. It can be seen that an overall good agreement is achieved, namely, the trends of the EF with the gap size and Ag particle size are the same, and the PIB structure array with a 160 nm Ag particle and 5 nm Al_2O_3 separation layer gives the largest SERS EF. Quantitative deviation between the simulation and experiment might come from the non-spherical shape of the Ag particles and surface roughness. In addition, it is noted that the evident enhancement corresponds to Ag particles larger than 130 nm, which means those smaller particles (<100 nm, see Figure 3) can be neglected for the EF estimation. In addition, it is noted that the evident enhancement corresponds to Ag particles larger than 130 nm, which means those smaller particles (<100 nm, see Fig. 3) on the wall contribute little to the total SERS enhancement.

Figure 5.9 SERS spectrum of the PIB with Ag deposition time of 40 s. The reference is a bulk Raman spectrum recorded from 10 mM R6G aqueous solution evaporated on a single crystal gold foil and has been magnified 10 times.

To test the reproducibility of our sample, SERS spectra from 15 random-selected places on the ordered array of PIB nanostructure substrate were recorded under identical experimental conditions Figure 5.11. For the Raman peak at 1360 cm⁻¹, the relative standard deviation (RSD) of the SERS intensity is about 11%. This low RSD indicates the structure and surface property of our substrate is reasonably uniform

Figure 5.10 Comparison of the estimated SERS EF and the simulated field enhancement of the PIB structure array substrate: (a) with different Al_2O_3 separation layer thicknesses; (b) with different Ag particle sizes. For the field enhancement from simulation, the largest $|E/E_0|^4$ values are chosen corresponding to the Max values in Figure 5.5 and 5.6.

Figure 5.11 SERS spectra of R6G on PIB structure array substrate from 15 randomly selected positions. Ag deposition time was 40 s and the Al_2O_3 separation layer is 5 nm thick.

5.4 Conclusion

Assisted by the nanosphere self-assembly and ALD, a simple process has been demonstrated for the controlled and reproducible fabrication of a novel ordered array of particle-in-bowl plasmonic nanostructures for SERS. The SERS enhancement is found to increase dramatically with the reduction of the separation layer thickness, which is due to increased plasmonic coupling. In addition, among various Ag particle sizes, the largest enhancement, with a SERS EF $\sim 3.8 \times 10^7$, comes from the PIB structure with ~ 160 nm Ag particles (when the gap thickness is fixed to 5 nm). Numerical simulations of the field distribution are also studied and the result is in good agreement with experiments. This fabrication method can be applied to fabricating other metal-based PIB structures in optimized dimensions towards a higher level of SERS EF. It is proposed that such ordered PIB plasmonic arrays are useful as functional components in high sensitive spectroscopy and biosensors.

Chapter 6

Application of ALD in other nanofabrication

6.1 ALD ZnO on multi-walled carbon nanotubes (MWCNT) and 3D ZnO Nanostructures

6.1.1 Introduction

CNT and inorganic composite materials have attracted much attention recently due to their potential application such as in photocatalyst, gas sensors, supercapacitors, and field emission devices.¹⁶⁴ Compared to the individual constituents, it has been reported that the optical and electrical properties of CNT–inorganic composites can be enhanced.¹⁶⁵ For example, when CNT films were employed as conducting scaffolds in a TiO₂ based photoelectrochemical cell, the photoconversion efficiency showed an enhancement by a factor of two.¹⁶⁶

CNT-ZnO represents one of most important members of the CNT-inorganic composites family, as ZnO is a n-type semiconductor with a direct wide band gap (3.37 eV) and large exciton binding energy (60 meV).¹⁶⁷ For example, an ultrafast nonlinear optical switching behaviour has been observed from ZnO coated CNTs.¹⁶⁸ The coaxial heterostructured nanotubes with a p-channel CNT combined with an n-channel ZnO shell may be integrated into logical inverters.¹⁶⁹

So far, various synthesis strategies towards CNT-inorganic hybrids have been established based on physical and chemical process, as summarized in recent review

articles.¹⁷⁰ ALD is capable of conformal and uniform deposition of thin films at atomic level, which been applied to coat various non-planar high-aspect-ratio substrates with a variety of materials including oxides and metals.⁷³ ALD coating on CNTs has been an interesting topic. However, compared to ALD on inorganic or polymers nanostructures, there are relatively few reports. Continuous amorphous Al_2O_3 layers deposited on CNTs has been reported by Kim *et al.*¹⁷¹ However, as for direct ALD ZnO on CNTs, the so-far available reports show only ZnO nanoparticles or morphological poor-defined ZnO layer. While such tube-particle structure is shown useful for field emission applications,¹⁷² more homogeneous coatings are desirable for CNT-based photonic devices. Kim *et al.* achieved relatively smooth ZnO coating on CNT using a thin ALD Al_2O_3 buffer layer.¹⁷³ However, the existence of an Al_2O_3 buffer layer breaks the direct contact of ZnO to CNTs and thus prevents the charge transfer, a process needed for functions of photoelectrochemical cells. Furthermore, the low optical quality of such ZnO layer, as seen from the weak UV emission, will hinder the photonic application of such hybrid nanostructures.¹⁷³

Here, we demonstrate the direct ALD of ZnO on vertical aligned multiwall carbon nanotube arrays. The resulting ZnO layers have a well defined morphology and higher smoothness compared to discontinuous nanoparticles in previous reports. We also demonstrate that the as deposited ZnO layer can be used as seed layer for the hydrothermal growth of ZnO nanorods (NRs). This provides a new method for the fabrication of ZnO NRs based three-dimensional (3-D) hybrid nanostructures, which

might be useful as photoelectrochemical anode materials. The PL properties of the ZnO coated CNTs and CNT-ZnO 3-D nanotrees will be discussed.

6.1.2 Experimental

ALD ZnO: The vertical aligned MWCNT arrays were grown by plasma-enhanced chemical vapour deposition (PECVD) reported elsewhere.¹⁷⁴ ALD of ZnO was carried out on a Beneq system (TFS 200) using Diethylzinc ($\text{Zn}(\text{C}_2\text{H}_5)_2$, DEZ) and water as the zinc and oxygen source, respectively. High purity N_2 was used as the process gas in our experiment. The reaction chamber was maintained at 1.0 mbar with a steady N_2 steam at 200 sccm during the whole deposition process.

Each ALD cycle consisted of a 250-ms precursor pulse and 10-s purging time with N_2 . The relatively short precursor exposures and long purging times were adopted in order to achieve uniform coatings on the closely stacked CNTs arrays. The shell thickness was controlled by the numbers of the ALD cycles. A typical deposition consists of 80 ALD cycles. For ALD of alumina (Al_xO_y), trimethylaluminum [$\text{Al}(\text{CH}_3)_3$] and water were used as aluminum and oxygen source, respectively. A thickness of 7 nm was obtained

from 60 cycles.

Hydrothermal growth ZnO NRs: Vertical aligned ZnO NRs were grown using the standard hydrothermal method. The ALD ZnO coated CNT substrates were immersed into a 35 mL aqueous solution of equimolar zinc nitrate and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) in an autoclave. The reaction was conducted at 95 °C for 5 h. After

reactions, the substrate was removed from the solution, rinsed with deionized water, and dried with N₂ blow.

Characterizations: The morphology of the as-fabricated samples was characterized with a JEOL JSM-6700F field emission scanning electron microscope (FESEM) and a JEOL JEM-1400 F transmission electron microscope (TEM). Photoluminescence (PL) measurements were carried out with a Renishaw system using 325 nm laser as the excitation source.

6.1.3 Results and discussion

The TEM image of the typical morphology of the PECVD CNTs prior to deposition is shown in Figure 6.1 (a). Most of the CNTs are multiwall tubes, and the average diameter of the CNTs is ~7 nm. Figure 6.1(b) shows the typical TEM image of the CNTs after ALD ZnO coating. It can be clearly seen that the as deposited ZnO shell is continuous and uniform along the tube. The thickness of ZnO shell is about 18 nm, corresponding to a growth rate of 0.22 nm per cycle. Such a growth rate is in consistent with the regular ALD ZnO process.^{175, 176} Figure 6.1 (d) and (e) show the SEM images of the ALD ZnO on aligned CNTs. One can see that the ALD process did not affect the overall alignment of the CNTs, and all the CNTs on the substrate were coated with a ZnO shell. For comparison, the result of ALD of 7 nm Al₂O₃ on the same CNTs is shown in Figure 6.1(e). The amorphous Al₂O₃ layer exhibits a long range smoothness and continuity as expected.

Figure 6.1 (a) TEM image of PECVD-grown CNTs. (b) TEM image of ALD ZnO-coated CNTs. (c) and (d) SEM images of ALD ZnO-coated CNTs. (e) TEM image of ALD Al_2O_3 -coated CNTs.

There are several factors that affect the morphology of the ALD ZnO layer deposited on CNTs. The first one should be the surface configuration of the CNTs. As a micromolecular form of carbon, CNT can be regarded as graphitic layers (sp^2 -hybridized carbon atoms) rolled up into a cylindrical form, thus a perfect CNT is chemically inert. However, there generally exist defects on the tube wall, such as bending in the nanotube, the finite size of crystalline domains, sp^3 -hybridized bonds, or functional groups created by oxidation.^{177, 178} Those defects or function groups make the CNT surface reactive to the atomic species of an ALD precursor. The Raman spectrum of the PECVD CNTs (Figure 6.2 curve a) shows a strong D band, indicating the existence of defects on the tube wall. The second factor is the ALD

processing parameters. It is known that one ALD cycle is consisted of two half-chemical reactions. After each-half cycle, the excess precursor needs to be purged out; otherwise it will contribute to a CVD reaction. The growth rate of the deposition should be higher than a regular ALD process if the CVD reaction occurs during the ALD process,. In our experiment, in order to exclude the unwanted CVD reaction we used short precursor exposures and long purging times. The growth rate of ALD ZnO in our experiment is comparable to the previously reports based on DEZ and water,¹⁷⁵ indicating that there is little CVD reaction in our case. Furthermore, the alignment of CNTs also matters. Note that in previous report, the authors used randomly oriented MWCNTs for ZnO ALD.^{173, 179} Compared to the vertical-aligned CNTs in our study, there is much less free space between the tubes, which makes the purge of the excess ALD precursors after each semi-cycle more difficult. Subsequently, additional CVD reactions may occur. This could explain why only poor-defined ZnO agglomerates were observed on CNTs in previous work. It is also noted that the growth rate (0.35 nm/cycle) was much higher than the regular ALD process (0.22 nm/cycle), further implying the occurrence of additional CVD reactions in their experiment.¹⁷³ In our experiment, we used vertical-aligned MWCNTs and a longer purge time to exclude possible CVD reactions. This contributes to the improved conformity and uniformity of ALD ZnO.

