Metal nanostructures for surface-enhanced Raman scattering and its coupling with ZNO

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**METAL NANOSTRUCTURES FOR
SURFACE-ENHANCED RAMAN SCATTERING AND
ITS COUPLING WITH ZNO**

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**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

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Summary

This thesis presents results on fabrication and characterization of plasmonic nanostructures for SERS-based molecule probing and plasmonic radiation engineering.

The projects can be divided into two main parts as follows:

Part A: Plasmonic nanostructures for SERS-based molecule-probing

In Chapter 3, we present the fabrication of sub-10 nm vertical gaps by simply combining two surface-engineering processes, atomic layer deposition (ALD) and capillary effect of aligned nanowires. The tunability of the resulting nanogap widths is realized by ALD coating thickness. Such metal nanogaps are able to sufficiently trapping molecules and enhance local field as plasmonic concentrators. As a result, they can serve as highly effective SERS substrates due to "hot-spot" effect, and the SERS signals show increase with the shrinking of gap width.

In the following Chapter 4, another type of metal nanostructures is also provided by a so-called "nanoimprinting" method that simply relied on hydrothermal treatment of substrates and also assisted by ALD surface engineering. Via this method, nanoholes down to sub-10 nm scale are formed on Pt thin films. The plasmonic concentration effect of the obtained ultrasmall nanoholes is also tested by SERS measurement. In this way, the sub-10 nm holes prove to be highly efficient to enhance local field and give rise to the SERS signals, indicative of their potential for molecule probing..

Part B: Plasmonic radiation engineering: super near-band-edge emission

Chapter 5 and 6 deal with the effect of metal nanoparticles on the photoluminescence of ZnO nanorods (NR) primarily via the local surface plasmons coupling effect. The novelty of this part is the introduction of nanogap between ZnO and metal using ALD. By systematical study of the effects of ALD gap thickness (1 – 20 nm) and metal nanoparticles (by sputtering), the optimal condition for largest enhancement of the ZnO near bandedge emissions are established. Consistent results of gigantic increase of near bandedge emission enhancement are obtained from both photoluminescence (PL) and cathodoluminescence (CL) spectroscopies, with the latter being applied to the optical properties of individual semiconductor/metal nanoheterostructures. The super emission is primarily proposed to be due to highly efficient plasmon-emitter coupling, which is benefitting from the ultrathin dielectric gap to enable localized plasmon mode as well as the coupling. It is proposed based on our experiments that the regime responsible for the super emission is different from the common Purcell effect. On this context, the thesis ends with Conclusion and suggestion for futur work in Chapter 7.

Publication

1. **Monan Liu**, Rui Chen, Giorgio Adamo, Edbert J. Sie, Tze Chien Sum, Kevin MacDonald, Nikolay Zheludev, Handong Sun, and Hong Jin Fan, Tuning the Influence of Metal Nanoparticles on ZnO Photoluminescence by Atomic-Layer-Deposited Dielectric Spacer (**Nanophotonics**, **2013**, **2**, **153-160**)
2. **Monan Liu**, Xianglin Li, Siva Krishna Karuturi, Alfred Iing Yoong Tok, Hong Jin Fan, Atomic Layer Deposition for Nanofabrication and Interface Engineering (**Nanoscale**, **4**, **1522**, **2012**)
3. **Monan Liu**, Li Sun, Chuanwei Cheng, Hailong Hu, Zexiang Shen, and Hong Jin Fan, Highly Effective SERS Substrates Based on Atomic-Layer-Deposition-Tailored Nanorod Scaffold (**Nanoscale**, **3**, **3627**, **2011**)

Chapter 1

Introduction

1.1 Introduction to Surface Plasmon Polaritons

The dazzling and colorful glow of noble metals have been fascinating people for centuries. However, it was not until very recent decades that people came to understand the phenomena, which all lead to a whole new world driven by Surface Plasmon Polaritons (SPPs).

1.1.1 Basics of Plasmonics

SPPs are electromagnetic (EM) waves that propagate along metal surface. Back to the early centuries, people have noticed the unique optical properties of noble metals and made use of them, like the technique for stained glass. However, it was only until recent decades that people began to understand the phenomena and explore the science behind. This started with Mie's solving the Maxwell's equations of a single gold sphere and successful to explain its absorption spectrum. Based on the theoretical foundation, people's interest in SPPs and light-scattering properties of metal nanoparticles (NPs) have been growing in the following decades[1-6]. Another significant phenomenon found in the early stage was the red-shifted new peak found in the spectral peaks of metal colloid[7]. This is due to plasmon coupling of two NPs in the close proximity of each other, as well as in a multi-particle aggregate.

As an elementary excitation, SPPs originates from the interaction between surface charges and the EM field, which brings about two consequences. First, the oscillation of the surface charge density driven by the EM field results in plasmonic mode with a larger momentum than that of free-space photon, i.e. $\hbar k_{SP} > \hbar k_0$ ($k_0 = \omega/c$ is the free-space wave vector.) The dispersion relation of SPPs can be given by solving the Maxwell equations under appropriate boundary conditions, which is

$$k_{SP} = k_0 \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}}$$

where ϵ_d and ϵ_m refer to the permittivities of dielectric and metal, respectively. For valid k_{SP} , the two permittivities must have opposite signs. That's why SPPs can exist at a metal/dielectric interface. The increased momentum is associated with the its surface-binding nature, which must be compensate if light is used to generated SPPs[1]. More basics about SPPs can be found in Figure 1.1. SPPs are transverse magnetic mode in the y direction. Also due to the surface charge distribution, the electric field is normal to the metal surface. Both make the field component perpendicular to the surface enhanced significantly close to the surface while decay fast away from it. The second consequence of the interaction between the surface charges and the EM field is the evanescent plasmonic field along the direction perpendicular to the surface. That is, the perpendicular component of the field decays exponentially with the distance away from the surface. The evanescent field (or near field) is a sheer reflection

of the bound and non-radiative nature of SPPs and decides the deep-subwavelength scale as a key feature of plasmonics [as shown in Figure 1.1 (b)].

Figure 1.1 Basics of SPPs. (a) They are transverse magnetic modes with $\mathbf{H}$ in the y direction. (b) The field in this perpendicular direction is evanescent, reflecting the bound, non-radiative nature of SPPs[1].

To generate SPPs using light waves, the missing part of momentum must be provided as mentioned above. There are three common methods to fulfil this[8-9]: (i) using prism-coupling to enhance the momentum; (ii) using a topological defect (a protrusion or hole in subwavelength-scale) to scatter light into localized surface plasmons (LSPs); (iii) momentum gain by a periodic metal structure on the surface. Upon generation, SPPs tend to propagate along flat metal surface (the propagation nature). However, it will also attenuate during the propagation by loss into the metal. The attenuation is decided by the dielectric function of the metal at oscillation frequency of the SPPs. For

example, the propagation length of silver in visible spectrum is in the range of 10 - 100 μm , the lowest among metals. That's why the loss of SPPs into metal was considered a serious problem for developing plasmonic devices in the past. Now with the renovation of the scale limit in nanotechnology, more compact integrations are available with component far below the SPPs' propagation length and lay the foundation for a plasmonic century.

1.1.2 Plasmonic concentration

As illustrated above, SPPs' bound nature enables its significant enhancement to the local field. Therefore, metal nanostructures based on this functionality show the greatest potential for the current application of SPPs. They are well developed as extreme light concentrators for plasmonic antennas, lenses, resonators, etc.

Traditionally, dielectric lenses and resonators have been used for light concentration or providing local field enhancement. They are able to enhance a range of linear and nonlinear phenomena, which are considered as convenient light manipulators. However, since the dielectric lenses work under the fundamental laws of diffraction, the traditional way of light-focusing has a limit of half wavelength ($\sim\lambda/2$). Similarly, the dielectric light resonator also has a limit mode volume $v_m \sim (\lambda/2)^3$. Due to its distinctive nature, plasmonic light concentrators (mostly based on metal nanostructures) don't have such limits. Plasmonic antennas and lenses can convert light radiation into intense,

engineered, localized field distributions or enable coupling to deep-subwavelength-guided modes[10]. In this strategy, light concentration or local-field enhancement can be provided wherever they are need as long as the plasmonic structure is assembled.

Metal structures supporting plasmonic concentration can be generally divided into resonate and non-resonate ones according to the oscillation response to light radiation. Resonate metal structures can be further divided into two branches based on their structure sizes and dimensions, which are quasistatic and retardation-based ones. Quasistatic structures refer to those with sizes much smaller than the free-space wavelength of the incident light. Or the surface plasmon resonance (SPR) of tiny metal particles (size ~ 10 nm) can be described under the quasistatic approximation that the entire structure experience a uniform electric field at any instant of time[10]. The dipolar SPR is electrostatically determined to happen at wavelengths $\varepsilon_m = -2\varepsilon_d$, which can be tuned by varying the metal species, particle shape or dielectric environment. Typical field distributions are shown by Figure 1.2 for both nanosphere and nanorod geometries.

With one or more dimensions extending to the resonant wavelength, such as the strip shown by Figure 1.3, quasistatic structures thereby evolve into retardation-based ones. The evolution features a optical-phase variation along the extending dimension and hence results in retardation effects in the structures' plasmonic behavior. Given the oscillation similarity between such

plasmonic concentrators and well-developed radiofrequency antennas, concepts have been borrowed from the latter for plasmonic structure designs. One successful example is the half-wavelength dipole antenna. In a simple way, wavelength-scale metal structures are treated as Fabry-Perot cavities with non-trivial phase-pick-up effect, such as metal nanowires and strips. Hence to first order, the resonate length of such structures is determined by $n\lambda_{\text{SPP}}/2$, where n is an integer and λ_{SPP} is the wavelength of the supported SPP mode[10]. These concepts can be extended to other SPP waveguide structures and realize successful designs for field concentration.

Figure 1.2 Effects of geometry and materials on electrostatic resonances of deep-subwavelength metal structures[11].

Figure 1.3 Retardation-based strip resonators[12].

Non-resonant effects usually lead to a broadband field enhancement and hence are considered to achieve further field concentration for such structure designs. Two typical examples are "feed gap"[13] and "lightening rod". A feed gap here generally refers to a dielectric gap inserted into metal structures. Although the physics behind the feed-gap effect is not very clear so far, two points of view are believed helpful to understand the concentration effect. One ascribes the field enhancement to the component jump due to boundary conditions[14]. The other, sitting on an electrostatic view, raises that the charge building on both sides of the gaps also shows certain positive effect on the field concentration. The other typical example for non-resonant enhancement is "lightening rod"[15-16]. For such structures, field localization is achieved at tips or ends as a direct result of field-continuity conditions. The effect can be easily understood in the electrostatic regime but it actually can be extended to retardation structures for a broadband enhancement as well[17]. Based on the above introductions, one can see that these effects lead the concentrator design to a multi-strategy route for extreme field enhancement.

Figure 1.4 NSOM measurements (top) and finite difference time domain simulations (down) illustrating SPP focusing using a tapped strip waveguide[18].

1.1.3 Plasmonic-enhanced radiation

When placed in an electromagnetic near-field, the radiation behavior of a light emitter can be significantly modified. Generally, the light-emission process can be engineered via three aspects: i) increasing optical excitation rate γ_{exc} , ii) modifying the radiative and non-radiative rates (γ_{rad} and $\gamma_{\text{non-rad}}$) iii) altering emission directionality[10]. For optical pumping below saturation, the final emission rate can be expressed as $\gamma_{\text{em}} = \gamma_{\text{exc}} [\gamma_{\text{rad}}/(\gamma_{\text{rad}} + \gamma_{\text{non-rad}})]$. In the excitation session, assuming the internal quantum structure of the emitter remains unchanged, the enhancement is shown to be $\gamma_{\text{exc}} \sim |\mathbf{p} \cdot \mathbf{E}|$, where $\mathbf{p}$ is the dipole moment and $\mathbf{E}$ is the optical electric-field vector. One can also tell by this conclusion that the enhancement has a direction preference along the emitter polarization. Upon excitation, the plasmonic structures are supposed to

"squeeze" the optical field into the concentration zone and enable near-field coupling between the emitter and the optical field. Besides field-enhancement, the coupling can affect the relaxation of the excited emitters at a more fundamental level and hence are the research focus around such structures.

Figure 1.5 Basics of CQED. *a.* A typical CQED system consisting of a single quantum emitter coupled coherently to one mode of an optical microcavity (with coupling constant g). While for incoherent processes, γ and κ refer to the rates of spontaneous emission and photon loss, respectively. *b.* The featured time evolution (the excited state) and spectrum for weak-(red) and strong-coupling (blue) regimes[19].

Before realizing the idea with structure design, one needs to learn the general background of the coupling between emitter and plasmonic field. A typical model for understanding the coupling is the cavity quantum electrodynamics (CQED) model[19]. The basic configuration to study CQED is

a single quantum emitter placed inside a dielectric microcavity. The quantum emitter can be a single molecule, quantum dot or other single level systems. By defining a coupling constant g , two coupling regimes, one coherent and the other incoherent, can be distinguished from each other. Here, another two rates are introduced to identify the regime, which are energy loss rate γ and photon loss rate κ during the emission process. For the case of strong-coupling regime, energy is exchanged between the emitter and the single mode cavity by $2g$ and characterizes the energy exchange rate. Such strong-coupling fulfils $g \gg \gamma$ and $g \gg \kappa$, where $2g$ is known as Rabi frequency[20]. It makes the emitter-cavity configuration forms a new coupled system with a new energy level.

On the contrary, if the coupling fulfils $g < \gamma$ and $g < \kappa$, the dominant regime is the weak-coupling one, which makes the dynamics incoherent. After being excited, the emitter loses its energy exponentially while its decay rates are strongly modified by the cavity in resonant mode[20]. This is known as "Purcell effect"[21]. The decay is enhanced when the emitter's transition frequency is in resonance with the cavity mode frequency, $\omega = c/\lambda$ (here c is speed of light and λ wavelength). Otherwise, it tends to be suppressed. The Purcell factor can be given out by the following formula only if both exact resonance and perfect dipole-to-field alignment can be fulfilled simultaneously,

$$P = \left(\frac{3}{4\pi^2} \right) \left(\frac{\lambda}{n} \right)^3 \frac{Q}{V}$$

where n for refractive index, Q for quality factor and V for quantization (mode) volume, respectively[20]. Although the CQED model was first raised in atomic physics and mostly used to study Fabry-Pérot cavities[22], it has also been extended to many solid-state systems now[23]. From this model, one can have a basic picture about the modified radiation process and get prepared to look deeper into the dynamics[20].

