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博士学位論文

**Shape-dependent Surface-Enhanced Raman
Scattering under Modal Ultrastrong Coupling between
Self-Assembled Gold Nanoparticles and Fabry–Pérot
Cavities**

(自己組織化金ナノ粒子とファブリ・ペロー共振器間のモード超強結合に
よる形状依存表面増強ラマン散乱)

HE ZHIYU

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2026年3月

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Chapter 1

General introduction

1-1. Optical detection of biomolecules

Biomolecules, including nucleic acids, proteins, lipids, carbohydrates and metabolites, are fundamental to living organisms as both structural components and key regulators of biological processes.¹ Their concentrations, structures and interactions undergo continuous changes in response to the physiological and environmental conditions.² Consequently, biomolecules are important target analytes in diverse fields such as biotechnology,³ food safety,⁴ environment monitoring,⁵ early-stage medical diagnostics.⁶ With the growing demand for efficient biomolecule detection in recent years, the development of sensing platforms that offer high sensitivity and selectivity while remaining low-cost and easy to operate has become an increasingly active area of research.⁷

A broad range of analytical techniques have been established for biomolecule detection, including chromatography-mass spectrometry⁸, electrochemical sensing^{9, 10} and optical spectroscopy. Among these, optical spectroscopy-based methods, such as fluorescence^{11, 12}, colorimetry¹³, chemiluminescence¹⁴, Raman scattering¹⁵ offer notable advantages including rapid analysis, cost-effectiveness and compatibility with portable instrumentation.^{16, 17} The optical detection strategies can be generally categorized into label-based and label-free approaches.¹⁸ The label-based optical detection typically involves functionalizing the signal-transduction platforms with recognition molecules (e.g. aptamers, antigens), enabling target-binding events to be converted into measurable optical signals.^{19, 20} The label-free strategy usually utilizes the biophysical properties of the target molecules such as refractive indices²¹ and intrinsic optical signatures²² to directly monitor their presence and behavior without the need for external labels.²³

1-2. Surface-enhanced Raman scattering (SERS)

Surface-enhanced Raman scattering (SERS), as one of highly sensitive molecule detection techniques, generates molecular fingerprint signals that are significantly amplified by enhanced light-matter interactions.²⁴⁻²⁷ When laser light interacts with a sample with molecules, most of the light undergo transmission, absorption or reflection, with a minor fraction being scattered, including elastic and inelastic scattering (**Figure 1-1a**).²⁸ The elastic scattering is known as Rayleigh scattering, where the scattered light has the same frequency as the incident light. In the inelastic scatterings, the scattered light has either higher or lower frequency than the incident light due to the light-matter interaction, which are known as Stokes Raman scattering and anti-Stokes Raman scattering, respectively. The Stokes Raman scattering involves energy transferring from photons to the molecule in ground vibrational state. In contrast, the anti-Stokes Raman scattering involves the photons obtaining energy from molecules in excited states. Therefore, the Raman scattering reveals the vibration and rotation information of molecules. Given that most of the molecules are in ground vibrational state at room temperature, the Stokes Raman scattering provides relatively strong signal, and it is more widely used for molecule analysis. However, the intrinsic Raman scattering signal is very weak. In 1970s, significant Raman signal amplification on noble metal surface, namely, SERS, was discovered by Fisherman et.al,²⁹ which predominantly involves the improved light-matter interaction in strong localized electromagnetic (EM) field.^{30, 31}

SERS through EM field enhancement primarily utilizes localized surface plasmon resonance (LSPR) of plasmonic nanostructures, such as gold and silver nanoparticles.³² When interacting with incident light, the collective oscillation of conductive bands in the plasmonic nanoparticles produces intense localized EM field (**Figure 1-1b**).³³ When the

nanoparticles approach to each other, the coupled localized surface plasmon further produce strongly intensified EM field in the gap, generating “hotspots” that greatly enhances the Raman scattering of the molecules located there (**Figure 1-1c**). The SERS enhancement factor (EF) is proportional to the localized EM field intensities, and the theoretical correlation between the EF and EM field intensity is expressed as

$$EF \propto \frac{|E_{loc}(\lambda_{ex})|^2 \times |E_{loc}(\lambda_{sc})|^2}{|E_0(\lambda_{ex})|^2 \times |E_0(\lambda_{sc})|^2}$$

where $E_{loc}(\lambda_{ex})$, $E_{loc}(\lambda_{sc})$ represent the local electric field strengths at the excitation and scattered (Stokes-shifted) wavelengths, respectively, and $E_0(\lambda_{ex})$, $E_0(\lambda_{sc})$ are the incident electric field strength.^{34, 35}

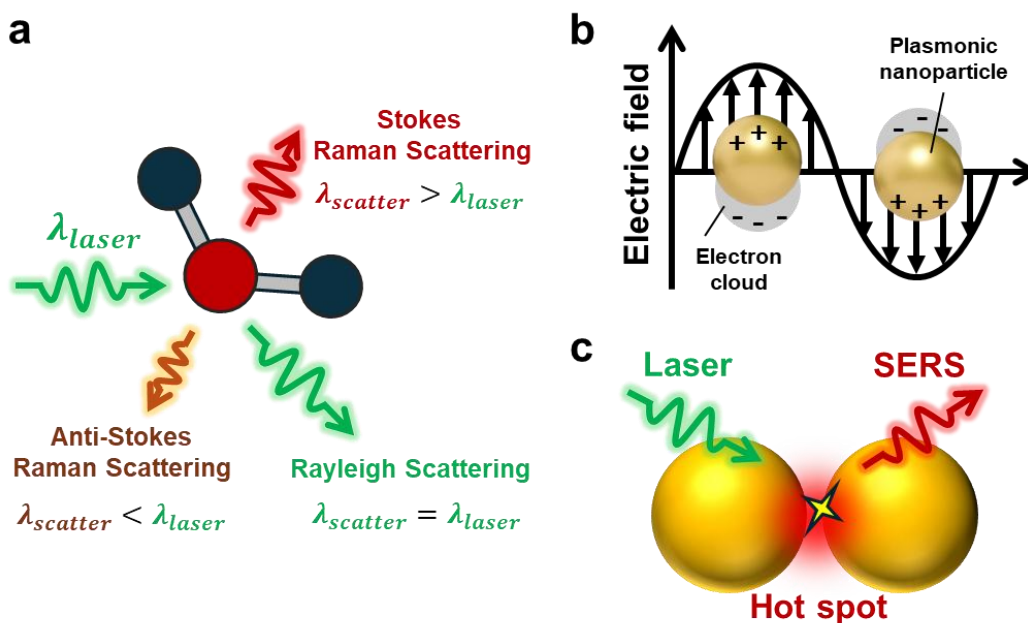


Figure 1-1. Schematic illustration of (a) Raman scattering, (b) LSPR of plasmonic nanoparticles and (c) SERS hotspots.

1-3. Gold nanoparticles (AuNPs) for SERS applications

Gold nanoparticle (AuNP) is a class of prominent materials for constructing SERS platforms. Besides the effective near field confinement due to the LSPR properties, AuNPs offer the advantages of better chemical stability than their silver counterparts. The AuNP-based SERS platforms are primarily fabricated by “top-down” and “bottom-up” methods (**Figure 1-2**).³⁶ The “top-down” method involves physical processes that breaking bulk gold into nanoscale, which allows precise engineering of the particle size, geometries and arrangements with limitations such as expensive instrumentations.³⁷ In contrast, the “bottom-up” fabrication is more cost-effective, and the controlled chemical reduction of gold precursors in liquid phase is among the most popular methods for synthesizing AuNPs.³⁸ In a typical colloidal AuNPs-based SERS platform, the optical hotspots are formed in the interparticle gaps of AuNP agglomerations via plasmon coupling, with the surface properties being tailored for facilitating the adsorption of signal reporter.³⁹ However, the formation of hotspots in the random agglomerations lack reproducibility, making it challenge to be applied for quantitative SERS analysis.⁴⁰ One of strategies for improvement is to control the self-assembly of AuNPs into nanoparticle array on solid substrates, which stably forms hotspots thereby improving signal reproducibility.^{41, 42} In recent years, several techniques have been developed to control the self-assembly of AuNPs on substrate such as drop casting, spin coating and air/liquid interfacial self-assembly.⁴³ Among them, the air/liquid interfacial self-assembly is attractive because closely packed AuNP film can be formed in centimeter-scale area with high uniformity.^{41, 44} Langmuir technique is representative, including Langmuir-Blodgett and Langmuir-Schaefer method (**Figure 1-3**). In these methods, nanoparticle monolayers float on the top of the water phase. By pushing the Langmuir barriers toward each other

to compress the air/water interface, the packing density of the nanoparticles can be maximized.⁴⁵ Then, the closely packed nanoparticle film is transferred onto solid substrates. In Langmuir-Blodgett method, the nanoparticle film is deposited across the substrate surface by lifting the vertically immersed substrate in the water phase. In Langmuir-Schaefer method, the nanoparticle film is transferred on the substrate that horizontally contact the air/water interface.⁴⁶ Consistently, the Langmuir technique enables minimized interparticle distances for the resultant AuNP films, forming dense hotspots with maximized EM field intensities.

