SPP/LSP coupled hybrid mode directed multi-functional surface-enhanced Raman system

Du, Luping

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**SPP/LSP COUPLED HYBRID MODE DIRECTED
MULTI-FUNCTIONAL SURFACE-ENHANCED
RAMAN SYSTEM**

DU LUPING

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY

SPP/LSP coupled hybrid mode directed multi-functional surface-enhanced Raman system

Du Luping

School of Electrical & Electronic Engineering

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Abstract

Surface plasmons (SPs) have generated a tremendous amount of interest in recent decades due to their intriguing features such as lateral spatial confinement, surface sensitivity and field enhancement. The consistent investigation of SPs leads to a wide scope of applications including ultrahigh-sensitivity biosensing, super-resolution imaging, sub-wavelength nanolithography, miniaturized photonic circuits, surface-enhanced Raman spectroscopy (SERS), etc.

In this thesis, a multi-functional surface-enhanced Raman system based on the SP-hybrid-mode is proposed and investigated. The system is grounded on a novel idea, which utilizes the giant electromagnetic enhancement arising from the strong coupling between surface plasmon polaritons (SPPs) and localized surface plasmon (LSP), the two different types of SP modes, and deals with the problems facing with SERS and other SP-based techniques.

First of all, as a fundamental investigation, two types of excitation configurations are proposed to achieve the plasmon-hybrid-mode: through a periodic metallic structure and via an attenuated total reflection configuration, respectively. In both approaches, the numerical investigation with three-dimensional finite-difference time-domain method shows that the coupling between the LSP and SPPs could result in a great improvement of electromagnetic enhancement compared to that from separate SP mode. Raman enhancement of more than 10^9 was predicted from the numerical simulation.

SERS experiment was carried out afterwards to verify the Raman enhancement. In the experiment, SPPs are excited by a tightly-focused radially polarized beam and interact with the nanospheres to generate the plasmon-hybrid-mode, exactly according to the second configuration aforementioned. The experimental result demonstrates

that silver nanospheres within the propagation region of SPPs are effectively activated and detected by a CCD camera. Raman enhancement presents 20 times improvement compared to the conventional nanoparticle-induced SPPs/LSP co-enhanced Raman spectroscopy. Surface-enhanced Raman scattering (also termed as SERS) from single nanosphere-film junction is realized, which is of significance for SERS as a quantitative analytical tool. It is also the basis for the following experimental work.

Subsequently, surface plasmon coupled-emission (SPCE) of SERS was studied. It is found that Raman signal originated from molecules sitting at the nanosphere-film junction can couple back to SPPs, and eventually radiates into the substrate side with high refractive index at SPP resonant angles. Collection efficiency of SERS can be improved with the help of SPCE. Meanwhile, due to the extremely narrow linewidth of Raman peaks, the SPCE curve of SERS can also be employed for measuring the propagation length of SPPs and quantitatively characterizing the point spread function of an SPCE microscopy.

Last but not least, as a promising application, the two-dimensional mapping of the strongly-dominant longitudinal field component of SPPs was realized based on the SERS imaging. Our method takes advantage of SERS from a single nanosphere-film junction where the enhancement factor is determined by the longitudinal component of coupled SPPs between the nanosphere and metal film. By scanning the nanosphere immobilized on the film over the propagation region of SPPs, We can map out the near-field SPP longitudinal field with super-resolution.

To sum up, a plasmon-hybrid-mode directed surface-enhanced Raman system is proposed in this thesis. By utilizing the coupling-effect between SPPs and LSP, Raman enhancement of more than 10^9 was predicted numerically and more than 10^8 was achieved experimentally. Moreover, collection efficiency of SERS originating

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Symbols and Abbreviations

List of Symbols

α : polarizability

β : wave-vector of SPP

ε : permittivity

ϕ : potential

φ : azimuthal angle

λ : wavelength

θ : incident angle

σ : cross-section

τ : transmission coefficient

ω : frequency

A : pitch

c : speed of light

d : distance

f : focal length

k : wave-vector

l : angular momentum

m : diffraction order

n : refractive index

r : radial coordinate

t : thickness

w : beam waist

x : x coordinate

y : y coordinate

z : z coordinate

H : magnetic field

L : propagation length

G : grating constant

R : radius

List of Abbreviations

ATR: attenuated total reflection

BFP: back focal/fourier plane

CCD: charge-coupled device

DDA: discrete dipole approximation

EBL: electron beam lithography

FDTD: finite-difference time-domain

FWHM: full width at half maximum

LSP: localized surface plasmon

NA: numerical aperture

NP: nanoparticle

NSOM: near-field scanning optical microscope

PMT: photomultiplier tubes

PSF: point spread function

PSP: propagating surface plasmon

RP: radially polarized

SERS: surface-enhanced Raman scattering / surface-enhanced Raman spectroscopy

SPs: surface plasmons

SPCE: surface plasmon-coupled emission

SPP: surface plasmon polariton

SPR: surface plasmon resonance

TM: transverse magnetic

TE: transverse electric

Chapter 1 Introduction

1.1 Motivation

Raman scattering is an inelastic scattering process between a photon and a molecule [1]. It was firstly observed in 1928 and quickly becoming an important branch of optical detection techniques due to its unique spectral features. Compared to the fluorescence of molecules, Raman spectrum is much sharper, with each peak representing the molecular vibrational or rotational mode, and hence enables the detection of uniquely identifying molecular fingerprints. However, the cross-section of Raman scattering is extremely small. It is 12-14 orders of magnitude lower than typical fluorescence cross-sections [2]. Thus, despite the rich information offered by regular Raman spectroscopy, it has not been the primary choice as a handy analytical tool.

The discovery of surface enhanced Raman scattering (SERS) opened a new avenue for Raman spectroscopy [3]. When molecules are residing at or near specific metallic nanostructure surface, the Raman scattering cross-sections are hugely enhanced, rendering them even comparable to that of fluorescence. The large signal enhancement allows vibrational spectrum to be measured from molecules that would otherwise be spectroscopically silent. In particular, the observation of single-molecule SERS by Kneipp, Nie, and their co-workers boosts the development of SERS [2, 4], and it rapidly becomes a powerful analytical tool for chemical and biological sensing application.

The enhancement effect plays a crucial role in SERS. Chemical and electromagnetic enhancement are widely believed the two main contributions, with

the latter being the dominant one [5-6]. The electromagnetic enhancement arises from the light-substrate interaction, which consists of the resonant excitation of surface plasmon modes (LSP, SPP, or both of them), the lightning rod effect, and the image field effect [7-8], with SP making the major contribution. The SP frequency and the induced electromagnetic enhancement are strongly dependent on the incident light wavelength, polarization, substrate morphology, and environment medium [9-10]. Researchers have made great effort to develop a robust SERS substrate to optimize the electromagnetic enhancement.

Noble metal nanoparticles (NPs) are the most widely used SERS substrate to enhance the Raman signals. With the fast development of nano-science and nano-technology, NPs of different sizes and shapes can easily be synthesized [11]. The electromagnetic enhancement of an individual NP ranges from several tens to several hundred, depending on its composite and shape [12-14]. In terms of Raman enhancement, it is on the order of $10^3 - 10^7$. Such Raman enhancement is mainly from the excitation of LSP and is relatively low among the family of SERS substrates.

As two NPs are put together (dimer configuration), with inter-particle separation on the order of several nanometers, the electromagnetic enhancement can substantially be improved [15-19]. This huge enhancement is believed due to the strong coupling between the LSP modes on each particle (LSP-LSP hybridization). Single molecule sensitivity has been realized on the dimer structures [20-21]. However, the nature of random formation of inter-particle junction makes it quite irreproducible, causing Raman enhancement with dramatic variations, often by many orders of magnitude. This significantly restricts its practical application as a robust SERS substrate.

An alternative junction is created in a NP-film gap mode system, in which one of

the NPs is replaced by a smooth metal film [22-30]. Experimental studies demonstrated that such NP-film junction configuration is capable of providing remarkably reproducible SERS-active hotspots compared with the NP-NP junction [27]. Moreover, due to the coupling between the LSP excited on the NP and the SPPs generated on the conducting surface (LSP-SPPs hybridization), the electromagnetic enhancement shows more advantageous than that on a dielectric substrate (such as glass, silicon or SiO_2), in which only LSP is present. The combination of high reproducibility with high Raman enhancement of NP-film junctions makes them a great potential as robust SERS substrates. However, in the preceding work regarding NP-film junction, there exist two main drawbacks.

Firstly, the SPPs formed on the smooth metal surface are induced by the NPs, which diffract the incident beam, generating the required wave-vector to match that of SPPs (NP-driven plasmon hybridization). Such an excitation approach is rather inefficient and hence limiting its Raman enhancement compared with that from NP-NP junction. Secondly, due to the vertical arrangement of an NP-film junction, an electric field component oriented vertically (perpendicular to the metal surface; also called as longitudinal field component) is preferred to efficiently excite an SP coupling mode at the junction [29, 31-37]. In the preceding SERS experiments, linearly polarized Gaussian beam was focused directly on to the NP-film junction. Although longitudinal electric field component does exist under this kind of excitation approach, it is the subordinate field component and the power utility is therefore quite low [38-39].

Hence, improving the excitation efficiency of SPPs and meanwhile increasing the electric field longitudinal component in a NP-film junction based SERS system is of great significance.

Surface plasmon virtual probe (SP-VP) generated by a tightly-focused radially polarized (RP) beam would be a great candidate as the excitation source for the aforementioned NP-film junction based SERS system [40]. RP light is a uniquely polarized light pattern whose distribution of electric field vectors is arranged radially around the optic axis of a laser beam. When a RP light is tightly-focused onto a metal-dielectric interface, the entire beam is p -polarized with respect to the interface, which enables the excitation of SPPs from all azimuthal directions to form an evanescent Bessel-like standing-wave at the focal region. Such evanescent standing-wave has a sharply-confined SPP spot at the center of focal plane, with the longitudinal field component dominating its total electric field [41-43]. The sharply-confined SPP spot is therefore termed as surface plasmon virtual probe. As a result, by using the SP-VP as the excitation source, both of the above drawbacks are overcome, and the NP-film junction configuration therefore can be as a robust SERS substrate, owing to its high reproducibility and Raman enhancement.

Before we use the SP-VP as the excitation source, it is important to map its near-field distribution above the metal film, particularly its longitudinal electric field component. However, there is no experimental technique up to now, which can effectively map the near-field distribution of SP-VP in the visible range, and hence verify the formation of it. The difficulty of mapping an SP-VP lies in that: first of all, due to the evanescent and sub-wavelength nature of SP-VP, the traditional far-field techniques, such as conventional optical microscopy, lose effectiveness; secondly, the field of an SP-VP is strongly-dominated by the longitudinal component, which is largely unmeasurable by near-field scanning optical microscope (NSOM), the most convenient tool to measure the field distribution of SPPs [42]. As a result, it would be of great significance if a novel detection technique is developed to efficiently and

accurately map the field distribution of SP-VP. An interesting thing is that: since the SP-VP can be as an optimized source for the excitation of SERS based on the NP-film junction, the NP-film junction, in turn, can be employed as an SP-antenna to detect the field distribution of SP-VP by means of SERS imaging. This is the second motivation of this thesis.

Finally, besides the SPPs contribution on the excitation of SERS signals, recent experimental work demonstrated that the emitted Raman radiation is also able to couple back to SPs with periodic metallic structure or nanoantennas, forming a “beam shaped” Raman scattering”. Such shaped emission of Raman scattering is able to improve its collection efficiency. Motivated by their work, in this thesis, we investigate the emission pattern of SERS from single NP-film junction. Because of the presence of a thin metal film, Raman scattering from the NP-film junction is able to couple back to SPPs supported at the air-metal interface, and eventually re-radiates into the substrate side with higher refractive index. The so-call surface plasmon coupled-emission (SPCE) [44-46] is able to improve the collection efficiency of SERS, and the SPCE curve of SERS can also be used for measuring the propagation length of SPPs and the point spread function of an SPCE microscopy.

1.2 Objective

Grounded on the discussion above, the main research focus of this thesis is to develop a robust SERS substrate based on the plasmon hybridization, which, accompanying with a suitable excitation source, can provide a relatively high Raman enhancement with high reproducibility, and extend it to other SPs-based applications. The objective is divided into three sub-items as following:

(1) From the excitation point of view, SP-VP excited by a tightly-focused RP beam is

introduced into the conventional NP-film junction based SERS system to improve further the Raman enhancement. We will investigate the plasmonic response of the new excitation scheme both from simulation and experiment, in term of Raman enhancement.

- (2) From the collection point of view, surface plasmon coupled-emission of SERS from single NP-film junction will be studied. Our investigation of SPCE will focus on the mechanism, the induced collection efficiency improvement of SERS and its corresponding applications.
- (3) From the characterization point of view, since SP-VP will be employed as the excitation source in our SERS system, accurately and efficiently mapping its near-field distribution is essential. As the final objective of the thesis, we propose a novel technique to detect the near-field distribution of SPPs (including SP-VP), which is based on the SERS imaging from single NP-film junction. The principle and performance of our method will be demonstrated.

1.3 Major Achievements

Below presents the major achievements in this thesis:

(a) Localized surface plasmon is excited by a surface plasmon virtual probe

To our best knowledge, it is our original work that LSP is excited by an SP-VP (film-driven plasmon hybridization), and the induced high electromagnetic enhancement is employed for SERS. Raman enhancement of more than 10^{10} was predicted from the numerical simulation and more than 10^8 was achieved in the experiment. The proposed configuration possesses both high Raman enhancement and reproducibility and hence is potential as a robust SERS substrate. The manuscript regarding this work is under preparation.

(b) Radially polarized beam is employed as the excitation source for SERS

Compared to the conventional linearly polarized beam, RP beam shows many advantages for the LSP/SPP co-enhanced Raman system based on the NP-film junction scheme. Firstly, RP beam is well known as the optimized source for the excitation of SPPs under a tight-focus configuration due to its full beam p -polarization. Secondly, a dominant longitudinal field can be generated at the center of focal plane, which is quite important for a NP-film junction due to its z -component sensitivity. The work is published on “Plasmonics”.

(c) Surface plasmon coupled-emission of SERS was studied, both theoretically and experimentally.

The SPCE of fluorescence has been extensively studied in the past decade, and is well known as a powerful tool for sensitive fluorescence detection. In this thesis, we experimentally demonstrated the coupled-emission of Raman scattering from NP-film junctions. It can serve as a sensitive detection tool for SERS. The work is accepted and published online on “Appl. Phys. Letts”.

(d) A novel method for mapping the dominant longitudinal field of SPPs was proposed and realized experimentally.

An efficient characterization of SPPs near-field distribution was a source of confusion in the past. The difficulty lies in that the field is dominated by the longitudinal field component which is largely unmeasurable by NSOM, the most convenient tool to measure the near field distribution of SPPs. In this thesis, we report a SERS based method that can predominately measure the longitudinal field of SPPs. Our method takes advantage of SERS from a single NP-film junction where the enhancement factor is determined by the longitudinal component of coupled SPPs between the NP and the film. By scanning the NP immobilized on the film, we can map out the longitudinal

field distribution of the SPPs, with super-resolution. The manuscript is ready for submission.

1.4 Organization of This Thesis

This thesis is organized into the following seven chapters:

Chapter 1 is the thesis introduction, encompassing the motivation for this work, its objectives, major achievements and organization.

Chapter 2 presents the background knowledge related with our work in this thesis, including surface plasmon polaritons, localized surface plasmon, surface enhanced Raman scattering and spectroscopy and radially polarized beam.

In Chapter 3, as a fundamental investigation, two different types of excitation configurations are proposed to realize the plasmon-hybrid-mode and their optical properties are numerically investigated.

Chapter 4 presents the experiments conducted to verify the high Raman enhancement induced by surface plasmon coupling mode.

In Chapter 5, the coupled-emission of SERS is studied.

Chapter 6 demonstrates the two-dimensional mapping of SPP longitudinal component based on the SERS imaging.

Finally, in Chapter 7, a brief summary concludes this work, describing all important findings and offer an outlook for possible routes to follow this work.

Chapter 2 Literature Review

Before we introduce our plasmon-hybrid-mode directed surface-enhanced Raman system, it is necessary to make a systematic literature review of the knowledge related with our work. More specifically, the unique properties of SPPs, including the dispersion relationship, the excitation and detection techniques, will be presented firstly, followed by the introduction of an LSP, containing its excitation mechanism and electromagnetic enhancement effect. Next, surface-enhanced Raman scattering will be reviewed, consisting of its mechanism, the concept of Raman enhancement and the SERS substrates that are investigated so far. Finally, the knowledge of radially polarized light will be introduced, including its unique beam profile and attractive properties as an excitation source of SPPs.

2.1 Surface Plasmons

The first scientific studies of SPs dated back to the beginning of twentieth century. In 1902, Robert W. Wood observed a dramatic drop in the optical reflection spectra measurement from metallic diffraction grating over a small change in incident angle [47]. Although Wood had no idea at that time to explain this anomaly due to SP, his work marked the beginning of the SP research area.

Nowadays, we have known that SPs are the coherent oscillation of the surface conduction chargers excited by an electromagnetic radiation, and there are two types of SP modes: SPP and LSP, respectively, with the difference between them illustrated in Fig.2.1..

Fig.2.1. Schematic diagrams illustrating a surface plasmon polariton (a) and localized surface plasmon (b), respectively [48].

In the case of SPP, plasmons are propagating in the horizontal directions along a metal-dielectric interface, for distances on the order of tens to hundreds of microns, depending on the material and excitation wavelength, and decaying evanescently in the vertical direction with $1/e$ decay lengths on the order of several hundred nanometers. Because of this, SPPs are also frequently called as propagating surface plasmons (PSPs) elsewhere. For the case of LSP, light interacts with metallic NPs much smaller than the incident wavelength. This leads to a plasmon that oscillates locally around the NP and a significant electric field enhancement around the surface of it. Due to their different schemes of oscillation with metallic structures, SPP and LSP are generally investigated separately and their specific applications are developed accordingly. In the following section, we will introduce the SPP and LSP, respectively.

2.1.1 Surface Plasmon Polaritons

(a) Dispersion relationship

The simplest geometry to support an SPP is that of a single, flat interface between a semi-infinite dielectric space with positive dielectric constant ϵ_1 and an adjacent conducting half space with dielectric function described as $\epsilon_m(\omega)$, as shown in Fig.2.2..

Fig.2.2. Single dielectric-metal interface for SPPs excitation and propagation.

Based on the Maxwell equations, for a TM mode (or a p -polarized beam), the electromagnetic fields at each half space can be expressed as [49]:

$$H_y(z) = A_1 e^{i\beta x} e^{-k_1 z} \quad (2.1)$$

$$E_x(z) = iA_1 \frac{1}{\omega \epsilon_0 \epsilon_1} k_1 e^{i\beta x} e^{-k_1 z} \quad (2.2)$$

$$E_z(z) = -A_1 \frac{\beta}{\omega \epsilon_0 \epsilon_1} e^{i\beta x} e^{-k_1 z} \quad (2.3)$$

for $z > 0$ (at the dielectric space), and

$$H_y(z) = A_2 e^{i\beta x} e^{k_2 z} \quad (2.4)$$

$$E_x(z) = -iA_2 \frac{1}{\omega \epsilon_0 \epsilon_m} k_2 e^{i\beta x} e^{k_2 z} \quad (2.5)$$

$$E_z(z) = -A_2 \frac{\beta}{\omega \epsilon_0 \epsilon_m} e^{i\beta x} e^{k_2 z} \quad (2.6)$$

for $z < 0$ (at the metal space), where A_1 and A_2 are the constants to be determined, $\beta = k_x$ is the propagation constant of the travelling waves and corresponds to the component of the wave-vector in the direction of propagation, k_i ($i=1,2$) are the components of the wave-vector perpendicular to the interface in the two mediums, respectively. The continuity of H_y and E_x at the interface requires that $A_1=A_2$, and

$$\frac{k_1}{\epsilon_1} + \frac{k_2}{\epsilon_m} = 0 \quad (2.7)$$

Eq. (2.7) clearly indicates that, on the one hand, $\epsilon_1 \cdot \epsilon_m$ should be negative to satisfy the condition since k_1 and k_2 are positive. This means that surface waves exist only at interfaces between materials with opposite signs of the real part of their dielectric permittivities, i.e. between a conductor and an insulator.

On the other hand, k_1 and k_2 in Eq. (2.7) represent the components of the wave-vector perpendicular to the interface in the dielectric and metal, and can be expressed as:

$$k_1^2 = \beta^2 - k_0^2 \epsilon_1 \quad (2.8)$$

$$k_2^2 = \beta^2 - k_0^2 \epsilon_m \quad (2.9)$$

Substituting Eq. (2.8) and Eq. (2.9) into Eq. (2.7) will give us the following equation:

$$k_{SPP} = \beta = k_0 \sqrt{\frac{\epsilon_1 \cdot \epsilon_m}{\epsilon_1 + \epsilon_m}} \quad (2.10)$$

This is the dispersion relationship of an SPP excited on a single dielectric-metal interface. For comparison, the corresponding calculation for a TE mode (or an s-polarized beam) leads to a condition of $A_1 \cdot (k_1 + k_2) = 0$, which is only fulfilled if $A_1 = A_2 = 0$. Therefore no surface mode exists for TE polarization. In other words, SPPs

only exist for TM mode or p -polarized beam.

