Coupled noble metal nanostructures for high-performance surface-enhanced spectroscopies

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NANYANG
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**COUPLED NOBLE METAL NANOSTRUCTURES FOR HIGH-
PERFORMANCE SURFACE-ENHANCED SPECTROSCOPIES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

COUPLED NOBLE METAL NANOSTRUCTURES FOR HIGH- PERFORMANCE SURFACE-ENHANCED SPECTROSCOPIES

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Abbreviations

SES	Surface-enhanced Spectroscopies
SEF	Surface-enhanced Fluorescence
SERS	Surface-enhanced Raman Scattering
SEIRA	Surface-enhanced Infrared Absorption
NP	Nanoparticle
SPR	Surface Plasmon Resonance
MNOMF	Metal Nanoparticle over the Metal Film
LSPR	Localized Surface Plasmon Resonance
SPP	Surface Plasmon Polariton
SNPD	Spiky Nanoparticle Dimer
SNP	Spiky Nanoparticle
SDD	Spiky Disk Dimer
3D	Three-dimensional
FDTD	Finite-difference Time-domain
Au	Gold
Ag	Silver
KR	Kretschmann-Raether
S-S	Sphere-to-sphere
T-S	Tip-to-sphere
T-T	Tip-to-tip
Si	Silicon
Q	Quality Factor
NIR	Near-infrared
EM	Electromagnetic
EF_{EM}	Electromagnetic Enhancement Factor
DNA	Deoxyribonucleic Acid
FF	Face-to-face
FE	Face-to-edge
EE	Edge-to-edge

LE	Low-energy
HE	High-energy
SD	Spiky Disk
TM	Transverse Magnetic

List of Publications

Peer reviewed publications

1. **A. Li**, S. Isaacs, I. Abdulhalim, S. Li, Ultrahigh Enhancement of Electromagnetic Fields by Exciting Localized with Extended Surface Plasmons. *J. Phys. Chem. C* 119 (33), 19382, (2015)
2. **A. Li**, and S. Li, Large-volume Hot Spots in Gold Spiky Nanoparticle Dimers for High-Performance Surface-Enhanced Spectroscopy, *Nanoscale* 6, 12921 (2014)
3. Y. Wang, K. Sentosun, **A. Li**, M. Coronado-Puchau, A. Sánchez-Iglesias, S. Li, X. Su, S. Bals and L. M. Liz-Marzán, Engineering the Structural Diversity in Gold Nanocrystals by Ligand-Mediated Interface Control. *Chem. Mater.*, 27, 8032, (2015)
4. A. Wan, T. Wang, T. Yin, **A. Li**, H. Hu, S. Li, Z. X. Shen, C. A. Nijhuis, Plasmon-Modulated Photoluminescence of Single Gold Nanobeams. *ACS Photonics*, 2, 1348, (2015)
5. L. Zhang, Y. Zhang, T. Hu, Q. Fan, W. Yang, **A. Li**, S. Li, W. Huang, and L. Wang, Refractive Index Dependent Real-time Plasmonic Nanoprobes on a Single Silver Nanocube for ultrasensitive Detection of the Lung Cancer-associated miRNAs. *Chem. Commun.* 51, 294, (2015)
6. Z. Zhang, **A. Li**, S. Cao, M. Bosman, S. Li, C. Xue, Direct Evidence of Plasmon Enhancement on Photocatalytic Hydrogen Generation over Au/Pt-Decorated TiO₂ Nanofibers. *Nanoscale* 6, 5217, (2014)
7. S. Pedireddy, **A. Li**, M. Bosman, I. Y. Phang, S. Li, X. Y. Ling, Synthesis of Spiky Ag-Au Octahedral Nanoparticles and Their Tunable Optical Properties. *J. Phys. Chem. C* 117, 16640, (2013)
8. Y. Tang, Z. Jiang, G. Xing, **A. Li**, P. Kanhere, Y. Zhang, T. C. Sum, S. Li, X. Chen, Z. Dong, Z. Chen, Efficient Ag@AgCl Cubic Cage Photocatalysts Profit from Ultrafast Plasmon-Induced Electron Transfer Processes. *Adv. Funct. Mater.* 23, 2932, (2013)
9. X. Zhang, Z. Li, S. Ye, S. Wu, J. Zhang, L. Cui, **A. Li**, T. Wang, S. Li, and B. Yang, Elevated Ag Nanohole Arrays for High Performance Plasmonic Sensors Based on Extraordinary Optical Transmission. *J. Mater. Chem.* 22, 8903, (2012)

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4. **A. Li**, and S. Li, Near-field and Far-field Properties of Spiky Nanoparticle Dimers. TechConnect World, Washington, DC, June 15-19, 2014. (poster presentation)
5. **A. Li**, and S. Li, Near-field and Far-field Properties of Spiky Nanoparticle Dimers. International Symposium on “30 Years of Surface Plasmon Resonance (SPR) in Biosensing”, Singapore, November 5-7, 2013. (poster presentation)

Summary

Noble metal nanoparticles (NPs) have been widely explored in surface-enhanced spectroscopies (SES) because of their ability to generate intense electric fields originating from the surface plasmon resonances. Particularly, coupled metallic NPs have attracted a lot of attentions in SES because they can generate much higher electric field enhancement than the single ones. In this study, two kinds of coupled structures, the dimer and the metal NP over the metal film (MNOMF), are examined using finite-difference time-domain method. Hot spots in these structures are optimized for high-performance SES.

Hot spots in dimers are usually confined within small volumes, limiting the sensitivity and reproducibility of SES. In this study, we show that Au spiky NP dimers (SNPDs) can provide large-volume hot spots, arising from the synergistic effect of “lightning rod effect” in spiky NPs and the interparticle coupling. The “hot spots volume” (defined as the whole volumes of all the regions with electric field enhancement larger than 1×10^4) in T–T SNPD is almost 5 times and 7 times larger than in the sphere dimer and spike dimer with the same 2 nm gap, respectively. In addition, further increased “hot spots volume” is achieved in crossed T–T SNPD, being ~ 1.5 times of that in T–T SNPD. At the same time, the electric field enhancement ($|E|^2/|E_0|^2$) in the tip-to-tip (T–T) SNPD with a 2 nm gap is as large as 1.21×10^6 . The results indicate a strategy to obtain huge-volume hot spots with large electric field enhancement in dimers by adding a bulky core at one end of the spindly building blocks.

We have shown SNPDs could provide hot spots with large volumes. Nevertheless, it is hard to fabricate SNPDs in experiments. Alternatively, spiky disk dimers (SDDs) on glass substrate may be fabricated using top-down lithography. We demonstrate crossed T–T SDD can generate much larger “hot spots volume” and much higher electric field enhancement than disk dimer. The results demonstrate the possibility to achieve large-volume hot spots in experiments.

In both SNPDs and SDDs, two adjacent particles are coupled in lateral direction. In experiments, it is difficult to achieve precisely controlled small gaps in dimers along lateral direction and hence limiting the enhancement of electric fields. On the contrary, MNOMF which offers coupling in vertical direction can provide even sub-1 nm gap, exhibiting great potentials for SES. In this study, we demonstrate a method to optimize the hot spots in MNOMF by exciting the localized surface plasmon resonances (LSPRs) using the surface plasmon polaritons (SPPs). We find the largest electric field enhancement and the highest surface-enhanced fluorescence intensity are obtained when the SPPs of the metal film are excited. The results show that exciting LSPRs using SPPs can generate 1-3 orders higher electric field intensity than direct exciting the LSPRs using incidence from free space. The ultrahigh enhancement is attributed to the strong confinement of the SPP waves in the vertical direction. The drastically intensified electric fields generated from excitation of LSPRs using SPP waves are extremely essential for sensitive refractive index sensing, high-performance SES, and enhancing the efficiency of optoelectronic devices.

Chapter 1 Introduction

This chapter gives a brief introduction to the whole thesis. Following a concise overview of previous researches, the problems existed in previous studies and the three hypotheses made in this work are stated. Then the objectives and scopes, the outline of this thesis, and the main findings and the significances of this work are listed.

1.1 Problem statement and hypotheses

1.1.1 Problem statement

Surface-enhanced spectroscopies (SES), for example, surface-enhanced fluorescence (SEF), surface-enhanced Raman scattering (SERS), and surface-enhanced infrared absorption (SEIRA), are highly sensitive techniques for chemical or biological detection.¹⁻³ In the past decades, noble metal nanoparticles (NPs) have been widely explored in SES because of their ability to generate intense electric fields originating from the surface plasmon resonances (SPRs).³⁻⁶ For excellent SES substrates, high reliability, reproducibility, and sensitivity are all required.⁷⁻¹⁰ It has been shown that huge electric field enhancement is essential for high sensitivity, and large “hot spots volume” is crucial for reliability and reproducibility.¹¹⁻¹⁴ In the past, lots of work has been performed to explore metallic nanostructures with large electric field enhancement for high-performance SES. Particularly, NP dimers and the metal NP over the metal film (MNOMF) have attracted a lot of attentions.

In dimer structures, drastically enhanced electric fields can be generated and localized at the interparticle junction, ascribing to the near-field interaction between two adjacent NPs.^{11-13, 15} However, hot spots in dimers are usually confined within small volumes, making it difficult for molecules to be adsorbed within small hot spots and consequently limiting the performance of NP dimers in SES. “Hot spots volume” in dimers can be increased by increasing the coupling surfaces.^{14, 16} Nevertheless, increasing coupling areas in NP dimers leads to weaker “lightning rod effect” and hence much smaller electric field enhancement within gaps.¹⁷

MNOMF can be easily fabricated by directly depositing NPs on top of the metal film. In MNOMF, intense electric fields are generated and localized at the junction between the NP and the film, ascribing to the coupling between the NP and its mirror image in the underlying metal film.¹⁸⁻²² Generally, the NP and metal film can sustain localized surface plasmon resonances (LSPRs) and surface plasmon polaritons (SPPs), respectively. Nevertheless, the SPPs of the underlying film were seldom considered in previous studies,

because SPPs cannot be directly excited using incidence from free space due to the momentum mismatch.²³

According to above-mentioned research background, the problems existed in current researches are summarized and listed:

- (1) For high-performance SES, it is important to obtain both high electric field enhancement and huge “hot spots volume”. Nevertheless, hot spots in dimers are normally confined within small volumes. And methods used to enlarge the “hot spots volume” in previous studies usually led to distinctly decreased electric field enhancement.
- (2) In MNOMF, the metal film can sustain SPPs. However, the SPPs of the underlying film in MNOMF were seldom considered in previous studies, because SPPs cannot be directly excited by incidence from free space due to the momentum mismatch.

1.1.2 Hypotheses

During the whole studies, three hypotheses are proposed:

- (1) We make the first hypothesis that Au spiky nanoparticle dimers (SNPDs) can provide huge “hot spots volume” and high electric field enhancement at the same time. According to previous studies, charges will accumulate at the sharp spikes of spiky nanoparticles (SNPs) due to the pronounced “lightning rod effect” of long spikes.^{24, 25} In addition, interparticle coupling in dimers also pumps up charges to interparticle junctions, resulting in drastically intensified electric fields confined at the narrow gaps.^{11, 15, 26} Taking advantages of both “lightning rod effect” of SNPs and strong interparticle coupling of dimers, SNPDs are anticipated to generate extremely intensified electric fields. Simultaneously, long spikes in SNPDs enable large coupling areas when they are in a side-to-side configuration, exhibiting great potentials to provide hot spots with large volumes.

- (2) Following the work about Au SNPDs, we make the second hypothesis that huge “hot spots volume” is not specific for free-standing SNPDs. We predict that hot spots with huge volume and large electric field enhancement can also be achieved in crossed tip-to-tip (T-T) spiky disk dimers (SDDs), even when the SDDs are placed on a glass substrate.

In crossed T-T SDDs, high electric field enhancement is anticipated because of the “lightning rod effect” of the spindly tip. At the same time, huge “hot spots volume” is expected ascribing to the large coupling areas between two parallel aligned tips.

(3) Considering the MNOMF system, we make the hypothesis that ultrahigh enhancement of the electric fields can be obtained when the SPP waves of the underlying metallic film is excited. We predict that the largest electric field enhancement can be obtained when the incidence angle is the SPP resonance angle of the metal film. When the incidence angle is the SPP resonance angle of the metal film, SPP waves can be generated at the metal-dielectric interface. The generated SPP waves can then hit the NP. Due to the strong confinement of the SPPs in vertical direction, a more efficient excitation of the LSPRs of the NP and consequently drastically enhanced electric fields are anticipated.

1.2 Objectives and scope

The overall objective of this study is to explore coupled noble metal nanostructures with extremely enhanced electric fields and huge “hot spots volume” for high-performance SES. In this study, Au SNPDs and Au crossed T-T SDDs are firstly investigated. Then taking the Au nanosphere over the Ag film as an example, the effects of the SPPs of the metal film on the hot spots in MNOMF are examined. The detailed objectives of this study are:

(1) To explore dimer structures that can generate both large electric field enhancement and huge “hot spots volume”. To investigate the extinction spectra, the electric field enhancement, and especially, “the hot spots volume” of Au SNPDs with various configurations, including T-T, tip-to-sphere (T-S), sphere-to-sphere (S-S), and crossed T-T configurations.

(2) To realize the huge “hot spots volume” and large electric field enhancement in experiments. To investigate the “hot spots volume” and electric field enhancement in SDDs with crossed T-T configuration.

(3) To investigate the effects of the SPPs of the underlying metal film on the hot spots in MNOMF. To optimize the electric field enhancement in MNOMF for high-performance SES.

1.3 Dissertation overview

The thesis consists of 7 chapters.

Chapter 1 is the introduction, including the problem statement, hypotheses, research objectives and scopes, the dissertation overview, and the findings and significances.

Chapter 2 gives a comprehensive literature review, including the SPRs of noble metal nanostructures, SES, noble metal nanostructures with hot spots, and methods to optimize the hot spots in metallic nanostructures for high-performance SES. Following the literature review, the research gaps are listed and the PhD in context of literature is provided.

Chapter 3 introduces the theoretical method used in this study, including the introduction of Maxwell's curl equations and the finite-difference time-domain (FDTD) method.

Chapter 4 investigates the hot spots in Au SNPDs. The influences of the SNPD configurations, the spherical core diameters, the hollow nanoshell core, and the polarization angle on the hot spots in Au SNPDs are studied. A methodology to achieve both huge "hot spots volume" and high electric field intensity in dimers is proposed.

Chapter 5 investigates the optical properties of Au crossed T-T SDDs. The "hot spots volume" and electric field enhancement in crossed T-T SDD are compared with those in disk dimer. The effects of glass substrate, disk diameter, tip width, tip length, structure thickness, gap size between two crossed tips, the longitudinal overlap distance between two crossed tips, and the polarization direction on the hot spots in crossed T-T SDDs are comprehensively investigated.

Chapter 6 investigates the effects of the SPPs of the Ag film on the hot spots in the Au sphere over the Ag film configuration. The electric field enhancement in the Au sphere over the Ag film at various incidence angles (including the SPP resonance angle of the Ag film) is calculated. The influences of the Si spacer thickness and the Au sphere diameter on the electric fields in the Au sphere over the Ag film are studied. The SEF experiments are performed to prove the theoretical predictions.

Chapter 7 shows the summary of this study and the future work.

1.4 Findings and significances

This research leads to three significant outcomes:

(1) The results shown in this study indicate that Au SNPDs are able to generate hot spots with simultaneously increased “hot spots volume” and electric field enhancement. Motivated by the huge “hot spots volume” in SNPDs, a method to achieve hot spots with huge volumes and large electric field enhancement in dimers is proposed by adding a bulky core at one end of the spindly building blocks. This finding is significant for designing and fabricating high-performance SES substrates. Previous studies showed that huge “hot spots volume” and large electric field enhancement are both important for excellent SES. However, hot spots in previous studies were generally confined within small volumes, limiting their performance in SES. And the methods used to increase the “hot spots volume” in previous studies usually led to obviously decreased electric field enhancement. The first finding breaks the general limitation that large “hot spots volume” usually comes with small electric field enhancement.

(2) In the following study, we show that simultaneously increased “hot spots volume” and electric field enhancement are not specific for SNPDs. We demonstrate that crossed T-T SDDs can also provide hot spots with both huge volume and large electric field enhancement. Even though SNPDs have been shown to provide hot spots with simultaneously increased “hot spots volume” and electric field enhancement, assembly of SNPs into SNPDs is difficult to control in current experiments. Compared with SNPDs, SDDs can be fabricated over large areas with well-controlled gaps using top-down

lithography. The finding about SDDs demonstrates the possibility to realize simultaneously increased “hot spots volume” and electric field enhancement in experiments. In addition, the results can serve as guidelines in fabricating and designing top-down lithography fabricated metallic substrates for high-performance SES.

(3) Finally, taking the Au nanosphere over the Ag film as an example, the effects of the SPPs of the metal film on the electric field enhancement in MNOMF are investigated. The Ag film is deposited on a prism in Kretschmann-Raether (KR) configuration to excite its SPPs. The results show that the largest electric field enhancement and the highest SEF intensity are obtained when the SPP waves of the underlying Ag film are excited. Because of the strong confinement of the SPP waves in vertical direction, SPPs can more efficiently excite the LSPRs of the NP, generating drastically enhanced electric fields. This finding is important for applications of MNOMF in sensitive refractive index sensing, high-performance SES, and enhancing the efficiency of optoelectronic devices.