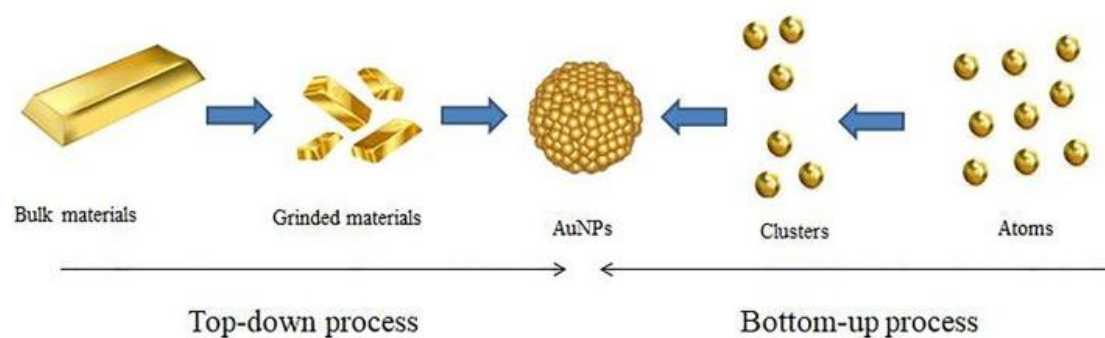


Figure 1-2. Top-down and bottom-up approaches for the synthesis of AuNPs.³⁶

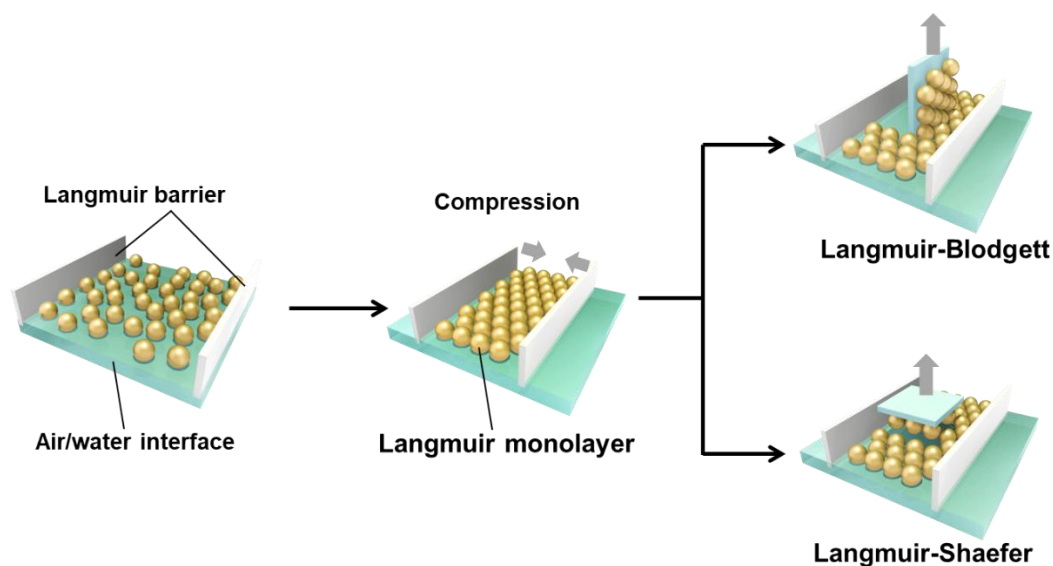


Figure 1-3. Schematic illustration of preparation of close-packed AuNP film via Langmuir-Blodgett and Langmuir-Schaefer method.⁴⁶

Besides controlling interparticle distance, the optimization of particle shape is another strategy to improve the SERS hotspots. Gold nanotriangle (AuNT) is a classical anisotropic nanostructure, which has been a popular material for SERS application owing to the significant near field enhancement at the three sharp vertices.⁴⁷ The self-assembled AuNT film fabricated by Langmuir-Schaefer method exhibits wide LSPR band ranges from visible to near-infrared region due to the plasmon coupling among the individual AuNTs (**Figures 1-4a, b**), which overlaps the excitation wavelengths and produces significant SERS signal (**Figures 1-4c, d**). In addition, the SERS enhancement can be further improved with assistance of functional substrate such as gold film, which rearranges near field distribution and intensity (**Figure 1-5**).⁴⁸

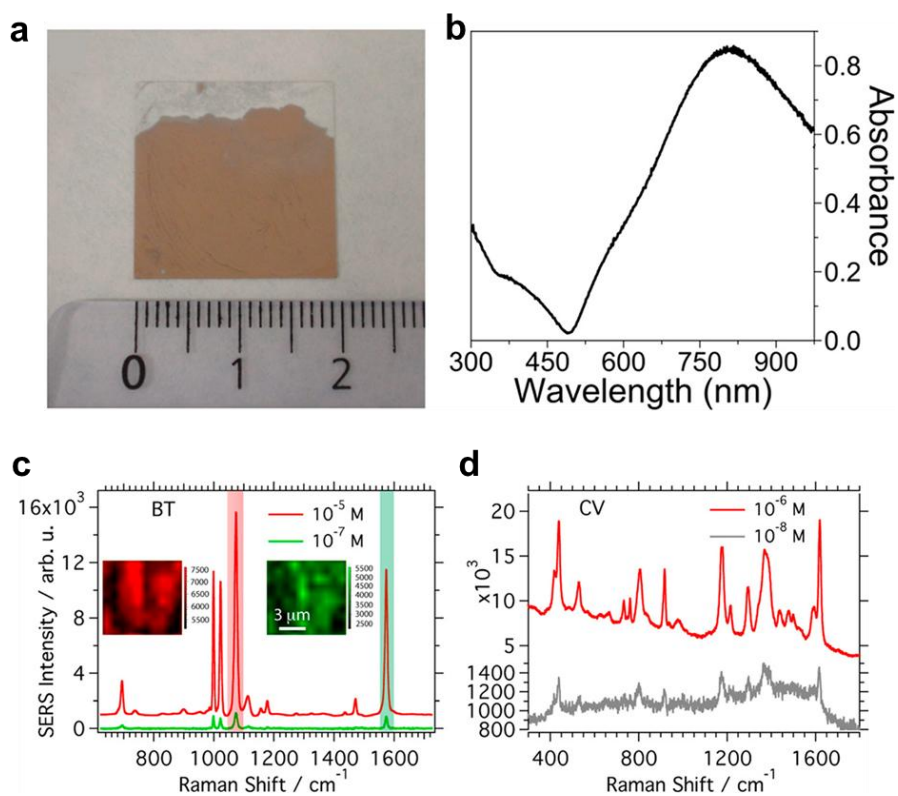


Figure 1-4. AuNT film for SERS application. (a) Photograph of self-assembled AuNT film on substrate. (b) Spectrum of the AuNT film. (c) SERS spectra of BT on AuNT film under the excitation of 785 nm. (d) SERS spectra of CV on AuNT film under the excitation of 633 nm.⁴⁹