Back to Eq. (2.10), since the permittivity of a dielectric ϵ_1 is always positive, and $\epsilon_1 \cdot \epsilon_m$ should be negative as predicted from Eq. (2.7), it means that ϵ_m needs a negative real part with absolute value exceeding ϵ_1 . Noble metals such as gold and silver have such large negative real part of permittivity with a small imaginary part, as shown in Fig.2.3. Therefore, at the interface between a noble metal and a dielectric, such as air, water or glass, surface plasmon modes at the metal/dielectric interface can exist.

Fig.2.3. Permittivities of silver and gold over the visible spectrum. Ref. [50]

Furthermore, if we express the permittivity of metal ϵ_m as $\epsilon' + i\epsilon''$, where ϵ' and ϵ'' represent the real and imaginary part of the permittivity and substitute it into Eq. (2.10), we can get the dispersion relationship, under the assumption that $|\epsilon''| \ll |\epsilon'|$, as following:

$$\beta = \beta' + i\beta'' \quad (2.11)$$

$$\beta' = k_0 \left(\frac{\epsilon' \epsilon_1}{\epsilon' + \epsilon_1} \right)^{1/2} \quad (2.12)$$

$$\beta'' = k_0 \left(\frac{\epsilon' \epsilon_1}{\epsilon' + \epsilon_1} \right)^{3/2} \frac{\epsilon''}{2(\epsilon')^2} \quad (2.13)$$

As a result, from Eq. (2.1) to Eq. (2.6), the SPPs decaying along the interface can be

described by β'' , which is responsible for an exponential damping of the electric and magnetic field amplitude. The $1/e$ decay length of the electromagnetic field density is defined as the propagation length L_x .

$$L_x = 1 / (2 |\beta''|) \quad (2.14)$$

This damping is caused by Ohmic losses of the electrons participating in the SPPs and finally results in heating of the metal. From Eq. (2.13), L_x is strongly dependent on the imaginary part of the permittivity of metal.

According to Eq. (2.12), the dispersion relationship of an SPP propagating along an interface between a metal and a dielectric is described as

$$k_{SPP} = \frac{\omega_0}{c} \left(\frac{\epsilon_1 \epsilon'}{\epsilon_1 + \epsilon'} \right)^{1/2} \quad (2.15)$$

Due to the negative permittivity of metal, the dispersion curve of an SPP always lies to the right of free space photon k_0 for all wave-vectors, as shown in Fig.2.4. As the frequency ω_0 increases, k_{SPP} deviates further from k_0 , leading to a larger wave-vector and shorter SPP wavelength. From the dispersion relation, it is obvious that SPP cannot be directly transformed from free space photon and the momentum mismatch must be compensated to couple the light with SPPs.

Fig.2.4 Dispersion relations of free space photons (A), free photons propagating in dielectric (B) and the surface plasmons (C).

(b) Excitation configurations

As presented previously, a unique feature of SPP is that the wave-vector k_{SPP} is always larger than that of light in vacuum over the visible spectrum (as shown in Fig.2.4 (A and C)). This means that SPP on a planar metal-dielectric interface cannot simply be excited by a light propagating in vacuum. It is possible only if the wave-vector of incident light is effectively increased such that an intersection occurs between their dispersion curves, as illustrated in Fig.2.4 (B and C). So far, there are several approaches proposed to excite an SPP, including the attenuated total reflection (ATR) configurations, near-field excitation configurations, and diffraction grating structures, etc.

(i) ATR configuration

Fig.2.5 ATR couplers for SPPs excitation. (a) The Otto configuration, (b) the Kretschmann-Raether configuration and (c) the objective configuration, respectively. Ref. [51]

A dielectric medium with larger refractive index ($n_2 = \sqrt{\epsilon_2} > 1$) is an easy way to increase the wave-vector of light, by a factor of n_2 , i.e., if a p -polarized light is propagating and impinging onto a metal surface with incident angle θ within the dielectric medium, its wave-vector becomes $\omega_0/c\sqrt{\epsilon_2}$, instead of ω_0/c in the vacuum. Under this circumstance, SPP can be excited at the metal-air interface as long as the in-plane wave-vector component of the incident light is equal to that of SPP, as illustrated in Eq. (2.16).

$$k_{SPP} = \frac{\omega_0}{c} \left(\frac{\epsilon_1 \epsilon_m}{\epsilon_1 + \epsilon_m} \right)^{1/2} = \sqrt{\epsilon_2} \sin \theta \frac{\omega_0}{c} \quad (2.16)$$

There are two configurations that can realize the ATR coupler to excite the SPPs at the metal-dielectric interface: the Otto configuration, which was proposed by Andreas Otto in 1968, and the Kretschmann-Raether configuration, which was proposed by Kretschmann and Raether shortly after Otto [52-53], respectively, as shown in Fig.2.5 (a) and (b). Both are using a prism as the coupler and the only difference is the location of metal film with respect to the prism. The Otto configuration is seldom employed due to its difficulty to control the distance between a prism and a metal, while the Kretschmann configuration is used frequently. A minor alteration to the Kretschmann configuration makes use of a high numerical aperture (NA) oil immersion objective lens to focus incident beam onto a metal-dielectric interface [54], as shown in Fig.2.5 (c). The index matching oil is used to optically couple metal coated glass slides to the objective lens. This configuration allows for exchange of metal film and integration with conventional microscopic system, making it well suited for applications in biosensing and imaging.

(ii) Near-field excitation

Fig.2.6 Schematic of launching SPPs by a near-field tapered fiber probe (a) or a scatterer (b). Ref. [51]

An alternative method is using a near field probe or scatterer to generate the required

larger wave-vector, as shown in Fig.2.6. In Fig.2.6 (a), a probe tip with aperture size much smaller than incident beam wavelength is illuminating onto the surface of a metal film in the near-field. Due to the small aperture size, the light transmitted from the tip will consist of increased wave-vector components, thus allowing phase-matched excitation of SPPs.

Similarly, if a nanoscale scatterer is present in the near-field region, for example, a randomly rough surface. When light illuminates the rough surface, the scatterer diffracts the incident light, generating the required wave-vector to match that of SPP and hence excite the SPPs near the area of the scatterer (see Fig.2.6 (b)). With these near-field approaches, the region of the area for launching SPPs can be greatly reduced. However, the launching efficiency is generally much lower than that of the ATR-based techniques.

(iii) Gratings

Fig.2.7 SPPs excitation based on grating configuration. Ref. [51]

The additional light momentum to excite SPPs can also be provided by light scattered via a periodic corrugation on a metal surface, as shown in Fig.2.7. The incident plane wave is diffracted by such a periodic structure into many orders, with some corresponding to the propagating plane waves and others the evanescent waves which can drive surface charge oscillations to form SPPs, as long as the incident light is *p*-polarized and the wave-vector matching condition is satisfied. For this type of SPP

coupler, the increase of wave-vector necessary to match its momentum is achieved by adding an additional grating momentum to the free-space wave-vector. For the simple one-dimensional grating structure, the SPP phase matching takes place whenever the condition $k_{SPP} = k_0 \sin \theta \pm mG$ is fulfilled, where θ is the incident angle, $G = 2\pi/\Lambda$ the grating constant and m ($= 1, 2, 3 \dots$) the diffraction orders. This method can preferentially excite a particular SPP mode with high efficiency.

(c) Detection techniques

SPPs are evanescent waves bound to the metal/dielectric interface, which brings complexity to detect them. Imaging of their propagation with far-field optics will be available only when the SPPs are coupled back to photons first. Three main methods have been reported in literature to detect SPPs.

(i) Leakage radiation microscopy

The first method is to detect the leakage radiation [55]. If an incident light can couple to an SPP mode through a substrate, the SPP is able to decouple to a propagation radiation as well through the substrate. More specifically, when a metal surface is rough, it will scatter the SPPs into a far-field radiation that can be detected with a microscope, as shown in Fig.2.8. Drawback of this technique is that the scattered field is measured, rather than the SPP itself.

Fig.2.8 The scheme of a leakage radiation microscopy

(ii) Fluorescence imaging

The second technique is aided by fluorescence [56]. With sufficiently low concentrations, the fluorescence shows little perturbation onto the SPPs under investigation. Hence, with this technique, one can visualize the SP mode by detecting the fluorescence over the surface. It provides a useful tool to study the propagation of SPPs and their interaction with surface structures and optical components. However, the resolution of this technique is restricted by the diffraction limit.

(iii) Scanning near-field optical microscope

The most widely used technique to study SPP's near field behavior is NSOM [42, 57-68], in which a bare tapered or metal-coated glass fiber is dipped into the SPP field to couple some of the light into the probe. SPPs are thus converted into propagating modes and guided towards to a detector. The resolution of this technique is comparable to the size of the tip aperture, which can approach to 100 nm or even less when etching techniques are used.

2.1.2 Localized Surface Plasmon

In addition to the SPPs at a planar metal-dielectric interface, LSP can be excited on other geometries, such as metallic particles or voids of various shapes. The frequency of an LSP can be determined by solving the Laplace's equation under quasi-electrostatic approximation, imposing suitable boundary conditions. The quasi-electrostatic approximation is valid if the size of nanostructure is much smaller compared to the wavelength corresponding to the LSP frequency [10].

Fig.2.9. (a) Schematic of a sphere-shaped noble metal NP interacts with a uniformly-distributed electromagnetic radiation. (b) Contour map of the electric field distribution of a dipole mode.

A metallic nanosphere embedded within a uniform electromagnetic radiation is the simplest configuration to excite an LSP, as shown in Fig.2.9 (a). If we assume the radius of the nanosphere is R , the dielectric constants of nanosphere and environment are ϵ_m and ϵ_0 , respectively, the solution of Laplace's equation for the electrostatic potential inside and outside the sphere can be expressed as the following forms:

$$\phi_{in}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm} r^l Y_{lm}(\theta, \varphi), \quad 0 \leq r \leq R, \quad (2.17)$$

$$\phi_{out}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l b_{lm} \frac{1}{r^{l+1}} Y_{lm}(\theta, \varphi), \quad r \geq R, \quad (2.18)$$

where $Y_{lm}(\theta, \varphi)$ is the spherical harmonic, l the angular momentum label of atomic orbitals, respectively. If we restrict our consideration to only the $l = 1$ solution and if $\mathbf{E}_0$ is in the x direction, the potential is simplified to $\phi = A r \sin \theta \cos \varphi$ inside the sphere and $\phi = (-\mathbf{E}_0 r + B/r^2) \sin \theta \cos \varphi$ outside the sphere, where A and B are constants to be determined. By imposing the boundary conditions (the continuity of ϕ and $\epsilon \partial \phi / \partial r$ at the surface of the sphere) onto the equations, the potential ϕ can be solved. The obtained potential is then used to determine the field outside the sphere, $\mathbf{E}_{out}$, which is

$$\bar{\mathbf{E}}_{out} = E_0 \hat{x} - \alpha E_0 \left[\frac{\hat{x}}{r^3} - \frac{3x}{r^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right] \quad (2.19)$$

where α is the sphere polarizability and $\hat{x}$, $\hat{y}$, $\hat{z}$ are the unit vectors for each axis.

The Laplace equation solution shows that the polarizability is

$$\alpha = \frac{\varepsilon_m - \varepsilon_0}{\varepsilon_m + 2\varepsilon_0} = \frac{\varepsilon' + i\varepsilon'' - \varepsilon_0}{\varepsilon' + i\varepsilon'' + 2\varepsilon_0} \quad (2.20)$$

where ε' and ε'' represent the real and imaginary part of the permittivity of the sphere.

According to Eq. (2.20), the magnitude of electric field outside the nanosphere is maximized when $\varepsilon' + 2\varepsilon_0 = 0$. This is just the dispersion relation used to determine the resonant wavelength of the dipole mode on a nanosphere. α in this case equals to:

$$\alpha = \frac{-2\varepsilon_0 + i\varepsilon'' - \varepsilon_0}{i\varepsilon''} = \frac{3i\varepsilon_0 + \varepsilon''}{\varepsilon''} = 1 + 3\frac{\varepsilon_0}{\varepsilon''}i \quad (2.21)$$

As can be seen, on the one hand, the polarizability is positively related with the dielectric constant of environment. In other words, we can increase the electric field outside the nanosphere under resonant conditions by increasing the refractive index of the environment. On the other hand, it is also negatively related with the imaginary part of the permittivity of metal nanosphere, this is why silver NPs/nanostructures generally present greater electromagnetic enhancement compared to the gold nanostructures due to the smaller ε'' , as can be seen in Fig.2.3.

Since an LSP is strongly confined to a small particle, it results in a significant electromagnetic field enhancement at the surface of particle due to the localization of free electrons driven by the excitation radiation (as shown in Fig.2.9 (a)). The electric field distribution around the nanosphere under resonant condition is shown in Fig.2.9 (b), which is a standard dipole mode ($l=1$), with electric field greatly enhanced at the two sides of nanosphere along the direction of incident electric field. As the size of the sphere increases, the contributions of higher multipoles, especially the quadruple term ($l=2$), become more and more important [9]. However, because the high order LSP modes will not be involved in this thesis, the corresponding background knowledge is

not covered as well.

If NPs under consideration possess shapes other than spheroid (triangle, cube for example), the Laplace equations under these circumstances become complex and no explicit solution exist anymore. In these cases, other numerical tools should be employed to study the light-particle interaction. Discrete dipole approximation (DDA) [12, 69-74] and finite-difference time-domain (FDTD) [75-78] method are the most widely used tools to solve Maxwell's equations to determine the local fields $\mathbf{E}(\omega)$ around the NP. In these methods, the particle structures are represented using finite elements. Thus, it is not difficult to describe a particle of any shape, and sizes up to a few hundred nanometers are within standard computational capabilities.

Fig.2.10 presents the LSP ($l=1$) excitation on an individual silver NP of various shapes, obtained with the DDA method. From the electric field contour maps in Fig.2.10, we can find that the maximum electric field under LSP resonant conditions is significantly improved for shapes with sharp edges, for example, nanocubes, nanotriangles and nano-spheroids with high long-to-short axis length ratio.

Fig.2.10. LSP excitation on an individual silver NP of different shapes. Ref. [9, 13]

2.1.3 Plasmon Hybridization

Plasmon hybridization occurs when two SP modes are excited simultaneously, with mode separation on the order of several nanometers or less. There are two types of plasmon hybridization: LSP-LSP and LSP-SPP hybridization, respectively. In this section, the mechanism of plasmon hybridization will be presented briefly and later in the section of SERS substrates, the applications of plasmon hybridization on SERS will be introduced.

a) LSP-LSP hybridization

When two metallic NPs are put together, with inter-particle separation on the order of several nanometers, LSP can be excited on each of the NPs, resulting in the electrons and ions driven to the two ends of NP surface along the direction parallel to the polarization of incident electric field, as shown in Fig.2.11 (a). Because of the small inter-particle separation, a strong Coulomb interaction between the two adjacent ends is present, which leads to a redistribution of the surface charges on each particle and hence a shift of resonant wavelength.

Fig.2.11. Demonstration of the LSP-LSP hybridization. (a) LSP mode excited on an individual NP. (b) LSP-LSP hybridization on a NP-NP junction configuration. The Coulomb interaction between the NPs leads to an energy splitting of the plasmon-hybridized modes. Ref. [79]

More specifically, as demonstrated by P. Nordlander, etc. in their theoretical

calculations, the particle-particle interaction will induce an energy splitting from their original LSP mode into the plasmon-hybridized bounding and anti-bounding modes [79] (Fig.2.11 (b)). The magnitude of splitting strongly depends on the strength of the Coulomb interaction between the two particles and hence on their spatial separation. In addition, the near-field electromagnetic enhancement within the gap between the two particles is significantly improved [13, 77, 80-81] (Fig.2.12), which is of great potential for applications in SERS.

Fig.2.12. Electromagnetic enhancement from LSP-LSP hybridization. Ref. [13]

b) LSP-SPP hybridization

There are two types of configurations supporting the LSP-SPP hybridization: periodic metallic structures and NP-film junction configurations, respectively.

For a periodic metallic structure (Fig.2.13 (a), as an example [82-83]), the wave-vector matching condition of SPPs is fulfilled via the two-dimensional grating, while the LSP is excited on each of the metallic NPs at specific incident wavelengths. A typical dispersion diagram of a two-dimensional periodic metallic structure is shown in Fig.2.13 (b) with the contour map. The horizontal lines marked with $l=1,2,3$ in Fig.2.13 (b) represent the excitation curves of LSP in the absence of SPP, while the

other four curves originated from a single point are the excitation curves of SPPs without the consideration of LSP. Similar to the case of LSP-LSP hybridization, energy splitting occurs when LSP and SPP are excited simultaneously, accompanying with a red-shift of resonant wavelengths with respect to their separate modes. The positions of the resonant wavelengths as well as the magnitude of their energy splitting can easily be tuned by changing the structural parameters (such as period, NP size, etc.). Such kind of double-resonance structures is well-suited as SERS substrates to improve the Raman enhancement.

Fig.2.13. Demonstration of the LSP-SPP hybridization. (a) A typical example of a two-dimensional periodic metallic structure supporting the LSP-SPP hybridization, in which LSP is excited on each of the metallic NPs while SPPs spreading all over the space between the NPs. (b) Dispersion diagram of a two-dimensional periodic metallic structure. Energy splitting occurs when SPP and LSP are excited simultaneously. Ref. [82-83]

NP-film junction is another configuration capable of supporting the LSP-SPP hybridization [31-37] (Fig.2.14 (a)). The separation between the NP and metal film is typically less than 10 nm (can be negative, meaning that the NP is embedded within the metal film), which is achieved by depositing a thin dielectric spacer layer between them. Similar to the particle-particle interaction, the Coulomb interaction between the NP and metal film plays a significant role on the resonant wavelengths of plasmon-hybridized modes. The stronger the interaction, the more remarkable the red-shift of

resonant wavelength with respect to a standalone NP (Fig.2.14 (e and f)). This also leads to a distinct response of a NP-film junction to the in-plane (transversal) and out-of-plane (longitudinal) electric field, as illustrated in Fig.2.14 (a and b).

Fig.2.14. NP-film junction induced plasmon hybridization. (a) Simplified representation of a plasmonic NP interaction with a gold film. The dipole parallel to the gold film is canceled out by the induced image dipole. (b) The dipole perpendicular to the gold film resonantly couples to the induced image dipole, and scatters into the far-field. (c) and (d) Experimentally observed far-field scattering from a 60 nm gold NP on a 45 nm gold film illuminated with polarization parallel (scattering is damped and is virtually undetectable) and perpendicular to the film (which couples to the vertically oriented dipole and is scattered into the far-field), respectively. (e) Color image and typical spectrum of 60 nm gold NPs in a quasi-uniform dielectric (at a glass-H₂O interface) and (f) on the surface of the 45 nm thick planar gold film (under dark-field illumination), which shows a red-shift of resonant wavelength.

Assuming the NP scatters as a polarizable dipole, an image dipole is induced in the film in response to the presence of a NP. The in-plane (induced by an in-plane electric field) dipole moments of the image are opposite to those of the NP, so that the net scattering from the NP vanishes when light is polarized such that the electric field is parallel to the film (Fig.2.14 (a and c)). The NP and its image can then only be polarized normal to the surface to get a far-field image of the NP (Fig.2.14 (b and d)). At the near-field, electric field is significantly confined within the NP-film gap under an out-of-plane field illumination [29, 37, 84] (Fig.2.15). The electromagnetic enhancement under resonant condition is greatly improved compared to a standalone

NP, for which only LSP mode is excited. This is very attractive for the application of SERS.

Fig.2.15. Electromagnetic enhancement induced by the LSP-SPP hybridization. Electric field is significantly confined within the NP-film gap. Ref. [37, 84]

2.2 Surface-enhanced Raman Scattering

Surface enhanced Raman scattering (SERS) is a phenomenon in which the Raman scattering cross-sections of molecules residing at or near specific metallic nanostructure surface are hugely-enhanced, even by factors up to 10^{14} , rendering them comparable to fluorescence cross-section. Since its discovery about 40 years ago, SERS has become one of the most spectacular applications of plasmonics to date. The large signal enhancement allows vibrational spectrum to be measured from molecules that would otherwise be spectroscopically silent. In addition, since each molecule has a distinct vibrational spectrum, SERS allows molecules on the enhancing metal substrate to be uniquely identified. The capability of obtaining fingerprint information of species has been widely used for *in-vitro* biosensing [85-95], chemical warfare detection [96-97], environmental pollutants identification [98-99], and a variety of other applications [100-102].

The mechanisms of SERS are systematically investigated since its first discovery. Chemical and electromagnetic enhancement are widely believed the two major

contributions, with the latter being awarded the main one [5-6]. The chemical enhancement arises from the chemical interaction between the adsorbates and metal surface, which includes the chemical bonding enhancement, resonance enhancement of a surface complex, and photo-induced charge-transfer enhancement (PICT) [103-104]. PICT is the most significant one. It describes the optical resonance excitation of charge-transfer state formed by the surface complex of the metal adatom and the adsorbate [105-107]. Generally, Raman enhancement induced by chemical interaction is on the order of 100.