Lastly, the growth of ZnO tends to crystallize and texture along *c*-orientation even at low temperatures. An uncompensated polarity exists in ultrathin ZnO films as predict from the first principles simulations.,¹⁸⁰ The involvement of polarity of ZnO

nanoclusters during the ALD process explains why the ZnO shells are not as smooth as the amorphous Al_2O_3 on CNT, as seen from the TEM image (Figure. 6.1e) and previous reports.^{171, 173}

Figure 6.2 (a) Raman spectral of CNTs before (curve a) and after (curve b) ALD of ZnO. (b) PL spectra of ALD ZnO coated CNTs. Insert (a): Raman spectrum in the range of $150\sim 650\text{ cm}^{-1}$ of ZnO coated CNTs.

Figure 6.2 (a) shows the Raman spectra of CNTs prior to (curve a) and after (curve b) ALD ZnO. It can be seen a G band appears at about $\sim 1580\text{ cm}^{-1}$ corresponding to sp^2 -hybridized carbon and a D band at $\sim 1346\text{ cm}^{-1}$ originating from disordered carbon.^{177, 178} In addition to the D band, the D' band as a shoulder of the G band appears at about 1614 cm^{-1} , which also originates from the disorder features due to the finite size effect of the crystalline domain or lattice distortion.¹⁷⁸ The intensity ratio of the D' over the G band ($I_{D'}/I_G$) increases with a decrease in the graphite crystalline domain. The D band and D' band peak are very strong, indicating that the CNTs we used has a considerable number of defects on the surface. After ALD ZnO, those D, D' and G band peaks changed only slightly. Additional Raman peaks from the ZnO shells appeared; the relatively strong peaks at 427 and 567 cm^{-1} correspond

to E_2^{high} and A_1 (LO) modes, respectively, and the peaks at 199, 321 and 1106 cm^{-1} attributed to $2E_2^{\text{low}}$, $E_2^{\text{high}}-E_2^{\text{low}}$ and 2LO, respectively. Those Raman peaks are in consistent with the previous reports of ZnO.¹⁸¹

The room temperature PL spectrum of ALD ZnO coated CNTs is shown in Figure 6.2 (b), in which the UV emission peak at about 390 nm (3.18 eV) corresponds to the near-band-edge emission of ZnO crystal. In addition to the UV emission, a broad visible emission peak is also observed, which appears to consist of two main components at ~560 nm and ~630 nm. The peak positions are similar to the PL of ZnO nanowire reported by Fan *et al.*¹⁸² It is generally believed that the visible emission of ZnO is due to the transition in defect states. Emission in the green spectra range is the most commonly observed defect emission in ZnO nanostructures and several different hypotheses have been proposed to explain this green emission, which is still under debate.^{183, 184} The orange-red emission is most often associated with oxygen interstitial.¹⁸⁵ Compared to the only available report so far on PL property of ALD ZnO,¹⁷³ the UV to visible emission ratio of our sample is significantly higher. That might be due to the high crystalline quality of the ZnO shell in our case.

Figure 6.3 (a) schematics of growth processes, (b) SEM images, and (c) PL spectrum of the CNT-ZnO 3-D hybrid nanostructure. Insert: large magnification SEM image.

Low-temperature hydrothermal growth is a popular method for synthesizing ZnO nanorods on various types of substrates. Hierarchical heterogeneous nanostructures can be realized based on hydrothermal growth of ZnO on nanostructured substrates.¹⁸⁶⁻¹⁸⁸ A prerequisite for ZnO hydrothermal growth of NRs is the seed layer, and the quality of the seed layer (e.g., crystallinity, smoothness, orientation). Here we demonstrate that the deposited ZnO shell can also be used as seed layer for hydrothermal growth of ZnO NRs on CNTs, without any further annealing process. Figure 6.3(a) schematically shows the growth processes of the CNT-ZnO 3-D hybrid structure. Figure 6.7 (b) shows the SEM images of the synthesized CNT-ZnO 3-D structure. The densely packed ZnO NRs are aligned roughly perpendicularly to the axis of the tubes. The size of the branched ZnO NRs is about 30 nm in the diameter and several hundred nm in length.

Figure 6.3 (c) shows the room temperature PL spectrum of CNT-ZnO 3-D hybrid structure. It shows a strong UV peak positioned at 385 nm with full width at half maximum (FWHM) of about 21 nm and a low and broaden peak in the visible range.

This is consistent with the generally obtained PL spectra of ZnO NRs growth by hydrothermal methods.¹⁸⁶ Compared with the ALD ZnO seed layer on CNTs, the UV emission intensity and the ratio of UV/visible peak of the CNT-ZnO 3-D hybrid structure is much higher. This is not surprising as the ZnO NRs are single crystalline while the ALD ZnO is a polycrystalline thin layer.

This method can be also applied on other 3D templates to fabrication ZnO NRs based 3D nanostructures, i.e. PS monolayers and Si pillars. Figure 6.4 (a) and (b) show the SEM images of an urchin like ZnO NRs architecture. It has been demonstrated the light scattering of the urchin-like ZnO NR based thin films is strongly improved compared to ZnO NR thin films grown on flat substrate.¹⁸⁹ Thus the urchin-like ZnO NR based thin films may find its application in nanostructured solar cells. Figure 6.4(c) shows the SEM image of the ZnO nanorods growth on a Si nanopillars arrays forming a ZnO/Si nanotree structure. After Ag-nanoparticle decorated, the ZnO/Si nanotree structure can be used as SERS substrate.¹⁹⁰

Figure 6.4 SEM images of ZnO NRs grown on (a,b) PS monolayer and (c) Si nanopillars. (d) Shows the SEM image of the Ag-nanoparticle-decorated ZnO/Si nanotrees used for the SERS application.

6.1.3 Conclusion

Direct ALD of ZnO thin layers on PECVD-grown CNTs have been successfully achieved. The deposited ZnO shell was found to be continuous and uniform along the tube. Raman and PL studies reveal that the ZnO shells are of reasonably good crystalline quality. Based on results of structural and optical characterizations, the ALD ZnO directly coated on CNTs are of improved quality compared to previous reports. Also we have demonstrated that the ALD ZnO can be used as seed layer for hydrothermal growth of ZnO NRs on CNTs, forming a CNT-ZnO nanotree structure, which are useful materials for electronic or energy-related applications. Using this strategy, various ZnO NRs based 3D nanostructures can be fabricated.

6.2 ALD of Fe_2O_3 using ferrocene and ozone precursors, and Ti doping

6.2.1 Introduction

As one of the most common form of iron oxide, hematite ($\alpha\text{-Fe}_2\text{O}_3$) has emerged as a promising photoelectrode material due to its favourable optical band gap (~ 2.2 eV), chemical stability in aqueous environments, sample abundance and low cost.¹⁹⁰⁻¹⁹⁵ Recently hematite has attracted more and more attention in energy applications such as photoelectrochemical cells for solar fuel generation.^{192, 195, 196} The theoretically predicted solar-to-hydrogen efficiency based a semiconductor with this band gap can achieve a value of 16.8%.¹⁹⁶ However, the experimental efficiencies of $\alpha\text{-Fe}_2\text{O}_3$ are notoriously lower than the predicted value. Such poor performance was primarily attributed to very short hole diffusion length (~ 10 nm) compared to the light penetration depth of several hundred nanometers.^{194, 195, 197} One possibility to overcome the drawback is to have non-conventional photoelectrode design, which is characterized by both short charge-collection distances and high surface areas. Such design will require techniques for controllable coating on pre-structured nano templates. For this purpose, ALD stands out to be a most convenient method due to its capability of conformal coating on arbitrary-shape surfaces and atomic level control in film thickness. ALD is based on cyclic self-limiting deposition reactions that prevent precursor reaction above the substrate surface. Owing to the self-limiting nature of ALD, various nanostructures, such as nanoparticles, nanotubes, nanowires, can be coated with oxides and nitrides thin films, or metal nanoparticles that are not

achievable by conventional physical or CVD method.^{73, 160, 198} The obtained low-dimensional nanostructures have been demonstrated in a wide range of applications, including catalysis, microelectronics, energy storage and conversion and sensing.^{146, 161, 198-201}

The first report of ALD α -Fe₂O₃ film was done by using ozone (O₃) and *tris*-(2,2,6,6-tetramethyl-3,5-heptanedionate)iron-(III) (Fe(thd)₃) as precursors.²⁰² However, the small growth rate (0.1 Å/cycle) and the low iron precursor vapour pressure limit its applicability to high aspect ratio structures. Subsequent reports of Fe₂O₃ deposition via ALD using ferrocene (Fe(Cp)₂) and oxygen as precursors required high temperatures (350~500 °C).^{203, 204} Also, ALD Fe₂O₃ using tertbutoxide (Fe₂(OtBu)₆) and water occurs only in a narrow temperature window between 130 and 170 °C and incites lots of carbon incorporation.²⁰⁵ Recently, Martinson and co-workers reported ALD Fe₂O₃ using O₃ and Fe(Cp)₂ with a modulated lower temperature window (200~350 °C) and it was capable of coating Si microtrenches with aspect ratio ~150 using longer dosing time.²⁰⁶ The self-limiting growth kinetics and surface reaction mechanism were elaborated therein. On the other hand, it was reported that ALD Fe₂O₃ using Fe(Cp)₂ and O₃ may show a decrease in growth rate after the first hundreds cycles,²⁰⁷ thus elongating the overall deposition time. For the consideration of practical application of ALD Fe₂O₃, it is desirable to have a shortened dosing time and linear growth mode (i.e., film thickness is proportional to the cycle number).