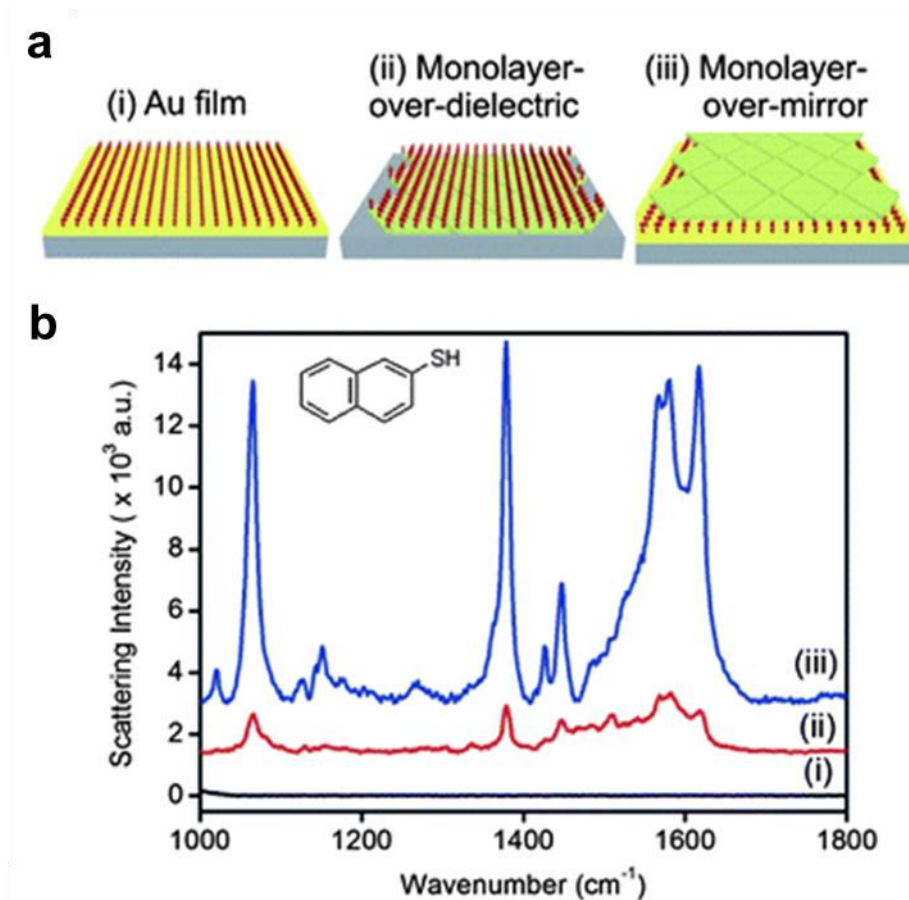


Figure 1-5. Enhancement of SERS performance of self-assembled AuNT film by a bottom Au mirror.⁴⁸

1-4. Fabry-Pérot (FP) cavity

Fabry-Pérot (FP) cavity, first introduced by Charles Fabry and Alfred Pérot in the late 19th century, have become a class of optical devices for efficient and controllable light confinement.⁵⁰ A conventional FP cavity is composed of two parallel mirrors with a sandwiched dielectric layer, which confines the light through the multiple reflection within the cavity structure.^{51, 52} If one of the mirrors has reflectivity less than unity, or even absent, the external incident light can enter the cavity and subsequently undergo multiple reflections inside the dielectric layer (**Figure 1-6**).

In an FP cavity structure, when a light wave is reflected by a mirror, it underwent phase shift. The interferences among the phase-shifted propagating light waves within the cavity form a standing wave pattern. The resonance of an FP cavity, known as cavity mode, requires the standing wave that is produced by destructive interference, and the wavelength (λ) can be estimated as

$$\lambda = \frac{2nd}{m - \varphi_r/\pi}$$

where n denote the effective refractive index; d denote the cavity length; m is the order of the cavity mode, which is an integer; and φ_r is the phase shift upon reflection at the interfaces, respectively.⁵³ It can be inferred that the cavity mode can be tailored by adjusting the thickness or the refractive index of the dielectric layer.^{54, 55}

The combination of FP cavities and plasmonic nanostructure for SERS applications has raised great research interest in recent years. In a typical FP cavity-based SERS substrate, plasmonic nanostructures are placed on the top of the semi-opened FP cavity, exposing the hotspots to enable the effective SERS signal generation. For example, Guo et al. investigated the SERS performance of silica-encapsulated AuNP aggregates on a SiO₂ layer deposited on a bottom Ag mirror, which forms a semi-opened FP cavity structure.⁵⁶ Benefitting from the enhanced light harvesting by the interference within the cavity structure, the SERS signal of trans-1,2-bis(4-pyridyl) ethylene (BPE) molecule attached on AuNP surface showed a 12-fold enhancement on the FP cavity compared with that on glass substrate (**Figure 1-7**). Moreover, the resonance property of the plasmonic structure/FP cavity combination can be tailored by adjusting the cavity length and refractive index, enabling precise alignment of the laser wavelength to maximize the EM field enhancement. Kim et al. demonstrated an FP cavity structure with actively modulated SERS (**Figure 1-8**).³⁵ In this case, the FP cavity structure consists of a porous

polymer perfluoro-(butenyl vinyl ether) (PBVE) layer on an Au film, with gold islands deposited on the top. The top gold island not only provide hotspots for SERS but also serves as a “shadow mask” to fabricate the porous PBVE layer. At an optimized thickness, the resonance frequency of the FP cavity is adjusted to be the same as the excitation, generating the maximized SERS intensity. When ethanol permeates into the porous PBVE layer, the effective refractive index changed, leading to a shift of the resonance thereby weakening the SERS intensity. When the dielectric layer is made from high refractive index material, such as TiO_2 and NiO , a semi-opened FP cavity without top mirror can also support cavity mode.⁵⁷⁻⁶⁰ When combine with plasmonic structures, the modifications of the resonance property could arise from the coupling between the LSPR mode and the cavity mode, known as “modal coupling”. Zang et al. investigated the SERS performance of a AuNP/ TiO_2 /Au film (ATA) structure, where a random AuNP array deposited on a semi-opened FP cavity composed of an ultra-thin TiO_2 film on an Au film (**Figure 1-9a**).⁶¹ The modal coupling results in significant enhancement and broadening of the absorption band (**Figure 1-9b**), which led to a 8-fold enhancement of SERS intensity compared to the AuNP array on glass (**Figure 1-9c**).

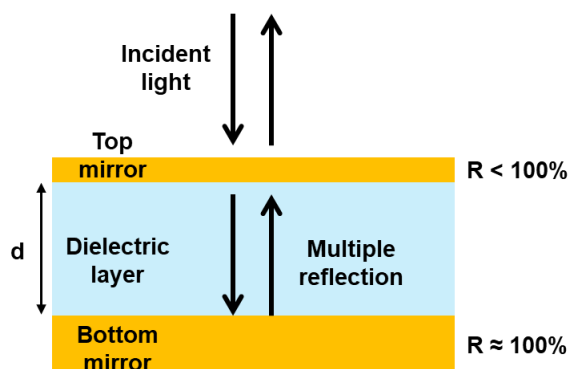


Figure 1-6. Schematic illustration of a Fabry Perot (FP) cavity composed of a dielectric layer sandwiched between two parallel mirrors. The light propagates through the semi-transparent top mirror with $R < 100\%$. Internal reflection occurs at the bottom mirror with $R \approx 100\%$, placed at a cavity length d from the top mirror. The incident light undergoes multiple reflections within the cavity structure.