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Chapter 2 Literature Review

This chapter gives a comprehensive literature review. The surface plasmon resonances of noble metal nanostructures are firstly introduced. Then, the applications of the noble metal nanostructures in surface-enhanced spectroscopies (SES) are presented. In addition, noble metal nanostructures with hot spots and methods to optimize the hot spots in metallic nanostructures for high-performance SES are also reviewed. Finally, following the literature review, the research gaps are listed and the PhD in context of literature is provided.

2.1 Surface plasmon resonances of noble metal nanostructures

SPR is the collective oscillation of conduction electrons at the surface of the nanostructures with a frequency in resonance with incident light.¹ Theoretically, any material with a negative real dielectric constant and a positive imaginary dielectric constant can support SPR.¹⁻⁴ Among all these materials, Au and Ag are the most widely used materials in plasmonics due to their high quality factor (Q), strong SPR in the visible or the near-infrared (NIR) regions, chemical inertness, and easy fabrication.⁴⁻⁶ Here, Q is defined as:⁵

$$Q = \frac{\omega(d\varepsilon_r/d\omega)}{2(\varepsilon_i)^2} \quad (2.1)$$

$\varepsilon_r, \varepsilon_i$ are the real and imaginary parts of the dielectric function of metallic NPs, respectively. Usually, ε_r determines the position of the resonance peak and ε_i relates to the damping and determines the shape and broadening of the resonance peak.⁷ Q directly shows the SPR strength, where larger Q indicates a stronger SPR and smaller Q means a weaker SPR. Q of SPRs for various materials is shown in Figure 2-1.⁴ Figure 2-1 shows that Ag nanostructure has higher Q than Au across most of the wavelength from 300 to 1200 nm. Nevertheless, compared with Ag, Au possesses pronounced chemical stability and resistance to oxidization and is more suitable for in vivo applications.⁸

Figure 2-1 Quality factor of the SPRs for various metals at the metal/air surface.⁴

Generally, there are two types of SPRs for noble metal nanostructures: SPPs and LSPRs.^{1, 4, 9, 10} For SPPs, plasmons travel along the metal-dielectric interface, and exponentially

decay into both media (Figure 2-2(a)).¹ SPPs are usually generated in structures with at least one dimension approaching the incidence wavelength, for example, thin metal films, nanowires, slits, films with nanoholes or grooves and so on. For the case of LSPRs, plasmons are generated for NPs much smaller than the incidence wavelength. The interaction between the incidence and the NP results in a plasmon oscillates locally around the NP with a frequency in resonance with the incident light, known as the LSPRs (Figure 2-2(b)).¹ LSPRs of noble metal NPs exhibit several unique wavelength-dependent phenomena.⁸ For example, metallic NPs can generate intense photon absorption, scattering, as well as extremely enhanced electric fields at their resonance wavelengths. Previous studies have shown that LSPRs of noble metal NPs strongly depend on the particle shape, size, composition, surrounding environment, and orientation when they are in aggregation status, enabling multiple ways to manipulate the plasmonic properties of noble metal NPs for desired applications.^{4, 7, 8, 11-13}

Figure 2-2 Schematic illustrations of (a) SPPs travel along the metal-dielectric interface and (b) LSPRs of a metallic nanosphere.¹

2.2 Noble metal nanostructures in surface-enhanced spectroscopies

SPRs enable several optical properties of noble metal nanostructures: intense photon absorption, scattering, and extremely enhanced electric fields at SPR resonance

wavelengths. Taking advantages of SPRs, various applications of noble metal NPs have been explored in the past decades.^{1, 2, 4, 8, 12} For instance, noble metal NPs have been widely used as refractive index sensors, ascribing to the sensitivity of LSPRs to the surrounding dielectric medium.^{2, 14-19} In LSPR refractive index sensing, introduction of analytes to the NP surface results in the local dielectric environment change and therefore leads to the shift of the LSPR position. Hence, the adsorption of analytes can be monitored by monitoring the shift of the LSPR position. Plasmonic ruler is another application of noble metal NPs. The resonance position of two coupled NPs changes as a function of the interparticle separation, forming the foundation of the plasmonic ruler.^{6, 12, 20, 21} According to the shift of the resonance position, the biomolecular distances can be measured, and the dynamic chemical or biological processes can be monitored.²² Noble metal NPs can also be used in cancer cell imaging and therapy through the enhanced thermal irradiation.²³⁻²⁸ In addition, noble metal nanostructures have been explored to improve the efficiency of optoelectronic devices.^{29, 30} Here, we focus our attention on the application of noble metal nanostructures in SES, for example, SERS, SEF, and SEIRA, which are sensitive techniques for chemical or biological detection. The applications of noble metal NPs in SES are ascribed to their ability to generate extremely enhanced electric fields stemming from SPRs.

2.2.1 Surface-enhanced Raman scattering

SERS is a highly specific, sensitive, and label-free technique for chemical or biological detection since Raman signals contain the detailed information of the vibrational energy levels of analytes.^{2, 31, 32} Generally, there are two principal mechanisms for the enhancement of Raman signals: the electromagnetic (EM) enhancement and the chemical enhancement, where the EM mechanism plays a major role.³¹⁻³⁵ The chemical enhancement mechanism arises from the charge transfer between the NP surface and molecule, which can explain the observation of selective enhancement of Raman scattering. When the Fermi level of the metal is at the half way between the lowest unoccupied molecular orbital and the highest occupied molecular orbital of the adsorbate, charge transfer excitations can occur at about half the energy of the inherent intramolecular excitations.³¹ The EM enhancement mechanism is associated with the

drastically enhanced electric fields generated by SPRs.³¹ For one thing, the strongly enhanced electric fields amplify the incident field, resulting in more photon-molecule interactions. For another thing, the intensified electric fields magnify the Raman scattered field, generating more detectable Raman scattered photons. A commonly used expression for describing the EM enhancement factor (EF_{EM}) considers both the incident field enhancement and the scattered field enhancement and is defined as:³⁶

$$EF_{EM} = |E(\omega)/E_0|^2 |E(\omega')/E_0|^2 \quad (2.2)$$

Where E is the local fields, E_0 is the incident fields, ω is the incident frequency and ω' is the scattered frequency. Therefore, it is important to get intensely enhanced electric fields at both ω and ω' for higher EF_{EM} in SERS. It has been demonstrated that the optimum condition for SERS could be obtained by engineering the LSPR wavelength falls between the exciting incidence and the wavelength of scattered photons.³⁷ By using a mixed dimer with double resonances matched the laser and Raman line of analytes respectively, larger SERS enhancement was achieved.³⁸ When neglecting the difference between the enhancement of emission light and that of incidence light, the EF_{EM} can be roughly calculated as $|E(\omega)/E_0|^4$.^{31, 34, 39}

2.2.2 Surface-enhanced fluorescence

Noble metal NPs also have been widely applied in SEF. In the process of SEF, the emission of resonant molecules near a metallic NP is strongly enhanced primarily due to the interaction between the intensified electric fields of the NP stemming from SPRs and the fluorophore in excited state.^{4, 40-43} In SEF, the excitation rate and decay rate of the molecule both increase.^{40, 41} For one thing, the enhanced electric fields induced by SPRs lead to increased excitation of fluorophores near metal surface. For another thing, fluorophore in excited state can interact with nearby metal NP to create plasmons which can create detectable emissions through radiation, resulting in decreased life times and therefore more emission cycles prior to photo bleaching. The nearby NP can also increase the intrinsic radiative decay rate of the fluorophore. In the past, SEF have been used for single molecule sensing, bio-imaging, medical diagnostics, and so on.^{40, 41, 44, 45}

2.2.3 Surface-enhanced infrared absorption

Similar to SERS, SEIRA is also a surface-enhanced vibrational spectroscopy and is usually used as a complementary technique of SERS to provide additional fingerprinting information of analytes in the infrared region.^{12, 46-48} In SEIRA, the enhancement of absorption is mainly associated with the intensified electric fields at the vicinity of metal NPs.⁴⁶⁻⁴⁸ Generally, the EM enhancement of SEIRA is proportional to the square of the local electric fields magnitude.^{48, 49} Serving as SEIRA substrates, metallic nanostructures should exhibit strong SPRs in the infrared region. For example, aggregated Au nanoshells have been used as effective SEIRA substrates due to their ability to provide a broad infrared SPR band.⁵⁰ It also has been demonstrated that assembled Au nanoshell arrays can be carefully manipulated to provide intense electric fields at both NIR and mid-infrared regions, simultaneously enhancing SERS and SEIRA.⁴⁹ Rodlike antennas and nanowires are also the commonly used nanostructures in SEIRA.^{51, 52}

2.3 Noble metal nanostructures with hot spots

As illustrated in part 2.2, strongly enhanced electric fields at the vicinity of metallic NPs stemming from SPRs play a dominant role in SES. It was shown that the greatly enhanced signals in SES mainly came from analytes positioned in the hot spots sites with intensely enhanced electric fields.⁵³⁻⁵⁸ During the past decades, considerable efforts have been devoted to investigating metallic nanostructures with optical hot spots. Particularly, intensely enhanced and highly localized electric fields can be obtained at the location outside sharp features of the nanostructures, or at the interparticle junctions between two adjacent nanostructures.^{57, 59-65}

2.3.1 Nanostructures with sharp features

Particle shape has significant effects on the optical properties of noble metal NPs.^{66, 67} It has been shown that NPs with anisotropic shape can provide highly tunable SPR bands, enabling applications in both visible and NIR regions.^{68, 69} For example, LSPR band of a nanorod can be easily controlled throughout the visible and the NIR region by gradually increasing its aspect ratio when the incidence is polarized along the nanorod length.^{19, 70} More importantly, NPs with anisotropic shape can generate much larger electric field enhancement confined at their sharp features than nanospheres.^{68, 69, 71-73} As shown in

Figure 2-3, extremely intensified electric fields can be generated at the sharp corners of the nanocube with a value much higher than in nanosphere.^{72, 73} The intensified electric fields at the sharp features of the NPs are because of the “lightning rod effect”.^{33, 74, 75} Hot spots generated at the sharp corner of nanocubes, the apex of the nanoprisms, the end of the nanorods, the tip of the nanocrescents, and particularly, the sharp tip of the nanostar or the spiky NP (SNP) have been applied in SES.^{61, 63, 71-73, 76-80}

Figure 2-3 Electric field enhancement for (A,B) a Ag nanocube and (C,D) a Ag nanosphere in water with 514 nm incidence. The polarization direction of incidence is indicated by the red arrow in (B, D). The scale bar in figure (A,C) is 10 nm.⁷³

Nanostar or SNP consists of a bulky spherical core and protruding sharp spikes. Previous studies showed that nanostar exhibited highly tunable LSPRs through visible to NIR spectral regions and provided drastically enhanced electric fields at its sharp tips.^{61, 81} In nanostar, the spherical core serves as a nanoscale antenna and an electron reservoir, significantly enhancing the electric fields of the spike plasmons when comparing with that of an isolated spike.⁶¹ Moreover, the protruding spike enables the localization of electric fields at its apex because of the “lightning rod effect”.⁶¹ Both of these two factors

result in the much larger electric fields in nanostar than in nanocube, nanorod, nanoprism, and so on.^{61, 82} In nanostar, each protruding tip can be a potential hot spot region depending on the polarization direction of incidence.^{61, 81, 82} With varying the polarization angle of incidence, the location with the largest electric field enhancement varies accordingly (Figure 2-4). In analogy to nanostar, SNP can also generate hot spots at the apexes of its sharp spikes. It was shown that spike length had a substantial influence on the resonance peak and the electric field enhancement in SNPs.⁸³⁻⁸⁶ The red most resonance peak exhibits obvious red shift with increasing spike lengths (Figure 2-5).⁸⁶ Meanwhile, significant increase of the electric field enhancement at the spike tip from ~ 180 to $\sim 10^4$ was observed with rising spike lengths from 50 nm to 137 nm.⁸⁶ SNP has been widely applied in the field of LSPR sensing, SERS, diagnostics, and photothermal therapy.^{28, 85, 87-95}

Figure 2-4 Electric field distributions of a Au nanostar at (a) 804 nm, (b) 717 nm, and (c) 594 nm, respectively.⁶¹

Figure 2-5 Influence of spike length on (a) extinction spectra and (b) electric field enhancement of Ag-Au spiky hollow octahedra.⁸⁶

2.3.2 Coupled nanostructures with nanoscale gaps

NP with anisotropic shape can generate intensified electric fields at its sharp features, ascribing to the “lightning rod effect”. Nonetheless, electric field enhancement in a single NP is relatively small. A more efficient geometry that can generate strongly enhanced electric fields is coupled metallic nanostructures with nanoscale gaps.^{12, 39, 53, 62, 78, 96} Upon aggregation, noble metal NPs are able to couple with adjacent ones through near field interaction, resulting in both the shift of their resonance positions and the drastically intensified electric fields localized at the interparticle junctions.^{6, 12, 62, 78, 97-99} The coupling between two adjacent metal NPs can be described by a plasmon hybridization model.¹⁰⁰ According to the hybridization model, plasmon response of a complex nanostructure with any shape can be expressed as the interaction or hybridization between simpler elemental parts in analogous to the molecular-orbital theory.¹⁰⁰

As shown in Figure 2-6(a), the plasmon resonance of a nanoshell composed of a silica core and a Au shell can be explained as the interaction between a solid Au sphere and a spherical cavity inside bulky Au. The interference results in a bonding plasmon mode with symmetric charge distribution at lower energy and an anti-bonding plasmon mode with anti-symmetric charge distribution at higher energy.¹⁰⁰ The interaction strength,

which determines the shift of the plasmon energy, depends on the shell thickness. Plasmon hybridization theory has been successfully used to describe many complex nanostructures since its initial demonstration. For example, the plasmon resonance of a Au nanostar could be explained as the hybridization of plasmon resonances of the core and the sharp tips.⁶¹ The splitting of plasmon resonance mode of two closely packed nanospheres was attributed to the hybrid coupling between each nanosphere, resulting in one bonding plasmon mode with lower energy, and one anti-bonding mode with higher energy (Figure 2-6(b)).⁴ In NP dimers, the coupling strength strongly depends on the gap size, where smaller gap leads to stronger coupling and therefore larger energy shift and higher electric field enhancement.

Figure 2-6 Plasmon hybridizations in (a) metal nanoshells¹⁰⁰ and (b) Ag nanosphere dimers with 2 nm and 10 nm gap⁴.

NP dimer is one of the simplest coupled structures with nanoscale gaps. In dimer structure, NP couples with the neighboring one through near-field interaction, generating extremely intensified electric fields localized at the interparticle junction. The hot spots confined within nanoscale gaps of dimers are essential for SES, and particularly, enable single-molecule detection.^{53, 58, 101, 102} The coupling effect in dimer structure is highly sensitive to the polarization direction of the incidence.¹⁰³⁻¹⁰⁷ As shown in Figure 2-7, the highest electric field enhancement in nanosphere dimer is obtained for incidence polarized along the interparticle axis, whereas the electric fields are excluded from the interparticle junction when the polarization of incidence is perpendicular to the dimer axis.¹⁰⁵ For parallel polarized incidence, the electric field enhancement within gap

regions also strongly depends on the interparticle separation.^{78, 108, 109} With increasing gap distance, a drastic decrease of the electric field enhancement is observed, resulting from the decreased coupling strength.^{78, 108, 109} In addition, the decrease of electric fields with rising interparticle separation follows an exponential equation (Figure 2-8).¹⁰⁹

Figure 2-7 Electric field distributions of the Ag nanosphere dimer at 514.5 nm with (a) 0°, (b) 30°, (c) 60°, and (d) 90° polarization angles.¹⁰⁵

Figure 2-8 Influence of gap size on (a) electric field distributions and (b) electric field enhancement at the gap center of Au nanoring dimers at their corresponding resonance conditions. The dotted line shows the exponential fitting result.¹⁰⁹

Figure 2-9 Contours of $|E|^4$ for (a) an isolated cylindrical rod, nanorod dimers with (b) end-to-end, (c) perpendicular, and (d) side-to-side configurations. The scale bar is 40 nm, the numbers in (b,c,d) represent the increase of $|E|^4$.³⁹

The geometry of the building blocks also has a significant influence on the optical properties of dimers.^{39, 78, 110-112} Generally, building blocks with anisotropic shapes provide larger electric field enhancement. For example, compared with spherical dimer, bowtie antenna composed by two opposing tip-to-tip prisms can provide larger electric field enhancement within gap region.^{45, 78} For dimers composed by NPs with anisotropic shapes, electric field enhancement within gap region further depends on the orientation of the building blocks. As shown in Figure 2-9, nanorod dimer with end-to-end configuration exhibits the largest electric field enhancement, followed by the rod dimer with perpendicular configuration, and then rod dimer with side-by-side configuration.³⁹

Coupled nanostructures with nanoscale gaps can be obtained by either assembly method using DNA or organic molecules as linkers or top-down lithography method.^{4, 6, 98, 113, 114} In assembly method, the gap distance can be controlled by the length of the linker selected, where gap distance as small as 1 nm can be achieved.¹¹³ However, hot spots generated from assembly are usually randomly distributed with low controllability and reproducibility, limiting their performance in SES.¹¹⁵⁻¹¹⁷ Compared with assembly method, lithography method can produce nanostructures with well controlled gaps.⁴ In the past, well-defined nanodisk dimers, nanoring dimers, nanorod dimers, and bowtie

antennas have been successfully fabricated over large areas using focused ion beam lithography or electron beam lithography.^{109, 118-120}

Figure 2-10 The dipole-dipole interaction between a Ag NP and a Au film separated by a silica spacer with small thickness d .¹²¹