Here, we describe a micro-pulse ALD process for growing Fe_2O_3 using $\text{Fe}(\text{Cp})_2$ and O_3 precursors and we explore the possibility of Ti doping. Compared to the previous report, the micro-pulse process exhibits a combination of lower precursor exposure and purge time, effectively faster growth speed, and capability of coating on high aspect ratio nanotemplates (nanorods and nanochannels). By introducing TiO_2 co-deposition, the commonly-observed nonlinear growth rate of Fe_2O_3 can be prevented, and simultaneously, a controllable Ti doping into Fe_2O_3 films can be achievable by adjusting the ALD cycle ratios of TiO_2 and Fe_2O_3 . For their potential application in photoelectrochemical cell and lithium-ion batteries, uniform coating on non-planar substrates have also been attempted with success.

6.2.2 Experimental

ALD of Fe_2O_3 and TiO_2 : ALD Fe_2O_3 was carried out on a Beneq TFS-200 system using $\text{Fe}(\text{Cp})_2$ (purchased from Aldrich, >98%) and O_3 (~300 sccm ultrahigh purity O_2 , BMT 830N) as the iron and oxygen source, respectively. The $\text{Fe}(\text{Cp})_2$ precursor was contained in a stainless steel bottle maintained at 65 °C, while the reaction chamber was maintained at 250 °C. High purity N_2 gas was used as the process gas in our experiment. The reaction chamber was maintained at 2 mbar with a steady N_2 steam at 250 sccm during the whole deposition process. In the micro-pulse process, the exposure time equals to the pulse time multiplied by the pulse numbers. Typically each $\text{Fe}(\text{Cp})_2$ exposure consists of $100 \times (100 \text{ ms filling of } \text{N}_2 + 100 \text{ ms wait time} + 100 \text{ ms pulse time})$, so that the exposure time for is $100 \text{ ms} \times 100 = 10 \text{ s}$. During such

exposure process the pressure of $\text{Fe}(\text{Cp})_2$ is maintained at about 13 mbar, as shown in Figure 6.5(a). Each O_3 precursor exposure consists 100×100 ms pulse time. Between the $\text{Fe}(\text{Cp})_2$ and O_3 exposure a 20-s purge with N_2 was used. The flow chart of precursor sequences of the micro-pulse process is shown in Figure 6.5(b). For convenience, the ALD timing sequences was expressed as t_1 - t_2 - t_3 - t_4 , where t_1 is the exposure time for $\text{Fe}(\text{Cp})_2$, t_2 is the purge time following the first exposure, t_3 is the exposure time for O_3 , and t_4 is the purge time following the second exposure. ALD of TiO_2 used TiCl_4 and H_2O as the precursors, and the precursor exposure time was 200 ms for both TiCl_4 and H_2O with 1 s N_2 purge in between.

Figure 6.5 (a) *In situ* $\text{Fe}(\text{Cp})_2$ pressure results during the micro-pulse process. (b) Flow chart of the precursor delivery for the micro-pulse process for Fe_2O_3 deposition.

Photoelectrochemical Measurements: The PEC performance of the electrodes was carried out in a three-electrode configuration under back-side simulated AM 1.5G illumination using a potentiostat (CHI760D, CH Instruments). Ag/AgCl in saturated KCl (+0.197V vs. normal hydrogen electrode, NHE) and a Pt foil were used as

reference and counter electrodes, respectively. The electrolyte used was a 1 M NaOH solution. The photoresponse was measured under chopped irradiation from a 150 W Xe lamp (Sciencetech SS150) equipped with an AM 1.5G filter, calibrated with a standard Si solar cell to simulate AM 1.5 illumination (100mWcm^{-2}).

6.2.3 Results and Discussion

Due to the self-limiting nature ALD, it is capable of conformal and uniform coating on both planar surface and high aspect ratio structures with an atomic control of thickness. A true ALD process (i.e., without CVD side reaction) will exhibit saturated surface reactions. Therefore, with increasing precursor exposure, it will appears a plateau in the growth rate. For the micro-pulse process in this study, the dose time equals to pulse time multiplied by the pulse. Figure 6.6(a) shows the Fe_2O_3 growth rate at 250°C to the exposure time. The ALD growth rate was calculated from the Fe_2O_3 thin film on Si (100) substrate with 200 cycles. The film thickness was determined by spectroscopic ellipsometry. It can be clearly seen that after a dose time of 5 s, the growth rate curve start to saturate with a plateau, in good accordance to the self-limiting characteristics of an ALD reaction. The curve can be fit to a Langmuir adsorption model, $Q = Q_m Kt / (1 + Kt)$, where Q is the growth rate, Q_m is the maximum growth rate, K is the Langmuir coefficient, and t is the dose time.

The fitting results in $Q_m = 0.5$, $K = 1.5$. The saturate growth rate, $0.5 \text{ \AA/cycle}$ is comparable to the previous report by Thomas et al. ($0.6 \text{ \AA/cycle}$),²⁰⁷ but smaller than that ($1.4 \text{ \AA/cycle}$) in the recent report by Martison et al.²⁰⁶ However, in their work the threshold exposure time for $\text{Fe}(\text{Cp})_2$ was 40 s and for ozone was 200 s, both much

longer than what we used (typically 10 s). Therefore, considering the shorter exposure and purge times, the overall growth speed in our experiment is effectively higher, which is 80 s for one full cycle (including 20 s N₂ purge). For the application in photoelectrochemical cells, in which the typical film thickness is around 10 nm, thus the film growth rate in our study is fairly acceptable. The reduction of the threshold exposure time could be related to micro-pulse process; the precursors enter the reaction chamber with a periodic disturbance, so that the gas flow passes over the surface like a wave. As a result, the adsorption of precursors on the sample surface is improved.

Figure 6.6 (a) Fe₂O₃ growth rate at 250 °C to dose time with 200 ALD cycles. The ALD growth rate was calculated based on the Fe₂O₃ film on Si substrate located at the centre of the reaction chamber during a single run. The solid line is the fit to the Langmuir adsorption model (see text). (b) Fe₂O₃ film thickness on Si substrate versus the number of Fe(Cp)₂/O₃ cycles using the dosing time of 10-20-10-20 (black curve). Shown also is the same plot for TiO₂ co-deposition with a cycle ratio of TiO₂/Fe₂O₃ = 1: 20 at 250 °C (blue curve).

A true ALD deposition is also characterized by a linear growth mode, i.e., film thickness is proportional to the cycle number. In our experiment, linear growth is observed on Si (100) substrate for the first 300 cycles with both $\text{Fe}(\text{Cp})_2$ and O_3 dosing time of 10 s (Figure. 6.6b), and the growth rate is calculated to be 0.5 Å/cycle. After 300 cycles, the growth rate decreases and film thickness increases only slightly with further more ALD cycles. This phenomenon has been observed in the previous report by Thomas et al.²⁰⁷ One possible reason for the growth rate reduction is the decomposition of the $\text{Fe}(\text{Cp})_2$ precursor. It has been reported that the decomposition of $\text{Fe}(\text{Cp})_2$ can be accelerated due to Fe- and C-coated vessels.²⁰⁸ Therefore, a self-catalytic process can occur such that the decomposition product (containing Fe and C) might, in turn, accelerate the decomposition of $\text{Fe}(\text{Cp})_2$ itself. Thus, the decomposition rate increases with ALD cycle number, resulting in a nonlinear growth. Interestingly, we found here that, by introducing one cycle of TiO_2 using TiCl_4 and H_2O after each 20 Fe_2O_3 cycles, a linear growth can be obtained up to 600 cycles, resulting in a film thickness of 33 nm (see Figure. 6.6b). This linear growth could be related to an elimination of the self-decomposition of $\text{Fe}(\text{Cp})_2$. The one-cycle TiO_2 layer might passivate the chamber and substrate surface and therefore retard the autocatalytic decomposition process. Therefore, the TiO_2 co-deposition can effectively maintain a constant growth rate, even at high cycle numbers. In the meantime, it also provides the opportunity for controllable Ti-doping by adjusting the cycle ratio of TiO_2 and Fe_2O_3 .

Figure 6.7 Distance dependence of the ALD growth rate inside the reaction chamber.

Triangle curve (blue): Fe₂O₃ film thickness measured at different locations away from the precursor inlet and along the precursor flow direction. Circle curve (red): Fe₂O₃ film thickness at different locations away from the centre and perpendicular to the precursor flow direction. The precursor dosing time is 10-20-10-20 and cycle number is 200. Deposition temperature is 250 °C.

It has been reported that ALD of Fe₂O₃ using Fe(Cp)₂ and O₃ shows a distance dependence of the growth rate.²⁰⁶ This phenomenon was also checked and confirmed in our experiment, as shown in Figure. 6.7. Along the precursor flow direction, the growth rate exhibits a slight decrease, flat and further decrease trend at positions measured away from the inlet point. The uniform range is about 16 cm, ~75% of the chamber diameter. Along the direction perpendicular to the precursor flow, the uniform range is about 12 cm, ~60% of the chamber size. Several mechanisms have been proposed to account for such distance dependence.²⁰⁶ One of them is related with the decomposition of precursors in the reactor chamber. The decomposition may

produce precursor concentration gradient, so that the precursor concentration in the gaseous phase drops both along the flow direction and in the perpendicular direction away from the centre. The lower gradient regions will have a lower growth rate. In addition, a catalytic decomposition of ozone over the Fe_2O_3 surface is also possible, which will also generate an O_3 concentration gradient away from the chamber centre.²⁰⁹

Figure 6.8 Growth rate of Fe_2O_3 films on Si (100) versus the deposition temperature (200 cycles) using the dosing time 10-20-10-20. The potential ALD window for Fe_2O_3 growth is indicated. Inset: Photograph of Fe_2O_3 film deposited on a glass slide at 250 °C.

In order to evaluate the ALD temperature window, Fe_2O_3 films were deposited in the temperature range from 160 to 325 °C. The precursor exposure time was fixed at 10 s. Figure 6.8 shows the dependence of growth rate on deposition temperature. It clearly shows that for temperatures higher than 200 °C the growth rate shows a plateau, while when the temperature lowers to 160 °C there is barely ALD growth.