Electromagnetic enhancement, on the other hand, arises from the interaction of light (both incident and scattered) with the substrate, including the resonant excitation of SPs, the lightning rod effect, and the image field effect [7-8], with the SPs make the major contribution. The resonant frequency of SP and the corresponding EM field strength are strongly influenced by the substrate morphology, environment medium as well as incident light polarization, as introduced in the preceding section. Therefore, by carefully controlling the shape, size, composition and the spacing of NPs and their assemblies, one can tune the SP frequency to obtain the optimized SERS substrate at any desired wavelength [10, 108].

2.2.1 Raman Enhancement

As mentioned above, the enhancement of Raman signals is due to two effects. Firstly, because of the chemical interaction between molecules and substrates, the Raman cross-section σ_{Raman} is modified to σ_{SERS} due to a change in environment of the molecule. Theoretical modeling suggests that CE is on the order of 100 [49].

A much more important factor arises from the enhanced electromagnetic field due to the excitation of SPs and the crowding of electric field lines (lightning rod

effect) at a curved metal surface [109-111]. This results in an enhancement of both the incoming and scattered light fields. If we denote $|E_{loc}(\lambda)|$ and $|E_0|$ as the amplitudes of local field at the Raman active site and the incident field, respectively, then $L(\lambda) = |E_{loc}(\lambda)|/|E_0|$ represents the electromagnetic enhancement factor, and the total power of Stokes beam under SERS conditions is eventually calculated as [49]:

$$P(\lambda_s) = N\sigma_{SERS} L(\lambda_L)^2 L(\lambda_s)^2 I(\lambda_L) \quad (2.22)$$

in which N is the number of Stokes' active scatterers within the excitation spot and I the intensity of the excitation beam. Generally, the difference in wavelength $\Delta\lambda = \lambda_s - \lambda_L$ between the incoming and emitted photons is much smaller than the line width of an SP mode, i.e., $L(\lambda)$ is approximately equal to $L(\lambda_s)$. Under this approximation, Eq. (2.22) becomes:

$$P(\lambda_s) = N\sigma_{SERS} L(\lambda_L)^4 I(\lambda_L) = N\sigma_{SERS} \cdot RE \cdot I(\lambda_L) \quad (2.23)$$

RE representing the Raman enhancement is defined as:

$$RE = |E_{loc}|^4 / |E_0|^4 \quad (2.24)$$

Eq. (2.23) is the most commonly used expression for calculating the enhancement of the power of Stokes beam. From this expression, we can find that the electromagnetic contribution to the total SERS enhancement is proportional to the fourth power of the field enhancement factor.

The physical basis of the electromagnetic enhancement consists of two main contributions: the resonant excitation of SPs on metallic nanostructures, and the lightning rod effect, respectively [49]. Of the two phenomena, only the plasmon resonance shows strong frequency dependence, while the lightning rod effect is due to the purely geometric phenomenon of field line crowding and the accompanying enhancement near sharp metallic features. Hence, we can further write the field enhancement factor $L(\lambda)$ as $L_{SP}(\lambda) L_{LR}$. In this thesis, we will focus our study on the

enhancement from the excitation of SPs, i.e., $L_{SP}(\lambda)$, only.

2.2.2 SERS Substrates

SERS substrate is the most widely studied topic in the area of SERS. In the practical diagnostic applications, an ideal SERS substrate should possess the following important features: (a), the substrate could produce a high Raman enhancement; (b), it is able to generate a reproducible and uniform response; (c), it has a stable shelf-life, and (d), it is simply to be fabricated. Over the past 40 years, a tremendous amount of SERS substrates was proposed and various techniques have been developed to generate these kinds of substrates. In the following section, we will review the development of SERS substrates, in detail.

(a) Roughened electrodes or island films

In the early stages of SERS, most substrates were made using electrochemically roughened electrodes or randomly deposited metal films, by means of oxidation-reduction cycles (ORC) or vacuum deposition methods. ORC is a simple method for preparing a SERS substrate. By employing an oxidation potential to the metal electrode, the electrode will be oxidized to soluble compounds or form a surface complex. A reduction potential will then reduce the dissolved species on the surface, forming surface nanostructures [3, 112] (Fig.2.16). By using this method, Raman enhancement for Au, Ag, and Cu can be on the order of 10^4 – 10^6 , while it is on the order of 10^1 – 10^4 for other transition metal substrates [113].

In parallel to EC-ORC, vacuum deposition is another common method to prepare SERS substrates. For this method, a thin layer of gold or silver is deposited onto a slide (such as Si wafer, glass, graphite, or even nano-structured substrates) [114-117],

yielding a collection of thin island films which is capable of supporting LSP. By controlling the substrate temperature and deposition rate, metal films with different SERS activities can be obtained.

Fig.2.16. Roughened electrodes as a SERS substrate formed by means of EC-ORC. Ref. [3]

The SERS substrates formed by the above methods do have some kinds of advantages. For example, they are of great stability and have less chance of being contaminated. However, both ORC and vacuum deposition methods have difficulty to produce uniform structures and lack of information regarding the SERS active sites, and therefore restrict their applications for quantitative analysis.

(b) Chemically-synthesized metallic NPs

With the vast development of nanoscience and nanotechnology, a variety of chemical methods were developed over the past decades to synthesize the NPs, including chemical reduction, chemical replacement, electrochemical reduction, ultrasonic decomposition methods, etc. [11, 118-122]. Metallic NPs of different sizes and shapes have been successfully synthesized using these methods (Fig.2.17).

Chemical reduction is the simplest and most widely used method, in which metal NPs are formed by reducing a metal salt in an aqueous or nonaqueous solution, with

the help of reductants [118, 123-125]. Compared with the ORC or vacuum deposition method, the use of chemically-synthesized metal NPs as SERS substrates possesses many advantages: (i) they are easily to be synthesized; (ii) the shape and size of NPs can be controlled by changing the reaction conditions to obtain the desired optical properties and optimize the electromagnetic enhancement; (iii) extremely high Raman enhancement is possible coming from the aggregated NPs, even for single-molecule detection [2, 4].

Fig.2.17. Chemically-synthesized metallic NPs with different shapes. (a): nanospheres, (b): nanocubes, (c): nanotriangles, (d): nanorods, (e): nanorices and (f): nanobeams. Ref. [119, 121]

Among various chemically-synthesized metal NPs, Au and Ag sols are the most widely used SERS substrates due to their strong SERS activity in the visible spectrum.

Theoretical calculations show that Raman enhancement of a standalone gold NP is around 10^3 – 10^4 , while that for a single silver NP can reach 10^6 – 10^7 [126-127]. Among different kinds of shapes, NPs possessing sharp edges, such as nanocubes and nanotriangles, present higher enhancement compared to nanospheres, owing to the “lightning rod effect” [109-111] at high-curvature-edges. The spectral reproducibility from Au or Ag sols is generally good enough for quantitative analysis; however, because of their weak field enhancement, they are only suitable for molecular systems with strong Raman signal. As a result, up to now, the use of sols for direct SERS detection is quite limited.

(c) Highly ordered SERS substrates

Highly ordered nanostructures are another important branch among the family of SERS substrates. The most intriguing advantage regarding highly ordered substrates is that they can provide a large area of dense SERS active sites with relatively high reproducibility. So far, there are many state-of-the-art methods developed to prepare highly ordered SERS substrates, including chemical assembly (CA) method [128-129], Langmuir Blodgett (LB) method [130-131], nanosphere lithography (NSL) method [132], and nanolithography method, respectively.

(i) Chemical assembly method

For the CA method, a compact layer of bi-functional molecules is firstly formed onto a solid substrate (such as Si and glass) with one moiety, which subsequently interacts with NPs by another moiety to form an ordered layer of NPs through the electrostatic or chemical interaction [112] (Fig.2.18). The surface coverage and uniformity of the assembled NPs layer primarily depend on the size, concentration, and surface charge of the NPs, as well as the type of bi-functional molecules used [112]. The most

attractive advantage of using CA method is that a substrate with large area but homogeneous SERS signal can be fabricated without any complicated equipment. Although the dispersion of NPs on the substrate during assembly process is still random, the signal is quite homogeneous over the whole surface because of the larger laser spot.

Fig.2.18. Highly ordered NPs formed by means of chemical assembly method. Ref. [112]

(ii) Langmuir Blodgett technique

For the LB technique, to prepare an ordered layer of NPs, the NPs are firstly dispersed into a volatile solvent that is immiscible with water, typically chloroform or hexane. The solution is then spread onto the water surface, where it spreads to an equilibrium surface pressure and evaporates, leaving behind a water-supported NPs film. An ordered layer of NPs will be generated eventually on the surface as a result of the compression of the layer through moving the barrier [131]. The film structures formed by different types of NPs are quite different with the LB technique. For example, highly ordered close-packed film of spherical and cubic NPs can easily be formed, whereas nanowires and nanorods tend to align perpendicular to the direction of compression and a rather ordered structure in a large area or a less ordered structure in a small area is formed, with respect to spherical NPs. So far, The LB method is able to

achieve the most uniform substrate based on the NP assembly method [112] (Fig.2.19).

Fig.2.19. Highly ordered NPs formed by means of Langmuir Blodgett method. Ref. [131]

(iii) Nanosphere lithography method

NSL method is another powerful tool to generate an ordered SERS substrate [132-136]. This method is both cost effective and relatively easy to be implemented.

The process involves dropping the coating polymer nanospheres on a substrate, allowing the nanospheres to self-assemble into a close-packed hexagonal array. The array is then used as a mask for the creation of several different SERS active substrates. To fabricate periodic nanotriangle arrays, metal (gold or silver) is directly deposited through the gaps in the nanosphere mask. A periodic array of nano-scale metal is left upon removal of the mask (Fig.2.20). Such metal surfaces have an extremely high density of SERS active sites. In spite of the inexpensive and rapid processes for fabricating a large array of nano-structured materials, they are limited by restricted lattice/interparticle spacings, shapes, and sizes that can be produced, as well

as a large range of defects that occur in the structure.

Fig.2.20. (a) Illustration of the process of NSL. (b) AFM image of an NSL-fabricated NP array in which the nanosphere mask has been removed. (c) AFM image of a film-over-nanosphere substrate in which the nanospheres remain on the surface. Ref. [48]

(iv) Nanolithography

Finally, a highly-ordered metallic array can also be formed with a top-down nanolithography method. During a nanolithography process, a photoresist layer (photoresist can be positive or negative) is firstly spun casted onto a solid substrate (glass, Si, or metal film). It is subsequently patterned with an electron beam, a focused ion beam, or an ultraviolet light to desired structures. After exposure and development, SERS-active metals are deposited on to the remaining photo-resist. A highly ordered

nanostructured SERS-active substrate is finally formed after lifting off, with a structure identical or complementary to that of photoresist pattern [137] (Fig.2.21).

The electron beam lithography (EBL) method is an ideal method for producing highly uniform and reproducible SERS substrates [138-142]. It enables us to control the particle size, shape, and spacing and to locate the plasmon resonance at almost any desired visible wavelength. Unfortunately, it is very expensive to produce large area substrates using EBL, unless the technique is combined with a nano-imprint lithography method. In addition, the improved reproducibility is usually accompanied by a decrease in the overall Raman enhancement and vice versa. Thus, a large amount of research has recently focused on fabricating structures in a way that provides the optimum balance between reproducibility and enhancement for use in chemical and biological sensing application.

Fig.2.21. Highly ordered NPs formed by means of nanolithography method. Ref. [137]

(d) SERS substrate with plasmon hybridization

As introduced in the section of plasmon hybridization, there are two unique properties associated with the surface plasmon hybridization: higher near-field enhancement and

energy-splitting of plasmon-hybridized modes, respectively, both of which can be employed for SERS.

Higher near-field enhancement

The superiority of a higher field enhancement is intuitive since the EM contribution to the total SERS enhancement is proportional to the fourth power of the field enhancement factor, as demonstrated in the section before. A well known substrate that employs this property is the NP-dimer structure, with inter-particle separation at the sub-nanometer scale (Fig.2.22). Raman enhancement on the order of 10^{14} has been asserted [143-144], which is capable for single-molecule detection.

Fig.2.22. SERS substrates of metallic NP cluster with inter-particle junction. (a): dimer and (b): trimer.

A direct visualization of the high field enhancement induced by the LSP-LSP hybridization was also experimentally demonstrated by F. Svedberg, etc. [16]. In their experiment, a diffusing Ag-NP within the aqueous solution was trapped with an optical tweezers and moved towards to another immobilized Ag-NP, both of which were adsorbed with Raman molecules. As can be seen in Fig.2.23, in the case that the two particles are separated far away, neither of them exhibits a SERS signal above the noise level. A clear SERS spectrum only appears when the optically-trapped particle is moved to the same position as the immobilized one and a SERS-active silver particle dimer is thus created.

Fig.2.23. Inter-particle junction created by optical trapping technique and employed for SERS. (a) SERS spectrum from a single immobilized particle (I) shows no signal. (b) An optically trapped particle (T), without SERS signal, is moved toward the immobilized one. (c) When brought into near-field contact, the particle pair (P) shows a strongly enhanced SERS signal. Ref. [16]

However, it is not easily to generate this kind of NP dimer or aggregate structures and position the detected specimens exactly at the inter-particle junction. Moreover, the SERS enhancement from NP aggregates will be strongly influenced by the size and shape of the NPs, as well as the inter-particle spacing and incident light polarization. Since the inter-particle spacing and arrangement for a NP aggregate is random, the spectral intensity originated from NP aggregates is therefore quite irreproducible.

To overcome the low reproducibility of NPs aggregates, an alternative type of junction is created by replacing one of the NPs with a smooth metal film, forming a NP-film gap mode system [22-30]. Experimental studies demonstrated that such NP-film junction is capable of providing remarkably reproducible SERS-active compared with the NP-NP junction [27] (Fig.2.24). Moreover, due to the coupling between the LSP excited on the NP and the SPPs generated on the conducting surface

[37], the EM field enhancement shows more advantageous than that on a glass substrate, in which only LSP mode is present. Hence, a NP-film junction shows a good balance between the reproducibility and Raman enhancement.

Fig.2.24. NP-film junction as SERS substrate, which presents remarkable reproducibility as well as high Raman enhancement. Ref. [27]

Energy-splitting of plasmon-hybridized modes

The energy-splitting of plasmon-hybridized modes can be employed for improving the Raman enhancement as well [145-149]. The mechanism behind it is that since the Raman peaks show a small wavelength-shift with respect to the incident illumination, by carefully designing the structural parameters of the substrate such that the resonant wavelengths of the bounding and anti-bounding plasmon-hybridized modes match the excitation wavelength plus another specific Raman peak, the Raman intensity of that peak can greatly be improved. For a clear demonstration, two of the examples are

shown in Fig.2.25 (for LSP-LSP hybridization) and in Fig.2.26 (for LSP-SPP hybridization), respectively.

Fig.2.25. Double-resonance SERS substrate with LSP-LSP interaction. (a) Schematic illustration of the structure. (b) Simulated extinction (solid line) and near-field intensity (dashed line) spectra. Near-field intensity spectrum shows intensity enhancement at a monitor point on the rod as a function of illumination wavelength. Near-field spectrum exhibits two pronounced resonances at $\lambda = 733$ and 798 nm. (c) Normalized field distribution, $|E|$, for illumination at $\lambda = 733$ nm and (d) for illumination at $\lambda = 798$ nm. (e) Carefully designed substrate with resonant wavelengths match the excitation wavelength and one of the Raman peak. (f) The improvement of Raman signal for the selected Raman peak. Ref. [145]

Fig.2.26. Double-resonance SERS substrate with LSP-SPP interaction. (a) Schematic and SEM image of the substrate. (b) Extinction cross-section and SERS spectrum of array with period of 780 nm. Dashed line illustrates the excitation wavelength. Ref. [147]

2.3 Radial Polarization

Radially polarized light is gaining growing attention in the past decade due to its advantages over the well known linearly and circularly polarized beams [150-162]. In particular, it was shown that when using a high NA objective lens, the RP beam can be focused to a much tighter spot compared with a linearly or circularly polarized beam. This is mainly attributed to the strong longitudinal electric field component generated at the focal plane [150, 153]. Owing to the unique properties of strong longitudinal component and small spot size, the RP beam is well suited for a variety of applications, including beam trapping [163], material processing [164], and optical memories.

2.3.1 Beam Profile

The beam profile of a RP beam is quite different from that of conventional polarized beams. Due to its singularity of polarization at the center, a RP beam has a donut

shape beam profile, with amplitude of electric field expressed as:

$$|\vec{E}_r| = \frac{r}{\omega_0} \exp[-(\frac{r}{\omega_0})^2] \quad (2.25)$$

where r is the radial coordinate and ω_0 represents the beam waist. Fig.2.27 presents the beam shape of a RP beam and the comparison with a linearly polarized Gaussian beam.

Fig.2.27. Beam shapes of a linearly polarized Gaussian beam (a) and a radially polarized beam (b), respectively. (c) The corresponding amplitude distributions. The white arrows indicate the direction of light polarizations.

2.3.2 Full p -polarized Beam

Because of its rotational symmetry of polarization, radially polarized light exhibits focusing characteristics quite different from linearly polarized light. Fig.2.28 shows the polarization characteristics of a linearly, radially, and azimuthally polarized light when focused on to a planar interface. The first one on the left shows the optical ray paths for a linearly polarized beam. In this case, the linearly polarized beam has an

electric field that is horizontal and oriented parallel to the y-axis. Following the ray paths through the lens we see that the electric field is perpendicular to the plane-of-incidence (*s*-polarized or TE mode with respect to the surface) in the y-axis/direction. Observing the electric field orientation in a similar manner along the x-axis/direction, the optical paths now cause the electric field to be in the plane-of-incidence (*p*-polarized or TM mode). Thus there is no optical symmetry and the surface at the focus is radiated by the varying degrees of either TM or TE type of polarization depending on the path the ray took through the lens.

Fig.2.28. Comparison of the focusing properties of a linearly, radially and azimuthally polarized beam.

However, due to the rotational symmetry of both the radially and azimuthally type of polarized beams, the beam is completely TM polarized (middle panel in Fig.2.28) in all directions with respect to the surface for the radially polarized beam and completely TE polarized (right panel in Fig.2.28) for the azimuthally polarized beam irrespective of the ray path taken through the lens. This characteristic of having complete TM polarization makes RP beams optimal for certain technological applications and an ideal candidate for a variety of experiments in surface physics.

2.3.3 SPPs Excitation Source

One of the most intriguing applications of radially polarized beams is to be employed as the excitation source of SPPs. As mentioned previously, surface plasmon excitation shows a strong dependence on the excitation polarization. In particular, under an ATR excitation configuration, only p polarization can excite an SPP. This leads to an interesting application of radially polarized beam in plasmonic focusing. More specifically, when a radially polarized beam is launched into a dielectric/metal plasmonic lens structures, the entire beam is p polarized with respect to the dielectric/metal interface (Fig.2.29), providing an efficient way to generate a highly focused surface plasmon through constructive interference and creating an strongly enhanced local field, with the longitudinal component dominants the total electric field (Fig.2.30). In contrast, if a highly focused linearly polarized beam is used to excite the surface plasmons, because of the destructive interference between counter-propagating surface plasmon waves, the focal field has a minimum at the geometric focus.

Fig.2.29. (a) Diagram of SPP excitation with highly focused RP beam. (b) Back Fourier plane image of the reflected beam, in which an axis-symmetric dark ring is observed that is due to the SPPs excitation. Ref. [40]

Fig.2.30. Calculated SP intensity distribution at silver/air interface with RP illumination. (a) Total intensity $|E|^2$; (b) longitudinal component $|E_z|^2$; (c) radial component $|E_r|^2$; (d) $|\nabla_{\perp} E_z|^2$ distribution, which is proportional to the NSOM signal detected by an apertured fiber probe. Ref. [40]

Chapter 3 Surface Plasmon Coupling Mode – Numerical Investigation

3.1 Chapter Introduction

Surface plasmon polaritons (SPPs) and localized surface plasmon (LSP) are two different types of surface plasmon modes. For an SPP mode, two conditions should be satisfied to excite an SPP: a p -polarized beam and the wave-vector matching condition, respectively. As mentioned before, there are several approaches to realize the wave-vector matching condition, such as ATR configuration, metallic grating configuration, near-field scatter, etc. For an LSP mode, a p -polarized beam is necessary as long as the excitation wavelength matches the resonant wavelength of specific metallic nanostructure. In previous research work by other groups, LSP was generally excited by free space propagating radiation, and LSP and SPPs were investigated separately for their specific applications. In this chapter, as a fundamental investigation, two types of excitation configurations are proposed and numerically studied, in which SPPs and LSP are excited simultaneously, resulting in a surface plasmon coupling mode (or called plasmon-hybrid-mode elsewhere).

The first one consists of a two-dimensional dielectric grating covered by a silver film with thickness of tens of nanometers. SPP excitation conditions are fulfilled through the metallic grating, while LSP is excited on the metallic bumps. Resonant wavelengths of SPPs and LSP can effectively be tuned via changing the structural period and the thickness of silver film. At specific wavelength, LSP and SPPs can co-exist, leading to a surface plasmon coupling mode.

For the second configuration, a RP light is tightly-focused onto a silver-air interface by a high NA objective lens. SPPs are thus excited under an ATR

configuration. The SPPs subsequently interact with a silver nanosphere on top of the silver film to excite the LSP.