Figure 2-11 Influence of the polyelectrolyte spacer thickness on (a) Electric field distributions ($|E|$) at 633 nm, (b) scattering efficiency, and (c) average $|E|^4/|E_0|^4$ at 633 nm for a 60 nm Au NP over a 45 nm Au film with 75° incidence angle.¹²²

The MNOMF, which can be easily fabricated by directly depositing NPs on top of the metal film, is another kind of structure that can provide nanoscale gaps. In MNOMF, the NP can couple with its mirror image in the underlying metallic film, resulting in both the red shifted resonance position and the intensely enhanced electric fields confined at the

junction between the NP and the film.^{121, 123-126} As shown in Figure 2-10, the p-polarized incidence can be decomposed into a horizontal field element (E_{in-x}) and a normal field element (E_{in-z}). Upon illumination, E_{in-x} excites the lateral dipole oscillation in Ag NP. When the Ag NP is close to the Au film, an anti-parallel image dipole oscillation can be induced in the Au film. In this case, the dipole moment in the Ag NP is cancelled out by the induced anti-parallel dipole moment in the Au film. Similarly, the E_{in-z} excites a normal dipole oscillation in the Ag NP. The normal dipole oscillation in the Ag NP can induce the normal image dipole oscillation in Au film. The normal dipole moment in Ag NP can then resonantly couple with the induced normal dipole moment in the Au film, generating the intensified electric fields at the junction between the Ag NP and the Au film. In MNOMF, the coupling strength between the NP and the underlying film can be well-controlled by adjusting the dielectric spacer thickness between the metallic NP and the film.^{121, 122, 125-129} As shown in Figure 2-11, with increasing the dielectric spacer thicknesses, obvious blue shift of the resonance position and distinct decrease of the electric field enhancement within gap are observed, ascribing to the decreased coupling strength between the Au NP and the Au film.¹²²

Working as sensing substrates, the MNOMF configuration possesses many advantages. For example, MNOMF can be fabricated using low-cost and simple methods over large areas by directly depositing the NPs on top of the metal film.^{65, 122, 125} In addition, the resonance position of the MNOMF can be well-tuned by precisely adjusting the dielectric spacer thickness.^{121, 122, 125-128} The accurate manipulation of the dielectric spacer thickness also enables the generation of highly uniform and reproducible gaps between the NP and the film, which is significant for highly sensitive and reproducible SES.^{122, 130, 131} Moreover, MNOMF provides coupling in vertical direction. For two NPs coupled in lateral direction, it is a challenging task to obtain very small gaps between them. Nevertheless, it is feasible to obtain small gaps in vertical direction. In the MNOMF, uniformly distributed gaps with sub-1 nm size can be developed, which is important for generating extremely enhanced electric fields in coupled nanostructures.^{122, 128, 129, 131} Due to the aforementioned advantages, MNOMF has been widely explored for high-performance SES.^{65, 125, 130-135} Previous studies showed that $\sim 60^\circ$ incidence angle gives

the largest electric field enhancement and the maximum SERS intensity for the MNOMF configuration, ascribing to the coherent superposition of the reflected field components and the incident field components (Figure 2-12).^{125, 136} In the past decades, the MNOMF has been extensively applied in SERS, plasmon-enhanced photoluminescence, and other techniques.^{116, 133, 137-139}

Figure 2-12 Effects of the incidence angle on (a) the measured SERS spectra, and (b) the electric field enhancement factors for a 35 nm Au NP over a 200 nm Au film separated by 3 nm SiO₂ dielectric spacer at 633 nm.¹²⁵

2.4 Methods to optimize the hot spots in noble metal nanostructures

High reliability, reproducibility, and sensitivity are required for good SES substrates.^{35, 95, 140-143} It has been shown that huge electric field enhancement is essential for sensitive SES, especially for single-molecule detection, and huge “hot spots volume” is crucial for reliable and reproducible SES.^{53, 58, 101, 110} Therefore, it is significant to optimize the hot spots in noble metal nanostructures for high-performance SES.

2.4.1 Methods to increase electric field enhancement

Literature review shown in part 2.3 indicates that lots of work has been done in the past to explore metallic nanostructures with intensely enhanced electric fields. It was shown that much larger electric field enhancement can be obtained by fabricating nanostructures with sharp features, ascribing to the “lightning rod effect”.^{61, 69, 72} For example, nanocubes can provide intense electric fields confined at their sharp corners.^{63, 71-73} Nanoprisms can generate intense electric fields localized at their apexes.^{76, 78} Nanostars or SNPs can produce strong local electric field enhancement at their sharp spikes.^{61, 86} In addition, researchers demonstrated that coupled nanostructures with nanoscale gaps were more efficient in generating intensely enhanced electric fields. In coupled metallic NPs, the NP couples with the adjacent one through near-field interaction, generating hot spots located at the interparticle junction.^{6, 12, 62, 98} In the past, coupled dimer structures have been widely explored for SES. It was found that the electric field enhancement in dimer can be optimized by manipulating its building blocks, where dimers composed by building blocks with anisotropic shapes are able to generate much larger electric field enhancement than dimers composed by nanospheres. For example, bowtie antenna composed by two opposing tip-to-tip prisms or crescent dimer composed by two opposing crescents can provide much larger electric field enhancement within gap region than nanosphere dimer.^{45, 78, 144} It was also shown that the electric field enhancement in bowtie antenna arrays could be increased by carefully decreasing the gap size between the two prisms or by decreasing the radius of curvature of the prism corners.¹²⁰ For dimers composed by building blocks with anisotropic shapes, the electric field enhancement within gap region also depends on the orientation of the building blocks. McMahon et al. showed that the largest electric field enhancement is obtained in nanorod

dimer with end-to-end configuration, whereas the electric field enhancement within gap region of rod dimer with side-by-side configuration is much smaller.³⁹

2.4.2 Methods to optimize hot spots volume

Previous studies mainly focused on exploring metallic nanostructures with extremely enhanced electric fields, where the largest electric field enhancement attracts the most attention.^{53, 57, 58, 60, 61, 77, 101} Nevertheless, hot spots in previous studies were generally in small volumes, making it difficult to direct analytes into small hot spots and consequently limiting the reproducibility of SES detection. In the past, several strategies have been performed to optimize the “hot spots volume” in noble metal nanostructures, including reducing cold spots areas and increasing coupling areas.¹⁴⁵⁻¹⁴⁸

Figure 2-13 Reducing cold spots areas in Ag nanocone arrays. (a) Helium ion microscopy image (45°) and schematic illustration of unprocessed Ag cone arrays. (b) Hot spots isolation process. (c) Raman spectra from unprocessed Ag cone arrays and processed Ag cone arrays with isolated hot spots.¹⁴⁶

Hot spots within metallic nanostructures can be optimized by decreasing the cold spots areas.^{146, 147} When screening the cold spots areas and only exposing the hot spots to surrounding medium, analytes are only allowed to adsorb at the hot spots sites, resulting in much larger Raman intensity from the same number of molecules, as demonstrated by Diebold et al. (Figure 2-13).¹⁴⁶ In their studies, ordered arrays of cones covered with aggregates of Ag NPs were firstly fabricated. In this kind of structure, hot spots are located at the sharp tip of each cone. Secondly, a positive-tone photoresist is spin-coated on the Ag cone arrays to cover the surface. This photoresist layer can prevent analytes from adsorbing on the Ag surface. Then, a femtosecond laser pulse is scanned over the photoresist, selectively removing the photoresist covering the hot spots and uncovering only the hot spots regions. In this hot spots isolation process, the exposure fluence plays a significant role in determining the hot spots areas to be exposed. At the optimum exposure fluence of 200 J/m^2 , Raman intensity from the same number of molecules adsorbed on hot spots isolated substrate is 27 times larger than that adsorbed on unprocessed substrate.

Despite the enhanced Raman intensity, hot spots isolation also helps to get more reproducible and reliable SERS detection (Figure 2-14).¹⁴⁷ Hot spots for concave nanocube are located at its sharp corners. Using a chemical etching process, hot spots isolation on Au concave cubes can be achieved (Figure 2-14(a)). Compared with bare concave cubes, Raman intensity for corner isolated concave cube is smaller (Figure 2-14(c)). However, considering the extremely small area of exposed corner, SERS enhancement factor for corner isolated concave cube is 2 orders greater than for bare concave cube. More importantly, Figure 2-14(d) shows that bare concave cube exhibits a wide variety of Raman signal intensities, while the variation of Raman intensity from hot spots isolated concave cube is extremely reduced, indicating a more reliable SERS detection using hot spots isolated cube. The narrow distribution of Raman intensity from hot spots isolated concave cube is because the analytes can only adsorb at hot spots sites with similar electric field enhancement. In aforementioned two examples, the improved performance in SERS by masking cold spots areas are because molecules are allowed to bind only at hot spots regions. However, masking cold spots areas only leads to the

relatively increased hot spots regions. The actual “hot spots volume” remains unchanged and is still small.

Figure 2-14 Reducing cold spots areas in Au concave nanocubes. (a) Illustration of the method used to uncover the concave cube corners. (b) SEM images of SiO₂-coated concave cube (A), coated with SiO₂ and etched obtaining a hollow shell (B), a bare concave cube (C), and corner-isolated concave cube (D). The scale bar is 100 nm. (c) Single-particle SERS from the four structures shown in (b). (d) SERS intensity distribution of single bare concave cube and corner-isolated concave cube.¹⁴⁷

Besides reducing cold spots areas, increasing coupling areas is another method used to optimize the hot spots in metallic nanostructures. Increasing the coupling areas was usually used to enlarge the “hot spots volume” in coupled nanostructures.^{110, 119, 145, 148, 149}

For example, enlarged “hot spots volume” in Au nanorod dimer was achieved by increasing the coupling areas through manipulating its gap geometry from a straight one to a slanted one, resulting in the improved SERS performance.¹¹⁹ By placing a Au nanosphere into a cylindrical hole in a metallic film, the same direction of the curvatures of the hole edge and nanosphere enables the larger coupling areas between hole-particle

pairs and consequently larger “hot spots volume”, generating larger SERS enhancement comparing with spherical dimers.¹⁴⁹ In nanosphere dimer, the coupling area is much smaller due to the opposite curvature of the two NPs at gap region.

Figure 2-15 Manipulating the coupling areas in Ag nanocube dimers for optimized SERS. (a) SERS spectra for Ag nanocube dimers with FF, FE, and EE configurations functioned with 4-MBT. The images on the right show the SEM images of the probed dimers. The scale bar is 100 nm.¹⁴⁸ (b) Illustration of the hot spots in nanocube dimers shown in (a).¹⁴⁸ (c) Electric field distributions at the junction of Ag nanocube dimers with 80 nm edge lengths and 2 nm gap size in FF, FE, and EE configurations at their corresponding resonance conditions (750 nm, 670 nm, and 670 nm, respectively).¹¹¹

The coupling areas in dimer can also be increased by controlling the orientation of its building blocks. As shown in Figure 2-15, nanocube dimer with face-to-face (FF) alignment produces hot spots with the largest volume, followed by nanocube dimer with face-to-edge (FE) and then edge-to-edge (EE) configurations.¹¹¹ The largest “hot spots volume” in FF cube dimer enables the largest number of molecules to be adsorbed within hot spots regions, resulting in the highest SERS intensity for FF cube dimer with a value being more than 10 times larger than that from EE nanocube dimer.¹¹¹ Figure 2-16 shows the comparison between nanopyramid dimers with different configurations for SERS.¹⁴⁵ In nanopyramid dimer with side-to-side configuration, coupling happens between one pair of parallel faces. While in stacked nanopyramid dimer, interparticle coupling occurs between four pairs of parallel faces. The increased number of coupling faces in stacked nanopyramid results in the greatly increased Raman-active volumes and therefore

enhanced Raman signals. Nevertheless, increasing coupling areas in NP dimer leads to a smaller curvature of the geometry at gap region, and consequently results in a much smaller electric field enhancement.¹¹¹ As shown in Figure 2-15(c), the electric field intensity in FF nanocube dimer is much smaller than that in EE nanocube dimer (Figure 2-15(c)). And in nanopyramid dimer, the highest electric fields are generated at the tip and edges of nanopyramid rather than the faces of nanopyramid (Figure 2-16(c)).

Figure 2-16 Manipulating the coupling areas in nanopyramid dimer for optimized SERS. (a) Schematic illustrations and SEM images of a single nanopyramid, a side-to-side nanopyramid dimer, and a stacked nanopyramid dimer. (b) Raman spectra of structures shown in (a) coated with a monolayer of methylene blue molecules at 633 nm. (c) Electric field distributions ($\log_{10}(|E_z|^2)$) of a single nanopyramid and nanopyramid dimers at 633 nm.¹⁴⁵

2.5 Research gaps based on literature review

The literature review indicates that extremely enhanced electric fields play a dominant role in SES. Many related works have been carried out to explore noble metal nanostructures with high electric field enhancement. Particularly, it was shown that:

(1) Comparing with the isolated NP, NP dimer can generate much higher electric field enhancement at the interparticle junction, ascribing to the coupling between two adjacent NPs.

(2) In MNOMF, the NP can couple with its mirror image in the underlying metallic film, generating intensely enhanced electric fields at the junction between the NP and the film.

By carefully analyzing the literature review, the research gaps are listed:

(1) High electric field enhancement and huge “hot spots volume” are both essential for high-performance SES. However, hot spots in dimers are usually confined within small volumes. Methods used before to increase the “hot spots volume” in dimers usually bring obviously decreased electric field enhancement at the gap regions.

(2) In MNOMF, the NP and the metal film can sustain LSPRs and SPPs, respectively. Nevertheless, the SPPs of the underlying metal film were seldom considered in MNOMF since SPPs cannot be directly excited using incidence from free space.

2.6 PhD in context of literature

To solve the listed research gaps shown in part 2.5, the following works are carried out one by one during my PhD study:

(1) Exploring NP dimers with both huge “hot spots volume” and large electric field enhancement for high-performance SES.

Firstly, Au SNPDs are investigated. We demonstrate that Au SNPDs can generate large electric field enhancement and huge “hot spots volume” at the same time, exhibiting great potentials for high-performance SES.

However, assembly of SNPs into SNPDs is hard to control, making it difficult to obtain SNPDs in current experiments. Therefore, following the work about Au SNPDs, Au crossed T-T SDDs are further investigated. We show that crossed T-T SDDs can also provide both huge “hot spots volume” and high electric field enhancement, because of the “lightning rod effect” and the large coupling areas between two parallel aligned nanobars. Since crossed T-T SDDs may be fabricated with well-controlled geometries using top-

down lithography, the results demonstrate the possibility to obtain both huge “hot spots volume” and high electric field enhancement in experiments.

(2) Investigating the effects of SPPs of the underlying metal film on the hot spots in MNOMF.

Taking the Au nanosphere over the Ag film as an example, the effects of the SPPs of the metal film on the hot spots in MNOMF are examined. In order to excite the SPPs at the top surface of the Ag film, the Ag film is deposited on a prism in KR configuration. We demonstrate that the largest electric field enhancement and the highest SEF intensity are obtained when the SPPs of the Ag film are excited. We show that SPP waves can more efficiently excite the LSPRs of the NP than incidence from free-space, ascribing to the strong confinement of the SPPs in vertical direction. The results demonstrate a strategy to optimize the performance of MNOMF in refractive index sensing and SES by exciting the LSPRs of NPs using SPP waves.

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Chapter 3 Theoretical Method

This chapter gives an introduction to the theoretical method used in this study. The Maxwell's equations are firstly provided, which can be used to describe the interaction between electromagnetic waves with any materials. Then the finite-difference time-domain (FDTD) method used to solve the Maxwell's curl equations is introduced. Both the rationale and the advantages of the FDTD method are presented.

3.1 Maxwell's curl equations

Maxwell's equations are the foundations of classical electrodynamics, classical optics, and electric circuits. The solutions of the Maxwell's equations can describe the interaction between incident light and any materials. In linear, isotropic and nonmagnetic medium, Maxwell's electric flux dependent equations are given by

$$\frac{\partial \vec{D}}{\partial t} = \nabla \times \vec{H} - \vec{J} \quad (3-1)$$

$$\frac{\partial \vec{B}}{\partial t} = -\nabla \times \vec{E} \quad (3-2)$$

And $\vec{D}$ ($\vec{B}$) is related to $\vec{E}$ ($\vec{H}$) by the following equations:

$$\vec{D} = \varepsilon(\omega) \vec{E} \quad (3-3)$$

$$\vec{B} = \mu_0 \vec{H} \quad (3-4)$$

Where $\vec{H}$, $\vec{B}$, $\vec{D}$, $\vec{J}$, $\vec{E}$ are the magnetic field intensity (A/m), magnetic flux density (Wb/m²), electric flux density (C/m²), electric current density (A/m²), and electric field intensity (V/m), respectively. $\varepsilon(\omega)$ and μ_0 are the electric permittivity (F/m) of the medium and the magnetic permeability (H/m) of free space.