Deposition at temperatures higher than 325 °C was not attempted, as it reaches the ALD temperature of $\text{Fe}(\text{Cp})_2$ and oxygen for Fe_2O_3 .²⁰⁴ Therefore, in our study the ALD window can be expected at 200~325 °C, similar to the previous report.²⁰⁶ Photograph of one representative sample of the as-deposited Fe_2O_3 film on glass substrate (Figure 6.8 inset) shows a red-orange colour.

X-ray Photoemission spectroscopy (XPS) was used to verify the Fe_2O_3 phase and Ti incorporation. Figure 6.9 (a, b) shows the survey scan from both pure and TiO_2 co-deposited ALD Fe_2O_3 films. Both spectra show the same features of Fe_2O_3 in Fe 2p and the existence of O, but only the TiO_2 co-deposited sample show the Ti element. The details of the Ti 2p peak are shown in Figure 6.9 (c). The binding energies of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ are observed at 464.3 and 458.5 eV, respectively, indicating a normal state of Ti^{4+} in the anatase TiO_2 .²¹⁰ Therefore, it could be inferred that the one cycle TiO_2 co-deposition has little effect on the chemical state of Fe. The increase in the Fe_2O_3 growth rate (Figure. 6.9b) could be due to the addition of TiO_2 itself, which was excluded in the calculations of growth rate.

Figure 6.9 (a) XPS survey scan of pure and TiO_2 co-deposited ALD Fe_2O_3 thin film on Si substrate. (b) Fe 2p details for the Fe_2O_3 and TiO_2 doped Fe_2O_3 thin films. (c) Ti 2p chemical states for the TiO_2 co-deposited film.

Raman spectroscopy is widely used to analyze the phase of iron oxides due to the distinct spectral of various crystal phases, hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4). Figure 6.10 (a) shows the Raman spectral of the 20 nm ALD Fe_2O_3 film deposited on a FTO substrate before and after thermal annealing. The as-deposited film shows no distinguishable Raman peaks because of its amorphous

structure. After post-annealing at 500 °C for 1 hr, the typical Raman peaks of α -Fe₂O₃ at 225, 293, 403 and 1318 cm⁻¹ are observed, consistent to previous report.²¹¹ The two peaks at 600 and 1100 cm⁻¹ come from the FTO substrate. No peak from other iron oxide phases can be detected, implying that crystal phase of the ALD iron oxide using ferrocene and ozone after post annealing is dominantly hematite (α -Fe₂O₃). Note that, due to the small thickness, X-ray diffraction characterization was not attempted as it is not expected to show evident features related to hematite. Figure 6.10(b) shows the UV-vis absorption spectral of the 20 nm thick ALD hematite thin films grown on the FTO substrate. The absorption onset at around 600 nm of the pure Fe₂O₃ sample is consistent with a 2.1~2.2 eV band gap of hematite reported in many other studies.²¹²⁻²¹⁴ While for the sample with TiO₂ co-deposition, the absorption edge blueshifts slightly, accompanied by a decrease in the absorbance.

Figure 6.10 (a) Raman spectra of the as-deposited 20 nm thick Fe₂O₃ film on FTO substrate (red curve) and after 500 °C ambient annealing for 1 hour (blue curve). (b) UV-vis absorption spectra of the 20 nm thick Fe₂O₃ film deposited on FTO substrate with and without TiO₂ co-deposition.

The ability of conformal coating of high-aspect-ratio structures is essential to the application of Fe_2O_3 in photoelectrochemical devices, for which a continuous electrical path needs to be established along the long dimension. For demonstration, both positive and negative templates were tested using the micro-pulse process.

Figure 6.11 Fe_2O_3 deposited on non-planar substrates. SEM images of (a) the pristine ZnO nanorods array and (b) after ~ 25 nm thick Fe_2O_3 deposition at 250°C with dosing time of 10-20-10-20. (c) SEM image of a $\sim 45\ \mu\text{m}$ thick AAO template (pore size $300\ \text{nm}$) after Fe_2O_3 deposition at 250°C with dosing time of 30-30-30-30. (d-f) enlarged views at different parts of the cross section.

Figure 6.11 shows the SEM images of the ZnO nanorods array and anodic aluminum oxide (AAO) template after ALD Fe_2O_3 . Details of the hydrothermal growth of the ZnO nanorods can be found in previous section 6.1.2. The aspect ratio

of the ZnO nanorods is about 20 (Figure. 6.11a). After 500-cycle ALD Fe_2O_3 (with TiO_2 co-deposition), the conformal coating of the nanorods can be clearly seen (Figure. 6.11b); the average diameter of the ZnO nanorods increases from 80 to 130 nm, corresponding to a thickness of the Fe_2O_3 layer of about 25 nm. The clogging at the bottom is a result of smaller gaps between the ZnO nanorods near the substrate surface, which is a common phenomenon in the hydrothermal growth of ZnO nanorods. For the AAO template with 300 nm-diametered pores and total depth of 45 μm , a longer dose time was used. Figure 6.11 (c) shows the cross section of 300-cycle ALD Fe_2O_3 coated AAO template with the dosing time of 30-30-30-30. Figure 6.14 (d-f) shows the cross section of the portion with the distance of ~ 10 , ~ 20 , and ~ 35 μm from the top, respectively. A uniform layer of Fe_2O_3 with thickness about 15 nm can be seen down to 10 μm . However, at the depth of 20 μm only discontinuous small particles can be observed, and near the bottom no Fe_2O_3 deposition is achieved. Therefore, with a 30 s dosing time, a uniform coating of porous structures with aspect ratio about 50 can be achieved with such a micro-pulse process.

To test the PEC performance of the ALD Fe_2O_3 and Ti-doped Fe_2O_3 thin films samples, current density versus potential measurements under simulated sunlight illumination (AM 1.5, 100 mWcm^{-2}) in a three-electrode cell were conducted. The photocurrent of the pure Fe_2O_3 film increases from the onset potential around 0.20 V versus Ag/AgCl and approaches a plateau at 0.6 V versus Ag/AgCl, as shown in Figure. The photoresponse of the Ti-doped samples are quite sensitive to the doping level. For the low doping level the photoreponse is almost the same to the pure Fe_2O_3

thin film. When the doping level becomes higher, there are two phenomena to be noticed. Firstly, the onset potential is shift to at about ~ 0.08 V, which is ~ 0.12 V lower than that of the pure Fe_2O_3 sample. The observed onset potential shift is quite similar the previous report. Secondly, the photocurrent density shows an increase, reach a maximum, and then decrease trend to the doping level. Therefore, the introducing of Ti co-deposition can further improve the photocurrent of the ALD Fe_2O_3 photo anode at lower bias voltages. The origin of the onset potential shift and increase of the current density is still unclear at this stage. One recent study reported that Ti doping can resurrect the dead layer of Fe_2O_3 film as photoanode.²¹⁵ The Fe_2O_3 and TiO_2 co-deposited thin films may find their applications in solar energy conversion devices.

Figure 6.12 J–V curves of the ALD Fe_2O_3 and Ti-doped Fe_2O_3 thin film samples under simulated solar light illumination.

6.2.3 Conclusions

Hematite (α -Fe₂O₃) has been deposited by ALD based on a micro-pulse process using ferrocene and ozone precursors. Typical ALD behavior is observed over a temperature window between 200 and 325 °C. The micro-pulse process exhibits shorter precursor exposure time (about 10 s for both precursors), a growth rate of ~0.55 Å/cycle, and the capability of conformal coating on structures with aspect ratios >50. By introducing ALD TiO₂ co-deposition to Fe₂O₃ with a cycle ratio of 1:20, the previously-observed decrease of the growth rate after the first hundred cycles can be prevented, and simultaneously Ti doping is achievable. The dense hematite films deposited on FTO substrate exhibits an optical band gap of about 2.1 eV. Uniform coating on high aspect ratio structures including dense arrays of ZnO nanorods and AAO template have also been demonstrated. The obtained hematite films on 3D substrates may find applications in lithium-ion batteries and photoelectrochemical devices.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

By combining NSL and ALD we have designed and fabricated three kinds of the metal nanostructures arrays, gold semishell arrays, metal nanoparticles on semishell (PoSS) arrays and particle-in-bowl (PIB) arrays, for SERS applications. These results demonstrate the usefulness of NSL and ALD in fabricating plasmonic sensors towards application in biomedical science and food security. The major accomplishments and contributions of this thesis can be summarized into the following four points:

(1) A recyclable SERS substrate based on ordered array of gold semishells on TiO₂ spheres. A facile and new strategy for the creation of recyclable SERS-active substrates based on the ordered array of Au semishells on hollow TiO₂ spheres has been demonstrated. The whole structure is fabricated by scalable techniques with good control including NSL, ALD, and metal evaporation. Raman measurements reveal that the ordered array of Au-TiO₂ composite can indeed be a high-performance SERS platform, which is highly sensitive (due to nanogaps between the Au semishells), stable, reproducible (uniform arrays) and recyclable (self-cleaning enabled by the UV photocatalytic characteristics of TiO₂). The unique recyclable capability provides a new opportunity in eliminating the single-use problem of

traditional SERS substrates and creates promising applications as a functional component in surface-enhanced spectroscopy and quantitative analysis.

(2) Ordered array of metal particles on semishell separated by ultrathin oxide: fabrication and SERS. Assisted by the NSL and ALD, we have demonstrated a controllable fabrication of novel ordered arrays of Ag particles on semishells (PoSS) with a high SERS effect. The particles are obtained via dewetting of sputtered Ag thin films and the particle size is tunable. The SERS signal from the PoSS array shows up to 10 times increase compared to the commonly-studied bare metal semishell arrays. The Raman signal enhancement depends on the size of the Ag particles, and the largest SERS enhancement factor is $\sim 2.5 \times 10^6$. The FDTD simulation reveals that the further SERS enhancement is attributed primarily to the increase of the local field and the density of plasmonic hot spots near the gap regions. The large SERS enhancement of such metal PoSS arrays suggests their potential application as functional components in chemical and biosensors.