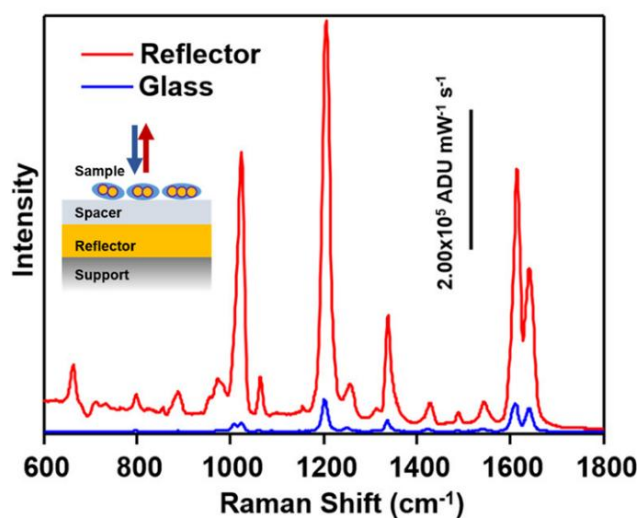


Figure 1-7. Enhancement of SERS signal by FP cavity. The red SERS spectrum is obtained from the AuNP aggregates on FP cavity, and the blue SERS spectrum is obtained from the AuNP aggregates on glass substrate. The inserted scheme illustrates the structure of AuNP aggregates on FP cavity.⁵⁶

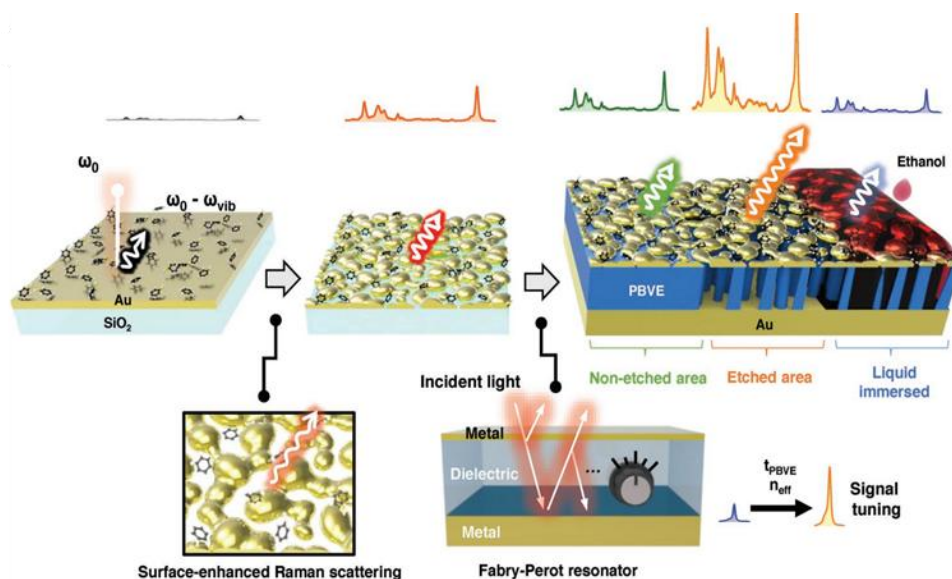


Figure 1-8. Schematic illustration of tunable SERS performance on an FP cavity. The SERS performance of the top gold island can be controlled by changing the thickness and effective refractive index of the underlying PBVE layer.³⁵

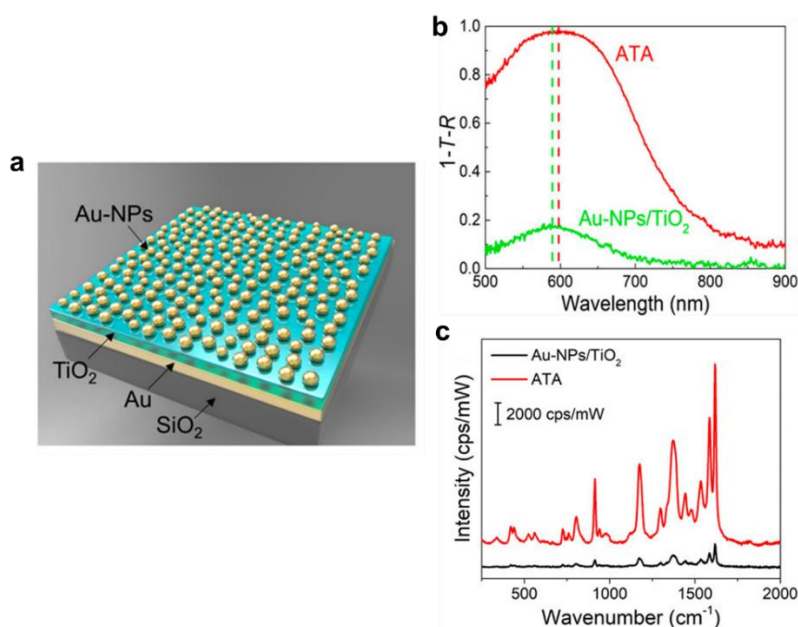


Figure 1-9. SERS enhancement by ATA structure. (a) Schematic illustration of ATA structure. (b) Absorption spectra of ATA structure and AuNP array on TiO_2 layer. (c) SERS spectra of crystal violet on ATA structure and AuNP array on TiO_2 .⁶¹

1-5. Modal strong coupling between LSPR and cavity mode

With rational design of both the FP cavity and the top plasmonic nanoparticle structure, the interaction between the FP cavity mode and the LSPR mode can be strengthened, allowing the system to enter the strong coupling regime, namely, modal strong coupling. A typical ATA structure that demonstrates the modal strong coupling has been reported by Shi et al., with the AuNP array partly inlaid into the underlying TiO₂ layer, which result in more than 99% visible light harvesting (**Figure 1-10a, b**).⁵⁸ In the modal strong coupling regime, the LSPR mode and the cavity mode hybridize to form new energy bands, known as the upper branches (UB) and lower branches (LB), which are separated by a characteristic energy splitting (**Figure 1-10c-e**).^{58, 62-65}

The modal strong coupling behavior is described by harmonic oscillation model, which is expressed as the following function:

$$E_{\pm}(\delta) = \frac{E_{LSPR} + E_{cavity}}{2} \pm \frac{1}{2} \sqrt{(E_{LSPR} - E_{cavity})^2 + |\hbar\Omega|^2}$$

where $E_{\pm}$ are the energies of the hybrid modes, known as UB and LB, E_{LSPR} and E_{cavity} are the uncoupled LSPR and cavity mode energies, respectively, and $\hbar\Omega$ is splitting energy.⁶⁶ When the LSPR mode energy E_{LSPR} and cavity mode energy E_{cavity} are overlapped, the new hybrid modes UB and LB would be generated. Once the two energy levels become equal, known as “tuning condition”, the energy gap between the two hybrid modes is the splitting energy $\hbar\Omega$. For strict identification of modal strong coupling, the splitting energy should surpass the band widths of the hybrid modes, which satisfy the following condition:

$$\hbar\Omega > \sqrt{\frac{\gamma_{UB}^2}{2} + \frac{\gamma_{LB}^2}{2}} = \sqrt{\frac{\gamma_{cavity}^2}{2} + \frac{\gamma_{LSPR}^2}{2}}$$

where γ_{UB} and γ_{LB} are the linewidths of the upper and lower bands, and γ_{cavity} and γ_{LSPR} are the linewidths of the bands generated from FP cavity and LSPR modes, respectively.^{58, 67-69} In addition, when the splitting energy $\hbar\Omega$ is higher than 0.2-fold of the energy of the non-interacting states of the LSPR and the cavity mode ($\hbar\omega_0$), namely, $\hbar\Omega > 0.2\hbar\omega_0$, the system is considered to reach the modal ultrastrong coupling condition.^{70, 71}