In both plasmon-hybrid-mode systems, the three-dimensional FDTD method is employed to investigate their plasmonic response. In particular, electromagnetic enhancement was studied under the surface plasmon coupling mode. The studies in this chapter will provide important information for the following experiments as well as the application based on the plasmon-hybrid-mode.

3.2 Surface Plasmon Coupling Mode Induced by Periodic Metallic Structure

3.2.1 Structure

Fig.3.1 shows the proposed structure studied in this section. Briefly, a two-dimensional array of SiO_2 cuboids with fixed size of $50 \times 50 \times 100 \text{ nm}^3$ is patterned on the Si substrate, with a layer of 40-nm-thick silver film covered on the surface. An array of cubic bumps is formed as viewed from the top. Obviously, such a structure can easily be fabricated using the conventional silicon process technology.

Fig.3.1. Schematic of the proposed structure and its cross-sectional view along the dashed line.

To obtain the plasmonic response of such a structure, the DiffractMod package based on rigorous coupled wave analysis in the commercial software R-Soft is applied. For water (as the environment), Si, and SiO_2 , the refractive indices are set to be 1.3364, 3.99, and 1.5458, respectively. For silver, which is a lossy material possessing wavelength-dependent dielectric constant, the refractive index is obtained from Ref. [50] in the visible range (400 nm - 800 nm). We choose water as the environment in this work because SERS are widely used in the area of bio-sensing and bio-imaging, in which the sample is typically aqueous.

3.2.2 Simulation Results

Fig.3.2 shows the absorption characteristics based on various configurations. Using the semi-infinite water-silver flat interface model (dashed line), the reflectance at the interface for normal incidence is: $R = ((n_0 - n_r)^2 + k^2) / ((n_0 + n_r)^2 + k^2)$, where n_0 is the refractive index of environment, n_r the real part of the refractive index of silver and k the imaginary part which gives rise to the absorption in the silver. For a 40-nm-thick silver film sandwiched between semi-infinite water and Si (dotted line), the absorption will decrease slightly and transmission appears due to the finite thickness of the silver film. Further, if we produce the two-dimensional infinite dielectric grating and cover the whole surface conformally by a 40-nm-thick silver film, multiple absorption peaks will present in the absorption spectrum due to the excitation of LSP and SPP (solid line). The broad ones denoted as peaks 2 and 3 in Fig.3.2 correspond to the first-order LSP and high order LSP, respectively, whereas the sharp one denoted as peak 1 corresponds to the SPP.

At normal incidence, the SPPs can be excited in a periodic structure satisfying

$$2\pi / \Lambda = k_0 \sqrt{(\epsilon_m \cdot \epsilon_e) / (\epsilon_m + \epsilon_e)} \quad (3.1)$$

where Λ is the structural period, k_0 the wave-number of light in vacuum, and ϵ_m and ϵ_e the permittivity of metal and environment, respectively. The term on the right hand side of Eq. (3.1) represents the wave-number of the SPP propagating along the single interface. Equation (3.1) predicts an SPP excitation wavelength of 670 nm for $\Lambda = 475$ nm, which is slightly longer than the numerical simulation result (637 nm). The difference is due to the modification of Eq. (3.1) for periodic bump structures. Fig.3.3 gives the near-field distributions at different resonant conditions in the solid-line curve in Fig. 3.2, which is obtained by applying the FullWave Package based on the FDTD method in R-Soft. In the simulation, the grid size is set to be 2 nm and the

periodic boundary conditions are set for X and Y directions and the perfectly matched layer for Z direction.

Fig.3.2. Absorption spectra based on: semi-infinite water-silver flat interface configuration (dashed line), 40-nm-thick silver film sandwiched between water and Si configuration (dotted line), and dielectric grating covered by 40-nm-thick silver film configuration (solid line).

For the numerical investigation, two methods are generally employed to estimate the Raman enhancement: the maximum enhancement factor ($EF_{\max}$) and the averaged enhancement factor (EF_{ave}), respectively.

For an arbitrary localized plasmon mode, for example, the dipolar plasmon mode on a sphere-shaped NP as shown in Fig.2.9 (b), the electric field is typically spatially-variant over the surface of particle. As a result, the enhancement factor for molecules adsorbing at different sites are different. The maximum Raman enhancement factor is therefore defined as: $|E_{\max}|^4/|E_0|^4$, where $E_{\max}$ is the maximum electric field over the particle surface from the excitation of plasmon mode while E_0 the incident electric field. The logic behind such definition is based on the assumption that the concentration of molecules and NPs within their specific solutions during preparation is comparable such that there are, statistically, only few molecules adsorbing at the NP. One typical example is the single molecule SERS (SM-SERS), in which only single molecule is attached on the NP. Under this circumstance, the maximum enhancement factor is meaningful since the SM-SERS is realized generally

in the case that the molecule is attached at the point with maximum electric field.

The averaged enhancement factor, on the other hand, is defined as:

$$EF_{ave} = \frac{\iint |E|^4 ds}{A \times |E_0|^4} \quad (3.2)$$

in which E represents the spatially-dependent electric field and A the area of the NP surface, respectively. Such definition is meaningful in the case that the concentration of Raman molecules is much higher than that of NPs, and thus the molecules are attached over the entire surface of NP.

The value discrepancy between the EF_{max} and EF_{ave} strongly depends on the structure that supports the SP mode. For the structure over which the intensity of electric field is not diverse significantly, the discrepancy is not huge. In this case, EF_{ave} is preferred because it describes the enhancement feature more precisely. However, in the case that electric field varies significantly over the surface of structure, the discrepancy can be very large. Under this circumstance, the EF_{max} describes more precisely the enhancement feature of the studied structure. This is because of the nonlinearity of Raman enhancement factor (forth-order effect). The molecules at the area near maximum electric field contribute most of the Raman signals detected from the system.

In the simulation part of the thesis, as many previous publications did, we adopt the EF_{max} to evaluate the enhancement feature of our proposed structure and configuration, because of the large variations of electric field over the surface of the studied structures. As shown in Fig.3.3, for the case of LSP and SPP, the EF_{max} is 3×10^7 for the high order LSP, 4×10^8 for the first-order LSP and 3×10^8 for the SPP, respectively. Apart from the high Raman enhancement, the highly regular hotspots are obviously produced. In the following section, we take the structural period and film

thickness as variables and investigate their effects on the Raman enhancement.

Fig.3.3. $|E|^2$ distributions at the top of cubic bumps along XY plane at various resonant conditions, i.e., the incident wavelength of (a) 450 nm corresponding to the high order LSP, (b) 637 nm to the SPP, and (c) 670 nm to the first-order LSP. The colorbar scale is set as $\log_{10}(|E|^2)$.

Fig.3.4 (a) shows a set of absorption spectra for the period ranging from 402 nm to 546 nm with a step of 24 nm. The peak absorption wavelengths are denoted as λ_{max} and their plots against the structural period for both the LSP and SPP are shown in Fig.3.4 (b). The red-shift trend of the resonant wavelength for SPP for increasing period can be predicted from the excitation condition [Eq. (3.1)]. As the structural period increases, the right hand side value in Eq. (3.1) should be lower accordingly to satisfy the condition. Because of the dispersion property of silver refractive index in visible range, a red-shift of excitation wavelength is required from calculation. For the LSP, the resonant wavelength is affected by the distance between bumps. For large structural period, meaning bumps are separated far away; the plasmon resonant wavelength shift is resulting from the long-range interactions. From Fig.3.4 (b), LSP resonant wavelength shows slightly blue shift as bumps distance is decreased, which is consistent with previous work [165-166].

The Raman enhancement shows a great dependence on the structural period because of the interaction between the LSP and SPP. In Fig.3.4 (b), two peaks can be found from the $|E_{max}(\lambda)|$ plot for the resonant wavelength of SPP at each period (green curve with triangles). The red (with circles) and black (with squares) curves clearly

show that there is an intersection between them, implying the occurrence of LSP and SPP at the same wavelength. In this case, strong coupling between the SPP and LSP will occur, leading to a considerable enhancement of the local electric field responsible for the right peak in the $|E_{max}(\lambda)|$ curve. As for the left peak at smaller wavelength, the analysis of the $|E(\lambda)|$ distribution shows that it is from the coupling between the SPP and the second-order LSP.

Fig.3.4. (a) Absorption spectra for various periods from 426 nm to 546 nm with a 24 nm increment; (b) absorption peak positions versus different periods for LSP (circles) and SPP (squares), with corresponding maximum local $|E|$ at resonant wavelength of SPP (triangles). The silver film thickness is 40 nm, the bump height is 100 nm and the environment is water.

Next, we consider the influence of the silver film thickness to the resonant wavelength and Raman enhancement. For a fixed structural period, the resonant wavelength of SPP remains constant approximately. For the LSP, as film thickness is increased, three aspects should be considered which can contribute to the wavelength shift. Firstly, the distance between the bumps decreases for increasing film thickness. As stated above, this causes slightly blue shifts of the resonant wavelength. Secondly, since the nanoparticle (bump here) is not pure metal, as film thickness increases, the effective refractive index of nanoparticle will change accordingly, which induces slightly blue shifts as well. Thirdly, the size and shape of the nanoparticle play an important role in determining the plasmon resonant wavelength. As film thickness increases, the size of nanoparticle largens and the shape becomes more oblate, both effects contribute to a

red-shift of plasmon resonant wavelength [9]. The tradeoff between these three factors results in the LSP resonant wavelength shift in a whole.

Fig.3.5. Absorption peak positions at various silver film thicknesses for LSP (circles) and SPP (squares), as well as the corresponding maximum local $|E|$ at resonant wavelengths of SPP (triangles). The structural period is fixed at 475 nm, the bump height is 100 nm and the environment is water.

Fig.3.5 presents the influence of the silver film thickness to the absorption peak positions. The factor of size and shape of the bumps seems to be dominant in our case because of the red-shift of resonant wavelength with the film thickness. As suggested in Fig.3.5, the resonant wavelengths of the LSP and SPP meet at silver film thickness of ~ 25 nm, leading to a significantly high electric field enhancement due to strong coupling between them. As the film thickness increases, the two resonant wavelengths deviate from each other, implying weaker interaction between the two modes and thus the decreasing Raman enhancement.

Fig.3.6 shows the electric field distributions under LSP and SPP coupling conditions in Fig.3.4 (b) and Fig.3.5. The co-existence of the LSP and SPP is clearly seen in both figures. Moreover, the electric field enhancement is greatly maximized under such a circumstance. The $EF_{\max}$ for these two cases are 1×10^9 and 2×10^9 , respectively, with improvement of 1 order of magnitude compared to those in Fig.3.3 and 3 orders compared to those without any modes. Such high Raman enhancement

ensures this structure as a potential substrate and this plasmon-hybrid-mode system as a potential mechanism for high sensitive molecule detection.

Fig.3.6. $|E|^2$ distributions under surface plasmon coupling conditions in Fig.3.4 (b) (left), and in Fig.3.5 (right), respectively. The colorbar scale is set as $\log_{10}(|E|^2)$.

3.2.3 Summary

We have investigated the plasmonic properties of a potential SERS substrate, on which both the LSP and SPP can be excited. The FDTD simulation shows that the resonant wavelengths of LSP and SPP can effectively be tuned via changing the structural period and the silver film thickness. LSP and SPP can co-exist at specific wavelengths such that the coupling between them can contribute to a considerable boost of Raman enhancement. Raman enhancement of more than 10^9 is achieved in the proposed structure, under the plasmon-hybrid-mode. This work illustrates a structure with large area, regular hotspots, as well as extremely high Raman enhancement. It is a good candidate for SERS substrates as it can be easily fabricated using conventional silicon process technology.

3.3 Surface Plasmon Coupling Mode Induced by a Tightly-Focused Radially-Polarized Beam

3.3.1 Excitation Configuration

Fig.3.7 presents the second optical configuration for a plasmon-hybrid-mode system. A standard glass cover slip with refractive index of 1.5 is coated with a 45-nm-thick silver film. A silver nanosphere with 60-nm-diameter is placed on the silver surface. The gap between the objective lens and the cover slip is filled with an index matching immersion oil. RP beam focused by a high NA objective lens is used as the excitation light.

Fig.3.7. Proposed optical configuration through a high NA objective lens for plasmon-hybrid-mode, in which a RP light is tightly focused onto a silver-air interface to excite SPPs, which subsequently interact with a silver nanosphere on top of the silver film to excite LSP.

To excite the SPPs at the silver-air interface, on the one hand, the incident wavelength and angle should satisfy the following wave-vector matching condition:

$$k_{sp} = k_0 n \sin(\theta_{sp}) = k_0 \sqrt{\frac{\epsilon_m \cdot \epsilon_0}{\epsilon_m + \epsilon_0}} \quad (3.3)$$

where n is the refractive index of glass and matching oil, k_0 the wave-vector of light in

vacuum, and ϵ_m and ϵ_0 the permittivity of metal and air, respectively. The calculation according to Eq. (3.3) indicates that resonant angle for the configuration ranges from 42 to 45 degrees over the 500 nm to 1000 nm spectrum region. This can readily be realized as long as the maximum angle allowed by the objective lens exceeds the SP resonance (SPR) angles. Meanwhile, the small variation of SPR angles ensures that SPPs can be excited over the spectrum range we are interested. On the other hand, a p -polarized beam is required to excite an SPP. For a RP beam, the entire beam is p -polarized with respect to the silver-air interface. Thus, SPPs can be excited from all azimuthal directions when a RP beam is tightly-focused onto a dielectric-metal interface. The interference of the counter-propagating SPPs enables the formation of an evanescent Bessel-like standing wave at the focal region. As can be seen later in this work, such evanescent wave is well-suited as the excitation source of LSP on a nanosphere-film junction.

3.3.2 Generation of Radial Polarization Numerically

Dissimilar with the conventional linear or circular polarization, radial polarization is spatially-variant, and thus requires a tactical way to generate it, both in simulation and experiment. In this thesis, a radial polarization derived from circular polarization is employed numerically, which is based on the FullWave package within the commercial software R-Soft.

Equation (3.4) and (3.5) shows the mathematical expression of a right-handed and a left-handed circularly polarized beam, respectively. RP light is indirectly achieved by the superposition of a right-handed circularly-polarized beam and a left-handed circularly-polarized beam with a 2φ phase difference, where φ is the azimuthal angle (Fig.3.8), as illustrated with Eq. (3.6).

$$E_{RC} = \vec{e}_x - j\vec{e}_y = (\cos\phi\vec{e}_r - \sin\phi\vec{e}_\phi) - j(\sin\phi\vec{e}_r + \cos\phi\vec{e}_\phi) = e^{-j\phi}(\vec{e}_r - j\vec{e}_\phi) \quad (3.4)$$

$$E_{LC} = \vec{e}_x + j\vec{e}_y = (\cos\phi\vec{e}_r - \sin\phi\vec{e}_\phi) + j(\sin\phi\vec{e}_r + \cos\phi\vec{e}_\phi) = e^{j\phi}(\vec{e}_r + j\vec{e}_\phi) \quad (3.5)$$

$$E_R = \frac{1}{2}(e^{j\phi}E_{RC} + e^{-j\phi}E_{LC}) = \frac{1}{2}e^{j\phi}[e^{-j\phi}(\vec{e}_r - j\vec{e}_\phi)] + \frac{1}{2}e^{-j\phi}[e^{j\phi}(\vec{e}_r + j\vec{e}_\phi)] = \vec{e}_r \quad (3.6)$$

Fig.3.8. Phases imposed onto a right-handed (a) and a left-handed circularly polarized light (b), respectively, to achieve a RP beam.

Fig.3.9. Input (a) and output (b) amplitude distributions of a RP light.

The amplitude of electric field of a RP light is set as:

$$|\vec{E}_r| = \frac{r}{\omega_0} \exp[-(\frac{r}{\omega_0})^2] \quad (3.7)$$

where r is the radial coordinate and ω_0 represents the beam waist. Such amplitude distribution of electric field possesses a donut-shape profile and is consistent with the real beam obtained experimentally. Fig.3.9 (a) gives the two-dimensional amplitude distribution as the input for the simulation according to Eq. (3.7). The output beam profile can be found in Fig.3.9 (b), which agrees well with the one we designed.

3.3.3 Realization of Tight Focus Numerically

The tight focus of a RP beam is realized by setting an initial equivalent phase function of lens in the source file, instead of using the bulky objective lens to save the computational memory and simulation time. The phase function is expressed as $\exp(-ikr^2/2f)$, where f represents the focal length. Combined with the amplitude and phases imposed onto the circularly polarized lights, the final source file for a tightly-focused RP beam is as following:

$$\bar{E}_{R_focus} = \frac{1}{2} \frac{r}{\omega_0} \exp[-(\frac{r}{\omega_0})^2] \exp(-ikr^2 / f) (e^{j\phi} \bar{E}_{RC} + e^{-j\phi} \bar{E}_{LC}) \quad (3.8)$$

In the simulation, beam waist ω_0 is set to be 6.5 μm and focal length f in the phase function is set to be 7 μm . Such value combination of ω_0 and f makes sure that the amplitude peak of the generated RP light lies around the SPR angle, which optimizes the excitation efficiency. Fig.3.10 shows a snapshot of the E_z component in the XZ plane during the simulation. The tight focus of a RP beam can clearly be seen, with the focal point marked by the circle with yellow color (number 1). The 45-nm-thick silver film is located 2.5 μm below the focal plane. This treatment is to separate the excited SPPs from the transmitted focused beam and hence reduce the influence from the transmitted light. The excitation of SPPs can also clearly be seen just above the silver film, which is indicated by the arrows with orange color (number 2). An operation time of 20 (expressed in the unit of cT) is employed to make sure the convergence of the simulation, as illustrated by the orange circle (number 3).

Fig.3.10. Illustration of a tightly-focused RP light realized by setting an initial equivalent phase function of lens in the source file; 1: the focal point of the system, which is determined by the phase function of lens; 2: indication of the excitation of SPPs from all directions; 3: convergence verification of the simulation to ensure the accuracy.

3.3.4 Simulation Results

In the following numerical simulation, refractive indices of glass and matching oil are set to be 1.5, and that of silver is obtained from Ref. [50]. The grid size within the silver film and silver nanosphere is set to be 2 nm to ensure the simulation accuracy, and the perfectly-matched layer boundary conditions are set for X, Y and Z directions.

Fig.3.11 presents the longitudinal field (E_z) distribution around the metal film under a tightly-focused RP beam, in the absence of a nanosphere on the metal film. The transversal component (E_r) is not shown here because its intensity is much smaller than that of the E_z component ($\sim 0.1|E_z|^2$) and hence plays a tiny role. An interference pattern can clearly be seen in Fig.3.11, with a sharply-confined spot

located at the center (SP-VP). This is due to the constructive interference of SPPs' longitudinal component under symmetrical geometry and polarization conditions and hence an evanescent Bessel-like standing wave is formed at the focal region. To verify the result obtained with our FDTD model, we also calculate the E_z field using the well-established Richard-Wolf vectorial diffraction theory.

Fig.3.11. $|E_z|$ distribution at XZ plane calculated by 3D-FDTD (contour map) and by Richard-Wolf diffraction theory (solid curve), for comparison. The results accord well with each other.

According to ref. [100], the E_z component of SPPs under a tightly-focused RP beam can be calculated as:

$$E_z(r, \varphi, z) = i2A \int_0^\alpha \cos^{1/2}(\theta) P(\theta) t_p(\theta) \sin^2(\theta) \times J_0(k_1 r \sin \theta) \exp[iz(k_2^2 - k_1^2 \sin^2 \theta)^{1/2}] d\theta \quad (3.9)$$

where α is the maximal angle allowed by the objective lens, θ the incident angle, $t_p(\theta)$ the transmission coefficient of a p -polarized beam at angle of θ , A a constant and $P(\theta)$ the pupil apodization function, respectively. The transmission coefficient is obtained using the transfer matrix method, with the result presented in Fig.3.12. The sharp peak at 44.2° corresponds to the resonant angle of SPPs, which is in line with the SPR angle predicted by the wave-vector matching condition in Eq. (3.3). By using the

Richard-Wolf method, the E_z field distribution along x direction at $z = 0$ was obtained and illustrated with the solid line in Fig.3.11. As can be seen, the positions of interference fringes agree well with that obtained with the FDTD model and hence verifying the validity of our 3D-FDTD model.

Fig.3.12. Transmission of a 45-nm-thick silver film sandwiched by semi-infinite air ($n=1$) and glass ($n=1.515$), obtained with the transfer matrix method.

Next, a silver nanosphere with 60-nm-diameter is placed at the center of SPP standing-wave just above the silver film, to investigate the nanosphere-SPP interaction. Fig.3.13 (a) presents a contour map of electric energy density around the nanosphere at a 532nm incident wavelength excitation. As can be seen, a vertically-oriented dipolar-like mode is excited by the longitudinal component of SPP standing-wave, with electric field at the nanosphere-film junction significantly concentrated and enhanced. To make sure the accuracy and reliability of the calculation, we extract the maximum electric field at the nanosphere-film gap by a first-order exponential-decay-fitting of the data near the interface along the red dashed line as indicated with the inset in Fig.3.13 (b), instead of simply using the maximum value obtained by the simulation. The fitting curve along with the original data can be found in Fig.3.13 (b), which shows an excellent agreement with each other. The derived fitting value $A+y_0$,

which represents the maximum intensity of electric field at the gap ($x=0$), will be used to characterize the enhanced electric field in the following work.