(3) Highly-ordered arrays of PIB plasmonic nanostructure for SERS. A simple process has been demonstrated for the controlled and reproducible fabrication of a novel ordered array of particle-in-bowl plasmonic nanostructures for SERS. All of the techniques we used here including NSL, ALD, and metal evaporation, are scalable techniques and with good control. With the reduction of the separation layer thickness, the measured SERS enhancement is dramatically increased. That could be due to increased plasmonic coupling. In addition, among various Ag particle sizes, the largest enhancement, with a SERS EF $\sim 3.8 \times 10^7$, comes from the PIB structure with

~160 nm Ag particles (when the gap thickness is fixed to 5 nm). Numerical simulations of the field distribution are also studied and the result is in good agreement with experiments. The fabrication method used here can be applied to fabricating other metal-based PIB structures in optimized dimensions towards a higher level of SERS EF. It is proposed that such ordered PIB plasmonic arrays are useful as functional components in high sensitive spectroscopy and biosensors.

(4) ALD in nanofabrications. During my Ph. D study ALD I have done some related work of ALD in nanofabrication. We have demonstrated that the ALD ZnO film can be used as seed layer for hydrothermal growth ZnO nanorod arrays. With this technique, we have successfully fabricated various 3-D hybrid nanostructures, including Si-ZnO nanotrees, urchin ZnO structure, and CNT-ZnO heterostructures. Those 3-D nanostructures may find applications in SERS or energy-related application. We have also demonstrated a micro-pulse process of ALD of Fe₂O₃ using ferrocene and ozone precursors and Ti-doping for photoelectrochemical water splitting.

7.2 Suggestions for future work

This thesis demonstrates the usefulness of ALD in SERS application. In addition to SERS, with the growing field of plasmonics, the requirement of ALD thin film to decorate various plasmonic nanostructure surfaces at low temperatures will also increase. Some recommended future works are as follows:

- (1) For most existing applications in plasmonic, SERS or biosensors the ALD material utilized is Al_2O_3 or SiO_2 .⁷⁴ Other ALD-processable materials such as HfO_2 , which have higher reflective indices, could also be employed.
- (2) A direct metal deposition by ALD appears also promising for applications in plasmonics. This would be particularly relevant for high aspect ratio 3D nanostructures, on which uniform coating of metal nanoparticles by physical sputtering is challenging. By using ALD, it is possible to obtain 3D metallic nanostructures that may show new plasmonic properties for both fundamental study and applications in SERS, plasmonic biosensor, as well as fuel cell catalyst.
- (3) Since the first report on shell-isolated nanoparticle enhanced Raman spectroscopy (SINERS) by Tian *et. al.* in 2010,⁸⁰ SINERS has attract renewed attentions recently. However, these studies are all based on quasi-spherical nanoparticles, whereas no reports are made on other shapes, such as rods, shells and triangles, although it is known that these shapes show much better plasmonic features than spheres. Through ALD thin dielectric layer coating, it shell-isolated nanoparticles of these non-spherical shapes can be realized for more efficient SERS substrates.
- (4) Recently the composite plasmonic structures have found new applications in SRES as they can provide further field enhancement by unique coupling. For example, the particle in cavity structure and semishell coupled with nanohole cavity structure, have been demonstrated to produce high SERS field

enhancements.^{65, 145, 146} One common feature of these composite structure is that the strong local fields are generated by the nanoscale metallic gaps. Using ALD dielectric thin layer as a SERS spacer or as a sacrifice layer, various nanogap based metallic structures could be produced for SERS applications. For example, figure 7.1 shows schematically a metal bowl-in-bowl nanostructure array with sub-10 nm gaps (left) and the circular nanogap arrays (right).

Figure 7.1 Schematics of a metallic bowl-in-bowl nanostructure (a) and circular nanogap array (b).

References

1. http://en.wikipedia.org/wiki/Surface_plasmon.
2. Jeanmaire, D. L.; Van Duyne, R. P. *J. Electronanal. Chem.* **1977**, 84, (1), 1-20.
3. Haynes, C. L.; Yonzon, C. R.; Zhang, X.; Van Duyne, R. P. *J. Raman Spectrosc.* **2005**, 36, (6-7), 471-484.
4. Schatz, G. C.; Young, M. A.; Van Duyne, R. P., Electromagnetic mechanism of SERS. Berlin: Springer-Verlag: 2006; pp 19-46.
5. Nie, S. M.; Emery, S. R. *Science* **1997**, 275, (5303), 1102-1106.
6. Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, 78, (9), 1667-1670.
7. Yonzon, C. R.; Haynes, C. L.; Zhang, X.; Walsh, J. T.; Van Duyne, R. P. *Anal. Chem.* **2003**, 76, (1), 78-85.
8. Haes, A. J.; Chang, L.; Klein, W. L.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2005**, 127, (7), 2264-2271.
9. Haes, A. J.; Hall, W. P.; Chang, L.; Klein, W. L.; Van Duyne, R. P. *Nano. Lett.* **2004**, 4, (6), 1029-1034.
10. Englebienne, P. *Analyst* **1998**, 123, (7), 1599-1603.
11. Raschke, G.; Kowarik, S.; Franzl, T.; Sönnichsen, C.; Klar, T. A.; Feldmann, J.; Nichtl, A.; Kürzinger, K. *Nano. Lett.* **2003**, 3, (7), 935-938.
12. Brockman, J. M.; Nelson, B. P.; Corn, R. M. *Ann. Rev. Phys. Chem.* **2000**, 51, 41-63.
13. Berger, C. E. H.; Beumer, T. A. M.; Kooyman, R. P. H.; Greve, J. *Anal. Chem.* **1998**, 70, (4), 703-706.

References

14. Malmqvist, M. *Nature* **1993**, 361, (6408), 186-187.
15. Willets, K. A.; Van Duyne, R. P., Localized surface plasmon resonance spectroscopy and sensing. In *Ann. Rev. Phys. Chem.*, 2007; Vol. 58, pp 267-297.
16. Ritchie, R. H. *Phys. Rev.* **1957**, 106, (5), 874-881.
17. Raether, H., Surface Plasmons on Smooth and Rough Surfaces and on Gratings. Berlin: Springer-Verlag: 1986.
18. Bohren, C. F.; Huffman, D. R., Absorption and Scattering of Light by Small Particles Wiley: 1998.
19. Moskovits, M. *J. Raman Spectrosc.* **2005**, 36, (6-7), 485-496.
20. Kreibig, U.; Vollmer, M., Optical Properties of Metal Clusters. Springer-Verlag: 1995.
21. Murray, W. A.; Barnes, W. L. *Adv. Mater.* **2007**, 19, (22), 3771-3782.
22. Michaels, A. M.; Jiang; Brus, L. *J. Phys. Chem. B* **2000**, 104, (50), 11965-11971.
23. Li, W.; Camargo, P. H. C.; Lu, X.; Xia, Y. *Nano. Lett.* **2008**, 9, (1), 485-490.
24. Nie, S.; Emory, S. R. *Science* **1997**, 275, (5303), 1102-1106.
25. Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, 26, (2), 163-166.
26. Osawa, M.; Matsuda, N.; Yoshii, K.; Uchida, I. *J. Phys. Chem.* **1994**, 98, (48), 12702-12707.
27. Tian, Z.-Q.; Ren, B., Raman Spectroscopy of Electrode Surfaces. In *Encyclopedia of Electrochemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2007.
28. Vo-Dinh, T. *TrAC, Trends Anal. Chem.* **1998**, 17, (8-9), 557-582.

References

29. Kneipp, K.; Kneipp, H.; Itzkan, I. *J. Phys.: Condens. Matter* **2002**, 14, R597.
30. Etchegoin, P.; Cohen, L. F.; Hartigan, H.; Brown, R. J. C.; Milton, M. J. T.; Gallop, J. *C. J. Chem. Phys.* **2003**, 119, (10), 5281-5289.
31. Moskovits, M. *Rev. Mod. Phys.* **1985**, 57, (3), 783-826.
32. Otto, A.; Mrozek, I.; Grabhorn, H.; Akemann, W. *J. Phys.: Condens. Matter* **1992**, 4, 1143.
33. Kravets, V. G.; Zorinants, G.; Burrows, C. P.; Schedin, F.; Casiraghi, C.; Klar, P.; Geim, A. K.; Barnes, W. L.; Grigorenko, A. N. *Phys. Rev. Lett.* **2010**, 105, (24), 246806-246810.
34. Li, K.; Stockman, M. I.; Bergman, D. J. *Phys. Rev. Lett.* **2003**, 91, (22), 227402.
35. Michota, A.; Kudelski, A.; Bukowska, J. *J. Raman Spectrosc.* **2001**, 32, (5), 345-350.
36. Kudelski, A.; Michota, A.; Bukowska, J. *J. Raman Spectrosc.* **2005**, 36, (6-7), 709-714.
37. Wrzosek, B.; Bukowska, J.; Kudelski, A. *J. Raman Spectrosc.* **2005**, 36, (11), 1040-1046.
38. Mi Lee, H.; Kim, K.; Kim, M. S. *J. Raman Spectrosc.* **1993**, 24, (10), 661-665.
39. Lee, T. G.; Kim, K.; Kim, M. S. *J. Raman Spectrosc.* **1991**, 22, (6), 339-344.
40. Leopold, N.; Cîntă-Pînzaru, S.; Szabó, L.; Ileşan, D.; Chiş, V.; Cozar, O.; Kiefer, W. *J. Raman Spectrosc.* **2010**, 41, (3), 248-255.
41. Feng, Z.; Liang, C.; Li, M.; Chen, J.; Li, C. *J. Raman Spectrosc.* **2001**, 32, (12), 1004-1007.