For well-designed plasmonic concentration structures, significantly enhanced localized-field can be achieved despite their specific structures, metal species or other relevant parameters. Therefore, when a emitter is brought close enough to the concentrator, it can relax rapidly under the LSP excitation owing to near-field coupling. The total decay rate ($\gamma_{\text{rad}} + \gamma_{\text{non-rad}}$) can increase according with the large optical density of states (LDOS) near the metal surface. Notably, large enhancement is attainable when the emitter's transition frequency matches the resonance frequency of the plasmons or further field localization is achieved by coupling to a second particle[24]. Once getting excited, the localized plasmons around the metal structures can either decay non-radiatively due to internal damping or re-radiate into free space[10]. As shown by Figure 1.6a, coupled plasmon-emitter systems can exhibit either increased or decreased luminescence depending on a series of parameters[25]. For plasmon-emitter coupling system, these metal structures are generally expected to behave similarly to optical antennas in some degree, that is to give rise to luminescence yields by gaining energy from nearby emitters and redistributing it to the

far-field. For example, such behavior has been demonstrated by the antenna-like angular emission of a single molecule coupled to a nearby metal particle regardless of the molecule orientation[26]. As long as elaborate designs can be applied to the plasmons and nearby emitters, superior emitters is available with increased light output and redirected light emission along preferential directions.

Figure 1.6 Plasmonic engineering of radiation. *a.* Fluorescence (rate γ_{em} normalized by that of an isolated molecule, γ_{em}^0) engineered by a metal NP with varying distance z from a molecule (red: theoretical, black: experimental)[25]. *b.* Fluorescence enhancement with varying hole diameter for a single molecule (red for fluorescence at saturation, $\eta_{F, sat}$; blue for below saturation $\eta_{F, low}$). *c.*

Spontaneous emission enhancement (denoted by factor F_p) with varied gap width L of a MDM slab[27]. d. Single plasmons generated and guided along a silver nanowire, with Γ_{rad} and Γ_{pl} denoting the spontaneous emission rates of a coupled quantum dot into free space and guided plasmons, respectively [28].

Subwavelength-scale metal holes can also give rise to excitation and decay rates of embedded emitters by means of coupling to guided SPP modes, as shown by Figure 1.6b[26]. With tuning of the hole diameter, varying enhancement will be contributed to the luminescence from the two effects. The largest one is observed around the cut-off excitation field of the fundamental guided mode, i.e. the very point corresponding to the minimization of the group velocity (also the maximization of the LDOS). Nanoholes paves an efficient way to single-molecule detection at high by confining both excitation and collection to a real nanoscale volume. Apart from LSPs from nanoparticles and nanoholes, propagating SPPs along MDM structures can also affect light emissions and raise enhancement over large area. An example is shown in Figure 1.6c, non-resonant enhancement can be also obtained for the spontaneous emission owing to the tight confinement of the modes between two metal films[27]. The emission is preferentially guided by plasmon modes and then out-coupled into free-space or dielectric waveguides. The subwavelength scale of the mode volume of SPPs is also ideal for quantum optic transmission, for example, by coupling a quantum dot to a CdSe silver nanowire as shown in

Figure 1.6d. In such a configuration, the optical signal is carried by a stream of SPPs propagating along the NW with high efficiency up to 50% [28].

1.2 Introduction to Surface Enhanced Raman Spectroscopy

1.2.1 Basics of SERS

Surface Enhanced Raman Spectroscopy (SERS) is a spectroscopic technique that provides greatly enhanced Raman signal from Raman-active analyte molecules pre-absorbed onto metal surfaces with special morphology[29]. The increases of SERS signal with respect to bulk Raman signal have been regularly observed to be on the order of 10^4 - 10^6 , up to for some specially-designed systems. There are two key features outstanding SERS from classic Raman spectroscopy, surface selectivity and high-sensitivity. With the shrinking of nanostructures and nanodevices on both size and dimension, normal Raman spectroscopy is no longer fit for the probing of such systems. This is because both the dissipation of incident laser into bulk and the interference from the overwhelming bulk signal under the classic spectroscopy scheme. Instead, for the case of SERS, the signal benefits from so called "surface-enhancement mechanisms" and hence is highly surface-selective. The surface signal simply overwhelms the bulk one and no subtraction is needed[29].

Two mechanisms are believed to be responsible for the signal enhancement of SERS, electromagnetic and chemical, respectively. The

electromagnetic mechanism is primarily dependent on surface roughness or specific morphology features, while the chemical one is ascribed to the internal quantum structure change in presence of chemical absorption. The chemical mechanism generally provides enhancement on an order or two magnitude[30], which is quite ignorable compared to the electromagnetic one. Therefore, for most cases, one can simply focus on the electromagnetic mechanism. Owing to both high selectivity and sensitivity, SERS can be widely explored for structural and molecular identification in a variety of chemical and biological interfacial systems. Recently, with the fast development of plasmonic concentration, this classic spectroscopy opens its second spring. The high-sensitivity and easy-operation make SERS a convenient tool to check the field enhancement qualitatively and in turn the largely-enhanced field can boost the signal intensity.

SERS was originally observed for analytes absorbed onto noble (Au, Ag, Cu) and alkali (Li, Na, K) metal surfaces, usually with excitation of visible or near-visible wavelength. Theoretically, any metal can be excited its SPPs and support surface enhancement. Noble and alkali metals are of preference for SERS is simply due to their accessible calculation and much stronger enhancement than other kinds of metal. With extended excitation wavelength, e.g. near ultraviolet, metals like Pt and Pd is also usable for SERS, showing enhancement of 10^2 - 10^3 [31].

Since the overall enhancement of SERS predominantly comes from electromagnetic mechanism, it is substantially determined by the surface roughness features of the metal substrates. Methods for developing such roughness mainly target leaving up small metal particles, particle aggregates or periodical nanostructures, all of which are supposed fulfill the surface roughness requirement (such as examples shown by Figure 1.7). According to roughness at different levels, it can be realized in a number of ways: surface oxidation-reduction of electrodes, thermal evaporation of metal, metal spheres or arrays via polystyrene lithography as well as other powerful lithography techniques. Based on the plasmonic concentration strategy, the roughness must be developed towards the subwavelength scale or deeper scale limitation, as it keeps stimulating the core nanotechnology.

Now looking back on the electromagnetic mechanism, the intensity of Raman scattered radiation along electromagnetic(EM) field incident on the analyte is shown by a simple relationship,

Figure 1.7 A timescale showing the development of SERS substrates[32-37].

where I_R is the intensity of Raman field and E is the total EM field exerted to the analyte. In detail, two parts contribute together to this field,

$$E = E_a + E_p$$

where E_a is the field on the analyte without surface roughness and E_p is the field due to existence of particular roughness feature[31, 38].

In the above sum-up formula for EM field E , E_a is the very incident field on the analyte from the excitation laser. Given that the field source is very far away, E_a is too small to generate stro

ng Raman signal by itself. This is one of the reasons why normal Raman spectroscopy is "famous" for its weak signal. However, for the case of SERS, the presence of E_p provides a extremely near field to the analyte. This is because E_p is excited directly on a local "roughness" (e.g. a metal particle) and exerts on the absorbed analyte in its most proximity. Due to the near-field nature of E_p , it's much larger to E_a and makes the dominant contribution to the total EM field. In other words, the magnitude of E_p is the decisive one to the intensity of Raman signal. Of course, it has already been shown that E_p is the field due to the LSP excited on a local roughness of the metal surface. It's not only a near field to the analyte but also an intense, highly- confined one owing to the localizing nature of SPP. This also result in large energy density on a local roughness and explains the above relationship between E and I_R . In this scheme, it's not difficult to bring forward that the SERS signal from analyte

absorbed between two metal particles will be further enhanced than that from a single particle[39].

1.2.2 "Hot spots" and an insight into plasmonic substrate design

As discussed in last session, the performance of SERS is essentially dependent on the surface roughness features of the supporting substrates, which are usually noble metal nanostructures prepared via a series of deposition techniques. Therefore, developing highly active SERS substrates becomes the key access to the enormous probing potential of this spectroscopy, which requires advanced designs for the nanostructures to provide enough "hot spots".

The concept of "hot spots" comes from the observations of single molecule SERS on dye molecules absorbed on colloidal metal particles[40-41]. It has not only brought SERS to the frontier of probing techniques but also left over a question: for the aggregates, where does the large field enhancement exactly come from? Now it is confirmed that all single molecule signals detected in the colloid aggregates come from pairs of directly adjacent metal particles rather than isolated single ones[42]. With these high-intensity regions being observed via various spectroscopy techniques, it became clear that the most-neighboring coupling between metal particles (neither long-range nor radiative coupling) is responsible for this field focusing effect. For example, in Figure 1.8(A), bright SERS signals can be detected directly from adjacent particles by a combination of SERS and AFM[43]. It can be also demonstrated by electrodynamic

calculations of an adjacent particle of the same material and geometry to show the intensity of the hot spot and its polarization dependence on the incident light [shown by Figure 1.8(B)][43]. This means the intense EM fields leading to the largely-enhanced SERS signals are quite located in the region between particle pairs. Or one can suppose there are "hot spots" in the interparticle regions, which are to be excited upon illumination of appropriate wavelength. These hot spots are the key factors that give rise to the Raman signals generated by the analyte molecules trapped in the very region and make the probing possible. That's why the structure design for SERS substrates needs a full sight into hot spots first.

There are two phenomena giving rise to hot spots, which are (1) "lightning rod" effects and (2) hybridized plasmons[42]. The first one, lightning rod effects, are actually a result of simply electrostatic screening and non-plasmonic phenomena. They are well existent for subwavelength metal gaps and rough metal surface. Considering the case for two adjacent metal structures, owing to the electrostatic screening, the incident EM field tends to be compressed or into the gap between the two structures rather than penetrate into metal[42]. The effects are metal and essentially frequency independent. It should be noted that this geometrical field focusing is only significant in the IR and terahertz regions with metal still being perfect conductors. For the visible and near IR regions, the conduction electrons on the structure surfaces are all involved into collective oscillations and known as plasmons. At resonance, these oscillations

Figure 1.8 "Hot spots" between adjacent particles. (A) Micrographs of gold nanoshells by (i) AFM and (ii) inelastically scattered light from 4-MBA coated nanoshells. SERS spectrum of (i) nanoshell pair and (ii) single nanoshells. (B) EM field enhancement at excitation wavelength 633 nm for (i) an isolated nanosphere and (ii) nanosphere pair (incident polarization along interparticle axis)[43].

give rise to intense optical fields confined to the metal surface. Moreover, the hot spots here are actually from interacting plasmons on the two proximate structure surface. They are a new "dimer" hybridized plasmons and no longer the same with those generated on an individual metal structure. Progress has

been made on metal geometry control over their surface plasmon properties by a series of recent work. With increasing experience of substrate optimization for surface-enhanced spectroscopies, a guiding principle for such design is in urgent need to provide sufficient and reproducible enhancement as well as controllable plasmon frequencies.

Figure 1.9 Plasmon hybridization

Among the wide variety of newly-developed engineering, plasmon hybridization (PH) is a leading principle for controllable and effective plasmonic substrate design, which also gives a simple picture for one to understand the interacting plasmons involved in complex metal structures. The general diagram of PH is to treat plasmons from two adjacent metal structures as two single quantum systems coupled to each other as described by molecule orbital theory[44]. It is a simple and intuitive model for understanding the origins of plasmons and predicting their resonant energies and EM field distribution over a certain metal structure. As shown in Figure 1.9, for example,

surface plasmons originating from a metal nanoshell is similar to the case of interacting plasmons from two adjacent structures, a metal and a cavity. From the simple view of two single quantum systems (e.g. H atom described by molecule orbital theory), the coupling is to lead to energy level splitting. For the actual case of hybridized plasmons, the split energy goes to a higher anti-symmetric and a lower symmetric dipolar plasmons, respectively. Here the interaction distance between the sphere and cavity plasmons are represented by the nanoshell thickness. By changing the thickness, tunable plasmons can be easily obtained and the resonant modes can be given out by PH model. These predicted modes have already been proved by comparing them to the results calculated using Mie scattering theory[45]. Calculation methods such as finite difference time domain (FDTD)[46-47] methods and discrete dipole approximation (DDA)[48] have been widely used to describe the near and far field optical properties of plasmonic substrates with complex nanostructures. Although they are powerful enough to make predictions on different structures, they are actually lack of necessary connections to the plasmonic origin. That's why we need models like PH to predict the performance of a certain plasmonic structure in the design of SERS substrates, which rationalizes the structures and provides a more "plasmonic" view to understand their properties.

The PH model is no doubt a powerful tool to rationalize and describe a plasmonic structure. Notably, it can also give rise to improvements beyond a theoretical scheme since it is a model constructed by interacting plasmons and

carries the topological information referring to a specific plasmonic structure. For example, in the comparison of SERS enhancements on single nanoparticle and dimers[43], the closing-gap issue was revealed which adds an important consideration to the design principle of SERS substrates (Figure 1.10). The discrepancy between theoretical predictions and experimental results made people re-consider the actual loading process of analyte molecule into the gap region of dimers. Although the closing up of the gap region gives rise to the hot spots, it blocks the way of molecules getting into the gap at same time. Not to mention that the case of a final direct contact of the dimers, which results in very different optical properties with relative to two directly adjacent particles with a gap. Theoretically, the SERS enhancement due to pure EM mechanism can be evaluated as follows:

$$G_{SERS} = \left\langle \left| E_{incident}(\omega_1) + E_{NS}(\omega_1) \right|^2 \left| E_{NS}(\omega_s) \right|^2 \right\rangle$$

It is an average around the structure surface and covers two parts of EM field intensity enhancement, one at the incident wavelength and the other at the Raman-shifted emission wavelength, respectively. Further evaluation of the biquadratic enhancement can be given by a approximated value of $|E(\omega_0)|^4$. Here one important point to be noted is that broad-band plasmons are superior to narrow-band ones since a sufficient bandwidth is needed to cover both the excitation and the Raman-shifted wavelengths.

With the understanding of PH diagram, one can start a plasmonic structure design for SERS substrates. According to their particular research focuses, people have developed a numbers of nanostructures under this framework. Given its well-defined and highly-tunable plasmon modes, nanoshell structures have been chosen as the starting point to practice the design work by a number of researchers. These work set good examples for using the PH model to modify a substrate structure by systematical study including comparisons between theoretical and experimental results. More importantly, their results highlight new points to enrich the design principle under PH framework, which give rise to extra field enhancement or strong wide plasmon band. Here are two examples, the symmetry-broken structure and the nanosphere arrays for strong wide IR plasmon band. Both show the power of PH model as a design principle for structures supporting enhanced and tunable plasmon modes while at the same time it can rationalize them and explain the observed optical properties.