Fig.3.13. (a) Contour map of electric energy density around the nanosphere at a 532 nm incident wavelength excitation. (b) Exponential-decay-fitting of the electric energy density in the vicinity of the nanosphere-film junction along the dashed red line as illustrated with the inset.

Fig.3.14 presents the maximum electric field enhanced at the gap plotting against the incident wavelength from 380 nm to 560 nm (blue curve). A controlled excitation scheme, in which the 45-nm-thick silver film was replaced by a glass film with identical thickness, was introduced in this study for the purpose of comparison. The calculated result with the same method is shown in Fig.3.14 with the red curve. Under the controlled scheme, the replacement of the metal film with a glass film avoids the excitation of SPPs at the film surface. In other words, the LSP excitation for the controlled one is totally due to the focused RP beam, rather than the SPPs standing-wave, and hence no SPP & LSP coupling mode exists.

As can be seen in Fig.3.14, from the resonant wavelength point of view, the peak of enhanced electric field occurs at 410 nm in the case of 45-nm-glass film, compared to the 500 nm resonant wavelength in the presence of SPPs. The red-shift of resonant wavelength is believed due to the strong interaction between the SPP standing-wave on the silver film and the LSP excited on the nanosphere and is in line with the preceding work [84]. From the perspective of field enhancement, the optimized

enhanced electric field is 6.6×10^6 under resonant condition in the case of 45-nm-thick silver film, while that from the controlled one is 1.35×10^5 . The significant enhancement effect for the proposed configuration attributes to two factors: from the excitation of SPPs and from the LSP/SPPs coupling mode, respectively.

Fig.3.14. Enhanced electric fields at various incident wavelengths ranging from 380 nm to 560 nm for the proposed (blue line) and controlled configurations (red line), respectively.

As introduced in the part of literature review, in a SERS system, the power of Raman scattering radiation can be calculated by the following formula:

$$P_{RS}(\nu_s) \propto N\sigma_{SERS} \cdot \frac{|E_{loc}|^4}{|E_0|^4} \cdot |E_0|^2 \quad (3.10)$$

where N is the number of Stokes-active scatters within the hotspot, σ_{SERS} the scattering cross-section, and E_{loc} and E_0 the amplitudes of the enhanced and incident electric field, respectively. In this work, SPPs are employed as the excitation source and hence Eq. (3.10) becomes:

$$P_{RS}(\nu_s) \propto N\sigma_{SERS} \cdot \frac{|E_{loc}|^4}{|E_{SPP}|^4} \cdot |E_{SPP}|^2 \quad (3.11)$$

As indicated in Fig.3.11, the field enhancement induced by SPPs is on the order of 10^3

$(|E_{SPP}|^2 \sim 35^2)$. Hence, that induced by LSP & SPPs coupling mode should be:

$$\frac{|E_{loc}|^2}{|E_{SPP}|^2} \approx \frac{6.6 \times 10^6}{10^3} = 6.6 \times 10^3 \quad (3.12)$$

and the total Raman enhancement is therefore on the order of 10^{10} . Similar calculation for the controlled configuration results in a total Raman enhancement on the order of 10^7 . Attention should also be paid on the field enhancement induced by LSP and SPPs coupling mode, which is on the order of 6.6×10^3 . This is greatly improved compared to the one shown in Fig.2.9 (b), in which a standalone silver nanosphere with exactly the same diameter is excited by a free-space propagating radiation and hence only LSP mode is present. The maximum field enhancement is 100 in that case and 225 for the controlled configuration in this study. It is 66 and 30 times improved, respectively, after introducing the SPPs as the excitation source of LSP.

Fig.3.15. Electric field distributions under resonant wavelengths for the cases of 45-nm-thick silver film (a) and 45-nm-thick glass film (b), respectively. The unit for x and y axis is μm and the scale bar is set as $\log_{10}(|E|^2)$.

Finally, the electric field distributions under resonant conditions are illustrated in Fig.3.15, for the case of 45-nm-thick silver and glass film, respectively. In Fig.3.15 (a), the presence of a metal film enables the excitation of SPPs. As a nanosphere placed within the SPP region, LSP will be excited on the nanosphere and interacts with the SPPs. The coupling between them results in a much higher field enhancement at the

nanosphere-film junction. In Fig.3.15 (b), it is clearly seen that a dipole mode is excited by the tightly-focused RP beam. The pure glass substrate only shows refractive index influence on the LSP mode.

3.3.5 Discussion

Film-driven and NP-driven plasmon hybridization

NP-film junction has been studied a lot in the past decade. One of the commons in the preceding work is that plasmon-hybridized gap mode at the NP-film junction is generally driven by the NP. More specifically, incident beam is focused onto a NP to excite an LSP on it. Meanwhile, the NP scatters the incident beam, generating the required wave-vector to excite the SPPs at the adjacent metal surface (Fig.3.16 (a)). The interaction between the LSP and SPPs leads to a plasmon-hybridized gap mode at the junction. Because of this, we term it the NP-driven plasmon-hybridized gap mode.

In our work, SPPs are firstly excited by a tightly-focused RP beam, forming an SP-VP at the metal surface. The SP-VP subsequently interacts with a NP above the metal surface to excite the LSP (Fig.3.16 (b)), leading to a plasmon-hybridized gap mode at the NP-film junction. As a result, the gap mode excited under this circumstance is termed as film-driven plasmon-hybridized gap mode.

Fig.3.16. Demonstration of the NP-driven (a) and film-driven (b) plasmon-hybridized gap mode.

The advantages of using our film-driven plasmon-hybridized gap mode for SERS are two folds, as discussed in the section of “motivations”. First of all, the excitation efficiency of SPPs is greatly improved by using the ATR configuration. In the case of NP-driven gap mode, the SPPs formed on the metal surface are induced by the NP, which diffracts the incident beam, generating the required wave-vector to match that of SPPs. Such an excitation approach is rather inefficient and hence limiting its Raman enhancement. Secondly, due to the vertical arrangement of an NP-film junction, a longitudinal field component is preferred to efficiently excite a gap mode at the junction. For an SP-VP excited by a tightly-focused RP beam, the portion of longitudinal field is 98% at 532 nm, 99% at 633 nm and more than 90% over the visible range. While in the case of NP-driven gap mode, a linearly polarized Gaussian beam is focused directly on to the NP-film junction. A longitudinal field component does exist under this kind of excitation approach. However, it is the subordinate field component and the power utility is therefore quite low (Fig.3.17). Although RP beam was also proposed as the excitation source for the NP-driven gap mode[84, 162], the portion of longitudinal component ($<80\%$) is still smaller than that of an SP-VP.

Fig.3.17. Transversal (left) and longitudinal (right) electric field distributions at the focal plane under a tightly-focused linearly polarized Gaussian beam. NA=0.98. The smaller the NA, the stronger (weaker) the transversal (longitudinal) field component.

3.3.6 Summary

We proposed and numerically investigated a potential plasmon-hybrid-mode system, in which a RP light is tightly-focused onto a silver-air interface to excite the SPPs. The SPPs subsequently interact with a silver nanosphere on top of the silver film to excite the LSP. In the simulation, RP beam is achieved by the superposition of a right-handed and a left-handed circularly polarized beam with 2ϕ phase difference. The FDTD simulation illustrates that the interaction between LSP and SPPs could result in a remarkable red-shift of resonant wavelength with respect to the nanosphere on a dielectric substrate, and a strong confinement of electric field at the nanosphere-film junction. Electromagnetic field enhancement induced by the film-driven plasmon-hybridized gap mode is on the order of 10^3 , presenting more than 30-fold improvement compared to that from standalone LSP mode. Raman enhancement of more than 10^{10} is achieved. It is 1000 times improved compared with the controlled configuration, which is frequently used in a conventional optical system.

Chapter 4 Surface Plasmon Coupling Mode for SERS

4.1 Chapter Introduction

In the previous chapter, we have numerically investigated two different types of plasmon-hybrid-mode configurations, in which SPPs are excited by a metallic grating structure and an ATR configuration, respectively. The electromagnetic enhancement was significantly improved under the surface plasmon coupling mode compared to that from the separate surface plasmon modes.

In this chapter, we will continue the work and investigate the performance of plasmon-hybrid-mode system experimentally. More specifically, the hybrid mode system induced by a tightly-focused RP beam will be introduced for surface-enhanced Raman spectroscopy. The reasons why we choose the second configuration for the experiment are three folds. Firstly, LSP is excited by an evanescent surface plasmon standing-wave, which is a novel idea. In the previous research work, LSP was generally excited by free space propagating radiations. Secondly, the preparation of structure is relatively easy. No complicated fabrication process is required and the only work is to immobilize silver nanospheres onto the silver film. Finally, using this configuration for SERS possesses many advantages, including easily formed, high predicted Raman enhancement and high reproducibility. These characteristics make it a potentially-robust SERS substrate.

The organization of this chapter is as following: firstly, the generation of a RP beam experimentally will be introduced; next, a sub-monolayer of silver nanospheres will be immobilized onto a 45-nm-thick silver film, and interact with SPPs excited by a tightly-focused RP beam. This experiment will present a qualitative view of the role

of SPPs playing on the total Raman enhancement. Finally, the concentration of silver nanosphere will be reduced such that surface-enhanced Raman scattering from single nanosphere can be studied. Under this circumstance, SPPs excited from all azimuthal directions will propagate toward to the center and interference with each other to form a surface plasmon virtual probe. We will then investigate the interaction of individual nanosphere with this virtual probe.

4.2 Generation of a RP Beam Experimentally

The experimentally generation of a RP light in this thesis is according to the method introduced in ref. [102], which was developed by a senior colleague in our group. The required optical components include: a linear polarizer (LP), a spiral phase element (SPE), an azimuthal-type analyzer (AA) and two half waveplates (HWs). An SPE is a transparent plate with refractive index n and thickness t that spirals up-ward (see Fig.4.1 (b)). The thickness of an SPE is carefully designed such that the phases imposed onto a beam after passing through it exactly compensates the build-in phase of the beam. An azimuthal-type analyzer is a specific kind of light polarizer with transmission axis along the azimuthal direction (Fig.4.1 (c)). i.e., only the E_ϕ component of a laser beam can pass through it while the E_r component will be absorbed. In our experiment, a commercially available “TSI 10901A Polarization Axis Finder” giving the azimuthal-type filter function was used.

The conversion from linear polarization into radial polarization is as following (Fig.4.1 (a)): a linearly polarized beam is firstly converted to a circularly polarized beam by a quarter waveplate (Eq. (4.1)). After passing through an azimuthal-type analyzer, the radial component is absorbed, with only the azimuthal component left

(Eq. (4.2)). A spiral phase element is then inserted to compensate for the geometric phase, resulting in a non-charge azimuthally polarized beam (Eq. (4.3)). Two half waveplates angled with 45 degrees between their optical axes are used finally to convert the azimuthal polarization into radial polarization.

Fig.4.1. Generation and verification of a RP beam experimentally. (a) Illustration of an optical configuration transferring a linearly polarized Gaussian beam into a RP beam. LP: linear polarizer, QW: quarter waveplate, AA: azimuthal-type analyzer, SPE: spiral phase element, HW; half waveplate. (b) Schematic view of an SPE and a real one. (c) Transmission axis of an azimuthal-type analyzer. (d) Verification of a RP beam by using a linear polarizer.

$$E_{LC} = \bar{e}_x + j\bar{e}_y = e^{j\phi}(\bar{e}_r + j\bar{e}_\phi) \quad (4.1)$$

$$\rightarrow j e^{j\phi} \bar{e}_\phi \quad (4.2)$$

$$\rightarrow j e^{j\phi} \bar{e}_\phi \bullet e^{-j\phi} = j \bar{e}_\phi \quad (4.3)$$

The experimentally-achieved RP light is shown in Fig.4.1 (d), which possesses a donut shape beam profile. This is due to the polarization singularity at the center of a

RP beam. A linear polarizer is employed to verify its polarization distribution. As a RP beam passes through a linear polarizer, the polarization along the transmission axis of the linear polarizer will transmit while that orthogonal to the axis will be absorbed, in between of these two directions, the polarized radiation is attenuated according to the law of Malus. Hence the observed profiles have two distinct lobes along a line parallel to the transmission axis of linear polarizer, as shown in Fig. 4.1 (c). In the following experiments, the generated RP beam will be used as the excitation source.

4.3 Nanosphere Sub-monolayer

4.3.1 Experimental Setup and Procedures

The schematic view of experimental setup is shown in Fig.4.2. RP beam as the excitation light is achieved using the method just mentioned before. An Olympus oil immersion objective lens (60 x, NA=1.49) is used to focus the collimated RP beam on to the sample, composing a 45-nm-thick silver film deposited onto a cleaned cover glass by electron beam evaporation, with 60-nm-diameter silver nanospheres assembled on it. Raman signals originating from rhodamine 6G (R6G) molecules sandwiched between the silver nanospheres and silver film are collected by an Ocean Optics TEC cooling Raman spectrometer (TE 65000). A CCD camera is used at the transmission direction to capture the Raman images of nanospheres, or at the back Fourier plane to get the reflected laser beam.

Fig.4.2. Optical schematic of a plasmon-hybrid-mode based surface-enhanced Raman spectroscopy. A 532nm RP beam is used as the illumination.

Silver nanospheres with diameter ~ 60 nm were purchased from nanoComposix. The self assembly of silver nanospheres on the thin film surface was carried out by the

following procedures: silver film with thickness of 45nm was first formed by electron beam deposition on a cleaned glass coverslip. The coated substrate was then immersed for around 30mins in a 10^{-7} M R6G solution to form a self-assembled monolayer (SAM) of R6G molecules. The sample was subsequently rinsed with DI water to remove excess molecules on the surface. Finally, a droplet of Ag colloids ($100\text{ }\mu\text{l}$, $\sim 10^{11}$ nanospheres / ml,) was applied onto the SAM/Ag plane and allowed to evaporate naturally, followed by water-rinsing and air-drying at ambient temperature. Dark-field image of the assembly of silver nanospheres on the silver film surface is shown in Fig.4.3. A sub-monolayer of silver nanospheres can clearly be seen, with most of the particles be isolated and uniformly distributed on the surface.

Fig.4.3. Dark-field image of immobilized silver nanospheres on a 45-nm-thick silver film.

4.3.2 Experimental Results and Discussion

Based on the Kretschmann configuration, SPPs can be excited to satisfy:

$$k_0 n_{oil} \sin \theta_{sp} = k_{spp} = k_0 \sqrt{\epsilon_m \cdot \epsilon_0 / (\epsilon_m + \epsilon_0)} \quad (4.4)$$

where k_0 is the wave-vector of light in vacuum, θ_{sp} the SPR angle, and ϵ_m and ϵ_0 the permittivity of metal and environment (air in our work), respectively. The predicted

resonant angle for 532 nm illumination according to Eq. (4.4) ($\theta_{sp} = 44.2^\circ$) is smaller than the maximum angle allowed by the oil immersion objective lens with 1.49 NA ($\alpha_{max} = 79^\circ$), which assures the excitation of SPPs in our work. Fig.4.4 presents the Raman images of nanospheres immobilized on the silver film captured by the CCD camera at various sample-objective lens distances (a-i), as well as the illustrations of three types of excitation schemes (j-l).

When the sample-objective lens distance is beyond the focal length (post-focal plane scheme), as shown in Fig.4.4 (j), RP beam will be focused on to the silver-air interface divergently, and so are the transversal components of wave-vector at silver film surface, which determine the propagating direction of SPPs. Since the entire beam for a RP beam is *p*-polarized, SPPs will be excited from all directions, forming an excitation circle, and propagate from the excitation circle divergently under the post-focal plane circumstance, as shown in Fig.4.4 (a), with the dashed yellow circle representing the excitation circle of SPPs. It can clearly be seen that silver nanospheres within the propagation region of SPPs are effectively activated, while those out of the SPP region cannot be detected due to their relatively low Raman enhancement. This demonstrates that the interaction of SPPs with nanospheres on top of the silver film can effectively excite the LSP on each nanosphere, leading to an impressive Raman enhancement. Attention should also be paid on the activated band with limited length, in which the intensity of Raman signals from activated nanospheres is gradually attenuated along positive radial direction. This is mainly due to the limited propagation length of SPPs and the exponentially-decaying of electric field as it propagates along radial direction.

Fig.4.4. Raman images of silver nanospheres immobilized on a silver film surface at various sample-objective lens distances obtained by a CCD camera (a-i), and the corresponding types of excitation schemes. (j): post-focal plane, (k): on-focal plane and (l): pro-focal plane schemes.

As the sample-objective lens distance decreases, the SPPs excitation circle becomes smaller since its size is proportional to the sample-focal plane displacement. However, as long as their distance goes beyond the focal length, SPPs will propagate from the excitation circle divergently, as demonstrated in Fig.4.4 from (a) to (d). Turning point occurs when the sample locates exactly at the focal plane of objective lens (on-focal plane scheme), as shown in Fig.4.4 (k). Under this circumstance, RP beam will be focused onto the silver-air interface into a minimum spot, within which SPPs are excited and propagate around. Likewise, silver nanospheres within the propagation region of SPPs will be activated and detected by the CCD camera (Fig.4.4 (e)). Further decrease of sample-objective lens distance results in the incident beam be focused onto the silver-air interface convergently (pro-focal plane scheme). Hence, SPPs excited under this circumstance will propagate convergently into the center from

the excitation circle, whose size becomes larger as sample-objective lens distance further decreases, as illustrated in Fig.4.4 (f-i). To sum up, SPPs excited by the RP beam plays a significant role on the Raman enhancement of the system. Meanwhile, our experimental result shown in Fig.4.4 indicates that a self assembly monolayer of metal NPs (adsorbed by detecting molecules) on a smooth metal film surface can serve as a far field characterization of the excitation and propagation of SPPs, instead of the near-field techniques such as NSOM.

Fig.4.5. Raman images of silver nanospheres obtained by a CCD camera when the sample locates exactly at the focal plane of the objective lens, with (a) and without (b) the SPPs excitation. (c) Demonstration of on-focal plane excitation scheme, under which incident beam is focused onto the interface into a minimum spot. (d) Reflected laser beam obtained at the back Fourier plane. The sharp dark ring represents a reflectivity dip thus indicating the SPPs excitation at the silver-air interface.

To further investigate the SPPs' contribution on Raman enhancement and conduct a direct comparison with the conventional NP-induced SPP&LSP coupling system, we focus our study on the on-focal plane excitation configuration, as illustrated in Fig.4.5 (c). Also shown in Fig.4.5 (d) is the reflected laser beam obtained by the CCD camera at the back Fourier plane. A sharp dark ring can clearly be seen at the reflected beam, representing that incident beam at this angle is efficiently coupled to the SPPs. Thus, as we control the RP beam size by an adjustable iris aperture just beneath the

objective lens, and monitor the reflected beam at back Fourier plane, we can conveniently switch “on” and “off” the excitation of SPPs.

Fig.4.5 (a) presents the Raman image of silver nanospheres with SPPs excitation under the on-focal plane configuration. It is captured when the dark ring just comes out at the reflected beam as we increase the incident beam size. While in Fig.4.5 (b), which gives the Raman image of silver nanospheres without the SPPs excitation, is captured when the dark ring just disappears as we decrease the beam size. The comparison between Fig.4.5 (a) and (b) clearly indicates that the existence of SPPs does lead to a significant improvement of Raman enhancement. Moreover, attention should be paid on the circumstance when the dark ring just disappears and hence no SPP is excited on the silver-air interface base on the TIRF configuration. In this case, incident beam is focused and interacts with the nanospheres on the film to excite the LSP, which is exactly the conventional NP-induced SPP&LSP co-enhanced system. In other words, our experiment demonstrates that the introduction of propagating surface plasmon into the conventional NP-film junction system brings on a significant improvement on Raman enhancement

Subsequently, Raman spectra of R6G molecules adsorbed on silver nanospheres at various RP beam sizes are obtained, as shown in Fig.4.6. The sample with much less nanosphere density is prepared by reducing the silver colloid concentration and immersion time. As can be seen from Fig.4.6, when RP beam size is too small to cover the SPR angle, SPPs cannot be excited and hence no Raman signals can be detected due to its limited Raman enhancement, as indicated by the black curve (a), which is obtained when the beam size is controlled such that the dark ring at the back Fourier plane just disappears. As incident beam size increases (red (b) and green (c) curves), the dark ring comes out, meaning that SPPs are excited and interact with the

nanospheres on the film surface. Raman enhancements under these circumstances are significantly improved and remarkable SERS signal can be detected. Further increase of beam size will not contribute to the Raman enhancement since the marginal beam cannot couple to the SPPS due to their larger incident angle than the SPR angle. Optimized condition occurs when the dark ring just totally comes out, with Raman spectrum shown with the green curve (c). A 10 folds magnification of the black curve indicates that Raman intensity for the smaller beam size is still 2 times weaker than that of the green curve, which means the introduction of propagating surface plasmon excitation based on a TIRF configuration induces an improvement of 20 times of the Raman enhancement.

Fig.4.6. Raman spectra of R6G molecules at various RP beam sizes, with a-f representing the increase of beam size. Laser power incident onto the sample is approximately 500 μ W. Integration time of 1 second was used to collect the Raman signals.