References

42. Marotta, N. E.; Beavers, K. R.; Bottomley, L. A. *Anal. Chem.* **2013**, 85, (3), 1440-1446.
43. van Lierop, D.; Larmour, I. A.; Faulds, K.; Graham, D. *Anal. Chem.* **2013**, 85, (3), 1408-1414.
44. Panikkanvalappil, S. R.; Mackey, M. A.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2013**, 135, (12), 4815-4821.
45. Kurouski, D.; Postiglione, T.; Deckert-Gaudig, T.; Deckert, V.; Lednev, I. K. *Analyst* **2013**, 138, (6), 1665-1673.
46. Yan, J.; Su, S.; He, S. J.; He, Y.; Zhao, B.; Wang, D. F.; Zhang, H. L.; Huang, Q.; Song, S. P.; Fan, C. *Anal. Chem.* **2012**, 84, (21), 9139-9145.
47. Cowcher, D. P.; Xu, Y.; Goodacre, R. *Anal. Chem.* **2013**, 85, (6), 3297-3302.
48. Zhang, L.; Xu, J. J.; Mi, L.; Gong, H.; Jiang, S. Y.; Yu, Q. M. *Biosens. Bioelectron.* **2012**, 31, (1), 130-136.
49. Su, Y. B.; Si, M. Z.; Zhang, D. Q.; Liu, R. M.; Lin, F. C. *Spectrosc. Spec. Analy.* **2012**, 32, (7), 1825-1828.
50. Qian, X.; Peng, X.-H.; Ansari, D. O.; Yin-Goen, Q.; Chen, G. Z.; Shin, D. M.; Yang, L.; Young, A. N.; Wang, M. D.; Nie, S. *Nat Biotech* **2008**, 26, (1), 83-90.
51. Millstone, J. E.; Hurst, S. J.; Métraux, G. S.; Cutler, J. I.; Mirkin, C. A. *Small* **2009**, 5, (6), 646-664.
52. Douketis, C.; Haslett, T. L.; Wang, Z.; Moskovits, M.; Iannotta, S. *J. Chem. Phys.* **2000**, 113, (24), 11315-11323.

References

53. Chen, G.; Wang, Y.; Yang, M. X.; Xu, J.; Goh, S. J.; Pan, M.; Chen, H. Y. *J. Am. Chem. Soc.* **2010**, 132, (11), 3644-3647.
54. Li, S. Z.; Pedano, M. L.; Chang, S. H.; Mirkin, C. A.; Schatz, G. C. *Nano. Lett.* **2010**, 10, (5), 1722-1727.
55. Talley, C. E.; Jackson, J. B.; Oubre, C.; Grady, N. K.; Hollars, C. W.; Lane, S. M.; Huser, T. R.; Nordlander, P.; Halas, N. J. *Nano. Lett.* **2005**, 5, (8), 1569-1574.
56. Chen, T.; Wang, H.; Chen, G.; Wang, Y.; Feng, Y. H.; Teo, W. S.; Wu, T.; Chen, H. Y. *Acs Nano* **2010**, 4, (6), 3087-3094.
57. Wei, H.; Hao, F.; Huang, Y. Z.; Wang, W. Z.; Nordlander, P.; Xu, H. X. *Nano. Lett.* **2008**, 8, (8), 2497-2502.
58. Yoon, I.; Kang, T.; Choi, W.; Kim, J.; Yoo, Y.; Joo, S.-W.; Park, Q. H.; Ihee, H.; Kim, B. *J. Am. Chem. Soc.* **2008**, 131, (2), 758-762.
59. Zhang, W.; Cui, Y.; Yeo, B.-S.; Schmid, T.; Hafner, C.; Zenobi, R. *Nano. Lett.* **2007**, 7, (5), 1401-1405.
60. Banaee, M. G.; Crozier, K. B. *Optics Letters* **2010**, 35, (5), 760-762.
61. Ye, J.; Van Dorpe, P.; Van Roy, W.; Borghs, G.; Maes, G. *Langmuir* **2009**, 25, (3), 1822-1827.
62. Charnay, C.; Lee, A.; Man, S. Q.; Moran, C. E.; Radloff, C.; Bradley, R. K.; Halas, N. J. *J Phys Chem B* **2003**, 107, (30), 7327-7333.
63. Lu, Y.; Liu, G. L.; Kim, J.; Mejia, Y. X.; Lee, L. P. *Nano. Lett.* **2005**, 5, (1), 119-124.
64. Wu, L. Y.; Ross, B. M.; Lee, L. P. *Nano. Lett.* **2009**, 9, (5), 1956-1961.

References

65. Huang, F. M.; Wilding, D.; Speed, J. D.; Russell, A. E.; Bartlett, P. N.; Baumberg, J. *J. Nano. Lett.* **2011**, 11, (3), 1221-1226.
66. Forestiere, C.; Pasquale, A. J.; Capretti, A.; Miano, G.; Tamburrino, A.; Lee, S. Y.; Reinhard, B. M.; Dal Negro, L. *Nano. Lett.* **2012**, 12, (4), 2037-2044.
67. Ahmed, A.; Gordon, R. *Nano. Lett.* **2012**, 12, (5), 2625-2630.
68. Natan, M. J. *Far. Disc.* **2006**, 132, (0), 321-328.
69. Suntola, T. *Materials Science Reports* **1989**, 4, (5), 261-312.
70. Bohr, M. T.; Chau, R. S.; Ghani, T.; Mistry, K. *Spectrum, IEEE* **2007**, 44, (10), 29-35.
71. Kim, H. *J. Vac. Sci. Technol. B* **2003**, 21, (6), 2231-2261.
72. Kim, H.; Lee, H.-B.-R.; Maeng, W. J. *Thin Solid Films* **2009**, 517, (8), 2563-2580.
73. Knez, M.; Nielsch, K.; Niimistö, L. *Adv. Mater.* **2007**, 19, (21), 3425-3438.
74. Im, H.; Wittenberg, N. J.; Lindquist, N. C.; Oh, S. H. *J. Mater. Res.* **2012**, 27, (4), 663-671.
75. Homola, J. *Chem. Rev.* **2008**, 108, (2), 462-493.
76. Cooper, M. A. *J. Mol. Rec.* **2004**, 17, (4), 286-315.
77. Whitney, A. V.; Elam, J. W.; Zou, S. L.; Zinovev, A. V.; Stair, P. C.; Schatz, G. C.; Van Duyne, R. P. *J Phys Chem B* **2005**, 109, (43), 20522-20528.
78. Im, H.; Lindquist, N. C.; Lesuffleur, A.; Oh, S.-H. *Acs Nano* **2010**, 4, (2), 947-954.
79. Dieringer, J. A.; McFarland, A. D.; Shah, N. C.; Stuart, D. A.; Whitney, A. V.; Yonzon, C. R.; Young, M. A.; Zhang, X.; Van Duyne, R. P. *Far. Disc.* **2006**, 132, (0), 9-26.

References

80. Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; WuDe, Y.; Ren, B.; Wang, Z. L.; Tian, Z. Q. *Nature* **2010**, 464, (7287), 392-395.
81. Mubeen, S.; Zhang, S.; Kim, N.; Lee, S.; Krämer, S.; Xu, H.; Moskovits, M. *Nano. Lett.* **2012**, 12, (4), 2088-2094.
82. Whitney, A. V.; Elam, J. W.; Stair, P. C.; Van Duyne, R. P. *J. Phys. Chem. C* **2007**, 111, (45), 16827-16832.
83. Barrios, C. A.; Malkovskiy, A. V.; Kisliuk, A. M.; Sokolov, A. P.; Foster, M. D. *J. Phys. Chem. C* **2009**, 113, (19), 8158-8161.
84. Formo, E. V.; Mahurin, S. M.; Dai, S. *Acs. Appl. Mater. Interface* **2010**, 2, (7), 1987-1991.
85. Zhang, X.; Zhao, J.; Whitney, A. V.; Elam, J. W.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2006**, 128, (31), 10304-10309.
86. Im, H.; Bantz, K. C.; Lindquist, N. C.; Haynes, C. L.; Oh, S. H. *Nano. Lett.* **2010**, 10, (6), 2231-2236.
87. Li, Y.; Duan, G.; Liu, G.; Cai, W. *Chem. Soc. Rev.* **2013**, 42, (8), 3614-3627.
88. Oh, Y.-J.; Park, S.-G.; Kang, M.-H.; Choi, J.-H.; Nam, Y.; Jeong, K.-H. *Small* **2011**, 7, (2), 161-161.
89. Duan, G.; Lv, F.; Cai, W.; Luo, Y.; Li, Y.; Liu, G. *Langmuir* **2010**, 26, (9), 6295-6302.
90. Liu, X.; Sun, C.-H.; Linn, N. C.; Jiang, B.; Jiang, P. *J. Phys. Chem. C* **2009**, 113, (33), 14804-14811.

References

91. Zhang, X.; Young, M. A.; Lyandres, O.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2005**, 127, (12), 4484-4489.
92. Lu, Y.; Liu, G. L.; Kim, J.; Mejia, Y. X.; Lee, L. P. *Nano. Lett.* **2004**, 5, (1), 119-124.
93. Haynes, C. L.; Van Duyne, R. P. *J. Phys. Chem. B* **2001**, 105, (24), 5599-5611.
94. Rybczynski, J.; Ebels, U.; Giersig, M. *Colloids Surf. A: Phys. Eng. Asp.* **2003**, 219, (1-3), 1-6.
95. Draine, B. T.; Flatau, P. J. *J. Opt. Soc. Am. a: Opt. Im. Sci. Vision* **1994**, 11, (4), 1491-1499.
96. BABUŠKA, I.; BANERJEE, U.; OSBORN, J. E. *Int. J. Computational Methods* **2004**, 01, (01), 67-103.
97. Futamata, M.; Maruyama, Y.; Ishikawa, M. *J. Phys. Chem. B* **2003**, 107, (31), 7607-7617.
98. Oubre, C.; Nordlander, P. *J. Phys. Chem. B* **2004**, 108, (46), 17740-17747.
99. Cao, Y. W. C.; Jin, R. C.; Mirkin, C. A. *Science* **2002**, 297, (5586), 1536-1540.
100. Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P. *Nat. Mater.* **2008**, 7, (6), 442-453.
101. Camden, J. P.; Dieringer, J. A.; Zhao, J.; Van Duyne, R. P. *Acc. Chem. Res.* **2008**, 41, (12), 1653-1661.
102. Graham, D.; Thompson, D. G.; Smith, W. E.; Faulds, K. *Nat. Nanotechnol.* **2008**, 3, (9), 548-551.
103. Maher, R. C.; Galloway, C. M.; Le Ru, E. C.; Cohena, L. F.; Etchegoin, P. G. *Chem. Soc. Rev.* **2008**, 37, (5), 965-979.