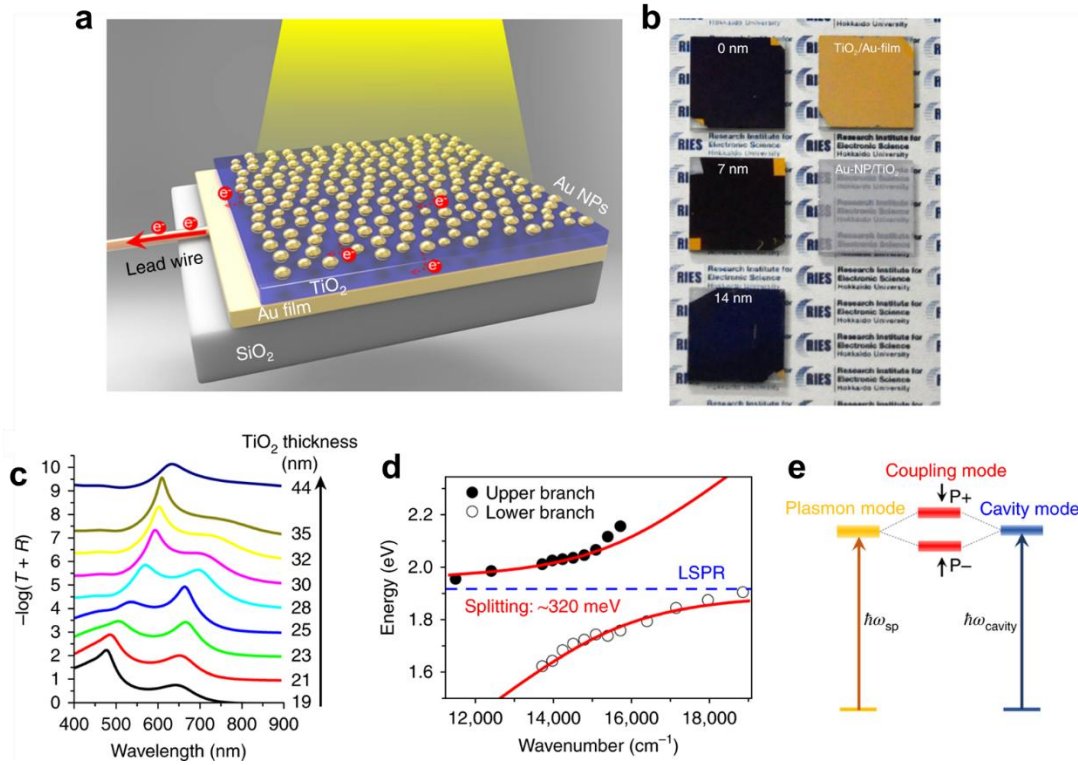


Figure 1-10. (a) Schematic of the ATA structure with partially inlaid AuNPs. (b) Photograph of ATA structures with different inlaid depths (left panel), TiO₂/Au film, AuNP/TiO₂ structures (right panel). (c) Absorption spectra of the ATA structure with various TiO₂ thicknesses. (d) Dispersion curve of the splitting absorption band. The energies of the upper branches and the lower branches were obtained from the splitting absorption bands. The red curves are the fittings using a coupled harmonic oscillator model. The blue dashed line depicts the LSPR energy of the AuNPs. (e) Energy-level diagram of the strong coupling between the cavity mode and the LSPR mode.⁵⁸

The modal strong coupling has also been explored on self-assembled AuNP films without inlaying into the semi-opened FP cavity. For example, Bonin et al. investigated the optical coupling on a AuNP film with particle size of ~50 nm placed on a thin FP cavity with cavity length of 35 nm.⁷² Band splitting was achieved along with boosted light absorption, however, the system did not satisfy the modal strong coupling condition under such a short cavity length due to the significant interplay between the large AuNPs and the bottom mirror, such as dipole-image interaction.⁷³ The effect from the bottom mirror would diminish when the cavity length increases to more than 100 nm, and clear mode splitting induced by modal strong coupling can be achieved.⁷⁴ Garcia et al. systematically investigated the effect of particle size and density on the modal coupling at thick cavity length range (100~200 nm), using a model consists of AuNP array placed on a NiO supported by an Au film (ANA).⁶⁰ The simulation results reveal that both increasing the nanoparticle size and the interparticle distance would facilitate the modal strong coupling (**Figure 1-11a**). Modal ultrastrong coupling was also demonstrated experimentally in this work, where densely packed AuNP films are prepared on the FP cavities formed by NiO/Au film through Langmuir-Schaefer method (**Figure 1-11b**). The splitting energy achieved by the AuNP films with particle sizes of 30 nm and 50 nm were 633 meV (**Figure 1-11c**) and 775 meV (**Figure 1-11d**), respectively.

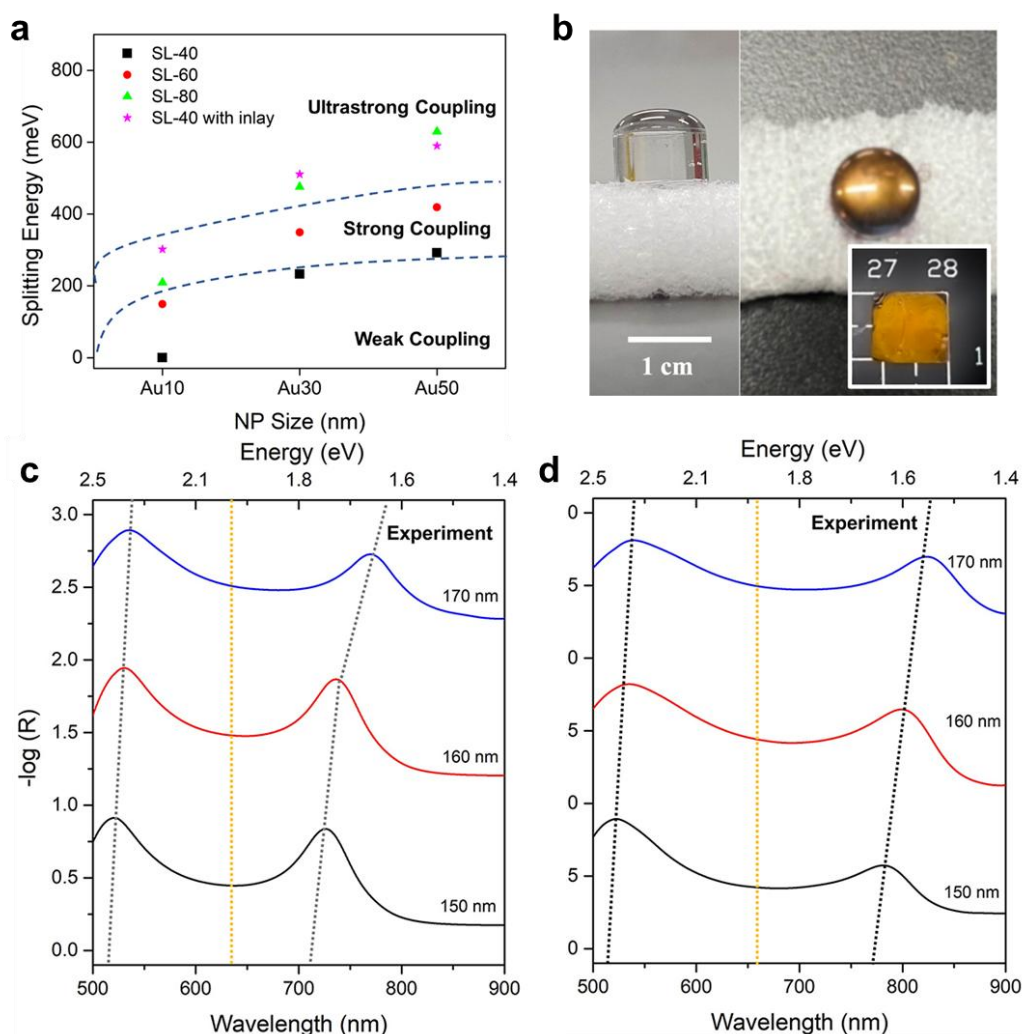


Figure 1-11. Realization of modal ultrastrong coupling on ANA structure. (a) Coupling regimes between LSPR and cavity mode at varying particle size and surface coverages. (b) Air–liquid interface self-assembly of AuNPs. (c, d) Absorption spectra of ANA structure with top particle size of (a) 30 nm and (d) 50 nm at different NiO thickness. The yellow dotted line represents the LSPR energy, and the black dotted curve traced the dispersion of the hybrid polaritonic states.⁶⁰

1-6. SERS under modal ultrastrong coupling conditions

The SERS performance of the self-assembled AuNP film under modal ultrastrong coupling condition was further studied by Suganami et al. (**Figure 1-12**).⁶⁹ AuNP colloids with ~15 nm in diameter were assembled into densely packed nanoparticle film, which are transferred on a FP cavity through Langmuir-Schaefer method. The FP cavity is

composed of a ~ 33 nm TiO_2 layer deposited on an Au film. With densely packed AuNP film on the FP cavity, the modal coupling can be strengthened into modal ultrastrong coupling regime while forming enhanced hotspots in large areas. This structure demonstrated modal ultrastrong coupling with a splitting energy of ~ 680 meV. The SERS signal of crystal violet (CV) on the AuNP film demonstrated a 78-fold enhancement compared with that on the TiO_2 film. This enhancement can be attributed to the markedly increased light absorption in the spectra range of the LB, which overlapped the excitation wavelength. Moreover, the signal homogeneity is demonstrated to be significantly improved even in the presence of small amount of analyte, owing to the quantum coherence effect under the modal ultrastrong coupling condition. The achievements by modal strong coupling demonstrated by above research provide a new approach for improving the SERS substrate design.