One example is nanoeggs, which is a core-shell structure evolving from concentric nanoshells[49-51]. The symmetry is broken by an offset of the dielectric core center from the original sphere center (offset values controlled by time in an anisotropic deposition). According to the PH diagram, the nanoegg

Figure 1.10 The closing gap issue.

plasmons can still be rationalized as hybridized plasmons from a sphere-cavity pair, only the coupling modes are not restricted to those of the same angular momentum. Experimentally, all the hybridized plasmon modes proved to be optically excitable and observable as a result of coupling from modes of all possible angular momentums. As shown by Figure 1.11(a), the hybridization peak displays a blue shift and asymmetrically broadening with an increasing offset value (i.e. increasing time). And the resulting mode at the thinner shell region turns out to be much stronger than in the concentric case.

The other example is nanosphere arrays shown by Figure 1.12(a). In the view of PH diagram, the nanogaps between patterned nanospheres form a well-defined periodical hot spot arrays. PH theory also points out this gap region scale should be confined to sub-10 nm range. The collection of dimer or junction plasmons in such periodical structures results in a strong broad hybridized mode, displayed by the near-IR broad peak in the extinction spectrum of Figure 1.11(b). This is due to the interaction of plasmons between

adjacent nanospheres which redistributes the majority part of energy to the lower level[50].

Figure 1.11 Symmetry-broken structure featured with (a) experimental, (b) calculated (FDTD) extinction-peak shift with varying deposition time/offset (black: concentric nanoshell; color: nanoeggs with core offsets) field redistribution and (c) calculated near-field distribution with varying core offsets[50].

Figure 1.12 Periodical nanostructures featured with a strong wide plasmon band. (a) SEM image of Au NP arrays on ITO glass. (b) Vis-NIR extinction spectrum of the arrays[52].

1.2.3 Nanostructured SERS substrates

As is shown by a series of reports on aggregated colloid substrates, the hot spot geometry which supports enormous enhancement is an interparticle nanogap between adjacent metal particles[53]. Although colloid aggregates are easy to form such geometry and able to provide large field enhancement, the geometry is neither reproducible nor controllable. Therefore, aggregated colloid substrates is not a good choice to for further development and research motivation. In this strategy, periodical nanostructures and well-defined planar geometry are no doubt of great superiority to be developed as SERS substrates.

A variety of nanostructures have been explored to develop SERS substrates of planar-geometry, including nanorods, nanorings, nanoshells,. Such planar substrates of periodical nanostructures support a series of hot spots, which originate from well-defined junction plasmons. These plasmon modes are decided by the dimensions of an elemental metal structure as well as the array topology. Within this scheme, the way towards highly effective SERS substrates through sub-nanoscale actually lies in the optimizations by three approaches, which are nanolithography, nanogap thickness control and hot spot geometry. These optimizations are not only targeted at the design of SERS

substrates, but also applicable for other plasmonic structures. Recently, a series of well-developed SERS substrates are no doubt approaching this goal with fast progress, illuminating the whole field with various ideas. Here three examples are chosen and discussed to show their concepts of SERS substrate design or optimization methods.

Figure 1.13 Self-closed gold nanofingers for hot spot arrays. (a-b) Self-closing driven by capillary force. (c-d) SEM images of the nanofingers before and after closing. (e) Schematic of molecule-trapping. (f) Field distribution (at 750 nm with finger diameter 136 nm)[54].

Optimization of structure techniques: self-closing nanofingers. For this optimization, the task is not simply to overcome the nanostructure complexity

or to break the scale limit. Fast and simple processing is also of great concern for developing more efficient and advanced nanotechnology. As shown by Figure 1.13, dense and periodical nanogaps are formed between self-closed gold nanofingers driven by microcapillary force in the exposure to analyte solution[54]. These gold nanofingers are prepared via nanoimprint lithography and post-deposition of gold. In this case, the self-closing still results in hot spot geometry with well-defined periodicity and plasmon modes. Furthermore, the substrate structure is able to trap molecules into the gap region during the closing process.

Figure 1.14 Sub-10-nm nanogap arrays assisted by ALD. (a) Field enhancement with a 5 nm gap shown by FDTD simulation. (b) Nanohole arrays confined by ALD. (c) Field distribution along the nanogap profile. (d) SERS result due to areas with nanogaps compared to non-nanogap areas[55].

Optimization of nanogap thickness: atomic-layer-deposition (ALD)-assisted nanogap formation. ALD is a powerful deposition technique known for its extreme control over thickness and 3-D conformability due to its real "layer-by-layer" deposition process (a detailed introduction is to be given in **Section 2.1.1**). It's very proper to be explored for the deposition of ultrathin dielectric nanogaps in sub-10 nm scale. Back to 2006, a metal-insulator-metal nanocavity structure with a 3 nm-thick SiO₂ gap has been prepared using this technique and highly nanometric confinement has been demonstrated due to the gap thickness[56]. Figure 1.14 shows a typical example of forming nanogaps via the fine-control on spacer thickness by ALD[55].

Optimization of hot spot geometry: a combination of genetic method and generalized multiparticle Mie theory[57-59]. It has been proposed that an alternative principle other than the PH model is also applicable for the design of plasmonic structures. If considering the optimization of a planar nanoarray as a real physical quantity, its degrees of freedom should consist of elemental nanostructure shape, size, geometrical arrangement and metal dispersion. Correspondingly, a series of general constraints can be enforced from several levels. For present technical limitations, constraints should be applied to ensure the plasmonic response of a nanostructure arrays, such as a minimum and a maximum dimension of elemental nanostructure, a minimum inter-structure separation, etc. As for measurement and probing manipulations, objective functions can be given such as local and average field enhancement values,

scattered power and the frequencies used for excitation (narrow and wide band optimizations) [60].

Figure 1.15 Genetically optimized plasmonic arrays. (a) SEM image of genetically optimized arrays. (b) Comparison of the field concentration between (b₁) genetic array, (b₂) dimer and (b₃) periodic grating. (c) Comparison of the near-field intensities of the three concentrating structures by both theoretical maximum spectra (d) and experimental SERS signals[60].

Figure 1.15 shows such an example for geometric optimization of plasmonic nanoarrays following the above diagram. It starts from generalized multiparticle Mie theory, which enables a multipolar expansion of the scattered field by vector spherical wave functions[61]. Then in this context, the total function is solved by the genetic algorithm for the maximized field enhancement. This biological approach is a branch of evolutionary algorithms,

which originate from evolutionary concepts such as nature selection and survival of the fittest. Due to the superiority of dealing with large ensembles of unknowns, the genetic algorithm has been proved feasible for a series of nano-optic problems[53, 62]. As shown in Figure 1.15(b)&(c), genetically-optimized particle arrays theoretically support significantly higher field enhancement than both dimer and periodic structures. And the experimental results of SERS measurement in Figure 1.15(d) have confirmed these predictions and indicated the geometric superiority of the proposed structures.

Another inspiring geometry is featured with "cascaded enhancement effect". It has been first demonstrated on self-similar metal nanospheres, or "nanolenses"[63]. For example, as shown by the inset schematic in Figure 1.16(a), the minimum sphere is sandwiched by two larger ones constructing atypical nanolense geometry. For such a nanolense containing n nanospheres, the cascaded enhancement coefficient is estimated to be $\sim Q^n$. With chosen radii of the nanospheres, the corresponding field enhancement can be simulated as shown by Figure 1.16(a). More elaborate designs can be developed to achieve cascaded enhancement, such as the nanogalaxies shown in Figure 1.16(b). The comparison based on Raman signal enhancement gives a full view of its dependence on both sphere size and interparticle gap width.

Figure 1.16 Cascaded enhancement effect supported by (a) nanolenses with simulated field enhancement [64] and (b) nanogalaxies with varied sphere radius and gap width compared to a dimer [65].

1.3 Objectives and significances of the studies

My Ph.D project includes contents of the following two parts:

Part 1: Fabrication of nanostructured plasmonic substrates and demonstration of their application as SERS substrates.

Part 2: Study of plasmon-enhanced radiation on semiconductor-dielectric-metal (SDM) structures.

The objective and significance of the first part:

Fabrication of plasmonic structures (nanogaps and nanoholes) using non-lithography methods for highly effective SERS substrates. Nanostructured

SERS substrates have become the first choice for both local probing and scalable research owing to their high controllability and reproducibility over aggregated particles. Theoretically, a sub-10 nm gap is needed in a typical plasmonic hot spot geometry for SERS due to the ultrahigh local electric field. For this purpose, developing cheap and scalable lithography-free techniques are always in need. In this part, our fabrication approaches rely on surface modifications of nanostructured templates. We first used ZnO nanorods as scaffold to obtain vertical nanogaps of well-defined hot spot geometry. For another approach, a simple template-free imprint recipe has been developed to the fabrication of random arrays of sub-10 nm nanoholes on pre-deposited Pt thin films. Such ultra-small holes have been proved to scatter light effectively into LSPs and enhance the local field by SERS measurement. Perspectival, such nanoholes make single-molecule probing possible. For both approaches, the resulting plasmonic structures (nanogaps and nanoholes) exhibit rich hot spot profiles and high efficiency for SERS measurements.

The objective and significance of the second part:

Metal plasmonic-enhanced photoluminescence of ZnO nanostructures. Plasmonic-engineered radiation is an interesting phenomenon including the observations of Purcell effect on plasmon-emitter coupling systems. Very recently, increasing efforts are being put on designing metal plasmonic nanostructures that are coupled with semiconductors for light emission

enhancement and their possible applications in light emitting diodes and nanoscale laser source. Based on a near-field coupling scheme and the precise thickness control of ALD, a series of semiconductor-dielectric-metal (SDM) nanostructures have been fabricated for a plasmonic-enhanced radiation study. By systematic photoluminescence (PL) measurements, a gap-thickness dependent enhancing mechanism has been demonstrated on both thin film and nanorod ZnO. Interestingly, our static and time-resolved luminescence results imply that the plasmonic-engineered radiation originates from a new coupling regime different from the two well-known regimes, that are strong coupling regime (Purcell effect) and weak coupling regime (Rabi splitting).

Chapter 2

Experimental techniques

2.1 Sample preparation

2.1.1 Atomic Layer Deposition for ultrathin dielectric gaps

Atomic layer deposition (ALD) has been rising very recently as an advanced deposition technique due to high demands on semiconductor processing. Back to the 1990s, with the fast development of semiconductor industry, the coating of continuous and pinhole-free films of high- κ dielectrics were one of the imperatives to ensure the accurate performance of semiconductor devices. Based on such demands, the technique of ALD has been developed and renewed, which is featured with unique conformality on high-aspect-ratio structures over all the other deposition techniques. Now over four generations, ALD has also become a key technique for the scaling-down of a great variety of micro- and nanodevices.

The outstanding conformality of ALD relies on its precise thickness control at Ångstrom or atomic layer level. This is because the deposition process of ALD is based on self-limited, sequential surface reactions. As displayed by Figure 2.1, for most ALD processes, the deposition undergoes binary reaction sequences to form a binary compound film. There are actually four steps in a *reaction cycle* of ALD:

Figure 2.1 Schematic representation of ALD

- (1) A self-limited reaction between reactant A and substrate surface;
- (2) A purge to remove remaining reactant A and gaseous by-products;
- (3) A self-limited reaction between reactant A and B;
- (4) A purge to remove remaining reactant B and gaseous by-products.

Reaction cycles are repeated until the total layer thickness reaches one's expected value. The domination of self-reactions makes ALD an absolute surface-controlled process and hence the deposition are substantially dependent on reaction parameters, i.e. the two reactants, substrates and reaction temperature.

The reaction control can be realized via various ALD reactor designs. Currently, most ALD reactors use a carrier gas flow pumped all the way to drive and manipulate the reaction process accurately. A typical reactor design is shown in Figure 2.2, which is synchronously modulated flow and draw. The design defines a very short residence time for reactant exposures by injecting

inert gas at the reactor inlet/outlet in the dose/purge step, respectively. In this way, the synchronized modulation of inert gas between inlet and outlet is realized simply by an injection shift and acquires a high-speed gas flow switching for the reactor.

Figure 2.2 Illustration of dose and purge modes of ALD.

2.1.2 Fabrication of plasmonic nanostructures

The fabrication of plasmonic nanostructures in this project is essentially a combination of *bottom-up* method and *surface engineering*.

Bottom-up method: As is known, top-down and bottom-up methods are two basic approaches to fabricate nanostructures on a substrate. Well-defined plasmonic structures can be developed via both methods. Top-down methods, such as soft lithography and electron beam lithography (EBL), have been widely explored to create surface patterns. In contrast, bottom-up methods here for plasmonic structures aim to guide metal nanoparticles (NPs) or clusters into organized surface structures by exploiting inherent interactions between the manipulated systems and the environment. Templates such as aligned ZnO

nanorods (NRs) have been widely utilized in bottom-up fabrications owing to their well-defined nanostructures and convenient growths.

Surface engineering: In the above strategy of bottom-up fabrication, the key session is how to realize the manipulation of metal NPs or how to drive the self-organization process. Given the subwavelength scale that this project has been focused on, the manipulation substantially relies on the surface properties of nanomaterials. Since the specific surface energy of such nanomaterials is relatively large, their surface properties can be easily engineered via flexible surface treating or modifications. In this project, various surface treatment or interactions have been exploited to change the surface properties of pristine nanomaterials, including capillary effect, ALD capping and hydrothermal treating. Especially, the combination of carefully controlled ALD capping with such internal universal effects turns out to reveal a rich and innovative profile of surface engineering.

2.2 Optical characterizations

2.2.1 Confocal Raman spectroscopy

Two confocal Raman systems have been used for optical characterizations in this project, WITEC CRM200 and Renishaw inVia Raman systems. Here taking Renishaw inVia Raman system for example, its schematic is shown in Figure 2.3. A 785 nm laser is coupled into the system and undergoes beam expanding to enlarge the spot size of the incoming beam. After being reflected

wise, the beam is split by holographic filters and directed separately to the microscope and the slit. The spot size of the laser beam is around $1\mu\text{m}$ at focus point with a $\times 100$ objective lens. The sample is located on a XYZ stage which can be moved manually along x - and y -axis. The Raman scattering light is collected via backscattering mode and so is the Rayleigh light.