References

104. Porter, M. D.; Lipert, R. J.; Siperko, L. M.; Wang, G.; Narayanana, R. *Chem. Soc. Rev.* **2008**, 37, (5), 1001-1011.
105. Zhang, B. H.; Wang, H. S.; Lu, L. H.; Ai, K. L.; Zhang, G.; Cheng, X. L. *Adv. Funct. Mater.* **2008**, 18, (16), 2348-2355.
106. Li, W. Y.; Camargo, P. H. C.; Lu, X. M.; Xia, Y. N. *Nano. Lett.* **2009**, 9, (1), 485-490.
107. Fang, Y.; Seong, N.-H.; Dlott, D. D. *Science* **2008**, 321, (5887), 388-392.
108. Han, X. X.; Jia, H. Y.; Wang, Y. F.; Lu, Z. C.; Wang, C. X.; Xu, W. Q.; Zhao, B.; Ozaki, Y. *Anal. Chem.* **2008**, 80, (8), 2799-2804.
109. Han, X. X.; Huang, G. G.; Zhao, B.; Ozaki, Y. *Anal. Chem.* **2009**, 81, (9), 3329-3333.
110. Liberman, V.; Yilmaz, C.; Bloomstein, T. M.; Somu, S.; Echegoyen, Y.; Busnaina, A.; Cann, S. G.; Krohn, K. E.; Marchant, M. F.; Rothschild, M. *Adv. Mater.* **2010**, 22, (38), 4298-4302.
111. Link, S.; El-Sayed, M. A. *J Phys Chem B* **1999**, 103, (21), 4212-4217.
112. Halas, N. J. *Nano. Lett.* **2010**, 10, (10), 3816-3822.
113. Smith, W. E. *Chem. Soc. Rev.* **2008**, 37, (5), 955-964.
114. Shen, C. M.; Hui, C.; Yang, T. Z.; Xiao, C. W.; Tian, J. F.; Bao, L. H.; Chen, S. T.; Ding, H.; Gao, H. J. *Chem. Mater.* **2008**, 20, (22), 6939-6944.
115. Hu, X.; Cheng, W.; Wang, T.; Wang, Y.; Wang, E.; Dong, S. *J. Phys. Chem. B* **2005**, 109, (41), 19385-19389.
116. Chen, H.; Wang, Y.; Dong, S. *J. Raman Spectrosc.* **2009**, 40, (9), 1188-1193.
117. Yoon, I.; Kang, T.; Choi, W.; Kim, J.; Yoo, Y.; Joo, S. W.; Park, Q. H.; Ihee, H.; Kim, B. *J. Am. Chem. Soc.* **2009**, 131, (2), 758-762.

References

118. Musumeci, A.; Gosztola, D.; Schiller, T.; Dimitrijevic, N. M.; Mujica, V.; Martin, D.; Rajh, T. *J. Am. Chem. Soc.* **2009**, 131, (17), 6040-6041.
119. Alessandri, I.; Depero, L. E. *Chem. Commun.* **2009**, (17), 2359-2361.
120. Cheng, C. W.; Yan, B.; Wong, S. M.; Li, X. L.; Zhou, W. W.; Yu, T.; Shen, Z. X.; Yu, H. Y.; Fan, H. J. *Acs. Appl. Mater. Interface* **2010**, 2, (7), 1824-1828.
121. Deng, S.; Fan, H. M.; Zhang, X.; Loh, K. P.; Cheng, C. L.; Sow, C. H.; Foo, Y. L. *Nanotechnology* **2009**, 20, (17), 175705-175712.
122. Wang, X. T.; Shi, W. S.; She, G. W.; Mu, L. X.; Lee, S. T. *Appl. Phys. Lett.* **2010**, 96, (5), 053104-053107.
123. Yang, L. B.; Jiang, X.; Ruan, W. D.; Yang, J. X.; Zhao, B.; Xu, W. Q.; Lombardi, J. R. *J. Phys. Chem. C* **2009**, 113, (36), 16226-16231.
124. Liao, Q.; Mu, C.; Xu, D. S.; Ai, X. C.; Yao, J. N.; Zhang, J. P. *Langmuir* **2009**, 25, (8), 4708-4714.
125. Ye, J.; Van Dorpe, P.; Van Roy, W.; Lodewijks, K.; De Vlaminck, I.; Maes, G.; Borghs, G. *J. Phys. Chem. C* **2009**, 113, (8), 3110-3115.
126. Ye, J.; Verellen, N.; Van Roy, W.; Lagae, L.; Maes, G.; Borghs, G.; Van Dorpe, P. *Acs Nano* **2010**, 4, (3), 1457-1464.
127. Ye, J. A.; Chen, C.; Lagae, L.; Maes, G.; Borghs, G.; Van Dorpe, P. *Phys. Chem. Chem. Phys.* **2010**, 12, (37), 11222-11224.
128. Wang, C. X.; Ruan, W. D.; Ji, N.; Ji, W.; Lv, S.; Zhao, C.; Zhao, B. *J. Phys. Chem. C* **2010**, 114, (7), 2886-2890.
129. Wang, T.; Hu, X. G.; Dong, S. J. *Small* **2008**, 4, (6), 781-786.

References

130. Aldeanueva-Potel, P.; Faoucher, E.; Alvarez-Puebla, R. A.; Liz-Marzan, L. M.; Brust, M. *Anal. Chem.* **2009**, 81, (22), 9233-9238.
131. Li, M. D.; Cui, Y.; Gao, M. X.; Luo, J.; Ren, B.; Tian, Z. Q. *Anal. Chem.* **2008**, 80, (13), 5118-5125.
132. Li, X. H.; Chen, G. Y.; Yang, L. B.; Jin, Z.; Liu, J. H. *Adv. Funct. Mater.* **2010**, 20, (17), 2815-2824.
133. Li, X. L.; Li, C.; Zhang, Y.; Chu, D. P.; Milne, W. I.; Fan, H. J. *Nanoscale Res. Lett.* **2010**, 5, (11), 1836-1840.
134. Li, Q. J.; Liu, B. B.; Li, Y. G.; Liu, R.; Li, X. L.; Li, D. M.; Yu, S. D.; Liu, D. D.; Wang, P.; Li, B.; Zou, B.; Cui, T.; Zou, G. T. *J. Alloys Compd.* **2009**, 471, (1-2), 477-480.
135. Blanford, C. F.; Schroden, R. C.; Al-Daous, M.; Stein, A. *Adv. Mater.* **2001**, 13, (1), 26-29.
136. Maarooof, A. L.; Cortie, M. B.; Harris, N.; Wiecezorek, L. *Small* **2008**, 4, (12), 2292-2299.
137. Cortie, M.; Ford, M. *Nanotechnology* **2007**, 18, (23), 235704-235710.
138. Akpan, U. G.; Hameed, B. H. *J. Hazard. Mater.* **2009**, 170, (2-3), 520-529.
139. Johnson, P. B.; Christy, R. W. *Phys. Rev. B* **1972**, 6, (12), 4370-4379.
140. Le Ru, E. C.; Blackie, E.; Meyer, M.; Etchegoin, P. G. *J. Phys. Chem. C* **2007**, 111, (37), 13794-13803.
141. Patoka, P.; Giersig, M. *J. Mater. Chem.* **2011**, 21, (42), 16783-16796.
142. Yang, S.-M.; Jang, S. G.; Choi, D.-G.; Kim, S.; Yu, H. K. *Small* **2006**, 2, (4), 458-475.

References

143. Li, X.; Hu, H.; Li, D.; Shen, Z.; Xiong, Q.; Li, S.; Fan, H. J. *Acs Applied Materials & Interfaces* **2012**, 4, (4), 2180-2185.
144. Kravets, V. G.; Zorinians, G.; Burrows, C. P.; Schedin, F.; Geim, A. K.; Barnes, W. L.; Grigorenko, A. N. *Nano. Lett.* **2010**, 10, (3), 874-879.
145. Im, H.; Bantz, K. C.; Lee, S. H.; Johnson, T. W.; Haynes, C. L.; Oh, S.-H. *Adv. Mater.* **2013**, 25, (25), 2678-2685.
146. Li, X. L.; Zhang, Y. Z.; Shen, Z. X.; Fan, H. J. *Small* **2012**, 8, (16), 2548-2554.
147. Liu, M.; Li, X.; Karuturi, S. K.; Tok, A. I. Y.; Fan, H. J. *Nanoscale* **2012**, 4, (5), 1522-1528.
148. Yang, L.; Jiang, X.; Ruan, W.; Zhao, B.; Xu, W.; Lombardi, J. R. *J. Phys. Chem. C* **2008**, 112, (50), 20095-20098.
149. Hu, M.; Ghoshal, A.; Marquez, M.; Kik, P. G. *J. Phys. Chem. C* **2010**, 114, (16), 7509-7514.
150. Wang, K.; Schonbrun, E.; Crozier, K. B. *Nano. Lett.* **2009**, 9, (7), 2623-2629.
151. Zumbusch, A.; Holtom, G. R.; Xie, X. S. *Phys. Rev. Lett.* **1999**, 82, (20), 4142-4145.
152. De Gelder, J.; De Gussem, K.; Vandenabeele, P.; Moens, L. *J. Raman Spectrosc.* **2007**, 38, (9), 1133-1147.
153. Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Chem. Rev.* **1999**, 99, (10), 2957-2976.
154. Kneipp, J.; Kneipp, H.; Kneipp, K. *Chem. Soc. Rev.* **2008**, 37, (5), 1052-1060.
155. Champion, A.; Kambhampati, P. *Chem. Soc. Rev.* **1998**, 27, (4), 241-250.
156. Wang, X.; Shi, W.; She, G.; Mu, L. *J. Am. Chem. Soc.* **2011**, 133, (41), 16518-16523.