3.2 Finite-difference time-domain method

3.2.1 General overview

For spherical metallic NPs and infinite long cylinders, Maxwell's equations can be analytically solved using Mie theory.¹ However, for other complex geometries, Maxwell's equations can only be solved using numerical methods, such as FDTD method, finite element method, discrete dipole approximation method, and so on.² FDTD method is a simply programmed, explicit time marching algorithm with second order accuracy.³ This method was originally proposed by Kane Yee in 1966, who replaced all time and space derivatives in Maxwell's equations with finite-difference (central-difference) expressions.⁴ FDTD method possesses some primary advantages.³ Firstly, there's no linear algebra in FDTD method, which decreases the computational overhead required to solve one specific problem. Secondly, modeling a structure is reduced to mesh generation instead of the complicated reformulation of an integral equation. Thirdly, the sources of errors are well known and restricted to make precise models. Moreover, being a time-domain method, the EM fields at any time during the FDTD simulation can be monitored

and shown through color videos, which is essential for the study of electrodynamics. And the solutions can cover a broad frequency range in one simulation. In the past decades, FDTD method has been widely applied in the field of plasmonics to study the near-field and far-field EM responses.^{2, 5-9}

3.2.2 Numerical methodology

Following Yee, uniformly spaced grids are introduced by dividing the selected space into various rectangular unit cells (Yee cells). The grid point of the space lattice is represented by

$$(i, j, k) = (i\Delta x, j\Delta y, k\Delta z) \quad (3-5)$$

For any function F of time and space assessed at a grid point is denoted as

$$F(i\Delta x, j\Delta y, k\Delta z, n\Delta t) = F_{i,j,k}^n \quad (3-6)$$

where i, j, k , and n are integers. $\Delta x, \Delta y, \Delta z$ are the dimensions of each grid along the x, y, z directions, and Δt is the time growth. Based on finite-difference expressions, the first partial space derivative of F in x direction at $t_n = n\Delta t$ is

$$\frac{\partial F_{i,j,k}^n}{\partial x} = \frac{F_{i+1/2,j,k}^n - F_{i-1/2,j,k}^n}{\Delta x} + O(\Delta x^2) \quad (3-7)$$

The first partial time derivative of F at the grid point (i, j, k) is

$$\frac{\partial F_{i,j,k}^n}{\partial t} = \frac{F_{i,j,k}^{n+1/2} - F_{i,j,k}^{n-1/2}}{\Delta t} + O(\Delta t^2) \quad (3-8)$$

which gives the second order accuracy both in space and time increments.

When solving Maxwell's curl equations using FDTD method, the magnetic and electric field components in a Yee cell are represented on discrete spatial grids and are shifted by half-grid points relative to each other.¹⁰ As shown in Figure 3-1, the magnetic field components are located at the center of the faces of a unit cell and the electric field components are at the middle of the edges.¹⁰ Each grid cube has a specific dielectric function $\varepsilon(\omega)_{i,j,k}$. Using FDTD method, the electric fields are solved at a specific moment of time. Then, the magnetic fields are solved at the next moment. This process is repeated again and again over the time. Consequently, the variation of the EM fields at each grid point can be deduced in time given the initial value.

Figure 3-1 Locations of electric field and magnetic field components in a rectangular unit cell of a 3D Yee lattice.¹⁰

Considering the x component of $\vec{E}$ in the Maxwell's curl equations:

$$\frac{\partial E_x}{\partial t} = \frac{1}{\varepsilon(\omega)} \left[\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} - J_x \right] \quad (3-9)$$

The discrete form of the x component of $\vec{E}$ at $(i, j, k, n - 1/2)$ is given by taking the finite difference approximation:

$$\begin{aligned} & \frac{E_x|_{i,j,k}^n - E_x|_{i,j,k}^{n-1}}{\Delta t} \\ &= \frac{1}{\varepsilon(\omega)^{n-1/2}_{i,j,k}} \left[\frac{H_z|_{i,j+1/2,k}^{n-1/2} - H_z|_{i,j-1/2,k}^{n-1/2}}{\Delta y} - \frac{H_y|_{i,j,k+1/2}^{n-1/2} - H_y|_{i,j,k-1/2}^{n-1/2}}{\Delta z} - J_x|_{i,j,k}^{n-1/2} \right] \end{aligned} \quad (3-10)$$

According to the semi-implicit approximation:

$$J_x|_{i,j,k}^{n-1/2} = \sigma_{i,j,k}^{n-1/2} \cdot E_x|_{i,j,k}^{n-1/2} = \sigma_{i,j,k}^{n-1/2} \cdot \frac{E_x|_{i,j,k}^n + E_x|_{i,j,k}^{n-1}}{2} \quad (3-11)$$

Where σ is the material conductivity. Assuming $H_z^{n-1/2}$, $H_y^{n-1/2}$, E_x^{n-1} are known at all spatial samples, then, $E_x(i\Delta x, j\Delta y, k\Delta z, n\Delta t)$ can be solved based on equation 3-10.

Similarly, $H_x(i\Delta x, j\Delta y, k\Delta z, (n + 1/2)\Delta t)$ can be solved from the finite-difference equations of the x component of $\vec{H}$ at (i, j, k, n) :

$$\frac{H_x|_{i,j,k}^{n+1/2} - H_x|_{i,j,k}^{n-1/2}}{\Delta t} = \frac{1}{\mu_0} \left[\frac{E_y|_{i,j,k+1/2}^n - E_y|_{i,j,k-1/2}^n}{\Delta z} - \frac{E_z|_{i,j+1/2,k}^n - E_z|_{i,j-1/2,k}^n}{\Delta y} \right] \quad (3-12)$$

Obviously, the renewed value of the electric field $\vec{E}$ (or magnetic field $\vec{H}$) at any lattice point in space depends on the stored value of the electric field $\vec{E}$ (or magnetic field $\vec{H}$) and the numerical curl of the local distribution of the magnetic field $\vec{H}$ (or electric field $\vec{E}$) in space, resulting in a marching-in-time process.

In FDTD method, the EM fields are solved as a function of time. EM fields as a function of frequency can be achieved using the Fourier transform:

$$\vec{E}(\omega) = \int_0^\infty e^{-i\omega t} \vec{E}(t) dt \quad (3-13)$$

To maintain the computational stability, the space increment and time increment must satisfy the “courant condition”^{3, 11}:

$$\Delta t \leq S_c \frac{\Delta}{c_0 \sqrt{D_m}} \quad (3-14)$$

where S_c is the Courant number that lies between 0 and 1, Δ is the minimal mesh size, C_0 is the wave-propagation velocity and D_m is the dimensionality.

To get accurate results, the grid size must be small enough to describe the structural features. Once Δ is selected, the maximum of time step can be determined. Generally, smaller mesh size and time step result in more accurate results but larger memory requirement. Therefore, a balance should be maintained between mesh size, time step and memory requirement. In addition, it is more important to choose proper time step than determine the appropriate mesh size. A slightly too large time step will lead to an exponentially increased error, resulting in an unstable and divergent result.^{3, 5}

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Chapter 4 * Large-volume Hot Spots in Gold Spiky Nanoparticle Dimers

Hot spots in coupled metal nanostructures are usually confined within small volumes, impairing their performance in surface-enhanced spectroscopies. In this chapter, we aim to explore dimer structures with both huge “hot spots volume” and high electric field enhancement. Using finite-difference time-domain method, we show that SNPD in a tip-to-tip (T-T) configuration generates the strongest electric fields lie in the gap region. The electric field enhancement ($|E|^2/|E_0|^2$) in a T-T SNPD with 2 nm gap can be as high as 1.21×10^6 . Moreover, the “hot spots volume” in T-T SNPD is almost 5 times and 7 times larger than that in sphere dimer and spike dimer with the same 2 nm gap, respectively. “Hot spots volume” in SNPD can be further augmented by manipulating the orientations of spiky nanoparticles, where crossed T-T SNPD generates the largest “hot spots volume” being 1.5 times of that in T-T SNPD. The results indicate a strategy to obtain both huge “hot spots volume” and intense electric fields in dimers by adding a bulky core at one end of the spindly building blocks.

* A. Li and S. Li, *Nanoscale*, 2014, 6, 12921-12928.

4.1 Introduction

Noble metal NPs have been widely explored for SES, because of their ability to generate enhanced electric fields originating from the SPRs.¹⁻⁴ It has been shown that the greatly enhanced signals in SES mainly came from analytes adsorbed at the hot spots sites with intensely enhanced electric fields.⁵⁻¹⁰ Therefore, lots of work has been done in the past to explore metallic NPs with optical hot spots. It was shown that intensified electric fields could be generated at the sharp features of nanostructures, ascribing to the “lightning rod effect”.¹¹⁻¹³ Compared with a single NP, a more effective structure to generate strongly enhanced electric fields is coupled metallic nanostructure with a nanoscale gap.^{2, 5, 14-17} Upon aggregation, drastically enhanced electric fields can be generated at the junction between two adjacent NPs. NP dimer is one of the simplest coupled structures with a narrow gap and has been extensively applied in SES.^{2, 9, 14, 15, 18, 19}

Excellent SES substrates require high reliability, reproducibility, and sensitivity.²⁰⁻²³ Previous researches showed that huge “hot spots volume” is crucial for reliable and reproducible SES, while large electric field enhancement is essential for sensitive SES.^{5, 10, 18, 24} However, hot spots in previous studies are usually confined within small volumes, making it hard to direct analytes into small hot spots. “Hot spots volume” in metallic NPs can be optimized by screening the cold spots areas and uncovering only the hot spots regions to surrounding medium.^{25, 26} Nonetheless, masking cold spots regions contributes nothing to increasing the “hot spots volume”. Hot spots are still in small size by reducing cold spots areas. Increasing the coupling areas by controlling the orientations of building blocks is another strategy to optimize the “hot spots volume” in NP dimers.^{9, 18} Nonetheless, increasing coupling areas leads to obviously decreased electric field enhancement in dimers.

In this chapter, a novel dimer structure named as SNPD is investigated. The results show that SNPD can provide both huge “hot spots volume” and large electric field enhancement, breaking the general restriction that increasing “hot spots volume” usually brings decreased electric field enhancement. In SNPD, SNP consisting of a bulky spherical core and a sharp spike is the building block. The optical properties of Au

SNPDs with various orientations are studied using 3D FDTD method.²⁷ We show that electric field enhancement ($|E|^2/|E_0|^2$) as high as 1.21×10^6 is obtained in T-T SNPD with 2 nm gap, which is much larger than in general dimer structures (normally at $\sim 10^4$). Moreover, ~ 5 times and ~ 7 times larger “hot spots volume” are achieved in T-T SNPD than that in sphere dimer and spike dimer with the identical 2 nm gap, respectively. More importantly, the results show that further increased “hot spots volume” can be achieved in crossed T-T SNPDs. Motivated by the studies about SNPDs, an approach to get hot spots with both huge volumes and intense electric fields in dimers is proposed by adding a bulky core at one end of the spindly building blocks.

4.2 Numerical method

The far-field and near-field properties of Au SNPDs are simulated using 3D FDTD method.²⁷ For all calculations, a total-field scattered-field plane wave source is chose to model the interference between the propagating plane wave and Au nanostructures. External medium is vacuum. The dielectric function of Au is achieved from Johnson and Christy.²⁸ To obtain precise results, 0.25 nm mesh size is used at the interparticle junctions of dimers and 1 nm mesh size is used in other regions. Convergence testing was cautiously done before all simulations to confirm the stability and accuracy of the calculations. In this study, all simulations are carried out using the FDTD simulation program (FDTD solutions 7.5, Lumerical solutions, Inc., Vancouver, Canada).

Here, all dimers are with at least 2 nm gaps. 2 nm or larger size gap allows the adsorption of large biomolecules at the interparticle junction, which is crucial for investigating large molecules. Figure 4-1 is the schematic drawing of a Au SNP, which is the building block of SNPDs. The SNP consists of a huge spherical core and a sharp surface spike. The spike is represented by a truncated cone with 22.5 nm bottom diameter (D_2), 10 nm tip diameter (D_1), and 50 nm spike length (L). The spherical core diameter (D) is 100 nm. The dimensions of SNP are chose based on previous studies by Pedireddy et al. and Chini's research group.^{29, 30}

Figure 4-1 Schematic drawing of a SNP composed by a spherical core and a sharp spike.

4.3 Results and discussions

4.3.1 Au spiky nanoparticle dimers with tip-to-tip, tip-to-sphere, and sphere-to-sphere configurations

Schematic illustrations of T-T, T-S, and S-S SNPDs are shown in the inset of Figure 4-2(a). The polarization direction and wave vector of incidence are represented by the red arrow and blue arrow, individually. Figure 4-2(a) shows the extinction spectra of T-T, T-S, and S-S SNPDs with 2 nm gap. The dotted line shows the extinction spectrum of a single SNP. As anticipated, notable red-shift of the resonance peak is observed in SNPDs because of the interparticle coupling.³¹ Moreover, upon coupling, T-T SNPD generates the largest red shift of the resonance position, followed by T-S SNPD and then S-S SNPD.

Figure 4-2(b) shows the electric field distributions for S-S, T-S, and T-T SNPDs at their low-energy (LE) resonance peaks indicated by the inverted triangle, triangle, and solid circle in Figure 4-2(a). The electric fields are mapped at the plane bisecting the center of the SNPDs and parallel to the polarization direction of incidence. The results show that intense electric fields are generated at both gap region and spike tips in S-S SNPD at the resonance wavelength of 844 nm. For T-S SNPD, electric fields are mostly located at the T-S gap region and the spike plasmon is weakly excited at the resonance wavelength of 1005 nm. At the resonance wavelength of 1143 nm for T-T SNPD, electric fields are confined at the T-T gap region, demonstrating that the resonance mode at 1143 nm is the

coupling mode at T-T gap. The results also show that electric field enhancement with a value as high as 1.21×10^6 can be obtained in T-T SNPD with 2 nm gap. This value is much larger than that in general dimer structures (generally with a value of $\sim 10^4$) with the same gap size.

Figure 4-2 Optical properties of SNPDs with various configurations. (a) Extinction cross sections for T-T, T-S and S-S Au SNPDs with 2 nm gap. (b) Electric field distributions ($\log_{10}(|E|^2/|E_0|^2)$) for three dimers at their resonance wavelengths labeled by inverted triangle, triangle and solid circle in (a). The scale bar is 50 nm.

Figure 4-3 Electric field distributions ($\log_{10}|E|^2/|E_0|^2$) of the S-S, T-S, and T-T SNPDs at their corresponding resonance peaks. The scale bar is 50 nm.

Besides the LE resonance peaks with large extinction cross sections, there are also other resonance modes appearing in the extinction spectrum of each SNPD. Calculated electric field distributions (Figure 4-3) show the resonance mode at 617 nm in S-S SNPD is dominated by the coupled plasmon resonance at the gap region. The resonance modes at 805 nm and 526 nm in T-S SNPD are dominated by spike plasmon resonance and sphere plasmon resonance, individually. And the resonance mode at 515 nm in T-T SNPD is dominated by sphere plasmon resonance. Since LE resonance mode provides the largest electric field enhancement, we focus our attention on the LE resonance peak in the following studies.

Figure 4-4 shows the LE resonance position and electric field enhancement of S-S, T-S, and T-T SNPDs with various interparticle separations. Here, electric field enhancement is calculated at the gap center of three SNPDs under their corresponding resonance conditions. With rising gap sizes, the coupling strength between two SNPs decreases, leading to both the blue shift of resonance peaks and the decrease of electric field enhancement for all dimers. Followed by a dipolar-coupling model³², the change of the resonance wavelength and the electric field enhancement for all SNPDs as a function of gap sizes are well fitted using single exponential equations. The fitting parameters are listed in Table 4-1 and Table 4-2, respectively. The results shown in Figure 4-4 directly indicate that T-T SNPD shows the largest red shift of resonance position and the highest

electric field enhancement when comparing with S-S, and T-S SNPDs with the same gap size, which can be explained by the best synergistic effect of "lightning rod effect" and interparticle coupling in T-T SNPD. Considering a SNP, charges will accumulate at the spike tip due to the "lightning rod effect". In T-T SNPD, the spike tip happens to be at the gap regions, promoting the near-field coupling at the T-T junction and consequently generating larger resonance peak shift and stronger electric field enhancement. However, in S-S SNPD, the "lightning rod effect" will attract charges away from the S-S gap regions, leading to weaker interparticle coupling strength and consequently smaller resonance peak shift and weaker electric field enhancement.

Figure 4-4 Effects of gap size on (a) resonance wavelength and (b) electric field enhancement of S-S, T-S and T-T SNPDs. The solid lines in (a, b) show the exponential fitting results. The dashed green line in (b) shows the maximum electric field enhancement (1.25×10^4) at the spike side of a SNP.

Table 4-1 Exponential fitting results ($y(x) = A_0 \cdot \exp(-x/D_0) + C$) for the resonance position as a function of gap separations for various dimer structures.

structure	$A_0(\text{nm})$	$D_0(\text{nm})$	$C(\text{nm})$	$R\text{-square}$
T-T SNPD	430.726	3.133	911.551	0.99301
T-S SNPD	285.785	2.665	867.856	0.99355
S-S SNPD	28.474	5.476	824.559	0.98287

Table 4-2 Exponential fitting results ($y(x)=A_0*exp(-x/D_0)+C$) for the electric field enhancement as a function of gap separations for various dimer structures.

structure	$A_0(\text{nm})$	$D_0(\text{nm})$	$C(\text{nm})$	$R\text{-square}$
T-T SNPD	3.11×10^6	1.380	3.88×10^4	0.99913
T-S SNPD	1.31×10^6	1.564	2.09×10^4	0.99375
S-S SNPD	6.47×10^5	0.532	5.92×10^2	0.87321

Figure 4-5 Comparison between a T-T SNPD and a spike dimer. (a) Extinction cross sections of a spike dimer and a T-T SNPD with 2 nm gap. (b) Electric field distributions ($\log_{10}(|E|^2/|E_0|^2)$) at the LE resonance peak for each dimer. The scale bar is 50 nm.