Figure 2.3 Schematic of confocal Raman system

2.2.2 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a contactless and nondestructive method for probing the electron structures of materials. When light is directed onto a sample for photo-excitation, it is absorbed with excessive part redistributed. With photo-excitation, the light emission for energy dissipation is called photoluminescence. The experimental setup for the PL measurement is shown in Figure 2.4. The PL measurements were performed at room temperature, and a continuous wave (CW) He-Cd gas laser emitting at 325 nm

was used as excitation source. The laser was focused onto the sample with spot size around 1 mm, and the emitted signal was collected into a 750 mm spectrometer and detected by photomultiplier using the standard lock-in amplifier technique. A long-pass filter is inserted before the spectrometer to avoid the influence from the laser beam.

Figure 2.4 Schematic of photoluminescence spectroscopy system

Chapter 3

Metal nanogaps for highly effective SERS substrates

3.1 Introduction

Plasmonic functionalization has been extensively studied and applied on a variety of nanostructures and nanodevices via a broad range of methods, from simple modifications by metal NPs to advanced nanolithography techniques. In spite of the specific metal type, geometry and resonant frequency, these well-designed plasmonic structures have been proved to be very effective for field concentration and succeed in boosting a number of techniques and devices, such as such as near-field scanning optical microscopy, photodetectors, nanoscale lasers, photovoltaics, catalysis[66-69]. In the strategy of field concentration, plasmonic structures can be divided into resonant and non-resonant ones. Both are able to provide field enhancement despite their different frequency responses. Resonant structures, such as single metal NPs and particle aggregates, usually gives enhancement at one order of magnitude or above. Non-resonant structures, such as "lightning rod" and "feed-gap", are often combined with resonant effect when considering a plasmonic structure design. Especially, the feed-gap structure enables strongly-localized field distribution within the gap region and outstands itself as a "hot-spot" geometry,

which has been illustrated by a series of newly-developed photonic nanostructures[70-72]. Sandwiched by two metal surfaces, the field concentration effect proves to be dominated by the gap width, resulting in even stronger field within thinner nanogaps. To tune the gap width down to sub-10 nm scale, we need to seek fine control over the distance between the two metal surfaces, e.g. by exploring ALD. Suppose we set two poles first, with diameter and separation distance both in nanometer scale, in this case ALD (e.g. a layer of dielectric capping) over the two nanopoles enables precise control on the pole diameter. By carefully thickening the two poles, nanogaps with thicknesses down to 5 nm or thinner can be finally formed and give rise to the local field intensity along three dimensions. Such scheme can be simply realized with well-prepared nanoarrays with good alignment. For example, since the material of ZnO is easily to be fabricated as vertically aligned structures, such as nanorod and nanowire arrays, it is ideal to be considered as the scaffold material for the fine-tune of nanogaps.

In this scheme, we built nanogap arrays for highly efficient SERS substrates by combining ALD and capillary effect as surface engineering method. Owing to the fine control of the deposition on atomic level, the nanogaps formed between close NRs can be well tuned between two kinds of gap profiles, wedge-like and uniform ones. With SERS measurement to show the local field enhancement, both kinds of profiles prove to support different enhancement to SERS signals, which shows a close dependence on the gap

profile, increasing significantly with the reducing of gap width and wedge angle. The nanogap arrays formed this way is a promising SERS substrate, due to their overall enhancement factor (EF) on the order of 10^5 and good scalability.

3.2 Experimental

Sample preparation. Well-aligned ZnO NR arrays were grown on *a*-plane sapphire substrates via chemical vapor deposition with thoroughly mixed ZnO and graphite powders as source material. The growth details was duplicated the recipe from a previous publication. The as-grown samples were cut into small pieces for the subsequent depositions of ALD coating and Ag sputtering. The gap-tuning layers of amorphous ZnO were coated by ALD, in which various ALD cycles were chosen for the thickness of 10, 20, 40, 50 and 60 nm, respectively. The outer layers of Ag were coated via DC sputtering (JFC-1600, JEOL). The sputtering was performed under power control of 20 kW and 10 mA for 40 s. Some samples were directly sputtered with Ag without the middle ZnO gap-tuning layer for control experiment. The morphology of the NRs was observed using both scanning electron microscope (SEM) and transmission electron microscope (TEM). For molecule loading, all the prepared samples were dip in aqueous solution of R6G molecules with a concentration of 5×10^{-5} M for 20 min. Then they were washed with deionized water for three times and then left in a dark room until dried naturally in air. The loading process was performed right before optical characterization.

Optical characterization. The SERS measurements were carried out on a WITEC CRM200 Raman system with a 532 nm line laser as excitation. The beam size of the laser is about 1 μm in diameter and the incident power was set to be 20 μW . At least three measurements were taken by selecting different detecting spots on each sample to assure the reproducibility. All the Raman spectra were obtained at room temperature with the same accumulation time and incident power.

3.3 Results and discussions

By combining the internal (capillary effect) and external (ALD capping) effects, the gap distance between adjacent NRs can be fine tuned down to sub-10 nm scale and two kinds of gap profile have been realized for hot-spot geometry, evolving from "wedge-like" to aligned one. As shown in Figure 3.1, the overall sample morphology displays a significant evolution with the increase of ALD capping thickness. Starting from aligned NRs [Figure 3.1(a)], the NRs are first drawn to bundled NRs [Figure 3.1(c)-(e)], then disassembled to thicker NRs with quasi-alignment [Figure 3.1(f)-(h)], referring to ALD thickness of 0, 10, 20, 40, 50 and 60 nm, successively. Here the reference sample in Figure 3.1(b) is sheer bundled NRs with nothing capped. Besides the starting aligned NRs and its analogue [Figure 3.1(a)&(b)], all the other samples had been made SERS-active with an outermost capping of Ag NPs over the

intermediate ALD layer. Notably, the ALD capping layer also serves as a solid dielectric surrounding besides tuning the NR thickness.

The formation and evolution of such substrate morphologies are a joint effect due to the co-existence of capillary effect and NR thickening by ALD capping. As described above, after the two-step capping on NRs, they were all dipped into the analyte solution, i.e. an aqueous solution of R6G. The capillary effect during such dipping process is a common phenomenon and has been observed on various nanomaterials exploited as SERS substrates, including nanowires, nanofingers, nanotubes, etc[54, 73-74]. In our sample system, it is the case for the ZnO-Ag sample in image (c). Now with the NR thickening by ALD capping, the capillary effect is to be suppressed due to poorer flexibility of each single NR and results in a "loose bundling" of the NRs [image (d)&(e)]. Such loose bundling of thickened NRs forms much thinner nanogaps with relative to those in the original bundling [image (c)]. When this NR thickening cross some critical value, one can expect that the capillary effect will no longer be dominate to the structure. That's the case for the samples referring to image (f)-(h). The further thickening (40 nm and above) finally suppresses the capillary effect and becomes dominant controlling factor of the structure, shifting the even thicker NRs back to quasi-alignment and forming thin and long uniform nanogaps. As expected, by introducing ALD capping, the hot-spot geometry based on ZnO NR scaffold can be flexibly tuned between two

Figure 3.1 SEM images of the nanorod scaffold plasmonic SERS substrates. (a) As-grown vertical-aligned ZnO NRs as the starting scaffold, (b) capillary scaffold of these pristine ZnO NRs and (c) ZnO-Ag, (d) ZnO(+10)-Ag, (e) ZnO(+20)-Ag, (f) ZnO(+40)-Ag, (g) ZnO(+50)-Ag, (h) ZnO(+60)-Ag as plasmonic SERS substrates. Numbers in the parenthesis denote the ALD coating thickness. Insets in images (f–g) show the top view of the quasi-aligned structure. The definition for the quasi-aligned and bundle structure can be found in the text.(scale bar: 500 nm)

nanogap profiles, i.e. thin wedge-like gaps and uniform ones. The wedge-like nanogaps have been proved to be a highly effective hot-spot geometry which focuses the optical field to the "wedge apex" or the NR tips. In such a "funnel" scheme, the apex gets "hotter" dramatically with the decrease of the nanogap thickness[75]. Therefore, by comparing the gap profiles in image (c)-(e), the sample ZnO(+10)-Ag is of the greatest expectation for enhancing SERS signals. The latter one, thin uniform nanogap has been shown to result in field redistribution along its thin long gap profile and also be able to provide certain enhancement[76].

Next, SERS results are exploited to evaluate the field concentration effects due to the specific nanogap profile of each sample. Figure 3.2 shows the SERS results of R6G molecules (molar concentration 5×10^{-5} M) dispersed on all the modified substrates, with that on pristine ZnO NRs and Ag thin films as references (No R6G related Raman signal can be observed on the pristine NR scaffold). As shown by Table 3.1, all the Raman bands match well with those of the characteristic spectrum of R6G as follows. By comparing the peak intensities of the SERS spectra between nanogap substrates and reference substrate, it can be found that all the hot-spot geometries of the samples show significant enhancement to the SERS signals. For the substrates of thin wedge-like nanogaps, ZnO(+10)-Ag shows the strongest

Figure 3.2 SERS spectra of R6G molecules with a concentration 5×10^{-5} M, collected from (a) bundled structure and (b) quasi-aligned structure, respectively. Both spectra include the results from two reference samples: pristine ZnO NRs and Ag thin films.

SERS enhancement, followed by ZnO-Ag and ZnO(+20)-Ag, successively. Combined with the observations on Figure 3.1(a)-(e), a trend of SERS enhancement vs. gap-tuning in the wedge-like profile can be revealed that with the reduce of nanogap width (tighter bundling of the NRs), the signals are enhanced even further. This is in good accordance with the theoretical results shown by Dawson et al., that the field enhancement is greatly reinforced by reducing the nanogap width between neighbouring posts, with enhancement

ratio up to 180 and above within a single gap[75]. For the substrates of thin uniform nanogaps, all the three also give notably strong enhancement to the Raman signals with a trend $\text{ZnO}(+50)\text{-Ag} > \text{ZnO-Ag}(+40) > \text{ZnO}(+60)\text{-Ag}$. By observing Figure 3.1(f)-(h), one can find that since the thick NRs have already gotten rid of capillary effect, the nanogaps are simply reduced with thicker ALD capping. However, when the capping finally gets thick enough to close a certain number of nanogaps, the "closing-gap" issue becomes notable and hence leads to a drawback to the overall performance of a SERS substrate[42]. That's the case for the substrate $\text{ZnO}(+60)\text{-Ag}$ in Figure 3.1(h). The basic trend here is still that the signal enhancement follows gap width inversely, which proves that gap- tuning works for both profiles.

Table 3.1 Assignment of characteristic Raman bands of analyte R6G.

Inner-molecule modes	C–C stretching	C–H in-plane bending	torsional and/or bending	C–C–C in-plane bending	C–H out-of-plane bending	C–O–C stretching
Characteristic Raman bands (cm^{-1})	1360 1507 1573 1650	1126 1183	518	614	774	1309

Figure 3.3 Enhancement factor (EF) due to narrowed nanogap plotted vs. ALD layer thickness. Inset shows a TEM image of a single ALD thickened NR with Ag nanoparticle capping.

In order to show the dependence of signal enhancement on ALD thickness, the enhancement factors (EF) of the above SERS results have been estimated based on the following formula,

$$EF = (I_{SERS} / I_{bulk}) / (C_{SERS} / C_{bulk})$$

where I_{SERS} and I_{bulk} denote SERS and bulk Raman peak intensities while C_{SERS} and C_{bulk} denote the molar concentration of R6G molecules in the aqueous solution used in the dipping step and that of R6G bulk sample, respectively. By picking out one of the characteristic bands, e.g. 1507 cm^{-1} , EFs can be estimated and plotted vs. ALD coating thicknesses, as shown in figure 3.3. This plot provides a straightforward quantification of both the SERS performance of

nanogaps and their dependence on our gap-tuning parameter. The overall high EFs illustrate that both kinds of nanogaps service as highly effective hot-spot geometries for SERS substrates, indicating their superiority as field concentration profiles, with overall EF above 5×10^5 and up to 2.64×10^6 . Such nanogaps primarily benefit from their further reduced gap width and wedge angle (the wedge-like ones)[75], both owing to the high flexibility and controllability of the proposed gap-tuning method. Moreover, the surrounding dielectric environment introduced in the method also serves as a shelter that reduces the scattering of the incident light to the scaffold. This particular additive distinguishes our nanogaps from the previous reports[54], which ensures the enhanced optical field can effectively contribute to the Raman signals. As for comparison, the wedge-like ones provide one single substrate [ZnO(+10)-Ag] with the highest EF over the whole sample system, while the uniform ones provide generally high EFs within the gap tuning range here. This is essentially due to their different redistributions of the field by the specific plasmon modes. Instead of focusing the field to NR tips, uniform nanogaps induce strong field enhancement along their thin long profiles, which makes them beneficial to the applications or devices that require global field enhancement over large surface area.

Figure 3.4 Absorbance of pristine ZnO NRs and SERS substrate of ZnO(+10)-Ag. The number in the parenthesis denotes the ALD coating thickness. Note that the decrease of absorption below 400 nm is due to the detector limit.

In order to identify the plasmon modes related to the nanogaps, we also try to acquire the absorption spectra of the substrates. As shown in Figure 3.4, taking the substrate with the strongest SERS signal as an example, the UV-vis absorbance (relative) of ZnO(+10)-Ag and pristine ZnO scaffold are plotted together for comparing observation. The strong and sharp peaks from both spectra in the range of 300-420 nm are attributed to the ZnO absorption in UV region. There is one more broad absorption for pristine ZnO NRs in the range of 500-650 nm, which is attributed to defects. No evident peak related to the SPR of Ag NPs can be observed in the spectrum for ZnO(+10)-Ag.

3.4 Conclusions

In this chapter, a simple surface engineering method combining ALD and capillary effect has been explored to fabricate tunable nanogaps for promising SERS substrates. With simply varying the coating thickness of ALD, both gap width and vertex angle can be fine tuned and hence two kinds of gap profiles (wedge-like and uniform) can be formed. The following SERS measurement on the nanogap substrates all show significant enhancement to the signals, indicating the great local field enhancement due to the nanogaps. This field enhancement increases with the decrease in gap width and angle, resulting in stronger SERS signals for the wedge-like gaps than for the uniform ones. So far, the nanogap arrays prove to be highly-active SERS substrates due to the scalable surface engineering method.