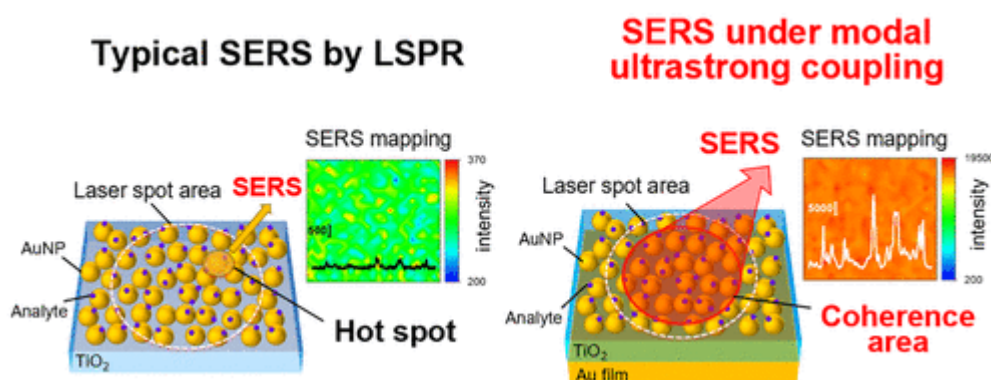


Figure 1-12. Improved SERS signal intensity and homogeneity on densely packed self-assembled AuNP array under modal ultrastrong coupling condition on a TA structure.⁶⁹

1-7. Objective

The self-assembled AuNP film demonstrates great potential in SERS applications. When it is integrated with FP cavity, the modified resonance property via modal strong coupling further improved its SERS performance. However, the study on the SERS under modal strong coupling conditions limited in small AuNPs on specific FP cavities, and the effects of modal strong coupling on the SERS performance remain insufficiently explored and warrant further investigation. Anisotropic AuNPs, especially AuNTs, exhibited great potential in SERS applications. However, they have received limited attention regarding their modal coupling with FP cavities, despite offering diverse surface properties and superior plasmonic performance compared to their isotropic counterparts.^{48, 49, 75} Moreover, the strong tip-enhanced field confinement of AuNTs renders them highly suitable for sensitive SERS applications,⁷⁵ with their performance expected to be further amplified by integration with FP cavities. In this thesis, I systematically investigated and compared the SERS performance of AuNP films composed of AuNT or gold nanospheres (AuNS) under the modal coupling with a semi-opened FP cavity structure consisting of a TiO₂ layer on an Au film (TA), with a focus on the effect of particle shape.

In Chapter 2, modal coupling behavior between the self-assembled AuNP film and the FP cavity was evaluated. AuNT and AuNS with approximately the same particle volume were synthesized through seed-mediated growth method. By using the Langmuir-Schaefer method, densely packed AuNT and AuNS films were fabricated on TA substrates, forming the AuNT film on TA (t-ATA) and AuNS film on TA (s-ATA) structures (**Figure 1-13, left**). The modal coupling behavior of these films was examined by varying the TiO₂ thickness, in conjunction with experimental measurements and finite-difference time-domain (FDTD) simulations.

In Chapter 3, the SERS performances of the t-ATA and s-ATA structures are investigated and compared (**Figure 1-13, right**). To find out the locations of hotspots in the t-ATA and s-ATA structures, the (EM) field distributions are evaluated by FDTD simulation. Then, SERS performances of the t-ATA and s-ATA structures were evaluated at different TiO_2 thicknesses using 4-MBA as the reporter. The particle shape effect on SERS performance under the modal ultrastrong coupling conditions are discussed.

In Chapter 4, I summarize the thesis and afford the significance and prospects.

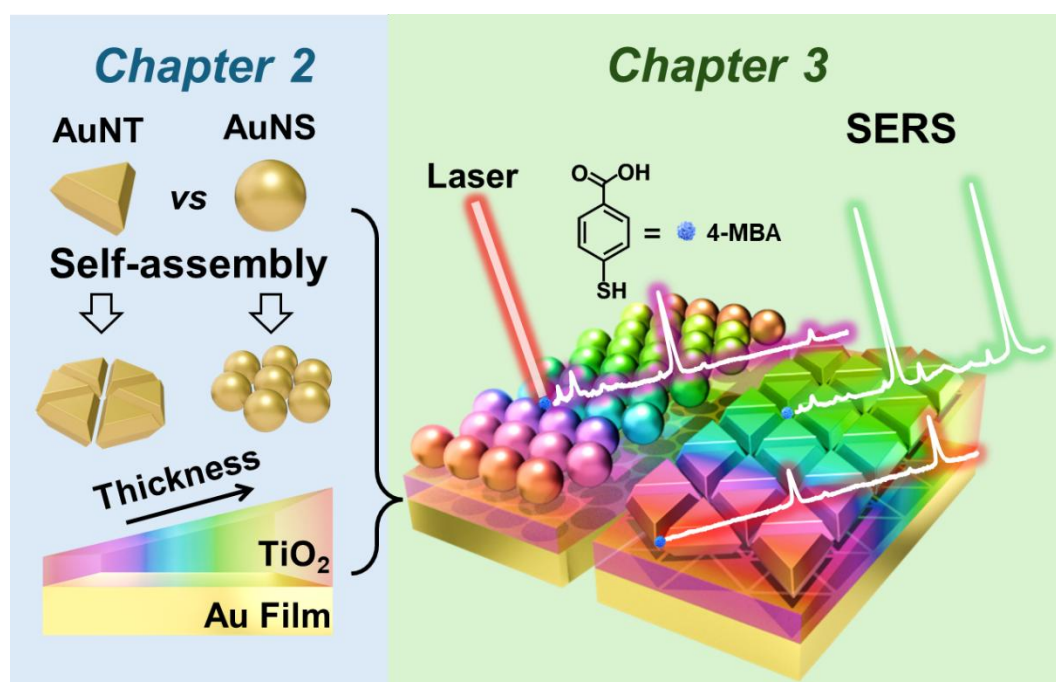


Figure 1-13. Schematic illustration of my doctoral thesis.

Chapter 2

***Investigation of modal coupling between
self-assembled AuNP films and FP cavities***

2-1. Introduction

The realization of modal strong coupling relies on rational design of the plasmonic-FP cavity system. The most straightforward way is to embed the plasmonic structures within a conventional FP cavity, which has been demonstrated to achieve modal ultrastrong coupling.⁷¹ However, the SERS application requires the exposure of the plasmonic structure to allow the analyte approach to the hotspots. Therefore, semi-opened FP cavities with plasmonic nanostructure placed atop are more desired. To achieve the modal strong coupling, on the one hand, the semi-opened FP cavity should have significant cavity mode. For example, a TiO₂ layer on Au film (TA) can support significant cavity mode at visible wavelength range due to the high refractive index of TiO₂. This TA structure has been frequently used as FP cavity to study modal coupling.^{57, 58, 62, 63, 76-79} On the other hand, the design of the top plasmonic structures is also important. Previous reported works used AuNP array with average diameter of ~14 nm prepared from heat evaporation, which were inlaid into the underlying TiO₂ layer and achieved modal strong coupling with coupling strength of ~320 meV.⁵⁸ The system can be further improved into modal ultrastrong coupling regime when the AuNPs are replaced by Ag-Au alloy particles.⁶³ Another extensively studied system uses gold nano disk array fabricated on TA structures by lithography, and the modal strong coupling was achieved with more than 100 nm-thick TiO₂ layers.^{57, 76} Recently, modal ultrastrong coupling with the underlying FP cavity has been achieved by dense AuNP films prepared from Langmuir-Schaefer method due to the high surface coverage.⁶⁰

Gold nanotriangles (AuNTs) exhibit multiple LSPR modes owing to their shape anisotropy.^{80, 81} When they were self-assembled in an edge-to-edge configuration, the plasmon coupling among adjacent AuNTs further complicates the LSPR characteristics,

potentially supporting multiple hybrid modes under strong coupling with a FP cavity. However, their modal coupling behavior with FP cavity remains systematically investigation.