In addition to the drastically intensified electric fields, huge “hot spots volume” can also be obtained in SNPDs. Figure 4-5 shows the comparison between a spike dimer and a T-T SNPD with the same gap of 2 nm. The spike dimer consists of two spikes, as shown in the inset of Figure 4-5(a). When adding a large spherical core at the end of the spike, increased extinction cross sections and obviously red shifted resonance peak are observed. Simultaneously, the addition of bulky spherical cores significantly intensifies the electric fields at the T-T gap regions (Figure 4-5(b)). The calculation results show that the maximum electric field enhancement in T-T SNPD is 1.21×10^6 . This value is ~ 15 times larger than that in spike dimer with a value of 8.18×10^4 . The extremely enhanced electric fields in T-T SNPD are associated with the “lightning rod effect”.^{12, 33, 34} In a single SNP, the spike is much sharper than the spherical core and therefore can attract charges to the spike tip, ascribing to the “lightning rod effect”. At the same time, the

intense interparticle coupling in T-T SNPD also contributes to pumping up charges into the gap junction. The collaboration of these two factors generates the drastically enhanced electric fields confined at the gap region of T-T SNPD. Figure 4-5(b) further demonstrates that electric fields in T-T SNPD are more delocalized along the sharp spikes when comparing with in spike dimer, suggesting a much larger “hot spots volume” in T-T SNPD. The results shown in Figure 4-5 suggest that simultaneously increased “hot spots volume” and electric field enhancement can be achieved in NP dimers by adding a bulky core at the ends of the spindly building blocks.

Table 4-3 Calculated “hot spots volume” for various nanostructures under their corresponding resonance wavelengths.

structure	resonance wavelength(nm)	“hot spots volume” (nm ³)	
		$ E ^2/ E_0 ^2 > 10^4$	$ E ^2/ E_0 ^2 > 10^5$
single spike	645.5	0	0
sphere dimer	633.5	493.5	0
spike dimer	778.5	335.5	0
S-S SNPD	844	1127	0
T-S SNPD	1005	2608	349
T-T SNPD	1143	2301	349

In order to demonstrate the huge “hot spots volume” in SNPDs, “hot spots volume” for sphere dimer, spike dimer, and SNPDs with the same 2 nm gap are calculated at their respective resonance wavelengths (Table 4-3). The hot spots are firstly defined as regions with electric field enhancement larger than 1×10^4 . And “hot spots volume” is defined as the whole volumes of all the regions with electric field enhancement larger than 1×10^4 . In this case, “hot spots volume” in T-T SNPD is ~5 times and ~7 times larger than that in sphere dimer and spike dimer, individually. The extremely enlarged “hot spots volume” in T-T SNPD is because of the synergistic effect of the interparticle coupling in dimers and the “lightning rod effect” of spiky geometry. The results show that “hot spots volume” in T-S SNPD is slightly larger than in T-T SNPD, and S-S SNPD provides the smallest “hot spots volume”. We also perform extra calculations by defining hot spots as

regions with electric field enhancement larger than 1×10^5 . With this definition, T-S SNPD and T-T SNPD exhibit the same "hot spots volume" of 349 nm^3 . And the "hot spots volume" for sphere dimer and spike dimer is 0. In previous researches, increasing "hot spots volume" usually brings decreased electric field enhancement.^{35, 36} Nevertheless, Table 4-3 quantitatively demonstrates that hot spots with both huge volume and large electric field enhancement can be achieved in SNPDs with T-T and T-S configurations, indicating the great potentials of SNPDs in high-performance SES.

4.3.2 Au spiky nanoparticle dimer with crossed tip-to-tip configuration

Further enlarged "hot spots volume" in SNPDs is anticipated when controlling the orientation of SNPs into a crossed tip-to-tip configuration, resulting from the increased coupling surfaces between two long spikes. Schematic of a crossed T-T SNPD is depicted in the inset of Figure 4-6(a). The overlap distance between two crossed spikes is labeled by s . The parallel distance between two spikes is 2 nm. As shown in Figure 4-6(a, b), the resonance position exhibits a volcano shift trend with rising s , i.e., the resonance position firstly red shifts and then blue shifts with continuously increasing s from 0 to 50 nm. The turning point is at $s \sim 25 \text{ nm}$. The volcano shift trend of the resonance position with rising s can be explained by the dipole-dipole interaction model shown in Figure 4-6(c).³⁷ For the dipole-dipole interaction (i), the attractive force between the positive charge of the right NP and the negative charge of the left NP weakens the repulsive forces within each NP, causing the decreased resonance frequency and therefore the red shifted resonance peak. And the resonance peak red shifts with decreasing interparticle separation. For the dipole-dipole interaction (ii), the attractive force between the negative (positive) charge of the upper NP and the positive (negative) charge of the lower NP can increase the repulsive action in both NPs, resulting in the blue shift of the resonance peak. For dipole-dipole interaction (ii), the resonance peak exhibits blue shift with reducing interparticle separation. For crossed T-T SNPDs with s smaller than 25 nm, the charge distribution at the resonance wavelength is similar to the charge distribution shown in (i) (Figure 4-6(d), $s=0 \text{ nm}$). In this case, rising s is equivalent to reducing the interparticle spacing, leading to the red shift of the resonance peak. When s is larger than 25 nm, the charge distribution in crossed T-T is similar to the charge distribution shown in (ii) (Figure 4-6(d), $s=50 \text{ nm}$).

Hence, the dipole-dipole interaction (ii) plays a dominant role. And the resonance peak exhibits blue shift with further rising s .

Figure 4-6 Effects of overlap distance s on the optical properties of crossed T-T SNPDs. (a) Extinction cross sections of the crossed T-T SNPDs with different s . (b) Shift of the LE resonance wavelength (left y -axis) and "hot spots volume" (right y -axis) for crossed T-T SNPDs as a function of s . (c) The dipole-dipole interaction model. The black arrows show the dipole moment. (d) Charge distributions and (e) electric field ($\log_{10}(|E|^2/|E_0|^2)$) distributions of crossed T-T SNPDs with s value of 0 nm, 25 nm and 50 nm at their corresponding resonance wavelengths. The scale bar is 50 nm.

Figure 4-6(e) shows the electric field distributions for crossed T-T SNPDs with s values of 0 nm, 25 nm and 50 nm at their corresponding resonance conditions. The electric fields in crossed T-T SNPDs are mostly localized at the junction between two spikes, stemming from the strong coupling between the negative charge at one spike and the positive charge at another spike. Previous research showed that electric fields were greatly decreased in Au nanorod assembly with side-by-side configuration.³⁸ However, Figure 4-

6(e) indicates that the maximum electric field enhancement in crossed T-T SNPDs is always larger than 1×10^5 when increasing s from 0 to 50 nm. The drastically enhanced electric fields at the junction between two parallel spikes in crossed T-T SNPD are believed to result from the addition of large spherical core at the end of spikes. When adding a large spherical core to the end of the spike, more charges will accumulate at the spike side due to the prominent “lightning rod effect”, generating stronger interparticle coupling and consequently larger electric field enhancement at the junction between two spikes.

In addition to the extremely enhanced electric fields, further enlarged “hot spots volume” can be obtained in crossed T-T SNPDs because of the large coupling areas between two long spikes. Table 4-4 shows the calculated “hot spots volume” for crossed T-T SNPDs with different s . When hot spots are defined as regions with electric field enhancement larger than 1×10^4 , “hot spots volume” in crossed T-T SNPDs is always ~ 1.5 times larger than in T-T SNPDs, irrespective of the value of s . When defining hot spots as regions with electric field enhancement larger than 1×10^5 , “hot spots volume” in crossed T-T SNPDs can still be ~ 1.5 times of that in T-T SNPD through manipulating s . The shift of “hot spots volume” (hot spots defined as regions with $|E|^2/|E_0|^2 > 10^5$) with increasing s is plotted in Figure 4-6(b).

Table 4-4 Calculated “hot spots volume” for crossed T-T SNPDs with various s under their corresponding resonance wavelengths.

crossed T-T SNPD	resonance wavelength(nm)	“hot spots volume” (nm ³)	
		$ E ^2/ E_0 ^2 > 10^4$	$ E ^2/ E_0 ^2 > 10^5$
$s=0$ nm	1007	3388.5	201.5
$s=10$ nm	1114.5	3310	397.5
$s=20$ nm	1155	3297	483
$s=25$ nm	1173	3324	557.5
$s=30$ nm	1155.5	3196	517
$s=40$ nm	1131.5	3271.5	523.5
$s=50$ nm	1104	3600.5	330

In SNPDs, the huge spherical core plays a significant role in increasing the “hot spots volume” and the electric field enhancement. Figure 4-7 shows the effect of the spherical core diameter on the extinction spectra of crossed T-T SNPDs. The LE resonance peak exhibits obvious red shift with increasing spherical sizes. At the same time, rising sphere core diameters leads to enhanced radiative damping, consequently generating gradually broadened resonance peaks. As shown in Figure 4-7, an extremely widened resonance peak is observed for crossed T-T SNPD with 400 nm spherical core.

Figure 4-7 Extinction cross sections of crossed T-T SNPDs with various spherical core diameters D . The overlap distance between two crossed spikes for each dimer is 25 nm.

Table 4-5 Calculated “hot spots volume” for crossed T-T SNPDs with various spherical core diameters D under their corresponding resonance wavelengths.

crossed T-T SNPD ($s=25$ nm)	resonance wavelength (nm)	maximum $ E ^2/ E_0 ^2$	“hot spots volume” (nm^3)	
			$ E ^2/ E_0 ^2$ $>10^4$	$ E ^2/ E_0 ^2$ $>10^5$
$D=50$ nm	980	2.04×10^5	1509	166.5
$D=100$ nm	1173	5.68×10^5	3324	557.5
$D=200$ nm	1343	9.94×10^5	5864	834.5
$D=300$ nm	1468	8.64×10^5	5469	773.5
$D=400$ nm	1675	5.14×10^5	3721	501

Table 4-5 shows the effect of the spherical core diameter on the “hot spots volume” and the maximum electric field enhancement in crossed T-T SNPDs. With gradually rising the sphere diameters from 50 nm to 200 nm, the “hot spots volume” and the largest electric field enhancement both exhibit great increase, resulting from the enhanced “lightning rod effect”. When increasing the sphere diameters, the spike tends to be relatively sharper, resulting in more prominent “lightning rod effect”. At the same time, serving as an electron reservoir, larger nanosphere can provide more electrons to be attracted to the spike side, leading to stronger electric field enhancement.¹² Nonetheless, the role of the spike becomes weaker when the spherical core is too large. In addition, gradually increased radiative damping with rising sphere core sizes also impairs the electric field enhancement. Therefore, decreased “hot spots volume” and maximum electric field enhancement in crossed T-T SNPDs are observed when further increasing the sphere diameters from 200 nm to 400 nm.

Noble metal nanoshells have been demonstrated to provide highly tunable resonance wavelength in the NIR by controlling the shell thicknesses.³⁹ Combining the advantage of shell structures, the resonance position of a spiky nanoshell dimer (SNSD) is expected to be tuned over a wider range of wavelength. Figure 4-8(a) shows the extinction spectra of Au crossed T-T SNSDs with different shell thicknesses. The schematic drawing of a crossed T-T SNSD is shown in the inset of Figure 4-8(a). The outer diameter of the nanoshell is 100 nm, and the shell thickness (t) ranges from 5 nm to 30 nm. The spike length (L) and the longitudinal overlap distance between two crossed spikes (s) are 50 nm and 25 nm, individually. In crossed T-T SNSD, both the high-energy (HE) and LE resonance modes exhibit obvious red shift with decreasing t . The red shift of HE resonance mode is reasonable since it is dominated by the SPRs of the bulky core. For the red shift of the LE resonance mode, it is also associated with the red shift of the nanoshell SPRs with decreasing t . With decreasing t , the coupling strength between the outer sphere surface plasmon and the inner cavity surface plasmon increases, leading to the red shift of the nanoshell resonance position.^{40, 41} Since the resonance mode of the SNP can be viewed as the hybridization between the bulky core and the sharp spike, the red shift of the nanoshell SPRs can accordingly induce the red shift of the spiky nanoshell SPRs and

consequently result in the red shift of the LE resonance mode of crossed T-T SNSD.¹² As shown in Figure 4-8(a), the LE resonance mode is red shifted from 1173 nm to 1293 nm as decreasing t from 30 nm to 5 nm. When t is larger than 30 nm, the extinction spectrum of a SNSD is almost the same with that of a SNPD, which is because of the finite penetration depth of the EM wave in metallic nanostructure. At optical frequencies, the penetration depth of the EM wave in metallic nanostructure is ~ 30 nm.⁴² When t is larger than 30 nm, the shell structure performs like a solid one.

Although t has a large effect on the resonance position, t only has a slight effect on the hot spots in crossed T-T SNSDs. As shown in Figure 4-8(b), with increasing t from 5 nm to 50 nm, the maximum electric field enhancement in crossed T-T SNSDs exhibits a small increase from 5.5×10^5 to 5.7×10^5 . Here, nanoshell with 50 nm shell thickness stands for a solid sphere with 100 nm diameter. At the same time, the “hot spots volume” of crossed T-T SNSDs shows a slight decrease with increasing t . About 150 nm^3 decrease of “hot spots volume” from 3467 nm^3 to 3324 nm^3 is observed when increasing t from 5 nm to 50 nm.

Figure 4-8 Effects of shell thickness t on the optical properties of SNSDs. (a) Extinction cross sections of Au crossed T-T SNSDs with different t . (b) Plots of the “hot spots volume” (left y-axis) and maximum electric field enhancement (right y-axis) for crossed T-T SNSDs with different t under their corresponding LE resonance wavelengths. A 50 nm shell thickness represents a solid sphere without hollow space.

Finally, we investigate the effects of polarization direction of incidence on the hot spots in SNPDs. Figure 4-9(a) shows that polarization direction of incidence has no effects on

the resonance position but only results in the change of the resonance peak intensity. With the increase of θ , the intensity of the 1173 nm resonance peak exhibits gradual decrease. When θ is increased to 90° , the peak located at 1173 nm cannot be observed any more. The effect of the polarization direction on the resonance peak intensity is in agreement with the phenomenon that has been observed in a single SNP.¹² Figure 4-9(b) shows the electric field distributions of a crossed T-T SNPD with differently polarized incidence. With rising θ , the electric field enhancement exhibit obvious decrease. When θ equals to 90° , the largest electric field enhancement is distinctly decreased to 10^3 . The greatly decreased electric field enhancement in crossed T-T SNPD is because spike mode in individual SNP cannot be effectively excited when θ equals to 90° (Figure 4-9(c)). In this case, the electric fields cannot be efficiently confined at the spike tip, leading to the pronouncedly decreased electric field enhancement at the interparticle junction of crossed T-T SNPD.

Figure 4-9 Effects of incidence polarization angle θ on (a) extinction spectra, (b) electric field distributions ($\log_{10}(|E|^2/|E_0|^2)$), and (c) charge distributions of crossed T-T SNPDs. The scale bar is 50 nm.

4.3.3 A strategy to obtain hot spots with both huge volume and large electric field enhancement in dimers

Motivated by the huge “hot spots volume” in crossed T-T SNPD, an approach to get both huge “hot spots volume” and large electric field enhancement in dimers is proposed by adding a huge spherical core at the end of the parallel aligned spindly building blocks. When adding a huge geometry to the end of a spindly structure, more charges will be accumulated at the spindly structure because of the “lightning rod effect”, generating

intense electric field enhancement at the interparticle junction. At the same time, parallel alignment of two spindly building blocks provides large coupling areas between them, generating hot spots with huge volumes localized at the junction between them. In order to confirm the efficiency of this strategy, simulations on Au cuboid dimers are carried out. The width, length, and height of Au cuboid are 25 nm, 50 nm, and 25 nm, individually. The edges of the cuboid are all rounded with a radius of 2 nm. The interparticle separation for all dimers is 2nm.

Figure 4-10(a) shows the extinction spectra of various cuboid dimers. The electric field distributions of all dimers are calculated at their corresponding resonance wavelengths labeled by the solid circles shown in Figure 4-10(a). The results show that electric field enhancement in cuboid dimers is always smaller than 1×10^4 , irrespective of the polarization direction of incidence and the arrangement of the Au cuboids (Figure 4-10(b~d)). For example, the maximum electric field enhancement in longitudinally aligned cuboid dimer is only 7.15×10^3 (Figure 4-10(c)). And for the parallel aligned cuboid dimer shown in Figure 4-10(d), electric fields are mainly distributed at the sharp corners of the cuboid, and the largest electric field enhancement in this case is only 1521. However, when adding a huge sphere at one end of each cuboid in the parallel aligned cuboid dimer, the maximum electric field enhancement at the junction between two cuboids is significantly increased to a value as high as 7.33×10^4 (Figure 4-10(e)). By defining hot spots as regions with electric field enhancement larger than 1×10^4 , “hot spots volume” in the parallel aligned cuboid dimer after adding the bulky spherical cores is calculated to be as large as 2893 nm^3 .

Figure 4-10 A strategy to get large-volume hot spots in cuboid dimers. (a) Extinction cross sections for dimers with different configurations. The black line is multiplied by 10 to show clearly. Electric field distributions of (b, d) parallel aligned cuboid dimers with differently polarized incidence, (c) longitudinally aligned cuboid dimer, and (e) parallel aligned cuboid dimer after adding a bulky spherical core at the end of each cuboid. All electric fields are calculated at their corresponding resonance wavelengths labeled by the solid circles shown in (a). The scale bar is 50 nm.