Chapter 4

Ultrasmall nanoholes for molecule trapping and probing

4.1 Introduction

Nanoholes are generally referred to holes perforated on metal thin films whose size and spacing distance are both in subwavelength scale[77]. Owing to both geometry[3] and surface plasmon resonance (SPR) effects, such nanostructures show peculiar optical properties, e.g. extraordinary optical transmission[78]. Nanohole arrays in noble metal thin films (e.g. Au films) prove to be more transparent at certain wavelength than the conclusion given by classical aperture theory[79-80]. Their response to specific wavelength is direct reflectance of SPR[81]. By studying the optical and spectroscopic properties of the nanohole arrays, it has been found that these properties can be well tuned by controlling the geometry of the arrays, including single hole shape and array periodicity[79, 82-83]. Each nanohole functions as an nanoantenna and focus light extremely to its apex[84]. Also the hole geometry itself decides its natural superiority for analyte restriction. Due to the subwavelength-scale periodicity, nanohole arrays are easy to be operated in optical wavelength range and hence is a desirable nanostructure for light manipulation. All these mentioned characteristics make nanohole arrays an ideal substrate for surface-enhanced spectroscopy[85-86].

SP-based molecule-probing or chemical sensing mainly explores the wavelength response of SPR and the EM field localization due to its excitation. The supporting nanostructures need further scale-breaking for both field confinement and molecule trapping[84]. Hence this throws a big challenge to both resolution and control on the hole shape and spacing of the imprinting method. The imprinting technique is the key session to realize this scheme. Recently, techniques such as soft lithography and electron beam lithography have been frequently used to perforate nanohole arrays into metal thin films. To achieve both extreme spatial and field localizations, ultrasmall nanoholes (size in sub-nanometer scale) and their arrays are of particular interest. At present, high-energy beams are the main technique for milling individual nanoholes on membranes, such as Si_3N_4 (using ion beam lithography)[87] and SiO_2 (using electron beam lithography)[88]. Most recently, optical methods such as laser ablation have been picked up to drill ultrasmall holes down to 4 nm[89]. Despite of the extreme high energy and cost of these mass or laser beams, the poor resolution and scalability are still serious limitations, not to mention that these high-energy lithography techniques so far not work well for metal thin films. Although alternative high-energy imprinting methods can directly drill naonholes on metal films[89], they still face applicability issues, such as poor spatial scalability and SPR excitations. A low energy and high throughput nano-imprinting method is in stringent need to build large patch of nanohole

arrays which support plasmon excitations and usable for molecule trapping and probing.

In this project, we propose a one-step method of using simple hydrothermal reaction process to form dense and random nanohole arrays on large pieces of Pt thin films (millimeter scale) which proves supportable by various substrates (sapphire, ZnO thin films and SiO₂). Both the size and density of the resulting nanoholes can be tuned by varying the chosen substrates and the control parameters of surface-engineering process. This method reaches a resolution down to 30 nm with tunable hole density from 10 to 20/μm and substrate scalability. Noticeably, the resulting nanoholes proves to be highly effective for exciting plasmons along the thin film surface, providing strong SERS signals of 4-adenosine triphosphate (4-ATP) molecules with an enhancement ratio of 5000 fold for the signal intensity (compared with as-sputtered Pt thin films).

4.2 Experimental

Sample Preparation. The original Pt thin films were deposited *via* DC sputtering (JFC-1600, JEOL) at room temperature onto various substrates selected for this project. The deposition was controlled by fixed sputtering current and time, 10 mA and 40s, respectively. Next, the starting Pt film underwent a series of surface engineering treatment, including ALD, hydrothermal reaction and a final wash-off. For ALD of ZnO as seed-layers, the

layer thickness was controlled by a fixed recipe to ensure the same thickness (50 nm) coated on all the samples. The deposition and control details can be found in Chapter 2. For the next hydrothermal treatment, the reaction time had been pre-tested several times and optimized to be 1 h fixed for all. Finally, after the hydrothermal reaction, all the samples were rinsed by diluted HCl solution several times to remove thoroughly the resulting ZnO NRs from the hydrothermal process. They were then dried naturally in air and so far ready for the following measurement.

Characterizations. The SERS measurements were carried out on a WITEC CRM200 Raman system with a 785 nm line laser as excitation. The beam size of the laser is about 1 mm in diameter and the incident power was set to be 2 mW. At least three measurements were taken by selecting different detecting spots on each sample to ensure the reproducibility. All the Raman spectra were obtained at room temperature with the same accumulation time and incident power. The AFM mapping was performed on a VEECO Dimensional-3100 AFM.

4.3 Results and discussions

The imprinting flow and steps are display by Figure 4.1(a), with SEM images in Figure 4.1(b) showing the as-processed morphology due to each step. The starting material is Pt thin films deposited via simple DC sputtering onto selected substrates. As shown by bold letters in Figure 4.1(a), the whole

imprinting procedure covers three steps, which starts with Step 1: ALD coating of a ZnO seed layer onto our as-deposited Pt thin films. Note that for a better control over the imprinting result, the multi-layer depositions so far are exactly the same for all the samples. The resulting surface morphology can be found in image (i), which turns out to be a layer of densely packed ZnO NPs with average size ~ 250 nm as well as separate nanoislands due to local aggregation. Given the uniform particle size distribution of the original Pt layer (also checked by SEM, images not shown here), such morphology indicates that even the medium deposition temperature of $200\text{ }^{\circ}\text{C}$ in a short time interval (within 5 min) still leads to strong aggregation of underlying Pt NPs. Those Pt "islands" exposed out of the ZnO layer are separated from each other whose sizes are in the range of $300\text{ nm} \sim 1\mu\text{m}$. Now moving forward to Step 2: hydrothermal treatment. This is a very routine hydrothermal reaction for growing ZnO NRs, which are merely by-product in our imprinting strategy. After such multi-layer substrates have undergone the reaction, it can be found in image (ii) that there is a coexistence of hydrothermally grown ZnO NRs and the resulting porous metal layer beneath. Compared with the sample morphology before this step, it is evident that the transformation of the metal layer occurs right during the hydrothermal reaction. Hence this step is regarded as the genuine "imprinting step", which imposes a comprehensive effect via the specific temperature, pressure and transport process during the nucleation of ZnO. And image (iii)

provides a further illustration of the above conclusion, which shows the resulting morphology of a synchronously-treated comparing sample only with

Figure 4.1 Imprinting steps shown by (a) schematic and (b) SEM images after each imprinting step.

the mixed solution replaced by DI water. In image (iii), the clear boundary of a layer of continuous Pt thin films can be easily identified. By checking the whole piece of sample it can be confirmed that no porous film are formed on the metal

films of such a comparing sample. This is a solid evidence to demonstrate that the hydrothermal reaction is the decisive step for the final formation of the nanoholes. The final step, Step 3, is simply rinsing and drying to removing any by-product and remaining chemicals from Step 2. After this step, the nanoholes on Pt thin films are quite observable and ready for the following characterizations. Image (iv) is a example of sparse nanoholes distributed on large piece of Pt thin films. From this image, one can find that the finally resulting metal layer are no longer packed particles piled on substrates but now large independent pieces with continuous surface and clear boundaries. Note that the sample in image (iv) is actually a piece supported by Si substrate rather than sapphire (the main substrates selected in this project). This piece also shows the wide applicability of the proposed imprinting method, since it doesn't rely on the supporting substrates.

Figure 4.2 Nanoholes imprinted on Pt thin films supported by different substrates, (i) dense region on sapphire, (ii) sparse region on sapphire and (iii)

ZnO thin films, with (iv) reference of the original morphology of Pt thin films (scale bar 2 μm).

Figure 4.2 displays a full view of the nanoholes imprinted on metal layer as described above on different substrates [image (i)-(iii)] as well as the original morphology of the starting Pt thin films from DC sputtering [image (iv)]. For a better comparison on the imprinting control of the sample morphology, all the three samples have undergone the very same treatment through each step. Figure 4.2(i) and (ii) are two regions formed on the same piece of sapphire substrate, with evident density difference. Figure 4.2(iii) are porous Pt thin films formed on ZnO films (1 nm Al_2O_3 buffered). For all the three samples, nanoholes with high density are imprinted on Pt thin films with average hole size estimated to be 10 nm. Due to the high density and relatively centralized size distribution of the nanoholes, they can be regarded as quasi-uniform arrays when exposed to laser beam illumination (around 1 μm in spot diameter).

From image (iv) showing the morphology of the starting Pt films, one can find that it's a layer packed by discrete Pt NPs, of sizes in the range of 130–500 nm in diameter. In the discussion around Figure 4.1(b), one confirmation has already been made that these dense tiny nanoholes are formed directly by the hydrothermal reaction based on the comparison of the sample morphologies with and without undergoing the reaction process. That is, with only the reaction temperature and heating time, the raw NPs will be transformed into large pieces of continuous thin films with improved smoothness [e.g. Figure

4.1(b)-(iii)] rather than films with dense nanoholes. Therefore, it can be inferred that the imprinting of ultrasmall nanoholes should be ascribed to the force imposed by the nucleation of ZnO NRs. Or the imprinting process is a comprehensive representation of the specific temperature, reaction time, vapor pressures, etc. That's why the hole size can be controlled by tuning reaction time and seed layer thickness. Note that the morphology difference in image (i) and (ii) is probably a result of the partial inhomogeneity of the metal deposition. Similarly, it can also be understood that in the case of ZnO thin film substrate [image (iii)], such dense ultrasmall nanoholes can be also imprinted only their size and density differs a little from the case of sapphire substrate [image (i) & (ii)].

Figure 4.3 SERS spectra of 4-ATP molecules as analyte trapped in (i) dense nanoholes, (ii) sparse holes on Pt thin films (on sapphire), (iii) ZnO thin films (with 1 nm spacer) and absorbed on (iv) as-deposited Pt thin films.

Next, we tried to explore these dense ultrasmall nanoholes for SERS-based molecule probing. All the three samples displayed in Figure 4.2 have been tested as SERS substrates with aqueous solution of ATP molecules as analyte (molar concentration 5×10^{-5} M). The measured SERS spectra are shown in Figure 4.3, for which the original Pt thin films are chosen as a comparing substrate. Two evident Raman bands can be observed in the spectra, which are centered at 1076 and 1582 cm^{-1} , respectively. By comparing with the Raman spectrum of solid 4-ATP sample[90], the two bands are identified to be the characteristic Raman bands of 4-ATP molecules, with noticeable frequency shift (1087 to 1076 cm^{-1} and 1592 to 1582 cm^{-1}). Although no one has reported any SERS results from 4-ATP absorbed on Pt surface so far, this shift should be probably due to the formation of chemical bond with the direct contact between thiol group in the molecule and Pt surface. The two characteristic bands located at 1076 cm^{-1} and 1582 cm^{-1} are assigned to a_1 vibration modes and b_2 vibration modes, respectively. As is observed from the spectra, all the three pieces of nanohole samples give evident SERS signals. These nanoholes set a drastic comparison with the original Pt films, which shows not a single characteristic peak from ATP molecules. The sample (i) gives stronger SERS signals than the sample (ii), which can be ascribed to the density difference of the nanoholes imprinted on them [referring to Figure 4.2(i) & (ii)]. Compared to the case of raw Pt films on which no Raman signal can be detected, the existence of

nanoholes prove to be able to excite SERS signals. The structure enables fully molecule probing and hence possess great potential as an activeSERS substrate.

Figure 4.4 AFM mapping of nanoholes on sapphire substrate in height mode:
(a) dense holes and (b) sparse holes.

For further learning the morphology of imprinted nanoholes, AFM mapping has been exploited for a higher resolution as shown in Figure 4.4. The mapping image (a) and (b) refer to the samples shown in Figure 4.2(i) and (ii), i.e. nanoholes in a dense region and a sparse region, respectively. Here, in absence of the interference from local electrons to imaging (the case in SEM), one can easily identify every single tiny holes and even their edges by observing the zoomed AFM mapping images. In this case, we are able to measure the nanohole sizes and estimate their densities. Taking image (a) as an example, the average hole size is statistically estimated to be 10 nm and the average density to be 38 holes per 300 nm (i.e. averagely 38 holes within a 300 nm circle) with average spacing 30 nm. The AFM mapping also provides the

profile information of the hole imprinting. By comparing the color brightness of image (a) and (b), it can be found that sample (a) shows more overall roughness than sample (b). For a clear picture on the hole profile, including the hole depth and local metal surface profile, one needs to rely on the cross-section analysis.

For cross-section analysis, we selected single nanoholes randomly in a AFM mapping, e.g. as shown by Figure 4.5(a) in which two single nanoholes have been located and marked. Now based on the cross-section plot of Figure 4.5(b), the profile of each nanohole can be told very clearly. Imaginarily, the imprinting process results in adjacent "nanohills" and these holes actually sit on top of each hill. Also, it's surprising that, based on the cross-section results, one can find that the average hole depth is actually down to 0.5 nm! By cross-section analysis on both single nanoholes and adjacent ones, the sample surface can be imaginarily schemed as in Figure 4.5(c), which are a series of adjacent nanohills with imprinted nanoholes sitting on top. This means the nanoholes imprinted by our method are able to trap molecules within a very small cone-like volume down to $10\text{ nm} \times 0.5\text{ nm}$ in diameter.

Figure 4.5 Nanohole profile shown by (a) AFM mapping in height mode, (b) AFM section analysis and (c) schematic profiling of the nanoholes.

4.4 Conclusions

In this chapter, we proposed a novel method by combining ALD surface engineering and hydrothermal treatment to perforate sub-10 nm nanoholes directly on metal thin films. This one-step imprinting takes place in the course of hydrothermal treatment as a complementary effect imposed by the nucleation of the byproduct under the specific chemical and physical environment. The resulting nanoholes are dense random arrays with average 10 nm in diameter and 30 nm in separation. The average density is estimated to be 38 holes within a 300 nm circle, which is probably dependent on both seed layer deposition and substrate (so far cannot be well controlled). The ultrasmall hole sizes make them effective as plasmonic concentrating centers. The nanoholes on Pt thin films have proved to be highly effective structures for molecule-probing as they

can boost SERS signals of 4-ATP molecules from absolutely undetectable to fully identified. The imprinting method shows great application potential for making sub-nanometer structures not only due to its simple and direct perforation process but also due to its spatial scalability (mm scale). So far no reported sub-nanometer nanoholes have been shown applicable to large pieces of metal thin films. Herein we have provided one possibility and the obtained substrate might be useful for single molecule trapping and probing.