4.3.3 Summary

In summary, we qualitatively-demonstrated that Raman enhancement of conventional NP-film junctions can significantly be improved by introducing the propagating surface plasmon excitation based on the TIRF configuration. Experimental results illustrate that silver nanospheres within the propagation region of SPPs are effectively activated and detected from Raman images by a CCD camera due to their impressive Raman enhancement. This intriguing phenomenon indicates that a self assembly monolayer of metal NPs adsorbed with detecting molecules on a smooth metal film can serve as a far field characterization of the excitation and propagation of SPPs, instead of the near-field techniques such as NSOM. Raman enhancement presents 20-folds improvement compared with the NP-induced SPP/LSP co-enhanced Raman spectroscopy. The impressive Raman enhancement along with its high reproducibility of NP-film junction makes this configuration an attractive candidature for the SPP-assisted gap-mode Raman spectroscopy.

4.4 Single Nanosphere

In the previous experiment, a sub-monolayer of silver nanospheres was immobilized on a silver film as the substrate for surface-enhanced Raman spectroscopy. Under this circumstance, SPPs excited by a tightly-focused RP beam interact with nanospheres very frequently and hence the interference of them is not notable.

In the following experiment, the density of nanospheres on the silver film is significantly reduced so that only single nanosphere is within the propagation region of SPPs. (Dark field image is shown in Fig.4.7). In this case, SPPs will propagate freely along the metal surface and interfere with each other, forming an evanescent standing-wave. An individual nanosphere will be moved into the SPPs region and the SERS from single nanosphere-film junction will be investigated. 4-mba molecule will be used in this section, due to its high power tolerance and pure Raman signals without fluorescence, instead of the R6G molecules we used before.

Fig.4.7. Dark-field image of silver nanospheres with much lower density immobilized on a silver surface. The yellow scale bar represents 5 μm .

4.4.1 Surface Plasmon Virtual Probe

Numerically, electric field in the vicinity of the focus can be calculated with the Richards-Wolf vectorial diffraction theory, with the results shown in Fig.4.8. Fig.4.8

(a) exhibits the longitudinal field distribution under an RP beam illumination. The transversal component is not shown here because of its much smaller intensity compared to the longitudinal field, hence playing a tiny role in our work. As predicted, because of the axially symmetric polarization of a PR light, SPPs excited from all azimuthal directions interfere and form a Bessel-like standing-wave pattern, which has a maximum intensity confined to a small region on the metal surface. It is therefore termed as a surface plasmon virtual probe (SP-VP).

Fig.4.8. Longitudinal electric field distribution in the vicinity of the focus for a radially-polarized (a) and a linearly-polarized Gaussian beam (b), respectively. (c) Electric field distribution around the silver nanosphere as it locates at the center of SP-VP.

Also shown in Fig.4.8 (b) is the longitudinal field distribution produced from a linearly polarized Gaussian beam with identical power, for the purpose of comparison. As can be seen, the maximum intensity shows approximately 4-folds improvement in the case of RP beam. The advantages of using a RP beam over a linearly polarized beam are obvious: on the one hand, the excitation of SPPs performs an angular filter function for the transmitted field. In other words, only the incident angles satisfying the wave-vector matching condition can excite the SPPs. For a RP beam, the donut shape beam profile shifts the power from center to higher inclination angle near the

SPR angle under a tight-focus configuration. This greatly improves the excitation efficiency of SPPs compared to a Gaussian beam, for which most of the laser power concentrated at the center. On the other hand, the Bessel-like standing-wave formed under a RP beam has only one peak at the center (Fig.4.8 (a)), while there are two longitudinal field lobes around the center in the case of a linearly polarized beam (Fig.4.8 (b)), which halves the efficiency since only one of the two lobes will be used.

Fig.4.8 (c) presents the electric field distribution at the same region after a silver nanosphere with 60-nm-diameter is placed at the center of the SP-VP, which is calculated using the three-dimensional FDTD method with 2nm grid size. The result clearly indicates that: firstly, the Bessel-like standing-wave pattern keeps well as that in Fig.4.8 (a) in the presence of a nanosphere, meaning that the nanosphere shows little influence on the excitation and propagation of SPPs, and hence the formation of SP-VP. This is crucial as we intent to harness the virtual probe for single-NP-SERS. Secondly, electric field is significantly concentrated at the nanosphere-film junction. The maximum electric field is more than 10^6 , which is much superior compared to that from a standalone nanosphere without the metal film. The high electromagnetic enhancement attributes to two factors: the formation of an SP-VP, which provides 10^2 - 10^3 enhancements, and the excitation of LSP/SPP coupling mode on the nanosphere-film junction, which is responsible for approximately 10^4 enhancements, as discussed in chapter 3.

4.4.2 Experimental Results

Fig.4.9. SERS spectra of 4-mba molecules from single nanosphere-film junction located at the center of SP-VP (Black) and without the excitation of SPPs (Red), respectively. The inset presents the simultaneously captured Raman image of an individual silver nanosphere, with SPPs excitation.

Experimentally, because of the small region of SP-VP, a piezo-scanning-stage (Physikinstrumente, P545, Nano XYZ stage) with 1-nm-resolution is used to search and position the individual nanosphere. A CCD camera placed at the image plane in the transmission direction is used to capture the Raman image of the nanosphere, monitoring the intensity as we move the scanning stage. An adjustable iris aperture placed just beneath the objective lens is used to manipulate the incident beam size. The black curve in Fig.4.9 shows the SERS spectrum of 4-mba molecules collected from a single nanosphere-film junction, with the inset showing the Raman image captured by the CCD camera at the position of maximum Raman intensity. Under the full beam illumination, nanosphere can clearly be seen, along with the Raman spectrum with good signal to noise ratio obtained by the spectrometer (black curve). As the beam size reduced such that the dark ring at the back Fourier plane just disappears (Fig.4.5 (d)), meaning that no SPP is excited in this case, nanosphere cannot be detected with the same exposure time as well as the Raman signals from the

spectrometer (red curve). This clearly illustrates that it is the SPPs, rather than the transmitted light, that contribute to the excitation of Raman signals.

Fig.4.10. Normalized Raman intensity from individual NP-film junction as it was scanned over the SP-VP region, plotting against the transversal axis (Line with stars), and the electric field distribution of an SP-VP obtained numerically by Richard-Wolf vectorial diffraction method (Line only).

While the above experiment indicates only the contribution of SPPs on total Raman enhancement, to confirm the formation of an SP-VP on the metal surface, a one-dimensional scanning of the stage is carried out, in which Raman spectra at various locations in the vicinity of focus are obtained with 20-nm-step size. Raman intensities at the peak of 1588.85 cm^{-1} are then refined and plotting against the lateral positions, with the scanning result presented in Fig.4.10 (line with stars). Also shown with the red line is the field distribution of SP-VP obtained numerically with the Richard-Wolf method, for the purpose of comparison. As can be seen from Fig.4.10, the experimental scanning result agrees well with the simulated longitudinal field distribution, both the pitch and the full-width at half-maximum (FWHM) of the central maxima. This provides strong evidence that SP-VP is does formed and responsible for the Raman enhancement in the experiment. Meanwhile, the scanning result also verifies the z-component sensitivity of a nanosphere-film junction. This is

reasonable because of its vertical arrangement, thus requiring a longitudinal electric field to efficiently concentrate the electrons near the nanosphere-film gap.

4.4.3 Evaluation of Raman Enhancement

Experimentally, the Raman enhancement factor can be evaluated with the following formula [167]:

$$EF = \frac{I_{SERS} / N_{Surf}}{I_{RS} / N_{Vol}} \quad (4.5)$$

where I_{SERS} is the intensity of SERS collected in the presence of a single nanosphere on the metal film and under a RP light excitation (with both SPPs and LSP), while I_{RS} the intensity of Raman scattering (non-SERS) collected in the absence of nanosphere and under an azimuthally polarized beam excitation to eliminate the contribution from propagating surface plasmon (without both SPPs and LSP). N_{Vol} is thus the average number of molecules in the scattering volume for the Raman measurement, while N_{Surf} the average number of adsorbed molecules in the scattering volume for SERS experiment. Assuming a uniform distribution of molecules over the silver film surface, the ratio of N_{Surf}/N_{Vol} is indeed the ratio of excitation area of SERS (A_{SERS}) and normal Raman scattering (A_{RS}). In our experiment, A_{SERS} is estimated to be $\pi (d/2)^2$, while A_{RS} to be $\pi (D/2)^2$, where $d/2$ ($\sim 5\text{nm}$) is the 1/10 decaying length of the electric field within the nanosphere-film junction and D ($\sim \lambda/2 = 266\text{nm}$) the spot size of a tightly -focused azimuthally-polarized light at the film surface, respectively.

Using a 1 second integration time and 10 mw laser power (the effective power illuminating onto the sample is much smaller than this value), I_{SERS} is measured to be 50 counts (Raman peak with maximum intensity, i.e., the 1588.85 cm^{-1} peak as shown in Fig.4.9). However, the value of I_{RS} cannot be obtained because of the limited

performance of our spectrometer. Even the integration time was increased to be 10min (the maximum period allowed by the spectrometer), we still cannot get the Raman spectrum in the absence of nanosphere under azimuthally polarized beam. Assuming a 4-counts-intensity of the noise, the enhancement factor is therefore estimated to be on the order of 10^6 , at the least.

While the 10^6 -Raman-enhancement evaluated above is obviously underestimated due to the instrumental limitation, an alternative method is employed to reevaluate it, which is based on the experimental work in Ref. [30]. In their work, a self-assembled monolayer (SAM) of 4-mba molecules was first adsorbed onto a thin gold film. Gold NPs with various shapes (including nanosphere) were then immobilized onto the SAM/Au film to form a sandwiched structure. As a result, their substrate is exactly the same with ours except that gold instead of silver was used. The novelty of our work is that SP-VP excited by a tightly-focused RP light are used as the excitation source for LSP, instead of a free-space radiation (e.g., a focused linearly polarized beam as did in Ref. [30]).

In our previous work, it is demonstrated that the Raman enhancement presents 20-folds improvement by introducing the SPPs; while in the absence of SPPs, it is just the case presented in Ref. [30]. Raman enhancement in their work (Au/nanosphere) was estimated on the order of 10^7 . Hence, that for our configuration should be at least 2×10^8 (20×10^7) since (1) silver presents a higher electromagnetic enhancement than gold and (2) a RP light shows great advantages compared to a linearly polarized light, as illustrated in Fig.4.8.

4.4.4 Summary

In summary, surface-enhanced Raman scattering from single nanosphere-film junction excited by a tightly-focused RP beam was achieved experimentally. Raman enhancement is estimated more than 2×10^8 by comparing with the conventional NP-induced SPPs/LSP co-enhanced Raman spectroscopy. SP-VP is confirmed to be formed at the metal film surface and responsible for the high Raman enhancement. It can be as an optimized source for a gap-mode surface-enhanced Raman spectroscopy, due to the SP nature of the virtual probe, which leads to a strong coupling between the LSP and SPPs, and the longitudinal property of electric field, which results in the electrons significantly concentrated within the gap between silver nanosphere and film.

Chapter 5 Directional Emission of SERS

5.1 Chapter Introduction

In the previous SERS experiments, we were from the excitation point of view, investigating the SPPs' contribution on total Raman enhancement in a plasmon-hybrid-mode directed Raman spectroscopy. In this chapter, we will from the perspective of signal collection, study the influence of SPPs on it.

When SERS signals emitted from molecules attached at a nanosphere-film junction, an intriguing phenomenon is that Raman scattering is able to couple back to SPPs in the presence of a thin metal film (SPPs are excited via a scatter in this case, as mentioned in the part of literature review), and eventually directionally-radiates into the substrate side with high refractive index at SPR angle. This phenomenon is called surface plasmon coupled-emission (SPCE).

SPCE was firstly discovered by J. R. Lakowicz for the fluorescence detection [44-46]. Since then, the SPCE has been extensively studied, and is emerged as a new and powerful tool for high sensitivity fluorescence detection [168-172]. Collection efficiency of $\sim 50\%$ was achieved and, meanwhile, the unwanted background signal can significantly be reduced, thus improving the signal-to-noise ratio [169]. This is of great significance for high contrast optical imaging. In addition, the SPCE spectrum at the back Fourier plane contains abundant optical parameter information of the excited SPPs. In particular, the wave-numbers and propagation length of the excited SPPs can rapidly be extracted from the SPCE ring without any mechanical movement or angle scanning. It can be used as a convenient SPP characterization tool.

Recently, the SPCE from quantum dots and carbon nanotubes were also investigated [173-175]. Meanwhile, recent experimental work demonstrated that the

emitted Raman radiation is also able to couple to SPs with periodic metallic structure [176] or nanoantennas [177-178], forming a “beam shaped” Raman scattering”. Such “shaped” emission of Raman scattering is able to improve its collection efficiency. In the following work, we investigate the coupled-emission of SERS from a single nanosphere-film junction based on the ATR configuration. We first explore the mechanism behind the phenomena of SPCE, following by the studies of emission patterns of SERS at the back Fourier plane and back image plane. We finally investigate the collection efficiency improvement of SERS induced by SPCE.

5.2 Mechanism

Fig.5.1. (a) Schematic view of the experimental setup investigating the SPCE of SERS from single nanosphere-film junction. (b) SERS spectrum of 4-mba molecules adsorbed at the junction.

Fig.5.1 (a) shows the schematic of experimental setup for the SPCE investigation from single-nanosphere-SERS. A collimated laser beam with 532-nm-wavelength is focused by a high NA oil-immersion objective lens (NA = 1.49) on to the sample, which composes of a single nanosphere (60-nm-diameter) immobilized on a thin silver film (measured thickness ~ 55 nm), with 4-mba molecules sandwiched between them. Raman scattering from 4-mba molecules (as shown in Fig. 5.1 (b)) couple back

to SPPs at the metal surface and directionally-radiates into the substrate side with high refractive index (the glass and oil side). The same objective lens is used to collect the SPCE of SERS while a second objective lens (NA=1.42 but without the use of oil) is used to collect the Raman scattering radiating directly at the transmission direction.

Fig.5.2. Three-layer system for the Fresnel coefficients calculation

For a three layer system composing of a 55-nm-thick silver film (n_2) sandwiched by semi-infinite air ($n_1=1$) and glass ($n_3=1.515$), as shown in Fig.5.2, the transmission coefficient for a p -polarized beam can be calculated as following:

$$\tau_p = \frac{t_p^{12} t_p^{23} \exp(ik_2 t \cos \theta_2)}{1 + r_p^{12} r_p^{23} \exp(2ik_2 t \cos \theta_2)} \quad (5.1)$$

where t_p^{12} and t_p^{23} are the Fresnel transmission coefficients for each of the respective two-layer interfaces and r_p^{12} and r_p^{23} the corresponding reflection coefficients. The two-layer coefficients can be calculated with the following equations:

$$t_p^{ij} = \frac{2n_{ij} \cos \theta_i}{n_{ij}^2 \cos \theta_i + \sqrt{n^2 - \sin^2 \theta_i}} \quad (5.2)$$

$$r_p^{ij} = \frac{n_{ij}^2 \cos \theta_i - \sqrt{n^2 - \sin^2 \theta_i}}{n_{ij}^2 \cos \theta_i + \sqrt{n^2 - \sin^2 \theta_i}} \quad (5.3)$$

$$n_{ij} \equiv \frac{n_j}{n_i}, \quad i=1,2; \quad j=2,3 \quad (5.4)$$

where θ_i ($i=1,2$) are the incident angles at each interface and are linked by the Snell's Law, k_i the wave-vectors at each layer and t the thickness of metal film, respectively.

Fig.5.3. Transmission features of the three-layer system under different circumstances. (a) Calculated transmittance plots against the incident angle (θ_3) when incident light illuminates from glass into air. (b) and (c) The transmittance plots against the incident angle (θ_1) and transmitted angle (θ_3), respectively, when incident light illuminates from air into glass. Wavelength is set to be 532 nm in the calculation.

First of all, we consider that incident light is illuminating from the glass side into the air side, passing through the thin silver film. Under this circumstance, θ_3 is the incident angle while θ_1 is the transmitted angle. The calculated transmittance T ($T = \tau_p^2$) plotting against the incident angle θ_3 according to Eq. (5.1) is presented in Fig.5.3 (a). A sharp transmission peak can clearly be seen around 44°. This corresponds to the resonant angle of SPPs as predicted from Eq. (2.16), and the high transmission coefficient is the well known field enhancement effect of SPPs generated at the air-silver interface.

Now, we consider that incident light is illuminating from air into the glass side. Under this circumstance, θ_1 is the incident angle while θ_3 is the transmitted angle. The calculated transmittance plotting against the incident angle θ_1 is illustrated in Fig.5.3 (b). As can be seen, over the whole range of available incident angles, the transmittance is very low. This is due to the special refractive index of metal, which has a small real part (high reflection) and a large imaginary part (high absorption). Situation is changed if we consider it from the perspective of transmitted angle, with the result shown in Fig.5.3 (c). It is interesting to find that a transmission peak is present at the curve. The corresponding transmitted angle is exactly the same with that in Fig.5.3 (a), and hence is the SPR angle. If we pick up the transmission curve at the small angles ($\theta_3 < 41.3^\circ$, 41.3° is the angle for total internal reflection), as shown with the inset, it is completely identical with that in Fig.5.3 (b), with the corresponding angles related with the Snell's law: $n_1 \sin(\theta_1) = n_3 \sin(\theta_3)$. Hence, the transmissions at small angles are totally due to the propagating incident radiations from the air side.

Now, we move our attention to the high transmitted angles ($\theta_3 > 41.3^\circ$). At SPR angle, the transmittance is calculated to be 600%. It is more than 300 times enhanced compared to that at small transmitted angles. Such giant enhancement is thus coming from the evanescent radiations at the air side, which have in-plane wave-vector component identical to that of SPPs supported at the air-silver interface and hence is able to couple to SPPs and re-radiate into the glass side at specific angle satisfying the wave-vector matching condition. It is therefore termed as surface plasmon coupled -emission due to its coupled nature of the transmitted emission with surface plasmon.

As a result, it is interesting to find that: in a conventional signal collection configuration, (for example, if the Raman signals in Fig.5.1 (a) are collected at the upper side), the collected signals are the propagating radiations originated from the

emitters and the collection efficiency is determined by the maximum angle allowed by the objective lens; while in an SPCE-based collection configuration, (for example, if the Raman signals in Fig.5.1 (a) are collected at the lower side by the oil-immersion objective lens), the collected signals are mainly from the evanescent radiations whose in-plane wave-vector component are identical to that of SPPs and hence the collection efficiency is determined by the radiation portion satisfying SPPs excitation condition and the SPPs-induced field enhancement effect.

In the following sections, we will investigate the SPCE of SERS from the perspective of Fourier plane and image plane, respectively. At the back Fourier plane, the SPCE spectrum reflects the wave-vector information of the excited SPPs and hence can be used for SPP characterization. At the image plane, the pattern obtained by a CCD camera is the real-space image of the nanosphere-film junction where 4-mba molecules sit and emit the Raman signals. Since the size of nanosphere-film junction is much smaller than that limited by the diffraction limit ($\lambda_0/2$), Raman scattering from a single nanosphere-film junction can be treated as a point source of SPPs and hence the Raman image of the junction is approximate the point spread function (PSF) of an SPCE microscopic system. We will then calculate the PSF theoretically for the purpose of comparison.

5.3 Results

5.3.1 Fourier Plane

As can be seen in Fig.5.1 (b), the Raman spectrum of 4-mba molecules presents three main peaks, which are 564.21 nm, 573.71 nm and 580.92 nm, respectively. Each peak has a very narrow linewidth (1 – 2 nm). To investigate the SPCE pattern at the back

Fourier plane, we calculate for each of the above peak wavelengths the transmission coefficients and plot them against the transmitted angle θ_3 , with the results shown in Fig.5.4 (a). One can see that the resonant angle slightly decreases as incident wavelength increases.

Fig.5.4 (b) shows the back Fourier plane image of SERS from 4-mba molecules. A bright and colorful SPCE ring is clearly seen. This corresponds to the transmission peaks as illustrated in Fig.5.4 (a) and is due to the excitation of SPPs at the silver-air interface, as analyzed above. The color of SPCE ring is green outside, red inside and yellow in between, which means that the resonant angle decreases as wavelength increases. This agrees well with the result shown in Fig.5.4 (a). The CCD camera cannot distinguish the colors clearly because the SPR angles are very close for the above three Raman peaks (can be seen as the picture zoomed in).

Fig.5.4. (a) Transmission coefficients of a 55-nm-thick silver film sandwiched by semi-infinite air and glass under 564 nm, 573 nm, and 581 nm incident wavelengths, respectively. The wavelengths are corresponding to the three main Raman peaks of 4-mba molecules. (b) Back Fourier plane image of SERS from 4-mba molecules. The coupled-emission of SERS forms the colorful SPCE ring.

Fig.5.5 presents the pixel intensity distribution along the white dashed line in Fig.5.4 (b). The horizontal axis is set as wave-number, which is derived from the angular information contained in the back Fourier plane image by $k = k_0 \times n_{oil} \times \sin\theta$, where k_0 is the incident wave-number in vacuum. As can be seen, the peak intensity at SPR

angle is 55 counts along this direction and averaged 70 counts across the whole ring; while at the non-resonant angles only the background noise is detected. The overall counts obtained over the SPCE ring are on the order of 10^5 , which provide strong evidence that collection efficiency of SERS at the substrate side of the sample is significantly increased with the help of SPCE. This is of great significance for a system in which signals need to be collected at the substrate side, such as a tip-enhanced Raman spectroscopy.