4.4 Conclusions

In summary, the first hypothesis is demonstrated in this chapter. We show that Au SNPDs can provide hot spots with both huge volume and large electric field enhancement, breaking the general restriction that increasing “hot spots volume” normally brings decreased electric field enhancement. The results show that electric field enhancement as high as 1.21×10^6 is achieved in T-T SNPD with 2 nm gap. Moreover, T-T SNPD exhibits ~ 5 times and ~ 7 times larger “hot spots volume” than sphere dimer and spike dimer, respectively. We further show that “hot spots volume” in SNPD can be improved by controlling the orientation of SNPs, where crossed T-T SNPD provides the largest “hot spots volume”, followed by T-S SNPD, then T-T SNPD, and finally S-S SNPD. Recent study showed that electric fields in SNP rapidly increase with increasing spike length.²⁹ In addition, SNP with longer spike can further increase the coupling areas between two spikes. Therefore, larger “hot spots volume” and higher electric field enhancement are anticipated in crossed T-T SNPD through fabricating SNP with longer spikes. The simultaneously increased “hot spots volume” and electric field enhancement in SNPDs are resulting from the cooperative effect of “lightning rod effect” and the interparticle coupling. Motivated by the huge “hot spots volume” in SNPDs, we suggest that hot spots with both huge “hot spots volume” and large electric field enhancement can be achieved in dimers by adding a large spherical core at one end of the parallel aligned spindly building blocks.

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Chapter 5 Obtaining Large-volume Hot Spots in Top-down Lithography Fabricated Nanoparticle Dimers

Au spiky nanoparticle dimers (SNPDs) were shown to provide both high electric field enhancement and huge “hot spots volume”. Nevertheless, the assembly of spiky nanoparticles into SNPDs is hard to control. Therefore, in this chapter, we aim to explore the top-down lithography fabricated nanoparticle dimers with huge “hot spots volume”. We show that the proposed Au crossed tip-to-tip spiky disk dimer provides 2.3 times higher maximum electric field enhancement and 2.5 times larger “hot spots volume” than disk dimer, because of the “lightning rod effect” and the large coupling areas between two parallel aligned tips. The effects of glass substrate, tip width, tip length, disk diameter, structure height, and gap separations between two crossed tips on the hot spots are also investigated. The results demonstrate the possibility to achieve the large-volume hot spots in experiments. In addition, the results can provide guidelines for designing and optimizing top-down lithography fabricated metallic nanoparticle dimers for surface-enhanced spectroscopies.

5.1 Introduction

Noble metal NP dimers have been widely explored for SES because of their ability to generate drastically enhanced electric fields localized at the interparticle junction.¹⁻⁸ Generally, NP dimers can be obtained by assembly method using organic molecules as linkers or by top-down nanolithography method.^{6, 9-13} However, dimers generated from assembly are usually with low controllability and reproducibility, limiting their performance in SES.¹⁴⁻¹⁶ Compared with assembly method, top-down lithography can be used to fabricate metallic NP dimers with well-controlled geometries.⁶ In the past, well-defined nanodisk dimers, nanoring dimers, nanorod dimers, and bowtie antennas have been successfully fabricated over large areas using focused ion beam lithography or electron beam lithography.^{2, 17-20}

Therefore, in this chapter, we aim to explore top-down lithography fabricated NP dimers with huge “hot spots volume”. The NP dimer studied in this work is constructed by respectively attaching a bulky disk to the end of two parallel aligned nanobars. For convenient description, we name this dimer structure as crossed T-T SDD through the whole paper. The SDDs may be fabricated with well-controlled geometries using top-down lithography. We suppose that huge “hot spots volume” are not specific for free-standing SNPDs. We predict hot spots with huge volume and large electric field enhancement should be generally achieved in dimers as long as the building blocks are composed by a bulky structure with a protruding spindly tip, even when the dimers are placed on a glass substrate. The results shown in this chapter indicate that large-volume hot spots are obtained in crossed T-T SDD, ascribing to the large coupling areas between two parallel aligned nanobars. At the same time, adding a bulky disk at one end of the nanobar makes more charges being accumulated at the nanobar due to the “lightning rod effect”, resulting in large coupling strength and hence large electric field enhancement at the junction between two nanobars. The effects of the glass substrate, tip width, tip length, disk diameter, structure height, gap size, and polarization direction of incidence on the hot spots in crossed T-T SDDs are also investigated, respectively.

5.2 Numerical method

Figure 5-1 illustrates the geometry of a Au crossed T-T SDD composed by two spiky disks (SDs) on a glass substrate. The SD is composed by a bulky disk with a protruding nanobar. The tip of the nanobar is rounded with a diameter being the width of the nanobar. The structure height, disk diameter, nanobar length, nanobar width, longitudinal overlap distance, and gap separation between two nanobars are labeled by h , d , l , w , s , and g , respectively. During the whole study, d , h , l , w , s , and g are 150 nm, 30 nm, 60 nm, 30 nm, 50 nm and 2 nm, individually. The effects of one parameter on the optical properties of crossed T-T SDDs are examined by gradually varying the parameter under study while keeping all other parameters fixed. The wave vector ($\vec{k}$) and polarization direction ($\vec{E}$) of incidence are labeled by the blue arrow and red arrow, individually.

Figure 5-1 Schematic illustration of a Au crossed T-T SDD on glass substrate.

3D FDTD method is used to calculate the near-field and far-field properties of crossed T-T SDDs.²¹ External medium is vacuum. A total-field scattered-field plane wave is chosen to simulate the interaction between the propagating plane wave and nanostructures. The Au dielectric function is achieved from Johnson and Christy.²² The dielectric function of glass is obtained from Palik.²³ Convergence testing is carefully performed to confirm the stability and precision of the simulations before all calculations. To get accurate results, a 0.25 nm mesh size is used at the gap region of dimers and a 1 nm mesh size is used in other parts of the nanostructure. In this chapter, hot spots are defined as regions with electric field enhancement ($|E|^2/|E_0|^2$) higher than 1×10^4 . “Hot spots volume” is defined as the whole volumes of all the regions with electric field enhancement higher than 1×10^4 . In this chapter, 3D FDTD method is carried out using the FDTD simulation program (FDTD solutions 8.6.3, Lumerical Solutions, Inc., Vancouver, Canada).

5.3 Results and discussions

5.3.1 Hot spots in crossed tip-to-tip spiky disk dimer on glass substrate

Figure 5-2 Effects of glass (SiO₂) substrate on the optical properties of crossed T-T SDD. (a) Extinction cross sections of a crossed T-T SDD with and without substrate. (b, c) Electric field distributions of the crossed T-T SDD without and with substrate at *xy*- and *xz*-plane at their corresponding LE resonance wavelengths. The scale bar in the zoomed in images at *xz*-plane is 10 nm. The scale bar in other images is 50 nm.

Using top-down nanolithography, SDDs are fabricated on substrate. Hence, the effects of glass substrate on the hot spots in crossed T-T SDDs are firstly investigated. As shown in Figure 5-2(a), resonance peaks show obvious red shift when placing the SDD on a glass substrate because of the larger refractive index of glass than that of vacuum. Figure 5-2(b,

c) shows that drastically intensified electric fields are mainly distributed at the junction between two crossed nanobars in crossed T-T SDD with and without glass substrate. But one difference is that anti-symmetric electric field distribution is observed in the crossed T-T SDD on glass substrate when viewing in xz -plane. Due to the interference of the underlying glass substrate, electric fields prefer to be localized at the bottom surface contacting the glass substrate. Calculations show that the “hot spots volume” and the maximum electric field enhancement in free-standing crossed T-T SDD are 3380 nm^3 and 1×10^5 , respectively, indicating that free-standing crossed T-T SDD can provide both huge “hot spots volume” and large electric field enhancement for high-performance SES. When placing the SDD on top of a glass substrate, both the “hot spots volume” and the electric field enhancement show decrease. Nevertheless, the effects of glass substrate on the hot spots in crossed T-T SDD are small. Crossed T-T SDD on glass substrate can still provide a huge “hot spots volume” of 2910 nm^3 and a maximum electric field enhancement as high as 9.9×10^4 . The results show that even when placing the crossed T-T SDD on a glass substrate, huge “hot spots volume” and large electric field enhancement can still be obtained. Since noble metal nanostructures are usually fabricated on a glass substrate using the top-down nanolithography, crossed T-T SDDs on glass substrate are investigated in the following work.

5.3.2 Comparison between disk dimer and crossed tip-to-tip spiky disk dimer

In order to demonstrate the large-volume hot spots in crossed T-T SDD, we compare the hot spots in a crossed T-T SDD with the hot spots in a disk dimer. All dimers are placed on a glass substrate. For the disk dimer, the disk diameter, thickness, and interparticle separation are 150 nm, 30 nm, and 2 nm, respectively. Figure 5-3(a) shows that two distinct resonance modes are observed in the extinction spectra of both disk dimer and crossed T-T SDD. Comparing with disk dimer, resonance peaks of crossed T-T SDD show obvious red shift with increased intensity. Calculated charge distributions (Figure 5-3(b)) indicate that the resonance peaks at 619 nm for disk dimer and 653 nm for crossed T-T SDD are ascribed to the quadrupole coupling modes. The resonance peaks at 1001 nm for disk dimer and 1455 nm for crossed T-T SDD are corresponding to the dipole coupling modes.

Figure 5-3 Comparison between a disk dimer and a crossed T-T SDD. (a) Extinction cross sections of a Au disk dimer and a Au crossed T-T SDD on glass substrate. (b) Charge distributions for the disk dimer and the crossed T-T SDD at their corresponding resonance wavelengths. The scale bar is 50 nm.

Figure 5-4 shows the electric field distributions of the disk dimer and the crossed T-T SDD at their corresponding resonance wavelengths. In disk dimer, electric fields are localized at the gap region between two disks at the resonance peaks (Figure 5-4(a)). In crossed T-T SDD, the electric fields are mostly confined at the junction between two crossed tips at its corresponding resonance wavelengths (Figure 5-4(b)). The results indicate that electric field enhancement at dipole coupling mode is always larger than that at quadrupole coupling mode for either disk dimer or crossed T-T SDD. Therefore, the following studies focus on the dipole coupling mode in crossed T-T SDD. Even though the electric field enhancement at quadrupole coupling mode is smaller than that at dipole

coupling mode, it should be noted that quadrupole coupling mode can still generate intense electric fields confined at the interparticle junction in both disk dimer and crossed T-T SDD. The intensified electric fields at quadrupole coupling mode are essential for the sensitive SES in the visible light region.

Figure 5-4 Electric field distributions ($\log_{10}(|E|^2/|E_0|^2)$) for (a) disk dimer and (b) crossed T-T SDD at their corresponding resonance wavelengths. The scale bar is 50 nm.

The electric field maps shown in Figure 5-4 qualitatively show that crossed T-T SDD can provide larger “hot spots volume” than disk dimer at their corresponding dipole coupling modes. To quantitatively demonstrate the optimized hot spots in crossed T-T SDD, the “hot spots volume” and the largest electric field enhancement in disk dimer and crossed T-T SDD are calculated, respectively. As shown in Table 5-1, the “hot spots volume” in crossed T-T SDD is 2910 nm^3 , being more than 2.5 times larger than that in disk dimer. Moreover, the maximum electric field enhancement in crossed T-T SDD is as high as 9.9×10^4 , being ~ 2.3 times of that in disk dimer. These results directly show that crossed T-T SDD can provide hot spots with both enlarged “hot spots volume” and increased electric field enhancement when comparing with disk dimer, exhibiting great potentials for highly sensitive SES. The increased “hot spots volume” in crossed T-T SDD is due to the increased coupling areas between two protruding nanobars. At the same time, nanobar with 30 nm width is much narrower than the nanodisk with 150 nm diameter. Hence, upon illumination, more charges will be accumulated at the nanobar because of the “lightning rod effect”, leading to stronger coupling between two tips and thus increased electric field enhancement at the interparticle junction.

Table 5-1 Calculated “hot spots volume” and maximum electric field enhancement in disk dimer and crossed T-T SDD at their corresponding resonance wavelengths.

structure	resonance wavelength (nm)	hot spots volume (nm ³)	maximum $ E ^2$
disk dimer	1001	1141	4.3×10^4
crossed T-T SDD	1455	2910	9.9×10^4

5.3.3 Effects of overlap distance between two crossed tips

Figure 5-5 Effects of overlap distance s on (a) Extinction cross sections and (b) resonance wavelength of dipole coupling mode (left y -axis) and “hot spots volume” (right y -axis) of crossed T-T SDDs.

For above-mentioned results in part 5.3.1 and part 5.3.2, the overlap distance (s) between two crossed tips is 50 nm. The extinction spectra and “hot spots volume” of crossed T-T SDD with various s are also investigated (Figure 5-5). With increasing s from 10 nm to 50 nm, the dipole coupling mode shows obvious red shift, whereas the shift of the quadrupole coupling mode is negligible. In addition, the variation of the dipole coupling peak decreases with increasing s . Further increasing s from 50 nm to 60 nm, a slight blue shift of the dipole coupling mode becomes observable. The first red shift and then blue shift of the resonance position with increasing s can be explained by a dipole-dipole interaction model.^{24, 25} A speedy increase of “hot spots volume” from 837 nm³ to 2464 nm³ is observed with increasing s from 10 nm to 20 nm (Figure 5-5(b)). However, when s is larger than 20 nm, the influence of s on the “hot spots volume” is small. The “hot spots

volume” in crossed T-T SDD only exhibits a variation of 446 nm^3 from 2464 nm^3 to 2910 nm^3 when increasing s from 20 nm to 60 nm . Since crossed T-T SDD with 50 nm overlap distance provides the relatively largest “hot spots volume”, overlap distance s is fixed at 50 nm in the following studies.

5.3.4 Effects of tip width, tip length, and disk diameter

Figure 5-6(a) shows the influence of w on the extinction spectra of crossed T-T SDDs. With increasing w , the dipole resonance mode shows obvious blue shift. The blue shift of the resonance position can be explained by two factors. For one thing, the resonance position of a single SD blue shifts with increasing w , which is akin to the blue shift of the resonance position with decreasing aspect ratio in a nanorod. For another thing, increasing w results in decreased “lightning rod effect” in a SD. Therefore, fewer charges are attracted to the tip, leading to weaker coupling strength between two SDs and hence blue shifted resonance position of the crossed T-T SDD. At the same time, decreased coupling strength between two SDs with increasing w leads to decreased electric field enhancement within gap region and hence a gradual decrease of the “hot spots volume” in crossed T-T SDD (Figure 5-6(b)). Contrary to the effect of w , increasing either l or d leads to the red shift of the resonance position, ascribing to the increased dipole moment and the enhanced “lightning rod effect” in a single SD (Figure 5-6(c, e)). Simultaneously, increased “lightning rod effect” also leads to more charges being attracted to the tip of a SD. Consequently, the coupling strength between two SDs becomes stronger, generating gradually increased electric field enhancement and enlarged “hot spots volume” with rising l or d (Figure 5-6(d, f)).

Figure 5-6 Effects of tip widths w , tip lengths l , and disk diameters d on (a, c, e) Extinction cross sections and (b, d, f) resonance wavelength (left y-axis) and “hot spots volume” (right y-axis) of crossed T-T SDDs. The solid lines show the linear fitting results.

Table 5-2 Slope of the resonance position and “hot spots volume” of crossed T-T SDDs as a function of w , l , and d deduced from Figure 5-6(b, d, f).

parameter	slope of resonance position	slope of “hot spots volume”
w	-9.27	-49.92
l	8.89	25.03
d	4.56	15.02

The shift of the resonance position and the “hot spots volume” in crossed T-T SDDs with varying w , l , and d can be approximately fitted using linear equations. The fitting results are shown by the solid lines in Figure 5-6(b, d, f). The slope of each line is deduced and listed in Table 5-2. The negative value of the slope for w indicates that both the resonance

wavelength and “hot spots volume” decrease with increasing w . The fitting results show that w has the largest influence on the resonance position and “hot spots volume” of crossed T-T SDDs, followed by l , and then d . In other words, the optical properties of crossed T-T SDDs are more sensitive to the dimensions of the protruding tip than the dimensions of the bulky disk. These fitting results can provide guidelines for designing and optimizing crossed T-T SDDs for high-performance SES.

5.3.5 Effects of structure height and gap size

Figure 5-7 Effects of structure height h on (a) extinction cross sections, (b) resonance wavelength (left y-axis) and “hot spots volume” (right y-axis), and (c) the maximum electric field enhancement of crossed T-T SDDs

Figure 5-7 shows the effect of h on the extinction spectra and hot spots in crossed T-T SDDs. The resonance position exhibits a gradual blue shift with increasing h (Figure 5-7(a)). When gradually increasing h from 30 nm to 80 nm, the “hot spots volume” in the crossed T-T SDD monotonously increases from 2910 nm^3 to 3599 nm^3 . However, when h

is larger than 80 nm, further increasing h leads to the decreased “hot spots volume” (Figure 5-7(b)). The first augment of the “hot spots volume” with rising h is due to the increased coupling areas between two crossed tips. However, increasing h simultaneously leads to decreased electric field enhancement within gap (Figure 5-7(c)). When h is larger than 80 nm, the effects of the increased coupling areas cannot compensate the effects of the decreased electric field enhancement, resulting in the decreased “hot spots volume”.