Previous studies in our lab employed amphiphilic surface ligand to fabricate closely packed monolayers of silver nanocube⁸² and AuNTs⁷⁵ with high homogeneity using Langmuir-Schaefer method. Building upon this approach, in this chapter, self-assembled AuNP films composed of AuNTs or gold nanospheres (AuNS) were prepared on TA substrates, forming t-ATA and s-ATA structures, respectively (**Figure 2-1**). By varying the TiO₂ thickness of the underlying TA substrate, the modal coupling behavior on the t-ATA and s-ATA structures are investigated and compared with a focus on the shape effect. Furthermore, the modal coupling behaviors were validated through finite-difference time-domain (FDTD) simulations.

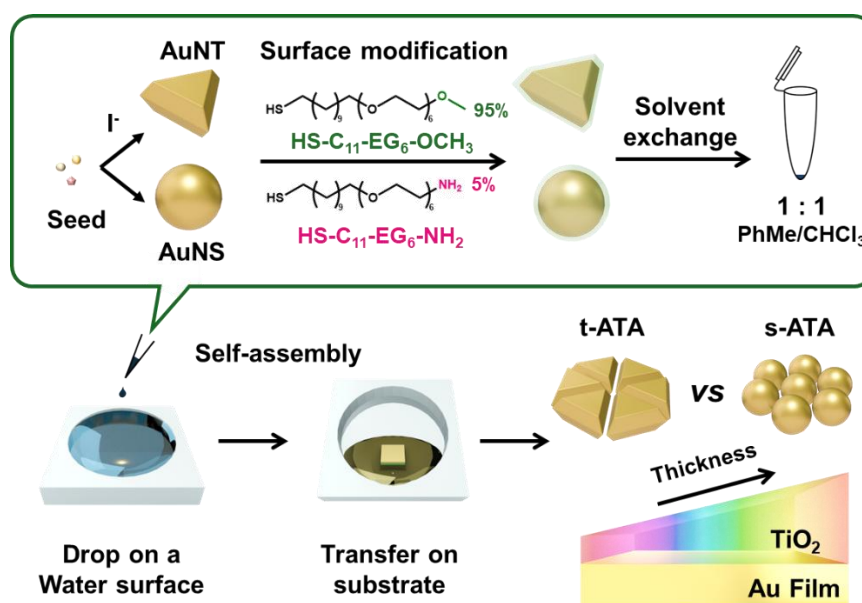


Figure 2-1. Schematic illustration of chapter 2. Preparation of self-assembled of AuNT film and AuNS film on TA substrate to form t-ATA and s-ATA substrate for evaluation of modal coupling behavior.

2-2. Experimental section

2-2-1. Chemical and apparatus

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, L-ascorbic acid (AA), NaI and NaBH_4 were purchased from Sigma–Aldrich. Oligo(ethylene glycol) ligands, Methoxy-hexa(ethylene glycol)-undecanethiol (HS-C11-EG6-OCH_3) and 20-(11-Mercaptoundecanyloxy)-3,6,9,12,15,18-hexaoxaicosane-1-amine (HS-C11-EG6-NH_2), were purchased from ProChimia Surfaces, Sp.zo.o (**Figure 2-2**). All other reagents were purchased from Wako Pure Chemical Industries, Ltd. (Japan). Quartz substrates with 1 mm thickness were purchased from Kenis, Ltd. (Japan). Indium tin oxide (ITO) substrates were purchased from GEOMATEC Co., Ltd. Ultrapure water (18.2 $\text{M}\Omega/\text{cm}$, Milli-Q, Millipore) was used to prepare all solutions.

The extinction spectra were recorded with a V-770 UV-vis spectrometer (JASCO Corporation, Japan). Reflection spectra were measured with a spectroscopic reflectometer (F20-UV, Filmetrics). Scanning electron microscope (SEM) images were obtained using a SU-8230 system (Hitachi High-Tech Co., Ltd., Japan). Transmission electron microscope (TEM) images were obtained using a STEM HD-2000 system (Hitachi High-Tech Manufacturing and Service Co., Ltd., Japan) with 200 kV acceleration voltage.

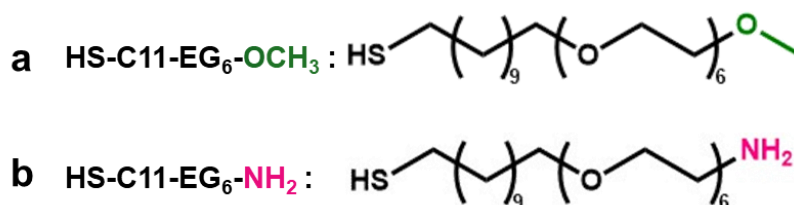


Figure 2-2. Chemical structures of the surface ligands used in this study.
 (a) Methoxy-hexa(ethylene glycol)-undecanethiol (HS-C11-EG6-OCH_3).
 (b) 20-(11-Mercaptoundecanyloxy)-3,6,9,12,15,18-hexaoxaicosane-1-amine (HS-C11-EG6-NH_2).

2-2-2. Preparation of AuNTs and AuNSs

AuNT colloids were prepared following a protocol reported by Liz-Marzán et al, including seed preparation, growth reaction and purification,^{49, 83} as shown in **Figure 2-3**. For preparation of gold seed in CTAC, 25 μL of HAuCl_4 (50 mM) was added into 4.7 mL of CTAC (0.1 M) with mild stirring, then, 300 μL of freshly prepared ice-cold NaBH_4 (10 mM) was rapidly injected into the CTAC/ HAuCl_4 mixture under vigorous stirring. The solution immediately turned brown, indicating the formation of gold seeds. The gold seed solution was stored at room temperature for 2 h, and then it was diluted 10 times before use. The growth reaction of AuNT was divided into two steps. (1) In the first step, two solutions were prepared. Solution A was prepared by adding 1.6 mL of CTAC (0.1 M), 8 mL of deionized water, 40 μL of HAuCl_4 (50 mM) and 15 μL of NaI (10 mM) were mixed in a 50 mL tube. For solution B, 40 mL of CTAC (0.1 M), 40 mL of deionized water, 1 mL of HAuCl_4 (50 mM) and 600 μL of NaI (10 mM) were mixed in a 100 mL tube. (2) In the second step, 40 μL and 800 μL of AA (0.1 M) were added into the solution A and solution B with gentle mixing. Then, 3.295 mL of solution A was removed, and 55 μL of the diluted seed solution was injected into solution A while stirring. After stirring for 2 s, all the solution A was rapidly poured into solution B, and solution B was stirred for 1 min, accompanied by color change from pink, purple to dark blue. The growth solution B was left undisturbed at room temperature for 2 h to finish the growth reaction. Finally, the resultant AuNT solution was centrifuged (2900 g, 1 h) at room temperature to remove the excess reagents, and the AuNTs were redispersed in 0.05 M CTAC solution.

In the step of purification, 5.625 mL of 25 wt% CTAC was mixed with 40 mL AuNT solution, making the final concentration of the CTAC to be 0.17 M. The AuNT solution was left under room temperature overnight, and the AuNTs would precipitate at

the bottom of the tube. Then, the supernatant was removed, and 50 mM CTAC was added to redisperse the precipitated AuNTs. The purification step was repeated 4–5 times to remove as many impurities as possible.

AuNSs were prepared from the method modified from the protocol of synthesis of AuNTs (**Figure 2-3**). The seed solution was the same as that of AuNTs. The growth solutions were prepared without addition of NaI, and the volume of seed solution added into the solution was 90 μL . The growth was finished in 2 h, and then the particles were washed by centrifugation.

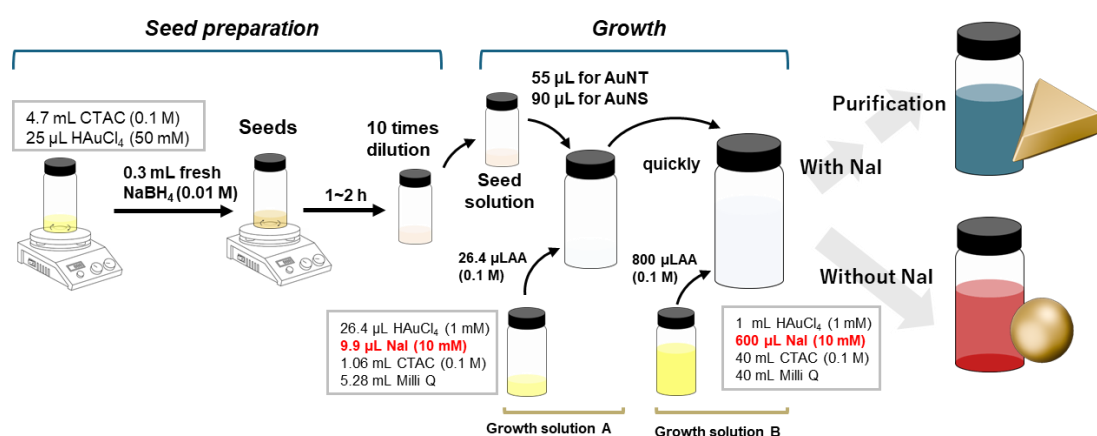


Figure 2-3. Schematic illustration of synthesizing AuNT and AuNS by seed-mediated growth method.