Chapter 5

Plasmonic radiation engineering: Giant near-band-edge emission of ZnO nanostructures

5.1 Introduction

Plasmonic-enhanced radiation is a unique phenomenon which results from the near-field mediation to an optical emitter by excited plasmon modes around metal nanostructures. The mediation from highly-confined plasmonic field essentially engineers the radiative decay of a nearby quantum emitter and shows significant modifications to both radiative and nonradiative decay rates as well as other optical properties[10, 91-92]. Besides the specific coupling regime, the strong local field itself gives direct rise to emission intensity due to its contribution to the absorption rate[10]. Moreover, possible coupling between different elementary excitations enables new decay channels and in this way the total decay rate gets enhanced as well as the emission intensity (Purcell effect[21]). Meanwhile, the sub-wavelength-scale confinement due to localized plasmons results in much smaller mode volume with relative to that of a classic emitter[10]. All the three mentioned aspects contribute together to the final emission enhancement. In a series of recent reports, plasmonic concentrators are assembled proximate to quantum emitters, which enables plasmon-emitter

coupling and have succeeded in engineering the radiation process from multiple aspects and profound levels[93-96].

As a typical semiconductor emitter, ZnO has a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. In the past decade, ZnO nanomaterials (NRs, NWs, etc), especially their aligned arrays, have been extensively explored for applications such as light emitting diodes (LED), UV optical switch, nanoscale lasers, etc[97-100]. Owing to their simple preparation and high optical efficiency, these nanomaterials are ideal representatives to be assembled with plasmonic structures as efficient quantum emitters with strong UV emissions. Given the wide variety of semiconductor materials applied in nano-optics as emitters and sensors, such assemblies targeting radiation engineering and enhancing are of great significance for boosting the efficiency and sensitivity of these devices[101-103].

In the past few years, a series of reports have been focused on ZnO nanostructures coated directly with noble metal particles, as shown in Table 5.1. These structures have been shown to support emission enhancement, e.g. by typical macroscopic PL spectroscopy, with enhancement ratios (UV-to-UV) less than 20. These enhancement have been well demonstrated as a result of Purcell effect with both observations of increased radiative decay rates and calculations of Purcell factors[20]. More significant enhancement is desirable and possible with other ingenious plasmonic structure designs.

Table 5.1 A summary of bandgap emission enhancement ratios of ZnO nanomaterials due to metal capping. In case of ZnO, the ratio refers to UV-to-UV.

Semiconductor nanomaterial	Metal	Form of metal and size	Enhancement Ratio	Ref.
Thin films	Ag	films of dense particles with sizes of 40–50 nm	50	[104]
Thin films	Ag, Au	films of dense particles, 10–250 nm thick	up to 10	[105]
Thin films	Al	50 nm-thick films	up to 14	[106]
Thin films	Au	~4.5 nm particles	18	[107]
Thin films	Pt	30 nm-thick pads array	12	[108]
Microrods	Ag	40 nm particles	~7	[6]
Nanowire	Ag	40 nm thin films and grating	up to 17	[109]
Nanorods	Pt	3–23 nm particles	up to 16	[110]
Nanorods	Pt	2–8 nm particles	up to 8	[111]

What else structures can boost the radiation even further? Given the three aspects from which an existing plasmonic field gives rise to a nearby emission, this question can be probably answered first by an extreme plasmonic concentration structure. With giant enhancement to the localized field, the near-field excitation of a quantum emitter as well as the follow-up coupling can

get reinforced in the greatest degree simultaneously. Back to 2005, In 2009, Zhang X. et al. proposed and realized a subwavelength-scale plasmonic laser based on a typical emitter-gap layer-metal structure[112]. This new compact lasers directly benefit from the super-localized hybrid plasmon mode which indicates the great potential of semiconductor-dielectric-metal (SDM) structure as a plasmonic concentrator. Herein in this project, we proposed a double-layer surface capping structure of metal/spacer and selected ZnO NRs as an example to show its luminescence-tuning effect. With such capping over the NR emitters, the structure enables strong tuning effect via the nanogaps between the core emitters and the outmost metal particles. Using PL spectroscopy to probe the tuning effect, great NBE emission enhancement has been observed for four kinds of outmost metal layers, Au, Pt, Ag and Al, with enhancement ratios on 2 - 3 orders in magnitude and defect emission strongly eliminated. Meanwhile, this enhancement is found to have a dependence on the middle nanogap thickness, that it decays very fast with thickening nanogaps. The capping structure has been also extended to ZnO thin films with varying Au capping (particle size and inter-particle distance) and a dependence on the metal layer morphology has been revealed by comparing their emission enhancements. By annealing a series of Au-capped NR samples with spacers, a similar conclusion can be obtained that the enhancement is closely dependent on the outer metal particle size and distribution. Time-resolved photoluminescence (TR-PL) spectroscopy has been finally conducted on a new series of Au-capped NR

samples with sub-5 nm spacers to probe the dynamics of the enhancing effect and may indicate a regime other than Purcell effect featured with reduced radiative decay rates.

5.2 Experimental

Sample preparation. Well-aligned ZnO NR arrays were grown on *a*-plane sapphire substrates via chemical vapor deposition where thoroughly mixed ZnO-graphite source powders and GaN/sapphire substrates were used. The growth details can be found in a previous publication.[113] Single-crystalline ZnO thin films were deposited on sapphire substrates via pulse laser deposition at 400 °C. The as-grown samples were cut into small pieces for the subsequent depositions of Al₂O₃ and metals. The middle layers of amorphous Al₂O₃ were coated by ALD, in which 40, 80 and 200 ALD cycles were used for the thickness of 5, 10, 25 nm, respectively. The outer layers of Au were coated via DC sputtering (JFC-1600, JEOL). Sputtering condition are unified for all the samples, i.e. 10 mA for current and 20 s' duration. Some samples were directly sputtered with Au without the middle Al₂O₃ spacer for control experiment. The morphology of the NRs was observed using both scanning electron microscope (SEM) and transmission electron microscope (TEM).

Optical characterizations. The PL measurements were carried out by excitation from a 325 nm line of a continuous-wave He-Cd laser at an incident angle of 45° and spectra were recorded in vertical direction. The laser power is 10 mW

(maximum power of the laser is 11 mW) with a spot size around 1 mm². At least three measurements were taken by selecting different detecting spots on each sample to assure the reproducibility. All the optical measurements were done at room temperature. Time-resolved PL (TR-PL) measurement was performed at room temperature by excited the samples with a 310 nm laser pulses generated from an optical parameter amplifier (Coherent TOPAZ™) which itself is pumped by a 100 fs, 1 kHz regenerative amplifier (Coherent Legend™). The laser spot size on the sample is 200 μm in diameter with an energy density of 10 μJ/cm² per pulse. The data were collected by an Optronis™ Optoscope streak camera combined with a high resolution CCD camera. For each sample, three measurements were taken by selecting different detecting spots on each sample to assure the reproducibility.

5.3 Results and discussions

5.3.1: Metal/dielectric/semiconductor nanorod structure for effective radiation engineering

The overall morphologies of the ZnO NRs after direct metal capping are shown in Figure 5.1 by both SEM and TEM images. The ZnO NRs, with a diameters in the range of 80–140 nm and a typical height of 1 μm, are vertically aligned due to an epitaxial growth on lattice-matching GaN layers. The bare ZnO NRs have very smooth surfaces. When coated with ALD Al₂O₃ gap layer, the NR surface smoothness is retained due to the “layer-by-layer” deposition

process of ALD. After the metal capping, the vertical alignment is retained but the NR surfaces become very rough which proves to be decorated with a discontinuous layer of NPs [see TEM image in Figure 5.1(c - f)]. The average size of gold NPs is about 5 nm with the sputtering condition commonly used in this project (see experimental part). It is not difficult to imagine the trend that with higher sputtering current or longer sputtering time the metal particles will grow bigger correspondingly. In addition, the NPs are not homogeneity in size as seen by TEM (see also below).

Figure 5.1 Morphology of the ZnO/Al₂O₃/metal nanorods. SEM images of (a) ZnO/Al₂O₃ 5 nm/Au trilayer nanorods and (b) ZnO/Al₂O₃ 5 nm/Ag trilayer nanorods aligned vertically on substrates. Inset in b) is the schematic top view of the trilayer configuration. (c-f) TEM images of a single ZnO/Al₂O₃ 5 nm/Metal nanorod, where the metal is Au, Ag, Pt, Al, respectively.

Before finding out how the spacer structure will affect the overall radiation process of the NR emitters, we first check the effect of a single dielectric or metal NP layer will do to the radiation. To isolate the impact of these two configurations, two samples, ZnO/Al₂O₃ and ZnO/Au, were used and compared with pristine ZnO NRs. The room-temperature photoluminescence spectra are displayed in Figure 5.2. The pristine NR shows a relatively weak UV emission peak due to near band edge (NBE) emissions and a very strong broad visible emission peak due to large numbers of surface defects. Now with a shell layer of 5 nm Al₂O₃ (which is the same spacer for the ZnO/spacer/metal samples to be discussed later), the peak for NBE emission remain almost unchanged while the defect emission peak is evidently suppressed. This is exactly due to a surface passivation effect by the dielectric capping layer (as well as polymer) [114-115]. As for the direct Au NP layer capping, the NBE emission is significantly enhanced, while the defect emission is nearly totally suppressed. The UV-to-UV enhancement factor is evaluated in the range of 6-10 fold. These results are in great accordance with the previous reports and the radiation enhancement has been well ascribed to be related to the Purcell effect. In a brief summary, we have shown from the above comparison (Figure 5.2) that:

(i) single-layer Al₂O₃ surface coating of the NRs has only a marginal effect to the NBE peak due to surface passivation effect;

(ii) direct metal nanoparticle capping supports the Purcell effect and leads to evident but still limited NBE emission enhancement.

Figure 5.2 A general comparison of the PL spectra of ZnO nanorods after different coating configurations, plotted in both (a) linear and (b) log scale. The 5 nm thick Al₂O₃ is by atomic layer deposition (ALD), the metal layers (denoted by M) are by magnetic sputtering. The spectra are obtained under the same

measurement condition. The spectra exemplified herein corresponds to gold, but the trend for other metals (Ag, Pt, Al).are essentially similar.

Next, we developed a series of ZnO/spacer/metal samples and measured their PL spectra to see how the spacer/metal capping affect the NRs' emissions. Figure 5.3 shows the compared PL spectra of this sample series, including four kinds of metals (Au, Pt, Ag and Al), in which the comparison is made to pristine NR emitters and the Al_2O_3 gap layer thickness is also varied as 5, 10 and 25 nm. Based on the comparisons in the four figures, one can find that (i) the spacer/metal capping boost giant NBE emissions for all the four kinds of metal tested; (ii) defect emissions have been totally quenched for all; (iii) a 5 nm dielectric gap provides the strongest enhancement and this enhancement attenuates very drastically with increasing gap layer thickness (up to 25 nm both NBE and defect emissions disappear).

For a clear picture of the function of this spacer/metal capping, let's take ZnO/spacer/Au as an example for further discussion and evaluation. As mentioned above, the inset TEM images shows that the outmost metal capping is a layer of noncontinuous NPs forming very rough surfaces and supporting possible plasmon excitations. The PL spectra display a full view of the luminescence-tuning effect of the spacer/metal capping. First, when a sub-nano

Figure 5.3 PL spectra showing the enhancement to the NBE emission of the trilayer ZnO NRs due to (a) Au, (b) Pt, (c) Ag, (d) and Al capping with 5 nm ALD Al₂O₃ spacers.

meter dielectric gap is introduced to the emitter/plasmon system, e.g. 5-nm for spectrum(ii) in Figure 5.3(a), one can find much larger enhancement to the UV peak with relative to spectrum(i) for pristine ZnO NRs. Note that since the enhanced UV emission is so strong that it's impossible to identify the emission peak for the pristine NRs if plotting it within the same scale, spectrum(i) in the four figures are all 10 times enlarged for clear identification of both its NBE and defect emission peaks. Next, if increasing the nanogap thickness, e.g. to 10 nm for spectrum(iii), one can find the NBE enhancement with relative to that of pristine NRs is also significant [note that peak (i) is 10 times enlarged], with

enhancement factors on the order of several tens in magnitude. This is actually still much stronger than those in the related reports so far (as shown in Table 5.1). What happens to the radiation if we increase the nanogap thickness further? To find out the answer, we made a jump on increasing the thickness, directly to 25 nm. The resulting PL is shown by spectrum(iv) and one can find this time NBE emission has been totally eliminated as well as defect emission. This means the function of the dielectric gap in engineering the radiation relies on its real sub-nanometer scale. Only gaps with sub-10 nm thickness works for this enhancement regime otherwise the engineering effects are all gone. The following observations on Figure 5.3(b) - (d) can be summarized to similar trends on the NBE peak intensity tuned by spacer thickness, that the sub-10 nm dielectric gap shows very extraordinary luminescence-enhancing effect with extremely strong NBE emission enhancement far beyond the enhancing limitation given by direct metal-capping. . We have also included a non-noble metal into the testing of the function of the metal/spacer capping, which is Al capping shown in Figure 5.3(d). Surprisingly, this metal gives even stronger enhancement to the NBE emission of NR emitters. Although possible oxidation may happen to the surface-layer atoms of Al particles, they can still work with the sub-nanometer spacer and give greater rise to the emission. The reason for this is unknown for now, which needs further probing to be revealed in future work. We further summarized the strongest emission enhancement due to the metal/spacer capping in Table 5.2, showing the enhancement factors due to all

four kinds of metal tested at 5-nm dielectric gap. It can be found they are all above 400 in magnitude, much larger than the case of direct metal nanoparticle capping without dielectric spacers listed in Table 5.1. Here the enhancement ratio difference directly reflects the metal specie difference.

Table 5.2 UV-to-UV enhancement ratios of metal-coated NRs with 5 nm.

Metal	Form of metal and size	Enhancement Ratio (UV-to-UV)
Al ₂ O ₃ 5nm/Au	5 nm particles	800
Al ₂ O ₃ 5nm/Pt	3 nm particles	470
Al ₂ O ₃ 5nm/Ag	15 nm particles	420
Al ₂ O ₃ 5nm/Al	Tiny nanoparticles with unknown size.	3960

From the above qualitative comparisons of the UV peak enhancement along varying dielectric gap, it's notable that the enhancement is very sensitive to the gap thickness, changing drastically within the tuning range of 20 nm. This feature is now shown quantitatively by Figure 5.4. The inset schematic gives a full view of the metal/spacer capping over the core NR emitter. It can be found for all the three noble metals tested, the thinnest gap of 5 nm provides the strongest enhancement, with enhancement factors all on the order of several hundred in magnitude. With increasing 5 nm on the gap thickness, both the

enhancement ratios referring to Au and Pt drop a whole order down to several tens in magnitude. When gap thickness is finally increased to 25 nm, it can be found the enhancement is totally gone for all three metals tested. It means this particular enhancement regime has completely collapsed due to the over-thickened gap. Such a close dependence on gap thickness can be hypothetically understood by the evanescence nature of surface plasmons, that they are bound tightly to the metal surfaces. Based on this hypothesis, it may indicate the plasmon effect in the luminescence tuning.