Figure 5-8 Effects of gap sizes g on (a) extinction cross sections, (b) resonance wavelength (left y -axis) and “hot spots volume” (right y -axis), and (c) the maximum electric field enhancement of crossed T-T SDDs.

The influence of g on the extinction spectra of crossed T-T SDDs is shown in Figure 5-8(a). With increasing g , the resonance peak shows obvious blue shift with decreased intensity due to the decreased coupling strength between two SDs. The decreased coupling strength also results in the decreased electric field enhancement with increasing g (Figure 5-8(c)). Figure 5-8(b) shows the influence of g on the “hot spots volume” in crossed T-T SDDs. When g is smaller than 5 nm, the “hot spots volume” is limited by the

geometrical volume of the gap space. Therefore, the “hot spots volume” increases with increasing g . Nevertheless, when g is larger than 5 nm, the decrease of the electric field enhancement plays a dominant role. Hence, the “hot spots volume” shows a drastic decrease with further increasing g .

Figure 5-9 Electric field enhancement ($|E|^2/|E_0|^2$) distributions in crossed T-T SDDs with different (a) structure heights h and (b) gap separations g . Only the electric field enhancements larger than 1×10^4 are counted.

In Figure 5-7(b) and Figure 5-8(b), a drastic decrease of the “hot spots volume” in crossed T-T SDDs is observed when h or g is larger than a certain critical value. For instance, when increasing h from 90 nm to 100 nm, the “hot spots volume” is drastically decreased from 3335 nm^3 to 1724 nm^3 . With rising g from 5 nm to 6 nm, the “hot spots volume” is significantly decreased from 3978 nm^3 to 265 nm^3 . To explain the drastic drop of the “hot spots volume”, we calculate the electric field enhancement distributions with various h (Figure 5-9(a)) and various g (Figure 5-9(b)). Since hot spots are defined as

regions with electric field enhancement higher than 1×10^4 , only the electric field enhancement larger than 1×10^4 is counted here. As shown in Figure 5-9, when g (or h) is 2 nm (or 30 nm), the electric field enhancement values spread almost all over the range from 1×10^4 to 1×10^5 . With increasing g (or h), the electric field enhancement values not only decrease but also exhibit narrower and narrower distribution. When g (or h) is 5 nm (or 90 nm), the electric field enhancement values are mainly located within the range from 1.0×10^4 to 1.5×10^4 . Therefore, with further increasing g (or h) to 6 nm (or 90 nm), continually decreased electric field enhancement makes the electric field enhancement values between 1.0×10^4 to 1.5×10^4 being smaller than 1×10^4 , leading to the sharp decrease of the “hot spots volume”.

5.3.6 Effects of polarization direction of incidence

Figure 5-10 Effects of polarization direction θ of incidence on (a) extinction cross sections and (b) “hot spots volume” (left y-axis) and maximum electric field enhancement (right y-axis) of crossed T-T SDDs.

Finally, the dependence of the optical properties of crossed T-T SDDs on the polarization directions (θ) of incidence is investigated. As shown in Figure 5-10(a), θ has no effect on the resonance position of the dipole coupling mode, but only affects its intensity. With rising θ , the intensity of the dipole coupling peak gradually decreases. When θ equals to 90° , the dipole coupling mode disappears. At the same time, both the “hot spots volume” and the electric field enhancement in crossed T-T SDD show obvious decrease with increasing θ (Figure 5-10(b)). The decreased “hot spots volume” and electric field enhancement is because the charges cannot be effectively confined at the tip of a SD with

increasing θ .

5.4 Conclusions

In conclusion, the second hypothesis is demonstrated in this chapter. We show that Au crossed T-T SDDs on glass substrate can provide hot spots with both much larger volumes and much higher electric field enhancement than disk dimer, ascribing to the increased coupling areas between two parallel aligned tips and the enhanced “lightning rod effect” in a SD. The results shown in this chapter make it possible to achieve the large-volume hot spots in experiments. We find that decreasing tip width, increasing tip length, and rising disk diameter all lead to the red-shifted resonance position and augmented “hot spots volume”, where the effect of tip width is the largest, followed by tip length, and then disk diameter. We further show that properly increasing structure height or gap separation can generate further increased “hot spots volume” due to the enlarged geometrical volume within gap regions. However, a drastic decrease of “hot spots volume” is observed when the structure thickness or gap separation is larger than one critical value, because the electric field enhancement not only decreases but also exhibits narrower and narrower value distribution with rising film height or gap size. The results can provide guidelines for optimizing top-down lithography fabricated metallic substrates for SES.

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Chapter 6 * Ultrahigh Enhancement of Electric Fields by Exciting LSPRs Using SPP Waves

Metal nanoparticle (NP) over the metal film (MNOMF) provides vertical coupling between the NP and the film, generating intense electric fields at the junction. In MNOMF, the surface plasmon polaritons (SPPs) of the underlying film were seldom considered in previous studies since SPPs cannot be directly excited using incidence from free space due to the momentum mismatch. In this chapter, we aim to explore the effects of the SPP waves of the underlying film on the hot spots in MNOMF. The SPPs of the metal film are excited by depositing the metal film on a prism in Kretschmann-Raether configuration. Taking Au NP over the Ag film as an example, we show that the largest electric field enhancement and the highest surface-enhanced fluorescence intensity are obtained when the SPPs of the Ag film are excited. The ultrahigh enhancement is attributed to the strong confinement of the SPP waves in the vertical direction. The drastically intensified electric fields are significant for highly-sensitive refractive index sensing, surface-enhanced spectroscopies, and enhancing the efficiency of optoelectronic devices.

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6.1 Introduction

Coupled metallic nanostructures can generate strongly enhanced electric fields localized at the interparticle junction, exhibiting great potentials for sensitive SES.¹⁻⁵ In coupled structures, small gaps are essential for generating strongly enhanced electric fields. Nevertheless, it is difficult to obtain small gaps in NP dimers coupled in lateral direction. Hence, the MNOMF system which provides coupling in vertical direction has received increasing attentions.⁶⁻¹³ In MNOMF, uniformly distributed gaps with sub-1 nm size can be fabricated.^{11, 14, 15} In addition, MNOMF can be fabricated over large areas using a low-cost and simple method by directly depositing the NPs on top of the metal film.^{7, 10, 16} Moreover, separation distance between the NP and the film can be well controlled by accurately adjusting the thickness of the dielectric spacer, resulting in both the well-tuned resonance position of the MNOMF and highly uniform and reproducible hot spots.^{9-11, 14, 16-19} In MNOMF, the NP couples with its mirror image in the metallic film, generating strongly intensified electric fields localized at the junction between the NP and the film.^{10, 17, 19-21} All these advantages make the MNOMF a good platform for SES.

Generally, the NP and the film can sustain LSPRs and SPPs, respectively. For periodic NP array on metallic film, the SPPs at the metal-dielectric interface has been shown to couple with the LSPRs or the Bragg waves of the NP array, generating higher electric field enhancement around the NPs.^{12, 13} However, the SPPs of the underlying metal film in MNOMF were seldom considered in previous studies, because SPPs cannot be directly excited using the free space incidence due to the momentum mismatch.²² In this chapter, taking the Au nanosphere over the Ag film as an example, the effect of the SPPs of the metal film on the electric field enhancement in MNOMF is examined. In order to excite the SPPs of the Ag film, the Ag film is deposited on a SF-11 prism in KR configuration. We show that the largest electric field enhancement and the highest SEF intensity are obtained when the incidence angle is the SPP resonance angle of the Ag film. The results indicate that SPP waves can more efficiently excite the metal NP than incidence from free space, ascribing to the strong confinement of the SPP waves in the vertical direction. The dependence of the electric field enhancement in Au sphere over Ag film system on Si spacer thickness and Au NP diameter is also examined.

6.2 Theoretical method

6.2.1 SPP resonance angle of a metal film

On a flat metal-dielectric interface, the frequency-dependent wave vector of the SPPs is,

$$k_{sp} = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (6-1)$$

where $k_0 = \omega/c$ is the free-space wave vector. ω is the frequency of the incident light, c is the velocity of light in vacuum. ϵ_m and ϵ_d are the complex dielectric functions of the metal and the dielectric medium (analyte), respectively. Equation 6-1 shows that the momentum of SPPs k_{sp} is larger than the momentum of a free-space photon k_0 with the same frequency. Due to the momentum mismatch, the SPPs of a thin metallic film cannot be directly excited by the free space incidence.²² In the present study, we deposit the metal film on a SF-11 prism in KR configuration to bridge the momentum mismatch.

In prism-based KR configuration, a transverse magnetic (TM) polarized light is launched from the prism side. The wave vector along the interface is:

$$k_x = 2\pi n_p \sin \alpha_p / \lambda = k_0 n_p \sin \alpha_p \quad (6-2)$$

where $k_0 = \omega/c = 2\pi/\lambda$, n_p is the refractive index of the prism, α_p is the propagation angle of the incidence in prism. In order to generate the SPPs on the metal-dielectric interface, it is compulsory to bridge the momentum mismatch between the incidence and the SPPs. Hence,

$$\sqrt{\epsilon_p} \sin \alpha_p = \text{Re} \left\{ \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \right\} \quad (6-3)$$

Here, $\epsilon_p = n_p^2$ is the dielectric constant of the prism. Equation 6-3 can be used to calculate the SPP resonance angle of the metal film. However, when a dielectric layer (for example, Si) is added on top of the metal film, equation 6-3 cannot accurately give the resonance angle. In this case, the Abeles 2x2 transfer matrix approach is used to calculate the SPP resonance angle. When the incidence angle is the SPP resonance angle of the metallic film, SPPs can be generated at the metal-dielectric interface.

6.2.2 FDTD simulations

The effects of the SPPs of the metal film on the hot spots in MNOMF are investigated

using 3D FDTD method.²³ Schematic illustration of the setup used to excite the SPPs of the underlying metal film in MNOMF is shown in Figure 6-1(a). A Au NP is deposited on the Ag film separated by a thin Si spacer layer. The thin Ag film is deposited on a SF-11 prism in the KR configuration. A TM polarized light with incidence angle α is launched from the SF-11 prism to gain momentum in the surface direction in order to excite the SPPs at the Ag film surface. In all calculations, the Ag film thickness is adjusted to maintain the highest contrast in the reflection spectrum, i.e., keeping the minimum reflection to be zero at the SPP resonance angle. The surrounding medium is water in all calculations since biological and chemical sensing usually happen in water environment. The dielectric function of Au is obtained from Johnson and Christy.²⁴ The dielectric function of Ag is achieved from reference 25²⁵, and the refractive index of Si is obtained from reference 26²⁶. To get accurate results, override mesh regions with 0.5 nm mesh size are used at the gap region between the Au sphere and the Ag film, and override mesh regions with 1 nm size are used to cover the Au sphere and Ag film. Convergence testing was carefully performed before all the calculations to confirm the stability and the accuracy of the simulations. In this study, all the calculations are carried out using the FDTD simulation program (FDTD solutions 8.6, Lumerical solutions, Inc., Vancouver, Canada).

6.3 Experimental details

SEF experiments using the Au nanosphere over the Ag film configuration are performed in air using spectrometer (specta Wiz). Rhodamine 6G molecules are used as the fluorophore. It has been shown that the maximum absorption of the Rhodamine 6G molecule appears approximately at 532 nm.²⁷ Therefore, 532 nm excitation is used in the SEF experiments. The Ag film is prepared by thermal evaporation method using PVD-75 purchased from Kurt J. Lesker Company. The thickness of the Ag film is controlled at 46~47 nm. The Ag film is deposited on SF-11 substrate which is attached to the SF-11 prism in KR configuration using index matching liquid. Then, one monolayer of Rhodamine 6G molecules is deposited on the Ag film using spincoating method. The colloidal solution containing 40 nm Au nanospheres is purchased from the BBI Solutions. The density of Au NPs in the colloidal solution is $\sim 1.1 \times 10^{10}$ NPs per 500 ml. We dilute

the colloidal solution with PBST to a concentration of 25% and then directly deposit the Au NPs from the diluted colloidal solution onto the Ag film using drop-coated method. Here, we assume the concentration of colloidal solution purchased from the BBI Solutions without dilution is 100%. Fluorescence intensity at two incidence angles of 36.25° and 60° is measured, corresponding to the on resonance condition and off resonance condition of the Ag film, respectively.

6.4 Results and discussions

6.4.1 Efficient excitation of the Au nanosphere using the SPP waves of the underlying Ag film

Figure 6-1 Exciting LSPRs of Au nanosphere using SPPs of the Ag film. (a) Schematic illustration of the setup used to excite the Au nanosphere LSPRs using SPPs of Ag film. The Ag film is coated on a SF-11 prism in KR configuration. α is the incidence angle inside the prism. (b) Electric field distributions and (c) the maximum electric field enhancement of a 40 nm Au sphere on 46.4 nm Ag film with 2 nm Si spacer at 655 nm with different incidence angles. The scale bar in each figure of (b) is 20 nm.

The effects of the SPP waves on the hot spots in the Au sphere over the Ag film configuration are investigated by adjusting the incidence angle to be the SPP resonance angle of the Ag film. Here, the diameter of the Au nanosphere is 40 nm. The thickness of the Ag film is 46.4 nm. The Au nanosphere and Ag film are separated by 2 nm Si spacer.

And the wavelength of the incidence is 655 nm. In this case, the SPP resonance angle of the Ag film is 53.775° . As shown in Figure 6-1(b), electric fields are dominantly confined at the gap region between the Au nanosphere and the Ag film when the incidence angle is away from the SPP resonance angle of the Ag film. The enhanced electric fields at the junction between the Au NP and the Ag film at off resonance angles have been demonstrated before and can be explained by the near-field coupling between the Au nanosphere and its mirror image in the Ag film.^{19-21, 28} When gradually adjusting the incidence angle to approach the SPP resonance angle (53.775°) of the Ag film, the electric fields at the junction between the nanosphere and the film become more and more intensely enhanced. At the same time, strongly intensified electric fields are distributed not only at the junction between the Au sphere and the Ag film, but also at the top of the Au sphere.

The maximum electric field enhancement in the Au sphere over the Ag film with various incidence angles is calculated and plotted in Figure 6-1(c). The results clearly show that electric field enhancement ($|E|^2/|E_0|^2$) as high as 2.5×10^5 is obtained when the incidence angle is the SPP resonance angle of the Ag film at 53.775° . Small deviation of the incidence angle away from the SPP resonance angle leads to a drastic decrease of the electric field enhancement. The full width at half maximum of the resonance response in Figure 6-1(c) is $\sim 1.87^\circ$. When the incidence angle is decreased to 45° , the maximum electric field enhancement is only 994, becoming more than 250 times smaller than the value at SPP resonance angle. In previous studies, incidence angle of $\sim 60^\circ$ was considered to generate the largest field enhancement in MNOMF.^{10, 18} However, according to our calculations shown here, the maximum electric field enhancement for 60° incidence angle is only 6.6×10^3 , being ~ 38 times smaller than the value obtained at the SPP resonance angle of 53.775° .

The greatly enhanced electric fields in the Au nanosphere over the Ag film at 53.775° are stemming from the generation of the SPP waves at the top surface of the Ag film, as demonstrated by Figure 6-2. Figure 6-2 shows the z component of the electric field (E_z) of a 46.4 nm Ag film deposited on a SF-11 prism with 45° , 53.775° , and 60° incidence

angles, respectively. Due to the momentum mismatch, SPP waves cannot be generated at the top surface of the Ag film when the incidence angle is 45° or 60° (Figure 6-2(b, d)). When the incidence angle is the SPP resonance angle of the Ag film at 53.775° , the momentum mismatch between the SPPs and the free space incidence is bridged. In this case, the SPP waves are efficiently generated at the top surface of the Ag film (Figure 6-2(c)). The generated SPP waves can then hit the Au nanosphere. Due to the strong confinement of the SPP waves in the vertical direction, the SPP waves can more effectively excite the Au nanosphere, generating much larger electric field enhancement at both the junction between the Au nanosphere and the Ag film and the top surface of the Au nanosphere.

Figure 6-2 Demonstration of the generation of SPPs at 53.775° . (a) Schematic illustration of a 46.4 nm silver film deposited on a SF-11 prism in KR configuration. The silver film is covered with 2 nm Si layer. (b~d) E_z distributions of the structure shown in (a) with 45° , 53.775° , and 60° incidence angles. The color bar applies to all the electric field maps. The scale bar is 200 nm.

For comparison purpose, the electric field distribution of a 40 nm Au nanosphere deposited on a free-standing Ag film at 655 nm with 53.775° incidence angle is also calculated (Figure 6-3). When moving away the SF-11 prism, SPP waves cannot be excited at the top surface of the Ag film due to the momentum mismatch between the SPPs and the free space incidence (Figure 6-3(a)). In this case, the LSPRs of the Au nanosphere is directly excited by the incidence that travels through the Ag film. Figure 6-3(b) shows that the maximum electric field enhancement in Au nanosphere over a free-

standing Ag film with 53.775° incidence angle is only 361, being ~ 693 times smaller than the value achieved from exciting the Au nanosphere using the extended SPP waves. The results demonstrate that excitation of LSPRs using SPP waves generates much larger electric field enhancement than direct excitation of LSPRs using incidence from free space.

Figure 6-3 No SPP waves generated for free-standing Ag film at 53.775° . (a) E_z distribution of a free-standing Ag film covered with 2 nm Si. (b) Electric field distribution of a 40 nm Au nanosphere on a free-standing Ag film separated by 2 nm Si at 655 nm with 53.775° incidence angle. The scale bars in (a) and (b) are 200 nm and 20 nm, respectively.