References

157. Tian, Z.-Q.; Ren, B.; Wu, D.-Y. *J. Phys. Chem. B* **2002**, 106, (37), 9463-9483.
158. Zhao, J.; Pinchuk, A. O.; McMahon, J. M.; Li, S.; Ausman, L. K.; Atkinson, A. L.; Schatz, G. C. *Acc. Chem. Res.* **2008**, 41, (12), 1710-1720.
159. GarciaVidal, F. J.; Pendry, J. B. *Phys. Rev. Lett.* **1996**, 77, (6), 1163-1166.
160. Liu, M. N.; Li, X. L.; Karuturi, S. K.; Tok, A. I. Y.; Fan, H. J. *Nanoscale* **2012**, 4, (5), 1522-1528.
161. Banholzer, M. J.; Millstone, J. E.; Qin, L.; Mirkin, C. A. *Chem. Soc. Rev.* **2008**, 37, (5), 885-897.
162. Qian, C.; Ni, C.; Yu, W. X.; Wu, W. G.; Mao, H. Y.; Wang, Y. F.; Xu, J. *Small* **2011**, 7, (13), 1801-1806.
163. Cortes, E.; Tognalli, N. G.; Fainstein, A.; Vela, M. E.; Salvarezza, R. C. *Phys. Chem. Chem. Phys.* **2009**, 11, (34), 7469-7475.
164. Eder, D. *Chem. Rev.* **2010**, 110, (3), 1348-1385.
165. Haremza, J. M.; Hahn, M. A.; Krauss, T. D.; Chen, S.; Calcines, J. *Nano. Lett.* **2002**, 2, (11), 1253-1258.
166. Kongkanand, A.; Dominguez, R. M.; Kamat, P. V. *Nano. Lett.* **2007**, 7, (3), 676-680.
167. Zhong, J.; Kitai, A. H.; Mascher, P.; Puff, W. *J. Electrochem. Soc.* **1993**, 140, (12), 3644-3649.
168. Zhu, Y. W.; Elim, H. I.; Foo, Y. L.; Yu, T.; Liu, Y. J.; Ji, W.; Lee, J. Y.; Shen, Z. X.; Wee, A. T. S.; Thong, J. T. L.; Sow, C. H. *Adv. Mater.* **2006**, 18, (5), 587-592.
169. Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, P. *Appl. Phys. Lett.* **1998**, 73, (17), 2447-2449.

References

170. Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, 106, (3), 1105-1136.
171. Lee, J. S.; Min, B.; Cho, K.; Kim, S.; Park, J.; Lee, Y. T.; Kim, N. S.; Lee, M. S.; Park, S. O.; Moon, J. T. *J. Cryst. Growth* **2003**, 254, (3-4), 443-448.
172. Min, Y. S.; Bae, E. J.; Park, J. B.; Kim, U. J.; Park, W.; Song, J.; Hwang, C. S.; Park, N. *Appl. Phys. Lett.* **2007**, 90, (26), 263104-263107.
173. Kim, D. S.; Lee, S. M.; Scholz, R.; Knez, M.; Goesele, U.; Fallert, J.; Kalt, H.; Zacharias, M. *Appl. Phys. Lett.* **2008**, 93, (10), 103108-103112.
174. Hofmann, S.; Cantoro, M.; Kleinsorge, B.; Casiraghi, C.; Parvez, A.; Robertson, J.; Ducati, C. *J. Appl. Phys.* **2005**, 98, (3), 034308-034316.
175. Guziewicz, E.; Kowalik, I. A.; Godlewski, M.; Kopalko, K.; Osinniy, V.; Wojcik, A.; Yatsunenko, S.; Lusakowska, E.; Paszkowicz, W.; Guziewicz, M. *J. Appl. Phys.* **2008**, 103, (3), 033515-033521.
176. Elam, J. W.; Routkevitch, D.; Mardilovich, P. P.; George, S. M. *Chem. Mater.* **2003**, 15, (18), 3507-3517.
177. Li, W. Z.; Zhang, H.; Wang, C. Y.; Zhang, Y.; Xu, L. W.; Zhu, K.; Xie, S. S. *Appl. Phys. Lett.* **1997**, 70, (20), 2684-2686.
178. Hirsch, A. *Angew. Chem. Int. Ed.* **2002**, 41, (11), 1853-1859.
179. Green, J. M.; Dong, L. F.; Gutu, T.; Jiao, J.; Conley, J. F.; Ono, Y. *J. Appl. Phys.* **2006**, 99, (9), 094308-094312.
180. Goniakowski, J.; Noguera, C.; Giordano, L. *Phys. Rev. Lett.* **2007**, 98, (20), 205701.

References

181. Cuscó R.; Alarcón-Lladó E.; Ibáñez, J.; Artús, L.; Jiménez, J.; Wang, B.; Callahan, M. J. *Phys. Rev. B* **2007**, 75, (16), 165202.
182. Fan, H. J.; Scholz, R.; Kolb, F. M.; Zacharias, M. *Appl. Phys. Lett.* **2004**, 85, (18), 4142-4144.
183. Djurisić, A. B.; Leung, Y. H. *Small* **2006**, 2, (8-9), 944-961.
184. Sarker, B. K.; Arif, M.; Stokes, P.; Khondaker, S. I. *J. Appl. Phys.* **2009**, 106, (7), 074307-074311.
185. Leiter, F. H.; Alves, H. R.; Hofstaetter, A.; Hofmann, D. M.; Meyer, B. K. *Phys. Status. Solidi. B* **2001**, 226, (1), R4-R5.
186. Cheng, C. W.; Liu, B.; Yang, H. Y.; Zhou, W. W.; Sun, L.; Chen, R.; Yu, S. F.; Zhang, J. X.; Gong, H.; Sun, H. D.; Fan, H. J. *Acs Nano* **2009**, 3, (10), 3069-3076.
187. Studenikin, S. A.; Golego, N.; Cocivera, M. *J. Appl. Phys.* **1998**, 84, (4), 2287-2294.
188. Zhang, W. D. *Nanotechnology* **2006**, 17, (4), 1036-1040.
189. Elias, J.; Lévy-Clément, C.; Bechelany, M.; Michler, J.; Wang, G.-Y.; Wang, Z.; Philippe, L. *Adv. Mater.* **2010**, 22, (14), 1607-1612.
190. Bjorksten, U.; Moser, J.; Grätzel, M. *Chem. Mater.* **1994**, 6, (6), 858-863.
191. Duret, A.; Grätzel, M. *J. Phys. Chem. B* **2005**, 109, (36), 17184-17191.
192. Sivula, K.; Le Formal, F.; Grätzel, M. *Chemsuschem* **2011**, 4, (4), 432-449.
193. Lin, Y.; Yuan, G.; Sheehan, S.; Zhou, S.; Wang, D. *Energy. Environ. Sci.* **2011**, 4, (12), 4862-4869.
194. Lindgren, T.; Wang, H. L.; Beermann, N.; Vayssieres, L.; Hagfeldt, A.; Lindquist, S. *E. Sol. Energy Mater. Sol. Cells* **2002**, 71, (2), 231-243.

References

195. Beermann, N.; Vayssieres, L.; Lindquist, S. E.; Hagfeldt, A. *J. Electrochem. Soc.* **2000**, 147, (7), 2456-2461.
196. Murphy, A. B.; Barnes, P. R. F.; Randeniya, L. K.; Plumb, I. C.; Grey, I. E.; Horne, M. D.; Glasscock, J. A. *Int. J. Hydrogen Energy* **2006**, 31, (14), 1999-2017.
197. Kennedy, J. H.; Frese, K. W. *J. Electrochem. Soc.* **1978**, 125, 1999-2017.
198. Marichy, C.; Bechelany, M.; Pinna, N. *Adv. Mater.* **2012**, 24, (8), 1017-1032.
199. Lin, Y.; Xu, Y.; Mayer, M. T.; Simpson, Z. I.; McMahon, G.; Zhou, S.; Wang, D. *J. Am. Chem. Soc.* **2012**, 134, (12), 5508-5511.
200. Lin, Y.; Zhou, S.; Sheehan, S. W.; Wang, D. *J. Am. Chem. Soc.* **2011**, 133, (8), 2398-2401.
201. Cheng, C.; Karuturi, S. K.; Liu, L.; Liu, J.; Li, H.; Su, L. T.; Tok, A. I. Y.; Fan, H. J. *Small* **2012**, 8, (1), 37-42.
202. Lie, M.; Fjellvåg, H.; Kjekshus, A. *Thin Solid Films* **2005**, 488, (1-2), 74-81.
203. Scheffe, J. R.; Francés, A.; King, D. M.; Liang, X.; Branch, B. A.; Cavanagh, A. S.; George, S. M.; Weimer, A. W. *Thin Solid Films* **2009**, 517, (6), 1874-1879.
204. Rooth, M.; Johansson, A.; Kukli, K.; Aarik, J.; Boman, M.; Hårsta, A. *Chem. Vap. Deposition* **2008**, 14, (3-4), 67-70.
205. Bachmann, J.; Jing, K.; Knez, M.; Barth, S.; Shen, H.; Mathur, S.; Gösele, U.; Nielsch, K. *J. Am. Chem. Soc.* **2007**, 129, (31), 9554-9555.
206. Martinson, A. B. F.; DeVries, M. J.; Libera, J. A.; Christensen, S. T.; Hupp, J. T.; Pellin, M. J.; Elam, J. W. *J. Phys. Chem. C* **2011**, 115, (10), 4333-4339.
207. Klahr, B. M.; Martinson, A. B. F.; Hamann, T. W. *Langmuir* **2010**, 27, (1), 461-468.

References

208. Dyagileva, L. M.; Mar'in, V. P.; Tsyganova, E. I.; Razuvaev, G. A. *J. Organomet. Chem.* **1979**, 175, (1), 63-72.
209. Dhandapani, B.; Oyama, S. T. *Appl. Catal. B: Environ.* **1997**, 11, (2), 129-166.
210. Wang, G.; Ling, Y.; Wheeler, D. A.; George, K. E. N.; Horsley, K.; Heske, C.; Zhang, J. Z.; Li, Y. *Nano. Lett.* **2011**, 11, (8), 3503-3509.
211. de Faria, D. L. A.; Venâncio Silva, S.; de Oliveira, M. T. *J. Raman Spectrosc.* **1997**, 28, (11), 873-878.
212. Kung, H. H.; Jarrett, H. S.; Sleight, A. W.; Ferretti, A. *J. Appl. Phys.* **1977**, 48, (6), 2463-2469.
213. Marusak, L. A.; Messier, R.; White, W. B. *J. Phys. Chem. Solids* **1980**, 41, (9), 981-984.
214. Gilbert, B.; Frandsen, C.; Maxey, E. R.; Sherman, D. M. *Phys. Rev. B* **2009**, 79, (3), 035108.
215. Zandi, O.; Klahr, B. M.; Hamann, T. W. *Energy. Environ. Sci.* **2013**, 6, (2), 634-642.