Fig.5.5. Pixel intensity distribution along the dashed line as shown in Fig.5.4 (b) plots against the wave-number derived from the transmitted angle.

Another useful property of this curve is that it can be described by a Lorentzian curve from which the FWHM encoding the propagation length of SPPs can be derived. The fitted curve with Lorentzian function is shown in Fig.5.5 with red line. The Lorentzian function is expressed as:

$$I = I_0 + \frac{2A}{\pi} \frac{w}{4(k - k_0)^2 + w^2} \quad (5.5)$$

where w represents the FWHM of the fitted curve and is equal to $0.10826 \mu\text{m}^{-1}$. The propagation length of the excited SPPs is hence $1/w$, which equals to $9.237 \mu\text{m}$. For the purpose of comparison, the propagation length derived from the transmission curve in Fig.5.3 is $9.14 \mu\text{m}$, in line with the one measured with the SPCE ring at the

back Fourier plane. The measurement error is believed from the limited CCD pixels near SPR angle and the background noises.

It is worth mentioning at this point that the SPCE curve from Raman scattering is more preferred for the measurement of SPP propagation length owing to its extremely narrow linewidth of Raman peaks compared to fluorescence. By filtering specific Raman peak, SERS from single nanosphere-film junction can approximately serve as a point excitation source of SPPs with single wavelength. Fluorescence spectrum, on the other hand, has a much wider linewidth. According to Fig.5.4 (a), as incident wavelength increases, SPR angle decreases. The eventual-transmission curve is hence the superposition of all of the transmission curves over the spectrum of fluorescence. This could lead to a much wider linewidth of the SPCE ring and hence a short SPP propagation length [175, 179].

5.3.2 Image Plane

To calculate the electric field distribution at the image plane, we adopt the method according to ref. [180]. In their general model, a point dipole on the metal-coated glass slide is excited by a p -polarized incident plane wave as shown in Fig.5.6. The point dipole is at a distance d away from the first interface and emits light at a different wavelength λ than the excitation wavelength λ_{inc} .

If we assume the electric field in the image plane is $\mathbf{E}_{\text{image}}$, according to ref. [180], it can be calculated by the following equations:

$$\overline{\mathbf{E}}_{\text{image}}(r, \varphi, z) = [E_{4,r}, E_{4,\varphi}, E_{4,z}] \quad (5.6)$$

$$E_{4,r} = -\frac{ik_4}{2} \left\{ \mu \sin \theta_d \cos(\phi_d - \varphi) [K_0' + K_2'] - \mu \cos \theta_d [2iK_1'] \right\} \quad (5.7)$$

Fig.5.6 Schematic of the imaging process within a 4f optical system of an SPCE microscope.

$$E_{4,\phi} = -\frac{ik_4}{2} \left\{ \mu \sin \theta_d \sin(\phi_d - \phi) [K_0^I - K_2^I] \right\} \quad (5.8)$$

$$E_{4,z} = -\frac{ik_4}{2} \left\{ \mu \sin \theta_d \cos(\phi_d - \phi) [2iK_1^II] - \mu \cos \theta_d [2iK_0^II] \right\} \quad (5.9)$$

$$K_0^I = \int_0^\alpha \sqrt{\frac{\cos \theta_4}{\cos \theta_3}} \sin \theta_4 (\tau_s + \tau_p \cos \theta_1 \cos \theta_4) J_0(k_4 r \sin \theta_4) \exp(ik_4 z \cos \theta_4) \exp(i\Phi) d\theta_4 \quad (5.10)$$

$$K_1^I = \int_0^\alpha \sqrt{\frac{\cos \theta_4}{\cos \theta_3}} \sin \theta_4 \tau_p \sin \theta_1 \cos \theta_4 J_1(k_4 r \sin \theta_4) \exp(ik_4 z \cos \theta_4) \exp(i\Phi) d\theta_4 \quad (5.11)$$

$$K_2^I = \int_0^\alpha \sqrt{\frac{\cos \theta_4}{\cos \theta_3}} \sin \theta_4 (\tau_s - \tau_p \cos \theta_1 \cos \theta_4) J_2(k_4 r \sin \theta_4) \exp(ik_4 z \cos \theta_4) \exp(i\Phi) d\theta_4 \quad (5.12)$$

$$K_0^{II} = \int_0^\alpha \sqrt{\frac{\cos \theta_4}{\cos \theta_3}} \sin \theta_4 \tau_p \sin \theta_1 \sin \theta_4 J_0(k_4 r \sin \theta_4) \exp(ik_4 z \cos \theta_4) \exp(i\Phi) d\theta_4 \quad (5.13)$$

$$K_1^{II} = \int_0^\alpha \sqrt{\frac{\cos \theta_4}{\cos \theta_3}} \sin \theta_4 \tau_p \cos \theta_1 \sin \theta_4 J_1(k_4 r \sin \theta_4) \exp(ik_4 z \cos \theta_4) \exp(i\Phi) d\theta_4 \quad (5.14)$$

In these equations, $J_n(\bullet)$ denotes the Bessel function of the first kind of order n , α the

maximum angle allowed by the objective lens, θ_d the dipole orientation with respect to z -axis, θ_i ($i=1,2,3$) the incident angles at each interface and are linked by the Snell's Law, θ_4 the polar angle of the wave-vector in medium 4, φ the azimuthal angle of the wave-vector, k_i ($i=1,2,3,4$) the wave-vectors at each layer and τ_q ($q = "p"$ or $"s"$) the Fresnel coefficients of a three-layer system for a p -polarized and s -polarized light, respectively. As we obtain the electric field distribution, the intensity that is detected in the image space is therefore as following:

$$I \propto (|E_{4,r}|^2 + |E_{4,\varphi}|^2 + |E_{4,z}|^2) / P_T \quad (5.15)$$

where the normalization factor P_T is the total power emitted by the dipole in the presence of a metal interface.

In our SPCE experiment, Raman scattering from 4-mba molecules is excited by the enhanced electric field at the nanosphere-film junction. On the one hand, the effective excitation area is determined by the linewidth of electric field at the junction, which is far below the size restricted by the diffraction limit, and hence we treat it as a point source. On the other hand, because of the vertical orientation of the junction, a longitudinal electric field is preferred for the excitation of localized surface plasmon. Thus, it is also reasonable to assume that the point dipole source is vertically oriented. In other words, θ_d is assumed to be 0. Finally, since the nanosphere is immobilized on the film surface, the dipole-film distance d should equal to zero. Under these circumstances, the Raman intensity distribution at the image plane becomes:

$$I_{\perp} \propto 4(|K_1^I|^2 + |K_0^{II}|^2) / P_T \quad (5.16)$$

Fig.5.7 presents the calculated PSF of an SPCE microscopy using Eq. (5.16) and the actual SPCE image of SERS obtained in the experiment. Incident wavelength of 573 nm was used in the calculation, which corresponds to the middle peak of the SERS

spectrum as shown in Fig.5.1 (b). It is interesting to find that the PSF of an SPCE microscopy has the rotationally symmetric and annular-like characteristic, with multiple rings extending out with decreasing intensity. More importantly, the PSF has a donut shape near the center. This is not seen in the PSF of a conventional microscopy, which has a maximum value at the center. Such unique PSF is mainly due to the angular selection of the excitation of SPPs. The comparison between the two figures shows a high degree of similarity in terms of their morphology (Fig.5.7 (c)).

Fig.5.7. (a) Calculated PSF of an SPCE microscopy. (b) The actual SPCE image of SERS from 4-mba molecules obtained at the back image plane. (c) Cross-section distributions across the center of (a) and (b), for the purpose of comparison.

Similarly, the SPCE image of Raman scattering at the back image plane is much more accurate for characterizing the PSF of an SPCE microscopy, due to the extremely narrow linewidth of Raman peaks. For the purpose of comparison, the PSF obtained with fluorescence by another group is presented in Fig.5.8 [180]. One can see that

both the locations and widths of the fringes for the experimental PSF are wider than those of the theoretical ones, which is mainly coming from the wider linewidth of fluorescence spectrum and hence the obtained PSF is actually the superposition of all of the PSF at each wavelength.

Fig.5.8. PSF of an SPCE microscopy obtained with fluorescence for comparison [180].

5.4 Discussion

In our experiment (combining the experiments in Chapter 4 and Chapter 5), SPPs are firstly excited by a tightly-focused RP beam. The SPPs subsequently interact with the silver nanospheres on the silver film, leading to a plasmon-hybridized gap mode with electric field significantly enhanced at the nanosphere-film junction. The enhanced electric field is then to excite SERS of 4-mba molecules sitting at the junction (Fig.4.9). Due to the scattering nature of SERS, the evanescent radiation component with in-plane wave-vector equal to k_{spp} is able to couple back to SPPs and eventually re-radiates into

the glass side at SPR angle, forming an SPCE ring at the back Fourier plane (Fig.5.4 (b)).

Attention now paid on the role of SPPs played in our gap mode SERS system, which is analogue to the one LSP played in a conventional SERS system. In a conventional one, the power of enhanced Raman radiation can be calculated as [181]:

$$P \propto N\sigma_{SERS} \cdot \frac{|E_{loc}|^4}{|E_0|^4} \cdot |E_0|^2 \quad (5.17)$$

where N is the number of Stokes-active scatters within the hotspot, σ_{SERS} the scattering cross-section, and E_{loc} and E_0 the amplitudes of the enhanced and incident electric field, respectively. The contribution from LSP is illustrated with the fourth-order factor, which is due to the enhancement of both the incident and emitted light field.

Similarly, in our system, incident light is first enhanced by the excitation of SPPs at the silver-air interface, as illustrated with Fig.5.3 (a). The emitted Raman radiation is finally enhanced through the SPCE, as shown in Fig.5.3 (c). The only difference arises from their different excitation schemes. LSP can be excited with light of appropriate frequency and polarization, irrespective of its wave-vector. Thus, the enhancement factors for the incoming and emitted light fields are very close and hence can be consolidated, leading to a fourth-order effect. The excitation condition for an SPP, however, is strongly wave-vector dependent, which is illustrated with the wave-vector matching condition (Eq. (2.16)). The additional condition results in an excitation of SPPs with incident light and an emission of the emitted Raman scattering at fixed angles (i.e., SPR angles) based on the ATR configuration.

Thus, the total power of Raman radiation collected can be expressed as:

$$P \propto N\sigma_{SERS} \cdot \frac{|E_{loc}|^4}{|E_{SPP}|^4} \cdot |E_{SPP}|^2 \cdot \text{CE}(\text{SPCE}) \quad (5.18)$$

The fourth-order factor illustrates the enhancement induced by the plasmon-hybridized

gap mode, while the last two terms represent the enhancement from SPPs, in terms of the SPPs excitation with incident light and collection efficiency (CE) improvement through SPCE, respectively.

Fig.5.9. Intensity comparison between the Raman signals of R6G molecules collected at the glass side through SPCE and collected directly at the air side (conventional). Integration time is 1s. Collection efficiency is shown to be enhanced through SPCE.

To illustrate the collection efficiency improvement through the SPCE, we now compare the intensity of Raman signal collected at the glass side (SPCE) to that collected at the air side (conventional), with the result shown in Fig.5.9. The improvement of collection efficiency can clearly be seen in Fig.5.9. The Raman intensity ratio (SPCE / conventional) is fluctuating between 3 and 5 as we move the stage, which is because of the non-uniform distribution of nanospheres immobilized on the metal film. Although the collection efficiency at the air side can further be magnified by using a higher NA objective lens, the bottom line here is that Raman signal collected via SPCE is comparable to that collected directly at the air side.

While such improvement does not seem notable for a SERS system, it is of great significance for a tip-enhanced Raman spectroscopy [155], in which, Raman signal is either side-collected with a long working distance objective lens (reflection mode), or

collected at the opposite side to the metallic tip with respect to the substrate (transmission mode). The collection efficiency under both configurations is very low. This, however, can significantly be improved by introducing a thin metal film as the substrate and hence SPCE occurs in the system. In addition, the SPP excitation with incident light can also greatly improve the excitation efficiency because of its field enhancement, as demonstrated in Eq. (5.18).

5.5 Summary

In this work, SPCE of SERS from single nanosphere-film junction was investigated. Because of the presence of a thin silver film, Raman scattering emitted from 4-mba molecules adsorbed at the junction is able to couple back to the SPPs and eventually directionally-emits into the substrate side with higher refractive index. Transmission coefficient is shown greatly enhanced at the SPR angle. It can be used to improve the collection efficiency of Raman signals at the back side of the excitation objective lens (SERS/TERS). Meanwhile, due to the extremely narrow linewidth of Raman peaks, SERS from single nanosphere-film junction can be employed as a point source of SPPs which possesses multiple single-wavelengths. By filtering specific Raman peak, it is well-suited for the measurement of propagation length of SPPs at back Fourier plane and quantitative characterization of PSF of an SPCE microscopy at image plane.

Chapter 6 SPP-Longitudinal-Component Detection with SERS Imaging

6.1 Chapter Introduction

In chapter 4, surface-enhanced Raman scattering from single nanosphere-film junction excited by SPPs has been realized. In that experiment, if we scanned a nanosphere-film junction over the propagation region of SPPs and extracted the Raman intensity at each point, we got an intensity distribution that agrees well with the longitudinal field component of SPPs. This intriguing result informs us that a nanosphere-film junction attached with Raman molecules can be employed as a novel SPP-antenna for characterizing the near-field distributions of SPPs.

As we know, an SPP has field components both in the direction perpendicular to (longitudinal component E_z) and in the surface plane (transversal component E_r), with relative strength determined by the dielectric constants of the metal and dielectric [65]. Over the visible spectrum, the longitudinal component is much stronger than its transversal (*e.g.*, $|E_z|^2/|E_r|^2 \approx 10$ and 16 for SPPs at an infinite silver-air interface at 532 nm and 633 nm incident wavelengths, respectively), and it is the longitudinal component that is responsible for most SPPs properties. As a result, it would be more meaningful if one can probe the longitudinal component and use it to characterize SPPs near-field behaviour.

Over recent decades, many state-of-the-art techniques have been developed characterizing SPPs, including fluorescence detection [56], leakage radiation microscopy [55], near-field electrical detection [182] and near-field optical microscopy [57-58]. The fluorescence and leakage radiation approaches are capable

of performing real-time imaging of the total intensity of SPPs; however, optical diffraction limit restricts their resolution, thus hinders a detailed analysis of SPPs. Near-field electrical detection of SPPs is still at the single-point detection stage and two-dimensional imaging of SPPs distributions remains challenging. NSOM is the pivotal detection technique, which enables SPPs imaging on sub-wavelength scales by means of a raster-scanning probe tip [42, 59-66, 68]. However, a critical issue associated with NSOM is that typically the transversal component of an electric field is preferentially picked up by an NSOM tip [65, 183], despite the larger contribution of $|E_z|^2$ to the total intensity. This jeopardizes the goal of detecting SPPs as we use a subordinated field to characterize the SPPs behaviour. Although there are other groups [42, 63] claiming that the detected signal of an apertured NSOM probe is proportional to $|\nabla_{\perp} E_z|^2$, the crucial point is that there are still no experimental methods to date that can detect directly and efficiently SPP dominant longitudinal component.

In the following work, as a continuation of chapter 4 and an important application of my PhD project, we propose a new method to map the near-field profile of SPPs. Our method takes advantage of SERS from a single nanosphere-film junction where the enhancement factor is determined by the longitudinal component of coupled SPPs between the NP and the film. By scanning the NP immobilized on the film, we can map out the field distribution of SPP's longitudinal component with super-resolution.

6.2 Principle

As mentioned in Chapter 4, the near-field coupling between propagating plasmon on the metal film and localized surface plasmon of the NP in a NP-film junction system offers a unique opportunity to extract the longitudinal component of the former plasmon. For example, considering the plasmon virtual probe produced from focusing a RP beam (Fig.6.1 (a)), where a plasmonic standing-wave interference pattern is formed on the metal film, free electrons and ions will then concentrate alternatively at the standing-wave nodes (Fig.6.1 (b)). Upon introducing a sphere-shaped NP, a vertically-oriented gap mode is excited at the nodes by the longitudinal electric-field of SPPs, while a laterally-aligned gap mode at the anti-nodes where the transversal electric-field dominates (Fig.6.1 (b)).

The NP-film interaction is governed by the Coulomb interaction between the surface charges of the localized dipolar plasmon mode on the NP and the propagating mode at the metal surface [31]. As demonstrated in previously experimental and theoretical work, plasmonic vertical gap mode presents a much stronger NP-film interaction, which results in a red-shift of the resonant peak position of the vertical mode with respect to the lateral one [31, 33, 36-37]. As a result, at a specific -incident wavelength, the near-field enhancement factor associated with the vertical gap mode can be much higher than the lateral mode (Fig.6.1 (c)). The enhanced electric field can be used to boost the SERS intensity of the molecules adsorbed within the particle-film gap. Therefore, by scanning and acquiring the SERS signals, it maps out indirectly the field-strength of the longitudinal component (Fig.6.1 (d)).

Fig.6.1. Working principle of plasmon-hybridized gap modes directed characterization of SPPs (a) Field feature of a typical SP-VP excited by a RP beam, which is essentially an evanescent Bessel-like standing-wave. (b) Illustration of a nanosphere-film junction interacting with the longitudinal (“A”) and transversal field (“B”) of an SPP standing wave. The longitudinal field will drive the harmonic oscillation of free electrons inside the nanosphere perpendicular to the metal film, leading to a vertically-oriented plasmon-hybridized gap mode; while a lateral gap mode will be excited by the transversal field. The different schemes of nanosphere/film interaction will result in an energy splitting of these two kinds of plasmon-hybridized gap modes. (c) Demonstration of the mode-splitting induced longitudinal field sensitivity. At specific incident wavelengths, field enhancement induced by the vertical gap mode is much higher. The enhanced electric field can be used to excite SERS signal of molecules at the nanosphere-film gap. Since the vertical gap mode contributes a higher Raman enhancement, the intensity of SERS can be used to characterize SPPs dominant longitudinal field. (d) Schematic diagram of plasmon-hybridized gap modes directed, SERS-based SPPs detection system. Diagram is not to scale.

6.3 Mapping SPP Fields with SERS Imaging

We first examine the SPPs which are excited on a 45-nm-thick silver film by a tightly-focused RP beam at a wavelength of 532 nm, under an ATR configuration with a high NA objective lens. To create the NP-film junctions, a sub-monolayer silver

nanosphere of 60-nm-diameter was self-assembled on the silver film by the thiol pairs of 4-mercaptobenzoic acid (4-mba) molecules sandwiched between them, which were also employed as the Raman probe of the evanescent surface plasmon fields. We have chosen this type of molecules because of their non-fluorescent nature which avoids the uncertainty induced by fluorescence such as “quenching effect”.

Fig.6.2. Mapping an SP-VP with SERS imaging. (a) Measured near-field distribution of plasmon virtual probe produced by a tightly-focused RP beam, compared with its calculated longitudinal (b) and transversal (c) electric field components. (d) Cross-section distribution comparison between the measured virtual probe and calculated longitudinal field component. (e) Statistical measurement of the central spot size of plasmon virtual probe with 50 randomly-selected nanospheres on the metal film, verifying the accuracy and reproducibility of our measurement. Incident wavelength is 532nm. Area of contour maps is $4\ \mu\text{m} \times 4\ \mu\text{m}$.

The mapping of SPP standing-wave pattern is presented in Fig.6.2 (a), which is obtained by raster scanning the nanosphere-film junction over the propagation region of SPPs and recording the intensity of SERS at each point. Because of the full beam *p*-polarization of a RP beam, SPPs can be excited along all azimuthal directions thus to form a sub-diffraction-limited evanescent plasmon virtual probe at the center. As

can be seen, the measured pattern is in excellent agreement with the calculated longitudinal component (Fig.6.2 (b)). Note that this result opposes to the transversal field distribution as shown in the calculation (Fig.6.2 (c)) which is the usual pattern obtained by NSOM. The agreement can be assessed quantitatively by plotting the intensity curves across the center (Fig.6.2 (d)).

The size of the center spot can be extracted subsequently. The result from 50 randomly-selected nanospheres is presented in Fig.6.2 (e). As shown, the measured spot sizes approximately follow a normal distribution (see the inset) with mean value of 188.93 nm ($0.355\lambda_0$) and standard deviation of 6.76 nm. The slight deviation from the theoretical value (185 nm) should attribute to the finite scanning step size (40nm). Both of the excellent agreement in the mean value and the small standard deviation indicate a high reproducibility as well as high accuracy of our measurement. To the best of our knowledge, this is the first direct measurement of the spot size of SP-VP in the visible range.

Fig.6.3 (a-c) present the mappings correspond to other typical polarized-beams including a tightly-focused linearly polarized Gaussian beam, a circularly polarized beam, and a linearly polarized optical-vortex beam of charge “1” [184], respectively. These measured results, on the one hand, verify further the longitudinal field sensitivity of our method; and on the other hand, also explicitly illustrate the capability of a RP beam to form the plasmon virtual probe owes to its properties of full beam *p*-polarization and in-phase plasmon excitation. This capability is missed for the other beams either because of the spatially-variant *p*-polarization (for Fig.6.3 (a), (c)) or because of out-of-phase SPPs excitation (for Fig.6.3 (a), (b)). This also verifies that a tightly-focused RP beam can be as the optimized source for the NP-film junction configuration.