6.4.2 Effects of Si spacer thickness

The dielectric spacer between the NP and the film plays a significant role on the electric field enhancement in MNOMF when exciting the LSPRs using the SPP waves of the underlying film. Figure 6-4(a) shows the electric field distributions of a 40 nm Au nanosphere over the 46.4 nm Ag film with various Si spacer thicknesses at 655 nm. The incidence angle for each case is the SPP resonance angle of the Ag film. The SPP resonance angles of the Ag film with 0 nm, 1 nm, 1.5 nm, 2 nm, 3 nm, 4 nm, 6 nm, 8 nm, and 10 nm Si spacers are 52.5° , 53.1° , 53.4° , 53.775° , 54.56° , 55.525° , 58° , 61.76° , and 67.9° , respectively. With increasing the Si layer thicknesses, the field distribution pattern becomes more and more symmetric. At the same time, electric fields at both the junction between the Au nanosphere and the Ag film and the top surface of the Au nanosphere exhibit obvious decrease with gradually increasing Si thicknesses. As shown in Figure 6-

4(b), the maximum electric field enhancement is obviously decreased from 6.3×10^5 to 2.1×10^4 when increasing the Si thickness from 1 nm to 10 nm. The results shown in Figure 6-4 indicate that the largest electric field enhancement is obtained in the Au sphere over Ag film without Si spacer layer. However, a dielectric spacer is in fact useful for practical applications. For example, the surface of the dielectric spacer can be purposefully functionalized for specific sensing. Moreover, the dielectric spacer can be used to control the resonance position of the MNOMF by adjusting its thickness.^{15, 19} Adding Si layer on top of the metal film has also been demonstrated to narrow the resonance dip in the reflection spectrum and increase both the sensitivity and figure of merit of refractive index sensing.²⁹

Figure 6-4 Effects of Si spacer thickness on (a) electric field distributions and (b) maximum electric field enhancement for a 40 nm Au nanosphere over a 46.4 nm Ag film at 655 nm. The incidence angles are the SPP resonance angles of the Ag film with different Si spacer thicknesses, respectively. The scale bar in each figure of (a) is 20 nm.

6.4.3 Effects of Au nanosphere diameter

Figure 6-5 Effects of Au sphere diameter on (a) electric field distributions and (b) maximum electric field enhancement for the Au spheres over Ag film separated by 2 nm Si spacer at 532 nm, 655 nm, and 785 nm, respectively. The scale bar is 50 nm. The incidence angles are the SPP resonance angles of the Ag film at 532 nm, 655 nm, and 785 nm, respectively.

In above-mentioned calculations, the diameter of the Au nanosphere is randomly fixed at 40 nm without considering the match of the LSPRs of the Au nanosphere and the SPPs of the underlying Ag film. Therefore, extra calculations are performed to see what happens when gradually varying the diameter of the Au nanosphere. Besides calculations at 655 nm, additional calculations at 532 nm and 785 nm are carried out since 532 nm and 785 nm excitations are usually used in SEF and SERS experiments. The Au sphere and Ag film are separated by a 2 nm Si spacer. The resonance angles of the Ag film at 532 nm, 655 nm, and 785 nm are 58.7° , 53.775° , and 52.15° , respectively. As shown in Figure 6-5(a), the maximum electric field enhancement is always located at the junction between the Au nanosphere and the Ag film, regardless of the incidence wavelength and the Au nanosphere diameter. In addition, the electric fields at the top surface of the Au nanosphere become less enhanced when increasing Au nanosphere diameters. Figure 6-

5(b) shows that electric field enhancement larger than 1×10^5 can be obtained at 655 nm and 785 nm by adjusting the Au sphere diameter. However, we notice that the maximum electric field enhancement at 532 nm is only $\sim 10^3$, being much smaller than that at 655 nm and 785 nm. The smaller electric field enhancement at 532 nm is associated with the lower Q of Au at 532 nm.³⁰ Figure 6-5(b) indicates that the optimum diameter of Au nanosphere for the electric field enhancement at 532 nm is ~ 40 nm. For 655 nm and 785 nm excitations, the optimum size of Au nanosphere is 60 nm and 100 nm, respectively. The increase of the optimum size of the Au nanosphere with increasing incidence wavelength is reasonable, considering the match of the LSPRs of the Au nanosphere and the SPPs of the Ag film. The LSPR position of Au nanosphere red shifts with rising diameters.⁷ Results shown in Figure 6-5(b) also indicate that the maximum electric field enhancement in Au sphere over Ag film is not sensitive to the size of the Au nanosphere when the sphere diameter is larger than 100 nm.

6.4.4 Surface-enhanced fluorescence

FDTD calculations indicate that much higher electric field enhancement can be obtained in MNOMF when the SPP waves of the underlying metal film are excited. The drastically intensified electric fields are extremely essential for high-performance SES, such as SEF, SERS, SEIRA and other spectroscopic techniques. In an attempt to experimentally prove the theoretical prediction, SEF experiments are performed in this study. Figure 6-6(a) shows the fluorescence intensity of a monolayer Rhodamine 6G covered on the Ag film with 532 nm excitation. The Ag film is attached to the SF-11 prism in KR configuration. The SPP resonance angle of the Ag film in this case is 36.25° . Fluorescence intensity at two incidence angles of 36.25° and 60° is measured, corresponding to the on resonance condition and off resonance condition, respectively. The fluorescence intensity of the monolayer Rhodamine 6G covered on the Ag film without Au nanosphere deposition is firstly measured. For the off resonance condition, the fluorescence intensity of Rhodamine 6G is very small with a value of ~ 0.7 (arbitrary units). When the incidence angle is the SPP resonance angle of the Ag film at 36.25° , fluorescence intensity of Rhodamine 6G is increased to ~ 3 . The enhanced fluorescence intensity from Ag film at 36.25° is ascribed to the enhanced electric fields at the Ag-air interface stemming from

the excitation of the SPP waves. When further depositing 40 nm Au NPs on top of the Ag film, increased fluorescence intensity is observed at both the off resonance and the on resonance conditions. At off resonance condition, the increased fluorescence intensity after depositing Au NPs is associated with the enhanced electric fields at the junction between the NP and the film. In Au sphere over Ag film, the Au NP can couple with its mirror image in the Ag film layer, generating intense electric fields at the gap region between the NP and the film.^{19-21, 28} When changing the incidence angle from 60° to the SPP resonance angle of 36.25° , ~ 24 times enhanced fluorescence intensity from Au sphere over Ag film configuration is observed. At the on resonance condition with 36.25° incidence angle, the fluorescence intensity from Au sphere over Ag film configuration is as larger as ~ 71 .

The extremely enhanced fluorescence intensity from Au sphere over Ag film at on resonance condition is because of the drastically intensified electric fields at the gap region between the Au sphere and the Ag film. As shown in Figure 6-6(b), much larger electric field enhancement is generated at the junction between the Au nanosphere and the Ag film at 36.25° than that at 60° . Previous studies showed that the fluorescence intensity in SEF strongly depends on the fluorophore orientation, the molecule-nanoparticle separation, and the geometry of the NPs.^{31, 32} Hence, either integrated electric field enhancement around the metal NP or the highest electric field enhancement qualitatively correlates with the fluorescence intensity. Here, we choose the highest electric field enhancement to qualitatively explain the fluorescence intensity in SEF. According to the calculations, the maximum electric field enhancement at 36.25° is 3.1×10^5 , while the maximum electric field enhancement at 60° is only 626.5. The calculation results qualitatively agree with the SEF experimental results.

Figure 6-6 Surface-enhanced fluorescence measurements. (a) Fluorescence intensity of a monolayer of Rhodamine 6G covered on a ~ 46 nm Ag film with and without 40 nm Au nanosphere deposition at 532 nm. The incidence angles for the on and off resonance conditions are 36.25° and 60° , respectively. The low intensity signals between 640 nm and 680 nm are zoomed in and shown in the inset. (b) Electric field distributions of a 40 nm Au sphere over 46 nm Ag film at 532 nm with 36.25° and 60° incidence angles. The gap between Au sphere and Ag film is 1 nm. The scale bar in (b) is 20 nm.

6.5 Conclusions

In summary, the third hypothesis is demonstrated in this study. We demonstrate that SPP waves can more efficiently excite the metal NP and hence generate much higher electric field enhancement than free space incidence, ascribing to the strong confinement of the SPP waves in the vertical direction. We show that the largest electric field enhancement

and the highest fluorescence intensity in Au sphere over Ag film system are obtained when the incidence angle is the SPP resonance angle of the Ag film. In addition, the electric field enhancement in Au sphere over Ag film highly depends on the Si spacer thickness, where drastic decrease of the electric field intensity with gradually increasing Si spacer thicknesses is observed. It is also shown that the optimum size of the Au nanosphere for electric field enhancement increases with increasing excitation wavelength, considering the match between the LSPRs and the SPPs. The drastically intensified electric fields generated from exciting the LSPRs of NP using SPP waves are extremely essential for applications of MNOMF in sensitive refractive index sensing, high-performance SES, and efficient optoelectronic devices such as better solar cells for energy harvesting.

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Chapter 7 Conclusions and Future Work

This chapter draws together the threads of this thesis. The contents of the whole thesis are summarized. The demonstration of the three hypotheses presented in chapter 1 is carefully illustrated. In addition, the opportunities for future work are listed.

7.1 Conclusions

This study aims to optimize the hot spots in coupled noble metal nanostructures for high-performance SES. The three hypotheses proposed in chapter 1 are proven one by one. In this study, we firstly explore dimer structures with both huge “hot spots volume” and large electric field enhancement. We demonstrate that Au SNPDs and Au SDDs are able to provide hot spots with large “hot spots volume” and high electric field enhancement at the same time, breaking the general restriction that increasing “hot spots volume” usually brings decreased electric field enhancement. Based on the studies about the Au SNPDs and SDDs, a strategy to get both huge “hot spots volume” and large electric field enhancement in dimers is proposed. In addition, we demonstrate that drastically enhanced electric fields in MNOMF can be obtained by exciting the LSPRs of the NP using the SPP waves of the underlying metal film. We show that the largest electric field enhancement and the highest SEF intensity are generated in the Au sphere over the Ag film configuration when the SPPs of the Ag film are excited.

The first hypothesis proposed in this study is that SNPDs can generate huge “hot spots volume” and large electric field enhancement at the same time. This hypothesis is firstly demonstrated by results shown in chapter 4. We show that electric field enhancement as high as 1.21×10^6 is obtained in T-T SNPD with 2 nm gap. Moreover, “hot spots volume” in T-T SNPD is ~ 5 times and ~ 7 times larger than in sphere dimer and spike dimer with the same 2 nm gap, respectively. We find that “hot spots volume” in SNPDs can be improved through manipulating the orientations of the SNPs, where crossed T-T SNPD exhibits the largest “hot spots volume”, followed by the T-S SNPD, then the T-T SNPD, and finally the S-S SNPD. The simultaneously enlarged “hot spots volume” and increased electric field enhancement in crossed T-T SNPDs are due to the cooperative effect of the “lightning rod effect” of the sharp spike in SNP and the increased coupling areas between two crossed spikes. For one thing, “lightning rod effect” enables more charges being accumulated at the sharp spike, resulting in intense electric field enhancement. For another thing, the large coupling areas between two crossed long spikes lead to large “hot spots volume”. Motivated by the studies about crossed T-T SNPDs, we propose a method to get hot spots with both large “hot spots volume” and

high electric field enhancement in dimers by adding a bulky core at one end of the parallel aligned spindly building blocks in dimers.

The second hypothesis proposed in this study is that large “hot spots volume” is not specific for free-standing SNPDs. We predict that high electric field enhancement and huge “hot spots volume” can also be achieved in crossed T-T SDDs, even when the SDDs are placed on a glass substrate. This hypothesis is demonstrated in chapter 5. We show that even though glass substrate brings a decrease of the electric field enhancement and “hot spots volume” in crossed T-T SDD, the crossed T-T SDD on a glass substrate can still provide a huge “hot spots volume” of 2910 nm^3 and a maximum electric field enhancement as high as 9.9×10^4 . We show that crossed T-T SDD exhibits much larger “hot spots volume” and much higher electric field enhancement than disk dimer, ascribing to the larger coupling areas between two tips and the “lightning rod effect” of spindly tip. These results further expand the applicability of the strategy proposed in previous investigations about SNPDs to get huge “hot spots volume” and large electric field enhancement. Currently, it is difficult to control the assembly of the SNPs into SNPDs. Comparing with SNPDs, SDDs possess a distinct advantage that SDDs can be fabricated using the top-down lithography with well-controlled orientations. Therefore, results shown in chapter 5 indicate the possibility to realize the large-volume hot spots in experiments for high-performance SES. In this study, we also show that either decreasing the tip widths or increasing the tip lengths and disk diameters of crossed T-T SDDs leads to the red-shifted resonance wavelength and augmented “hot spots volume”, where tip width has the largest effect, followed by tip length, and then disk diameter. In addition, further enlarged “hot spots volume” can be obtained by properly expanding the gap separation between two tips or properly increasing the structure height. These results can provide guidelines to optimize the top-down lithography fabricated metallic substrates for high-performance SES.

Finally, the third hypothesis is demonstrated in chapter 6. Taking the Au nanosphere over the Ag film as an example, we demonstrate that ultrahigh electric field enhancement can be obtained in MNOMF when exciting the LSPRs of the NP using the SPP waves of the

underlying metal film. The SPP waves of the Ag film are excited by depositing the Ag film on top of a prism in KR configuration. We show that the largest electric field enhancement and the highest SEF intensity of the Au sphere over the Ag film are obtained when the incidence angle is the SPP resonance angle of the Ag film. When the incidence angle is the SPP resonance angle of the underlying metal film, SPP waves are generated at the top surface of the metallic film. Due to the strong confinement of the SPP waves in vertical direction, the SPP waves can more efficiently excite the NP, generating much higher electric field enhancement than free space incidence. We also show that the electric field enhancement is highly sensitive to the Si spacer thickness, where drastically decreased electric field enhancement is observed with gradually increasing the Si spacer thickness from 0 nm to 10 nm. It is also shown that the optimum size of the Au sphere for electric field enhancement increases with increasing incidence wavelength, which can be explained by the match between the LSPRs and the SPPs. The drastically enhanced electric fields generated from exciting the LSPRs of NPs using SPP waves are extremely important for sensitive refractive index sensing, high-performance SES, and high efficiency of optoelectronic devices such as better solar cells for energy harvesting.

7.2 Future work

Inspired by the results shown in this work, some future works about the MNOMF are recommended.

(1) In the SEF experiments shown in chapter 6, the Au NPs are diluted with PBST with a concentration of 25%. SEF experiments using Au NPs with various concentrations are also performed. When respectively depositing the Au NPs with various concentrations on top of the Ag film, we notice that Au NPs diluted with 25% concentration gives the largest fluorescence intensity (Figure 7-1). To optimize the performance of the MNOMF in SES, it is important to fully understand the reason for the optimum enhancement of SEF using Au NPs with 25% concentration. We hypothesize that the influence of the Au NP concentration on the SEF intensity can be understood by examining the influence of the Au NP concentration on both the electric field enhancement and the number of hot

spots. To confirm this hypothesis, further theoretical calculations will be performed in the next study.

Figure 7-1 Fluorescence intensity of a monolayer of Rhodamine 6G covered on a ~46 nm Ag film with various concentrations of 40 nm Au nanospheres deposited on the Ag film at 532 nm. The low intensity signals between 640 nm and 680 nm are zoomed in and shown in the inset. The incidence angles for the on and off resonance conditions are 36.25° and 60° , respectively.

(2) We also notice that the fluorescence peak in the SEF experiments shown in chapter 6 is at ~655 nm, exhibiting a large red shift comparing with the fluorescence range of the Rhodamine 6G molecules which is usually from 555 nm to 585 nm.^{1,2} The spectral shift in metal-enhanced fluorescence has been observed before for Rhodamine 800 dissolved in glycerol on copper substrate, but the shift was much smaller.³ The large shift of the fluorescence peak in our experiments may be associated with the plasmons of noble metal NPs.^{4,5} It may also be due to the chemical change of the fluorophore caused by the intensely enhanced electric fields. Further investigations of this fluorescence peak shift are needed.

(3) Results shown in chapter 6 indicated that electric field enhancement in Au sphere over Ag film at 532 nm is much smaller than that at 655 nm and 785 nm. We attribute the smaller electric field enhancement at 532 nm to the low Q of Au at 532 nm. However, 532 nm excitation is usually used in SEF. Hence, it is necessary to optimize the electric field enhancement in MNOMF at 532 nm. Therefore, we will explore different material

combinations of the NP and the film, and see which combination gives the highest electric field enhancement at 532 nm. By investigating the effects of materials on the electric field enhancement in MNOMF, we aim to optimize the electric field enhancement in MNOMF at various incidence wavelengths.

(4) NP dimers have long been demonstrated to generate intense electric fields confined at the interparticle junction. Dimer structures with well-controlled geometries can be fabricated over large areas using top-down lithography. However, it is difficult to obtain gaps smaller than 5 nm using top-down lithography, impairing the electric field enhancement in dimers. Inspired by the drastically enhanced electric fields obtained from exciting the LSPRs using the SPP waves, the influences of SPPs of the underlying metal film on the electric field enhancement in dimer structures will be examined in the future studies. We hypothesize that when placing a dimer on top of a metal film, SPP waves can be used to enhance the electric fields at the gap region of the dimer. In this case, extremely enhanced electric fields can be generated in dimers even with large gaps.

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