Figure 5.4 Enhancement ratio dependence on gap thickness for three kinds of metal species. Inset schematic shows the double-layer capping over a NR. Here the enhancement ratios for different metals are relative and have no meaning for comparison.

5.3.2. On the plasmonic nature of the radiation-enhancement regime

Next, we introduced another series of thin film samples to testify the universality of the spacer/metal capping structure for highly effective luminescence-tuning. As is known, ZnO thin films fabricated by PLD method are of high crystallinity and emission quality. And by comparing the enhancement ratios in Table 5.1, it can be found that ZnO materials with direct metal-capping generally obtain stronger emission enhancement on thin film samples. Therefore thin film emitters are also very suitable candidates for testing the radiation engineering effect.

The spacer/metal capping (the same as that for the above NR samples) is directly applied to ZnO thin films pre-fabricated by PLD. The surface morphology of the capping can be referred to Figure 4.2(iv), which is composed of dense metal particles with average size ~ 250 nm. The similar emission comparison is displayed in Figure 5.5, with relevant inset absorbance spectra. The spectra for three kinds of metal NP layer (the same deposition control as in **Part I**) show no characteristic absorption peaks, in accordance to previous reports[116]. The absorption of the tested sample, ZnO/Al₂O₃/Au, shows a strong UV shoulder well ascribed to ZnO NBE excitons. The visible wavelength part of the spectrum almost overlaps with that of Au NP layer. In the emission comparison between ZnO, ZnO/Al₂O₃ and ZnO/Al₂O₃/Au, one can find the spacer/metal capping also give great rise to the NBE emission of the thin film sample, much stronger than that of pristine ZnO thin films. More importantly, the absence of defect emission for the pristine thin film sample

isolates the NBE emission process in the radiation process of these samples. In other words, there's no possible way for energy transferred from other levels to the NBE excitons here. Based on the results for the thin film samples, the enhancing effect to the luminescence of ZnO films cannot be induced by energy transfer.

Figure 5.5 PL spectra showing the NBE emission enhancement to ZnO thin films. Inset shows the characteristic absorbance of metal thin films (Au, Ag and Pt) and Au/spacer capped ZnO thin films (unified deposition conditions and substrates for all).

We have also studied the metal deposition dependence of the tuning effect by varying the deposition parameters. Figure 5.6 shows two series of samples to show the metal-deposition influence to the luminescence. Figure 5.6(a) displays the comparisons between a series of thin film samples. It can be

clearly observed that there is almost no defect emissions from the pristine ZnO thin films. Note that the original metal capping refers to the deposition condition of 10 mA 20s, the depositions maintaining the current while prolonging the time duration must lead to larger NPs, otherwise to smaller ones. In this emission comparison, one can find that the 15 s deposition should results in significantly stronger NBE emissions! When the time keeps shortening to 10 s, the NBE emissions gets back again, below the level of that of the sample from the original 20 s' deposition. Similarly, for NR samples in Figure 5.6(b), we varied the deposition conditions of Pt capping and find significant change to their luminescence. The capping of "20 mA 20 s" raises much strong enhancement than that of "10 mA 30 s" to the radiation. As a summary, for both the thin film and NR samples, their luminescence is evidently dependent on the resulting metal deposition. By varying the deposition parameters, the luminescence of the spacer/metal capped films can be also be tuned.

Figure 5.6 Emission enhancement rising from various metal particle morphologies (referring to various deposition conditions in parentheses). (a) Comparing PL spectra of Au-capped ZnO thin film samples with spacers. (b) Comparing PL spectra of Pt-capped ZnO NR samples with spacers (deposition parameters denoted by current and time duration together).

Next, we studied the annealing effect on the regime behind this spacer/metal capping. It has been shown previously that annealing at 400 C ° in air has little effect on the intrinsic PL properties of pristine ZnO NRs; the NBE emission almost stays intact while the defect emission might become even

stronger [117]. Now for spacer/metal capped samples, the overall morphologies of the capped NRs are shown by TEM images(a_{1,2}) and (b_{1,2}) in Figure 5.7, which especially gives a full view of the morphology transformation of the outmost Au NPs from before to after annealing. The outmost Au capping resulting from the same deposition control, no matter for samples with [image (a₁)] or without spacers [image (b₁)], are both originally a layer of dense and uniform NPs with average size estimated to be 5 nm. Generally, after being heated, the Au NPs gets larger and much more separated from each other for both samples [image (a₂) & (b₂)]. Besides partial growing-up, the Au NPs on ZnO NRs without spacers [image (b₂)] also shows drastic size deviation from their original sizes. Compared with the closely-packed uniform particle layer before treatment in image(b₁), the annealing has almost broken up the particular original particle topology, leaving randomly scattered particles of wild size distribution (much smaller or larger than the original 5 nm). The effect of thermal annealing to the PL spectra was illustrated in Figure 5.7 (a3) and (b3).

Figure 5.7 Annealing effect on the radiation engineering. TEM images showing surface morphology of Au-capped NR without spacers (a_1) before and (a_2) after annealing and (a_3) their comparing PL spectra. TEM images showing surface morphology of Au-capped NR with spacers (b_1) before and (b_2) after annealing and (b_3) their comparing PL spectra.

Based on the comparison spectra in Figure 5.7(a₃) for Au capped ZnO NRs without spacers, before annealing the sample shows comparable NBE and defect emissions (the defect emission was not completely suppressed here probably due to the insufficient surface capping). After annealing, the NBE emission is alleviated while the defect emission has regained its dominant status with much larger intensity than that of NBE peak. According to the comparison of outmost Au layer morphology before and after annealing [Figure 5.7(a₁)&(a₂)] for this sample, it is noted that the annealing treatment mainly causes the dissociation and growth of surface-capped Au NPs, exposing out certain parts of the ZnO surfaces and subsequently “releasing” the defect emissions into free space. As for the Au-capped ZnO NRs with spacer, after annealing, amazingly, the dominating NBE peak is drastically quenched and instead the sample shows both weak NBE and defect emissions. Recalling the radiation enhancing comparisons in **Part I**, one can notice that this annealing retreatment actually restores the NR emissions to its pristine status. This means since the annealing leads to the collapse of the particular Au NP topology responsible for the radiation engineering regime, it radically destroys the regime underlying the spacer/metal capping. On the whole, the annealing effect confirms that the luminescence-tuning is a regime relying exactly on our precisely controlled spacer/metal capping that is sensitive to the size and distance fluctuation of the metal nanoparticles.

Sum of the first 6 spectra.

The experimental data (in blue) is a sum of the absorption spectra of gold, ZnO and the TEM substrate.

Figure 5.8 Electron energy loss spectroscopy (EELS) experiment was conducted using STEM, in which the ZnO/Al₂O₃ (5nm)/Au trilayer nanorods were dispersed on a carbon-coated TEM grid. The collective plasmon frequency of the nanoparticle gold films is found to be ~2.30 eV.

To further verify the existence of the plasmons on metal NPs, we explored Electron energy loss spectroscopy (EELS) to detect the plasmons. Figure 5.8 is the analyzed EELS spectra based on the detection of a piece of ZnO/Al₂O₃/Au sample. The total spectrum has been fitted by multi-peaks and the results are easy for one to assign the three spectra. The yellow base spectrum is identified to be carbon electrons, which comes from the supporting carbon grids. The red spectrum shows a sharp shoulder around 3.5 eV and is assigned to ZnO NRs. The last one, the black spectrum, shows a significant peak centered around 2.25 eV, which is the very SPR peak we are looking for. It is very close to the SPR energy of Au NP of size ~100 nm[116].

5.3.3 Thinner nanogap effect probed by both static and time-resolved PL

To further study the enhancement dependence on spacer thickness, we developed a new series of samples with even thinner nanogaps. By combining both TR-PL and PL characterizations, we aimed to reveal the gap width effect on the metal-capped NR emitters with ultimate fine tuning of 1 nm scale. The Al_2O_3 nanogaps between the core NR and outmost metal were fabricated via ALD, tuned from 1 to 5 nm by 1 nm per step. Particularly, the comparing PL measurement was carried out subsequently by two times on each piece of sample for before and after metal/spacer capping (rather than by cutting it into two pieces for comparison). That is, the deposition step was arranged closely following the first PL measurement and on finishing it, the second PL measurement was immediately carried out on the samples.

As shown in Figure 5.9, the PL spectra of pristine ZnO and metal/spacer capped NRs are displayed together for comparison. Since the PL results of the five pieces of pristine NR samples are relatively close to each other, they have been summarized as an average spectrum. Pristine NRs show two peaks as being tested before, a NBE emission and a much stronger defect emission. While all the capped samples show only NBE emission peak, which mean the quenching of defect emission still happens as in the former series of samples and as being shown by relevant reports. For the comparison between the capped samples with relative to the pristine one, it can be found that they all show

significant NBE emission enhancement. The inset plot provides a full view of the enhanced NBE emission along gap tuning in whole tuning range covering both **Part I** and **Part III** (1-25 nm). Combining those spectra in Figure 5.9 with the table, one can find that from 1 to 5 nm, the enhanced emission shows a fast increasing trend with two evident stages divided by 3 nm. In the hypothesis of existing metal plasmons, such a trend could be understood by two competing effects: (i) enhancement of spontaneous emission rate due to metal particles; (ii) decreased coupling probability with increasing spacer thickness[118].

Figure 5.9 PL spectra of Au-capped ZnO NRs with thinner nanogaps(1-5 nm).

Inset is UV-to-UV enhancement ratio plotted against gap thickness in the full tuning range (1-25 nm).

Table 5.3 UV-to-UV enhancement ratios of Au-capped NRs with sub-5 nm nanogaps.

Gap width	1 nm	2 nm	3 nm	4 nm	5 nm
Enhancement factor	5	11	85	481	543

Figure 5.10 Time-resolved photoluminescence (TR-PL) of Au-capped ZnO NRs with sub-5 nm nanogaps. Solid lines are the best fit to the linear part of the experimental data.

To further understand the enhancement regime due to spacer/metal capping, we explored TR-PL spectroscopy to probe the decay dynamics of these samples. As shown in Figure 5.10, the TR-PL results of the thinner-gap samples have been plotted logarithmically with their exciton lifetimes listed in the figure as well. The lifetime of pristine ZnO NRs are fitted by double channels, giving out the decay lifetime as 154 ps. Now by comparing all the thinner-gap samples with this lifetime, one can find that there are also two stages during the lifetime variation with the gap thickness. From 1 to 3 nm, the lifetime of the 1, 2 and 3 nm-gap thickness NRs are much shorter than that of pristine NRs, corresponding to a possible increase to the radiative decay rate. This can be most-likely ascribed to Purcell effect[21, 119]. For the 4 and 5 nm-gap thickness samples, however, the lifetime become longer than that of pristine NRs, corresponding to a possible decrease to the radiative decay rate. This may indicate an enhancement regime other than conventional Purcell effect, which needs further research to testify.

5.4 Conclusions

In this chapter, we proposed a metal/spacer surface-capping structure for effectively tuning the luminescence of ZnO NRs. The radiation enhancement effect and its dependence on the spacer thickness, as well as the dependence on different metals and thermal annealing effect, have been comprehensively

characterized. The great enhancement effect is strictly dependent on a precise control over the double-layer capping, including gap thickness and sputtering condition of metals. The dielectric gap bridges the outmost plasmons and the core emitter without direct contact and is applicable on a series of metals, including Au, Pt, Ag and Al, providing strong emission enhancement up to nearly 4000 fold (UV to UV).

We first conducted a systematical study on the metal/spacer capping functionality over ZnO NRs by macroscopic PL characterization, focusing on the emission dependence on both the dielectric gap thickness (5–20 nm) and metal species. From 5 to 25 nm, the NBE emission intensity first increases and then drops fast with the increase of the gap thickness beyond 10 nm. This serves a strong indication of the near-field (off-resonant) coupling of metal plasmons to the core NRs. This emission enhancement and gap-thickness effect are also observed in other metal species, except for their absolute quantities of enhancement ratio. Following this part, further tuning has been made to the metal layer for both NR and thin film samples. The emission enhancement varies with the morphology change of the capped metal layer (size, thickness and inter-particle distance). One particular indirect evidence is that, thermal annealing of the metal-capped NRs causes a significant quenching of the NBE emissions, regardless of single metal layer or bi-layer capping. Finally, time-resolved PL measurements on sub-5 nm gap samples reveal that the lifetime and emission intensity of the NBE excitons shows consistent trend

along with the fine-tuning of gap thickness in the range of 1–5 nm. TR-PL result may indicate the existence of a different coupling regime, or another unknown reasons from Purcell effect, that has contributed to the emission enhancement beyond 3 nm.

Chapter 6. Single nanowire study by cathodoluminescence spectroscopy

6.1 Introduction

Cathodoluminescence (CL) is extensively explored spectroscopy for near field detection of microstructures as well as nanostructures with minimum damage. As an powerful contactless detecting technique, it has been well utilized from mineralogy analysis[120] to electronic band study[121] (especially on dopants' effect). Recently, the detection by CL has been spread further to a series of dynamics study owing to its effective electron excitation with both high controllability and resolution, such as tracing transitions, e-h pair recombination and surface plasmon excitation[122]. Using focused electron-beam as the excitation source, the spatial resolution of CL is down to 10 nm and mainly relies on the electron beam quality. Better spatial resolution is achievable on those assemble to STEM down to a few nanometers. Such high resolution is very desirable for subwavelength-scale nanostructures, such as quantum emitters and plasmonic structures for electro-optic probing.

The conventional excitation of surface plasmons is via photons. The spatial resolution of the probing is hence limited by the spot size of light beam available in prevailing optical spectroscopy techniques, such as scanning near-field microscopy (SNOM), down to 50 nm. In the case of CL probing, electron beam is able to be focused to a selected detecting spot of

sub-nanometer scale along the sample surface. That's also the case for EELS, which has been successfully explored to study plasmons on metal spheres[123-125] and carbon structures[126]. Contrary to pure optical probing, techniques such as CL and EELS relies on focused high-speed electrons and are able to provide lasting feedback information of the sample with much more localized and efficient excitations. So far, they have been proved to succeed in generate both localized and propagating surface plasmons on different structures. As details, in the CL excitation of plasmons, the energy of incident electrons couples to the plasmonic modes of the target structure and subsequently radiate into far fields[127]. Given that the CL spectroscopy is a function of the beam spot location, it thoroughly collects the optical emissions from all parts of the sample and hence is particularly ideal for detecting modes with an efficient radiative decay channel[127]. A series of recent reports have well explored those benefits of CL and successfully mapped plasmon modes based on various metal structures clearly showing local field distribution within real-nanometer scale[122, 127].