Fig.6.3 The mapping of SPP patterns under a tightly-focused linearly polarized Gaussian beam (LPGB), a circularly polarized beam (CPB) and a linearly polarized optical-vortex beam (LPVB) of charge “1”, respectively, to verify further the longitudinal field sensitivity of our method and show the distinct SPP patterns under different incident polarizations. From top to bottom: measured, calculated $|E_z|^2$ and calculated $|E_r|^2$, respectively. From left to right: LPGB, CPB and LPVB, respectively. Area of contour maps is $4\ \mu\text{m} \times 4\ \mu\text{m}$. Incident wavelength is 532 nm.

Compared to the current widely-used NSOM system, our method shows advantages in many aspects. First of all, by making use of the energy spitting of plasmon-hybridized gap modes and SERS imaging, the strongly dominant longitudinal surface plasmon fields are detected. While for a NSOM system, it was demonstrated, from both experiment and theoretical calculation, that the current commercially-available NSOM tip is more sensitive to the transversal electric field in the visible range. For a direct comparison, the counterpart of measurements for all of the above polarizations

by NSOM can be found respectively in Refs. [42, 63, 68] (as shown in Fig.6.4), where the measured patterns coincide with those of the transversal components, even if intensities of longitudinal components are 16 times (as calculated by $|\varepsilon_m/\varepsilon_d|$) [65] stronger under 632 nm incident wavelength for silver film as used in their work.

Fig.6.4. Comparison of SPPs distribution obtained with NSOM [42, 63, 68] (top) and our SERS imaging (bottom). From left to right: linearly polarized Gaussian beam, radially polarized beam, and linearly polarized optical vortex beam, respectively.

Secondly, the influence from transmitted light is significantly suppressed, which is clearly shown in Fig.4.9. The transmitted light shows a great influence on the conventional plasmon detection techniques, particularly for the method with direct-detection scheme such as aperture-type NSOM. For an aperture-less-type NSOM system, the collection signal is generally the Rayleigh scattering from metallic tip. Although Rayleigh scattering possesses a large scattering cross-section, its wavelength is exactly the same with the illuminating wavelength and hence is hardly extracted from the incident light. Raman scattering, on the contrary, shows a small wavelength shift with respect to the illuminating one. It can easily be extracted by using a notch (or long-pass) filter. Meanwhile, because of the excitation of

plasmon-hybridized gap mode, Raman scattering can significantly be enhanced by more than 10^8 for a NP-film junction excitation scheme. This greatly compensates for the small cross-section of normal Raman scattering. Finally, the turbulence induced by the SP-antenna in our method is much smaller than that induced by the NSOM tip. This is, on the one hand, because of the smaller size of nanosphere (can be less than 50 nm) than that of NSOM tip (typically more than 50 nm); on the other hand, localized plasmon will be excited at the metallic NSOM tip-end, which complicates the detected signals. In our method, localized plasmon is utilized to generate the longitudinal field sensitivity and to enhance the Raman scattering and hence the turbulence from it does not exist.

6.4 Numerical-Modelling with FDTD Method

In order to obtain the responses of a nanosphere-film junction to SPPs' longitudinal and transversal field, we place the nanosphere at the node (point "A" in Fig.6.1 (b)) and anti-node (point "B" in Fig.6.1 (b)) of SPP standing-wave respectively and carry out a wavelength scan. The simulated result is shown in Fig.6.5 (a), with vertical axis representing the normalized maximum electric field at the nanosphere-film gap. It is seen that both the resonant wavelength of lateral (480 nm) and vertical (500 nm) gap mode show remarkable red-shift with respect to the nanosphere standing on a glass substrate (410 nm), because of the Coulomb interaction between the nanosphere and silver film. However, the red-shift of vertical gap mode is more notable due to the stronger interaction. This can clearly be seen in Fig.6.5 (b) and Fig.6.5 (c), which give the electric field vectorial distributions in the vicinity of nanosphere under resonant conditions of lateral and vertical gap mode, respectively.

Fig.6.5. Numerical-modelling of a nanosphere-film junction interacting with SP-VP. (a) Normalized maximum electric field at the nanosphere-film junction plots against the wavelength, when the nanosphere placed at the standing wave node (point “A” in Fig.6.1 (b), vertical gap mode), anti-node (point “B” in Fig.6.1 (b), lateral gap mode), and on a glass substrate, respectively. (b) and (c) Electric field vectorial distribution in the vicinity of nanosphere-film gap, in the case of lateral and vertical gap mode, respectively. (d) Calculated averaged Raman enhancement for each mode, which is employed to evaluate the field sensitivity of a NP-film junction. Left vertical axis is set as $\log_{10}(\text{RE})$.

In the case of lateral gap mode, electric field generally travels horizontally inside the nanosphere and bends to the metal surface gradually because of the attraction between the lateral sides of nanosphere and the metal surface. It is just opposite to the case of vertical gap mode, under which the electric field insider the nanosphere travels vertically and the Coulomb attraction occurs between the lower side of nanosphere and the adjacent metal surface. This leads to a much higher concentration of electrons near the junction and a tighter interaction volume, both of which indicate a stronger nanosphere-film interaction.

Fig.6.6. Contour maps of electric field distribution. (a) and (b) Vertical and lateral gap mode in the XZ plane. (c) and (d) The corresponding modes in the nanosphere-film gap plane, respectively. Colorbar scale is set as $\log_{10}(|E|^2)$. The arrows represent the electric field orientation of SP-VP in the absence of nanosphere. Incident wavelength is 532 nm.

The field distribution of each mode is illustrated in Fig.6.6. For both cases, the electric field is strongly concentrated at the nanosphere-film gap (Fig.6.6 (a) and Fig.6.6 (b)), but is much confined and hence a higher field enhancement for the vertical gap mode. In the horizontal gap plane, the pattern is axial-symmetric for the vertical gap mode (Fig.6.6 (c)), while it is dipolar-like for the lateral (Fig.6.6 (d)), with mode orientation parallel to the polarization of electric field in the absence of nanosphere. The mode disparity also indicates a higher nanosphere-film interaction for the vertical gap mode owing to its larger effective interaction area.

Raman enhancement (RE), the parameter to evaluate the field sensitivity of a NP-film junction, can be calculated thereafter by the following expression:

$$RE_p = \left(\sum_{i,j} \frac{|E_{ij}^{loc}|^4}{|E_{ij}^{SPP}|^4} \cdot |E_{ij}^{SPP}|^2 \right) / |E_p^{SPP}|^2 \quad (6.1)$$

in which E_{ij}^{loc} denotes the localized electric field amplitude at the horizontal gap plane,

E_{ij}^{SPP} the amplitude of SPP in the absence of nanosphere, and p (“ z ” or “ r ”) represents the excitation longitudinal or transversal electric field, respectively. The calculated RE plotting against the wavelength is shown in Fig.6.5 (d). One can see that the nanosphere-film junction doesn’t exhibit a uniform response over the visible range, i.e. it is sensitive to the transversal field in the shorter wavelength range because of the lateral gap mode, and turns into the longitudinal field sensitivity gradually as incident wavelength increases. The extent of longitudinal field sensitivity is determined by three factors: the magnitude of red-shift of vertical gap mode with respect to the lateral; their relative peak RE (i.e. $\max(RE_z)/\max(RE_r)$, depending on the field enhancement and mode pattern), and their relative mode losses, respectively, with the first one making the major contribution. Although the longitudinal field sensitivity at longer wavelengths is at the expense of RE , as can be seen in Fig.6.5 (d), the RE is still higher enough for the excitation of Raman signals and hence for the measurement of SPPs. Meanwhile, by carefully designing the structural parameters of NP-film junction (e.g., the size, shape, and composition of NP), one can tune the resonant wavelength of gap modes to reach an optimized balance between RE and longitudinal field sensitivity at each incident wavelength.

6.5 Summary

In conclusion, we have reported a novel method to directly and accurately map the dominant longitudinal component of SPPs. The method relies on the longitudinal field component preferentially exciting LSP and enhancing the electric field in SPCM. Meanwhile, the adverse influences from transmitted and scattering light are significantly suppressed because of the relatively low Raman enhancement compared with that arising from SPPs, leading to an extremely clean and pure SPP detection.

Worth mentioning is the point that SPCM is not limited to SPP detection under tightly-focused configurations. As long as the nanosphere can be replaced with a Raman probe attached metallic tip and equipped with a feedback circuit (analogous to tip-enhanced Raman spectroscopy[185]), it can be extended to detect SPPs excited under any type of configuration. We believe that SPCM, in combination with NSOM, will provide a deeper and more complete understanding of SPP behaviour and open new developments in SPP-based applications.

Experimental apparatus: An Olympus oil immersion objective lens (60 x, NA=1.49) was used to focus the collimated incident beam on to the silver-air interface to excite the SPPs. Raman images of immobilized Ag nanospheres on Ag film were captured with a Thorlabs digital CCD camera. Meanwhile, Raman signals emitted from 4-mba molecules located at the nanosphere-film junction were obtained with an OceanOptics TEC cooling spectrometer (QE 65000). A piezo-scanning stage (Physikinstrumente (PI), P545.3R7) was applied initially to position the nanosphere at the centre of focal plane, by monitoring the intensity of Raman signals from spectrometer and CCD camera, and subsequently to raster scan the nanosphere over the SPP region to get the near-field SPP distribution.

SPP mapping and measurement: After an isolated individual nanosphere was found (checked with a CCD camera) and positioned at the centre of focal plane, Raman signals emitted from 4-mba molecules were sent for further amplification to a Hamamatsu photomultiplier tube (PMT), instead of the spectrometer. The PI scanning stage, the acquisition of data from the PMT, and real-time displaying of SPP distribution were all realized and coordinated via Labview software, as shown in Fig.6.7. For two-dimensional mappings, the scanning range and step size were set to 5

$\mu\text{m} \times 5 \mu\text{m}$ and 50 nm respectively; for SPP spot-size measurements, the scanning range in the X direction was set at 400 nm to trace the cross-section distribution across the centre, and that for the Y direction was set to 4 μm for the actual measurements. The step size for both directions was set to 40 nm.

Fig.6.7. Front view of the Labview program coded for two-dimensional mapping of SPP's longitudinal component.

Chapter 7 Conclusions and Future Works

7.1 Conclusions

In this thesis, we proposed a multi-functional surface-enhanced Raman system and investigated it both from simulation and experiment. Our system is based on a novel idea, which employs the fascinating electromagnetic enhancement stemming from the SPP&LSP coupling mode (plasmon-hybridized mode), and deals with the limitations/problems facing with the current SERS and other plasmon-based techniques.

First, with surface-enhanced Raman spectroscopy, electromagnetic enhancement from SP coupling mode was proved to be much superior to that from separate modes. Raman enhancement of $10^9 - 10^{10}$ has been achieved numerically. Meanwhile, the existence of SPCE in the presence of a thin metal film leads to a directional emission of SERS, which is able to improve the collection efficiency of Raman signals. Moreover, the reproducibility of NP-film junctions is verified much higher than that of inter-particle junction (dimer structure). Hence, from the perspective of the balance among Raman enhancement, collection efficiency and reproducibility, our plasmon-hybridized mode system is of great potential as a robust SERS substrate. Both air and water can be as the environment for the specimens in our system. The specimens should have a small thickness (<10 nm) because the field enhancement from a NP-film junction strongly depends on the separation between the NP and metal film. Gases can also be the specimens in our system.

Secondly, the SPCE spectrum obtained at the back Fourier plane contains optical parameter information of the excited SPPs. In particular, the wave-numbers and propagation length can rapidly be extracted from the SPCE ring without any mechanical movement or angle scanning. Although the SPCE spectrum from

fluorescence has been employed for the measurement of propagation length of SPPs before, the advantages of using SERS is prominent, due to the extremely narrow bandwidth of Raman peaks, small physical size of NP-film junction and avoidance of using a thin dielectric layer as a spacer.

Finally, a direct and efficient detection of the dominant longitudinal component of SPPs is realized based on our plasmon-hybridized mode system, which takes advantage of SERS from a single NP-film junction where the enhancement factor is determined by the longitudinal component of coupled SPPs between the NP and the film. The proposed technique tackles the problems associated with conventional NSOM system. It gives rise to the state-of-the-art near-field measurement with comparative advantages including:

- (i) Direct longitudinal component detection. To our best knowledge, this is the first technique which can directly and efficiently detect the SPPs dominant longitudinal component.
- (ii) Super-resolution. A resolution of less than 50 nm can be achieved.
- (iii) Less influence from transmitted and scattered light.
- (iv) Less turbulence induced by the probe.
- (v) Quantitative analysis. As an example, we measured for the first time the size of a sharply-confined SPP spot under a tightly-focused RP beam excitation. Such a measurement is a puzzle for a long time because of the drawbacks of NSOM system and lack of alternative approaches.

7.2 Future Works

7.2.1 Surface Plasmon Virtual Probe Directed Tip-enhanced Raman Spectroscopy

(a) High sensitivity, multi-functional tip-enhanced Raman System

Another attractive usage of surface plasmon virtual probe is as the excitation source for tip-enhanced Raman spectroscopy (TERS). TERS is a derivative application from surface-enhanced Raman spectroscopy, in which a NP is replaced with a metallic tip, equipped with a feedback circuit to keep the tip-sample distance constant, such as an AFM head or STM head. By raster scanning the tip over the sample and extracting the Raman spectrum at each point, a spectroscopic image of the detected sample can be generated with sub-diffraction limit resolution. This is one of the most intriguing advantages of TERS.

Fig.7.1. High sensitivity, high resolution tip-enhanced Raman spectroscopy based on surface plasmon virtual probe and surface plasmon coupled-emission.

Since the metallic tip of an AFM head is always vertically-oriented, as shown in Fig.7.1, a longitudinal electric field component is intrinsically required. General approach in the past is using a tightly focused linearly polarized beam, in which two

longitudinal field lobes is formed around the centre of focal plane. However, this method suffers from the efficiency problem because the longitudinal field in the focal plane is generally a subordinated component and hence the utility of power is low.

Surface plasmon virtual probe is just different. On the one hand, as mentioned in chapter 6, the relative strength of z-component over r-component of an SPP is determined by the dielectric constants of the metal and dielectric[65]. Over the visible spectrum, the longitudinal component is much stronger than its transversal, and so does for an SP-VP. This significantly improve the incident power utility while suppress the background noise induced by the transversal component. On the other hand, just as did and proved in our previous experiments, the coupling between the SPPs and LSP could result in a much higher Raman enhancement compared to that from separate mode. It is exactly the same as we employ the SP-VP as the excitation source for TERS. Furthermore, SPCE from tip-enhanced Raman scattering will occur as well in the presence of a thin metal film. This will greatly improve the collection efficiency of a TERS system because Raman signals need to be collected at the back side of objective lens. Finally, as discussed in the conclusion section in chapter 6, as long as the nanosphere can be replaced with a Raman probe attached metallic tip and equipped with a feedback circuit, our SPP detection technique can be extended to detect the SPPs excited under any type of configuration. This is readily realized as we introduce the AFM head into our previous system.

Taking all of these unique properties into account, the introduction of an AFM head into our previous system will lead to a SP-VP directed high sensitivity tip-enhanced Raman system, which is, at the same time, capable of realizing the super-resolution spectroscopic imaging of physical samples and super-resolution near-field imaging of SPP's longitudinal component.

(b) Controllable inter-particle junction excited by SP-VP

The dimer structure is widely accepted to generate the greatest Raman enhancement, owing to the strong coupling between the LSP modes on each particle. However, the nature of random formation of inter-particle junction makes it quite irreproducible, causing Raman enhancement with dramatic variations. This greatly restricts its practical applications. Bearing this situation in mind and continuing the work in part (a), if we immobilize an individual metal nanosphere on the thin silver film and accurately move it just under the AFM metallic tip, a vertically-oriented inter-particle junction is formed, and entirely under control, just as shown in Fig.7.2.

Fig.7.2. Controllable vertically-oriented dimer structure based on AFM tip, excited by an SP-VP

Since the inter-particle junction is vertically-oriented, an SP-VP could be a great candidate for the excitation of LSP under this circumstance because of its dominant longitudinal component. More interestingly, an SPP-LSP-LSP coupling mode will be generated. This could further improve the Raman enhancement compared to conventional inter-particle junction excited by propagating radiation, which is proved by the preliminary result as shown in Fig.7.3. Similarly, the existence of SPCE from Raman scattering will greatly improve the collection efficiency of such TERS-based

inter-particle system at the back side of objective lens. Since this structure and surface plasmon hybrid mode system is entire new, there should be more interesting phenomena behind this and hence a systematic investigation is necessary and quite meaningful. In particular, how the dimer structure responds to the SP-VP and to what extent the Raman enhancement could be improved are worthy studying.

Fig.7.3. Near-field distribution around a vertically-oriented dimer structure excited by a surface plasmon virtual probe, with 480 nm incident wavelength. The white scale bar represents 100 nm.

7.2.2 All-in-one Surface & Tip-enhanced Raman System

Our ultimate objective is to build up an all-in-one surface & tip-enhanced Raman system, which consolidates all of the functionalities mentioned previously into an integrated system. The schematic of such all-in-one system is presented in Fig.7.4.

From the setup point of view, it has three main parts:

- (a) Light Source, including a 532 CW laser, an optical valve (LP + HW), a polarization converter and a beam expander. It is used to generate and expand a RP beam.
- (b) Excitation part, composing of a high NA objective lens, a piezo-scanning stage, an AFM tip or nanosphere. SP-VP will be generated and employed as the excitation

source to interact with optical antennas, such as nanosphere-film junction, AFM tip, etc.

- (c) Collection part, which consists of CCD cameras, spectrometer and PMT, to collect the Raman signals with the help of SPCE.

Fig.7.4. Schematic view of an all-in-one surface-enhanced Raman system. HW: half waveplate; LP: linear polarizer; BS: beam splitter; BFP: back Fourier plane; IP: image plane; Spec: spectrometer; PC: personal computer; NS: nanosphere.

From the perspective of functionality:

- (a) When single NP is used. Firstly, it can be as a robust substrate for SERS (high Raman enhancement, high reproducibility, and high collection efficiency). Secondly, it can be used as a convenient tool for measurement of SPP's propagation length by analyzing the SPCE ring obtained at the back Fourier plane. Finally, it can be used to map the longitudinal component distribution of SPPs. In particular, an SP-VP will be imaged and used as the excitation source for our system.

- (b) When the AFM tip is used. It can be used as an SP-VP directed high sensitivity tip-enhanced Raman system, which is, at the same time, capable of realizing the super-resolution spectroscopic imaging of physical samples and super-resolution near-field imaging of longitudinal component of SPPs excited under any kinds of configurations.
- (c) When AFM tip and NP are used together. A controllable vertically-oriented dimer structure is formed and excited by an SP-VP. The giant Raman enhancement is of high potential to realize the single molecule fingerprint detection.

Authors Publications

Journal papers:

1. **L. P. Du**, X. J. Zhang, T. Mei, and X. C. Yuan, "Localized surface plasmons, surface plasmon polaritons, and their coupling in 2D metallic array for SERS," *Opt. Express* **18**, 1959-1965 (2010).
2. **L. P. Du**, G. H. Yuan, D. Y. Tang, and X. C. Yuan, "Tightly focused radially polarized beam for propagating surface plasmon-assisted gap-mode Raman spectroscopy," *Plasmonics* **6**, 651-657 (2011).
3. **L. P. Du**, D. Y. Tang G. H. Yuan, S. B. Wei and X. C. Yuan, "Emission pattern of surface enhanced Raman scattering from single nanoparticle-film junction," *Appl. Phys. Lett* **102**, 081117 (2013). (2013).
4. **L. P. Du**, D. Y. Lei, G. H. Yuan, H. Fang, X. Zhang, Q. Wang, D. Y. Tang, C. J. Min, S. A. Maier and X. C. Yuan, "Mapping plasmonic near-field profiles and dynamics by Surface-enhanced Raman scattering," communicated (2013).
5. **L. P. Du**, D. Y. Tang and X. C. Yuan, "Film-driven plasmon hybridization on a nanoparticle-film junction system," in preparation (2013).
6. **L. P. Du**, D. Y. Tang and X. C. Yuan, "Launching structureless plasmon lenses with focused radially polarized beam," in preparation (2013).
7. S. B. Wei, J. Lin, Q. Wang, G. H. Yuan, **L. P. Du**, R. Wang, L. Xu, M. H. Hong and X. C. Yuan, "Singular diffraction-free surface plasmon beams," *Opt. Lett.*, accepted (2013).

Conferences:

1. **L. P. Du**, D. Y. Tang and X.-C. Yuan "Radially polarized beam induced plasmon-hybrid-mode for surface-enhanced Raman spectroscopy" International Conference on Nanophotonics, Beijing, (2012)
2. **L. P. Du**, D. Y. Tang and X.-C. Yuan "Theoretically modeling of tip-enhanced Raman scattering under linearly and radially polarized beam with DDA method" *Advances in Optoelectronics & Micro/nano-optics*, Guangzhou, (2010)

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