Given both high spatial resolution and efficient electronic excitation of CL spectroscopy, it's also ideal to probe plasmon-emitter coupling system. So far there are few reports on using CL to detect enhance radiation or plasmon-emitter coupling. Since CL is conventionally used for phosphor detection, someone did try to enhance phosphorescence via near-field plasmons[128]. However, the enhancement is almost negligible, which

indicates plasmons probably cannot be coupled to phosphorescent emitters efficiently. Here we choose single ZnO nanorod as a quantum emitter and use CL to probe the luminescence-tuning by spacer/metal. With the high resolution, we are able to detect multiple spots along a single NR for obtaining more precise emission information. Also single NW mapping is available to directly show the intensity and spatial distribution of the emission. We verify that the luminescence tuning by spacer/metal capping can be well-detected by CL as well and this is the first time to use CL for the single NW detection and mapping of metal-modified ZnO.

6.2 Experimental

Sample preparation. Well-aligned ZnO NW arrays were grown on *a*-plane sapphire substrates via chemical vapor deposition from source material of thoroughly mixed ZnO-graphite powders, with GaN/sapphire substrates pre-coated gold. The growth details is elaborated in Chapter 5 and can also be found in a previous publication[113]. The as-grown samples were cut into small pieces for the subsequent depositions of Al₂O₃ and metals. The coating of Al₂O₃ was realized by ALD (Beneq TFS-200) using trimethylaluminum (TMA) and water as the aluminum and oxygen as source to obtain a series of desirable thicknesses (performed at 200 °C with a film growth rate of ~0.13 nm/cycle). The outmost layer of metal nanoparticles was coated via DC sputtering (JFC-1600, JEOL). The morphology of the NWs was observed using both

scanning electron microscope (SEM) and transmission electron microscope (TEM).

Cathodoluminescence characterizations. The CL excitation and measurement were performed on a SEM (CamScan CS3200 with LaB6 cathode). In details, the excitation was realized by illuminating the sample with a 30 kV electron beam, a beam current of ~1.2 nA and acquisition times varying from 0.01 s to 0.5 s depending on the signal intensity. The acquisition times were set to be 0.5, 0.1 and 0.01 s for pristine ZnO NWs, ZnO/Al₂O₃/Pt, and ZnO/Al₂O₃/Au NWs, respectively. The CL maps reach a spatial resolution of ~20 nm. The electron beam was focused onto the sample through a small hole in a short-working-distance parabolic mirror mounted directly above it to collect the light emitted from the sample over approximately half of the available hemispherical solid angle. The mirror directs the collected light out of the SEM chamber to a hyperspectral light collection system (spectrum analyser and liquid-nitrogen-cooled CCD detector). This setup allows building CL maps of the NWs with spatial and spectral information about the sample (each point in the map contains the full spectrum of the emitted light).

6.3 Results and discussions

For the CL study, both the pristine and metal/spacer-coated NRs are prepared and measured together under the same beam condition. TEM images

of the nanorods can be seen in Figures 5.1. The e-beam can excite the ZnO excitons and possible metal plasmons.

For CL measurement, the NWs have been specially pre-dispersed as displayed by the schematic in Figure 6.1(a). The substrate were pre-divided into two half regions, one for dispersing pristine ZnO NWs and the other for metal coated ZnO NWs with Al_2O_3 spacers. Given the resolution of CL (20 nm), the NW dispersion needs to be thoroughly for the e-beam to isolate a single NW. As shown in Figure 6.1(b), within the image view, several single NWs can be easily located since they are over 500 nm away from their most neighboring NWs.

The experimental configuration for CL excitation and collection is shown schematically in Figure 6.2. The dispersed NW samples were excited perpendicular incident electron beam through a tiny hole on top of the parabolic mirror. Possible excitation process of surface plasmons can be hypothesized as follows: the valence band electrons of the outmost Au NPs are excited and driven into collective oscillations corresponding to plasmon mode with gigantic enhancement to the local field. Meanwhile the NBE excitons of the inside ZnO NWs are also excited and ready for both radiative and non-radiative decay.

Figure 6.1(a) Schematic of the TEM sample: Si substrates on which with both pristine and the Al_2O_3 /metal-coated NWs are dispersed and spatially separated.
(b) SEM of the dispersed NWs on Si substrate.

Figure 6.2 Schematic of the CL excitation and collection configuration.

The luminescence of three single NWs (pristine ZnO, ZnO/ Al_2O_3 /Pt and ZnO/ Al_2O_3 /Au), were then collected through a grating monochromator, which allows resolving spectral characterizations, as shown by Figure 6.3. As for a unified comparison between the luminescence enhancement, the spectra have

already been calibrated by acquisition time for 0.5 s per point. For each single NW, the scanning has been directed along it from one end to the other. In the figures, the black, red and blue spectra are referring to the acquisition locations in the left, middle and right part along a NW, respectively. Meanwhile, monochromatic CL images were obtained through mapping at wavelengths 370 and 520 nm, as displayed together with the corresponding spectra. These images were mapped by scanning the electron beam along the NWs with setting the grating monochromator to a specific wavelength. Under strong coupling of the electron beam to the eigenmodes of the plasmons, the scanning reveals the standing-wave patterns of these plasmons[129].

We first look at the CL spectra. The pristine single NW shows the same peak pattern as PL, a strong sharp NBE emission centered at 370 nm and a broad weak defect emission centered at 520 nm. For two metal/spacer capped single NWs, the luminescence pattern is also similar to their PL, showing a greatly-enhanced strong NBE emission with defect emission almost quenched. Based on the comparison of calibrated spectra with the same scaling, one can find that both metal/spacer capped single NWs gives much stronger emission than the pristine one, with overall enhancement factors over 10-fold for a single NW (even stronger than most of the reported macroscopic PL results).

Figure 6.3 CL spectra and mapping of single NWs, scanned from left to right along each NW (black spectra: left, red spectra: middle, blue spectra: right). (a) Pristine ZnO NW, (b) a single NW capped by Pt/5 nm Al_2O_3 and (c) a single NW capped by Au/5 nm Al_2O_3 , with insets showing images mapped at 370 and 520 nm. The length of the mapped NWs are evaluated to be (a) 2.6, (b) 3.1 and (c) 2.2 μm .

The CL intensity mappings provide information on the spatial homogeneity of the luminescence along the NW length (note that the resolution is insufficient to provide spatial distribution cross the NW diameter). For the mappings of the pristine ZnO single NW at both 370 and 520 nm, one can find the image brightness (referring to the local field intensity) is generally uniform along the wire except that the 370 nm-mapping shows a much brighter end. The field distribution shown by both images is in accordance with the NBE peak intensities (left-middle-right). As for the CL images of the metal/spacer capped NWs (scanned at 370 nm), one can find that there's an evident longitudinal field distribution along the NW. From left to right, the longitudinal field distribution shows a dark-bright-dark-bright pattern for the Pt/spacer-capped NW and a bright-dark-bright pattern for the Au/spacer-capped one. The exact reason behind is still unclear based on data available. As demonstrated by a series of reports, metal capped NWs can be regarded as nanoantennas, showing a dipole field distribution along the cavity[130]. This dipole field distribution is a key feature of plasmon modes, distinguishing them from those of semiconductor NW cavity. Their resonant energy and mode distribution are closely dependent on the cavity length and capped metal species. It is hypothesized that in this study, the inhomogeneous intensity distribution of the metal/spacer capped NWs is an indirect evidence for the plasmonic nature of the emission regime.

To further show the emission enhancing effect of the metal/spacer capping, one can refer to the following Table 6.1 and Table 5.1. The UV-to-UV

enhancement factors in both tables are calculated by comparing the luminescence of their NBE peaks. Recall that Table 5.1 display all the previous reports on macroscopic PL study of the emission enhancing effect due to simple metal capping. It can be found that these macroscopic measurements generally give enhancement factors in the range of 7-18. As is known, the size of the laser beam in a macroscopic PL system is usually several micrometers in diameter, covering a large ensemble of NWs in a single measurement. For our CL results, the emission enhancement ratios of the two capped single NWs are approximately 16 and 32, respectively, much stronger than most reported macroscopic results. This is a solid evidence to further confirm the unique enhancement regime of our metal/spacer capping towards NW emitters, indicating its powerful radiation engineering effect.

Table 6.1 *UV-to-UV enhancement ratios of metal/spacer capped single NW calculated from the NBE peak intensity.*

Metal/spacer capped single NW	ZnO/Al₂O₃/Pt	ZnO/Al₂O₃/Au
Enhancement ratio	16	32

6.4 Conclusions

In this chapter, CL spectroscopy has been applied for the first time to probe the emission properties of a metal/spacer capped individual ZnO NWs.

Both pristine and capped NWs are dispersed on conductive substrates for the electron beam to easily isolate them for single NW probing. The obtained CL spectra show similar peak patterns as those of macroscopic PL results in Chapter 5, that is, compared to pristine single ZnO NW, the metal/spacer capped NWs exhibit greatly enhanced NBE emission and the defect emissions are totally quenched. The metal/spacer capped NWs show evident non-uniform intensity distribution along the NW length, which could indicate the dipole nature of the exciton-plasmon mode. While the results is still preliminary rather than complete, it tells that CL, equipped with the capability of panchromatic mapping, is a useful technique for the study of plasmon-exciton coupling in a high spatial resolution. More systematic work is needed to explore the effects of NW length and diameter on the coupling efficiency.

Chapter 7

Conclusions and future work

7.1 Conclusions

In general, this thesis can be categorized into two main parts. The first part is focused on metal plasmonic nanostructures for surfaced enhanced Raman spectroscopy and molecule probing. Their properties for plasmonic field concentration towards inorganic molecule probing have been well characterized by SERS measurements. The second part is a comprehensive study using both macroscopic PL and microscopic CL on the greatly-enhanced near bandgap emission of ZnO nanorods (NRs) based on metal/ Al_2O_3 capping. The extraordinary radiation engineering featured with ultrahigh emission enhancement has been ascribed primarily, among other possibilities, to plasmonic coupling with ZnO excitons.

Part 1 Plasmonic nanostructures for molecule probing

Atomic layer deposition (ALD)-featured surface engineering methods have been elaborately designed and applied for easy fabrication of plasmonic nanostructures. Owing to their ultrasmall dimension, these structures are able to support highly localized plasmon modes and thus give great rise to the strong local electric field. With specific plasmonic structure profiles of nanogaps or nanoholes, they are ideal for trapping analyte molecules and providing effective

hot-spot geometry. We have demonstrated their outstanding performance as effective SERS substrate, and prospectively, even for single molecule-probing.

Part 2 Photoluminescence enhancement of ZnO by metal/spacer capping

A metal/spacer capping around ZnO NRs has been designed with the assistance of ALD and the induced NBE emission enhancement has been observed by both macroscopic PL spectroscopy and microscopic CL spectroscopy. Both measurements show clearly more significant enhancement of near bandgap emissions of ZnO NRs compared to generally-studied direct metal capping. Featured by the precisely variable thickness of the ALD nanogap (i.e., spacer), the capping structure shows a close dependence on the gap thickness. Such structure proves to be universally effective for all the four kinds of metals tested (Au, Pt, Ag and Al), although the absolute enhancement ratios vary. The mechanism behind the emission enhancement phenomenon is proposed to be related to plasmonic coupling with ZnO excitons, but other possibilities could not be completely ruled out. Evidence of the plasmonic nature includes the sensitivity of the emission with gap thickness, and metal particle. Apart from macroscopic characterizations, the single NW probing by CL spectroscopy has further confirmed the powerful radiation engineering effect of the capping structure as well as its generality to different metals within the similar size range (around 10 nm). Notwithstanding the plasmonic nature, the coupling regime appears not to be the conventional Purcell effect, as implied by the time-resolved PL measurement. With the gap thickness below 3 nm, the

emission enhancement is similar to simple metal capping (below 20 fold) with increased radiative decay rates (Purcell effect). However with larger gap thickness (>3 nm), the enhancement ratios are more drastic but the decay rate is comparable to or even higher than that of pristine ZnO. Our results may stimulate more in-depth exploration on this topic. Some of proposals are as follows.

7.2 Future work

(1) Novel and hierarchical nanostructures for giant plasmonic field concentration

We have shown that by elaborately combining ALD with other surface engineering methods, a variety of nanostructures can be well developed from raw metal layers with real nanometer scale localization of the fields. Moreover, it has been shown that the combination of various nanostructures may result in more effective field concentration. For example, self-similar structures supporting cascaded enhancement effect have been demonstrated by a series of recent reports[131-132]. Owing to the effective local field enhancement, these novel structures are promising candidates for optical biosensors based on SERS.

Our work about plasmonic nanostructures can be continued in these two directions, self-similar structures and ultrasensitive sensor configurations. For the first one, ALD can be combined with other kinds of nanostructuring

techniques, such as imprint lithography, electrodeposition, electrophoretic deposition, or self-assembly of dispersed nanoparticles, nanospheres, etc. The role of ALD can be multiple including template fabrication, nanostructure stabilization, and gap narrowing. For the other direction, conventional plasmonic biosensors are based on propagating plasmon polariton on surfaces of flat and thin metal films. Very prototype devices have been constructed based on LSP nanostructures with hot-spots. In particular, the metal nanohole work can be further studied for a deeper understanding of the ultrahigh field concentration. One possibility is to apply the imprint lithography to generate large-scale arrays of nanohole on a gold surface, which can be then further shrunk in size using ALD.

(2) Extensive study on the metal/spacer-induced emission enhancement of ZnO and its application

The emission enhancement rendered by the metal/spacer capping over ZnO NRs featured with longer carrier lifetime is an interesting phenomenon among the huge community of ZnO. Both the gigantic emission efficiency and the decay dynamics distinguish it from any other emission process known so far (to the best of our knowledge). Therefore the nature and detailed dynamics of the process is of great necessity to be explored. We are keen to find out if such an efficient plasmon-emitter coupling is dominated by a more general rule and even decode it. Besides, the extremely high emission efficiency endows the capping structure with great potential for constructing highly-efficient

nano-optical or optoelectronic devices, such as light-emitting diodes, UV photodetectors, and photocatalyst of ZnO, as well as other semiconductor materials (e.g., ZnSe and CdTe). Careful matching of the energies needs to be confirmed for plasmons and the emitters to couple with each other. Furthermore, it is planned to study the effect of other dielectric spacer materials, for which a different spacer thickness dependence is reasonably expectable. Systematic simulations will be also carried out to understand the plasmonic behavior of the capped metal layer.

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