2-2-3. Surface modification of AuNTs and AuNSs

The AuNSs and purified AuNTs were dispersed in 0.05 M CTAC. The AuNT or AuNS solution (6 mL) was centrifuged (2900 g, 30 min, room temperature), and 5400 μL supernatant was removed, followed by addition of 4560 μL of deionized water and 840 μL amphiphilic ligand solution (95% HS-C11-EG6-OCH₃ and 5% HS-C11-EG6-NH₂, 1 mM). The solution was left at room temperature overnight for ligand exchange. Then, the

above step was repeated once to ensure that the AuNTs and AuNSs were modified with 5% cationic ligands.

2-2-4. Preparation of TA substrates

Quartz substrates were cleaned by sequential ultrasonication in acetone, methanol, and deionized water for 5 minutes, followed by drying with a stream of nitrogen gas. To prepare TA substrates, 100 nm-thick gold films were deposited onto the quartz substrates using a sputtering system (ULVAC, QAM-4-STs), with a 2 nm chromium adhesion layer. A 2 nm-thick titanium layer was additionally deposited onto the Au surface to facilitate subsequent TiO₂ deposition. TiO₂ films were then deposited on the Au films via atomic layer deposition (ALD) using a commercial system (Picosun, R-200 Adv) at 300 °C, employing titanium tetrachloride (TiCl₄) and water (H₂O) as precursors. The film thickness was characterized using a film measurement system (Filmetrics F20-UV, Ver 4.0). For stable attachment of AuNT and AuNS films in the subsequent steps, the substrates were immersed in a 1 mM ethanolic solution of dodecylphosphonic acid for over 30 minutes, followed by annealing at 120 °C for 1 hour to obtain hydrophobic surfaces.

2-2-5. Preparation of self-assembled AuNP films on substrates

Ligand-coated AuNT (3 mL) or AuNS (1 mL) were sequentially washed with ethanol and chloroform by centrifugation, then redispersed in 13 µL of a chloroform/toluene mixture (1:1 v/v). A homemade Teflon container (3 cm diameter) was filled with 9.4 mL of phosphate buffer (5 mM, pH 7.1), and the nanoparticle dispersion was gently dropped onto the aqueous surface, forming a thin nanoparticle layer at the air/water interface. Subsequently, 5 mL of the aqueous phase was removed, and the container was tilted by

approximately 30°. An additional 2.5 mL of the aqueous phase was further removed using a pipette, inducing a compact arrangement of the nanoparticles. The resulting assembled nanoparticle film was then transferred onto the hydrophobic indium tin oxide (ITO) or TA substrates (**Figure 2-4**). The extinction spectra of the AuNT and AuNS films were recorded on ITO substrates by a V-770 UV-vis spectrometer (JASCO Corporation, Japan). Since the 100 nm-thick bottom Au film blocks light transmission, the extinction of the t-ATA and s-ATA structures was evaluated by measuring the reflectance (R) and plotting $-\log R$ as a function of wavelength using a spectroscopic reflectometer (F20-UV, Filmetrics).

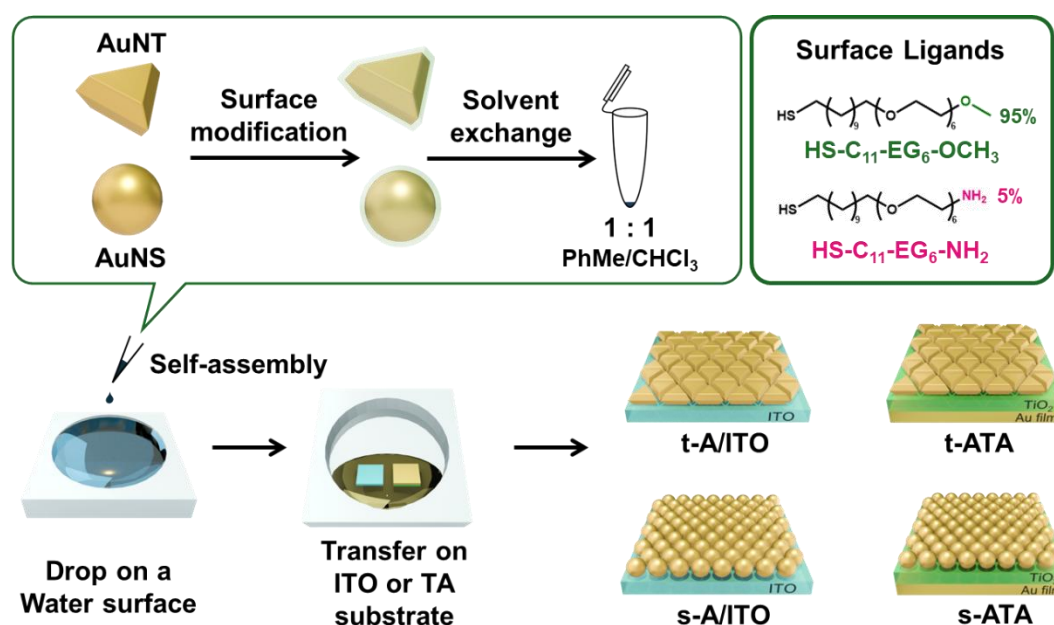


Figure 2-4. Schematic illustration of preparation of self-assembled AuNT and AuNS film on ITO or TA substrates using Langmuir-Schaefer method.

2-2-6. Curve Fitting by Harmonic Oscillation model for determination of coupling strength

To construct the dispersion curve, the energies of the hybrid modes were plotted as a function of the effective cavity mode energy in the presence of the top AuNT or AuNS films at various TiO₂ thicknesses. These dispersion relations were fitted using a harmonic oscillator model:

$$E_{\pm}(\delta) = \frac{E_{LSPR} + E_{cavity}}{2} \pm \frac{1}{2} \sqrt{(E_{LSPR} - E_{cavity})^2 + |\hbar\Omega|^2}$$

where $E_{\pm}$ are the energies of the UB and LB hybrid branches, E_{LSPR} and E_{cavity} are the uncoupled LSPR and cavity mode energies, respectively, and $\hbar\Omega$ is splitting energy.

2-2-7. Evaluation of modal coupling behavior by FDTD simulation

FDTD simulations were conducted using commercial software (Lumerical Solutions) to calculate the optical spectra and near-field distributions of AuNT and AuNS films on FP cavities. Basic unit cells were modeled under periodic boundary conditions in the x- and y-directions. The details of the models are shown in **Figure 2-5**. The AuNT were modeled as octahedrons based on reported facet information (**Figure 2-5a**).^{84, 85} The edge length and thickness were set to 70 nm and 30 nm, respectively. The interparticle distance was set to 4 nm, corresponding to the estimated thickness of the ligand layer.⁸⁶ Each AuNT was coated with a 2 nm-thick dielectric shell (refractive index = 1.4). For AuNS, the particle diameter was set to 45.6 nm to match the volume of AuNT (**Figure 2-5b**). Their arrangement was based on SEM observations, and a 2 nm ligand layer was also modeled, with the same 4 nm interparticle distance. The surrounding medium was assumed to be air. The dielectric function of gold was taken from experimental data by P. B. Johnson and R. W. Christy.^{87, 88} TiO₂ was modeled as a dielectric with an average refractive index of 2.4. Additionally, a 1 nm-thick dielectric layer (refractive index = 1.4) was placed on

top of the TiO_2 layer. Simulations were carried out using circularly polarized plane waves at normal incidence to excite all possible resonant modes, considering the imperfect periodicity of the nanoparticle assemblies. A uniform mesh size of 1 nm was used throughout the simulations.

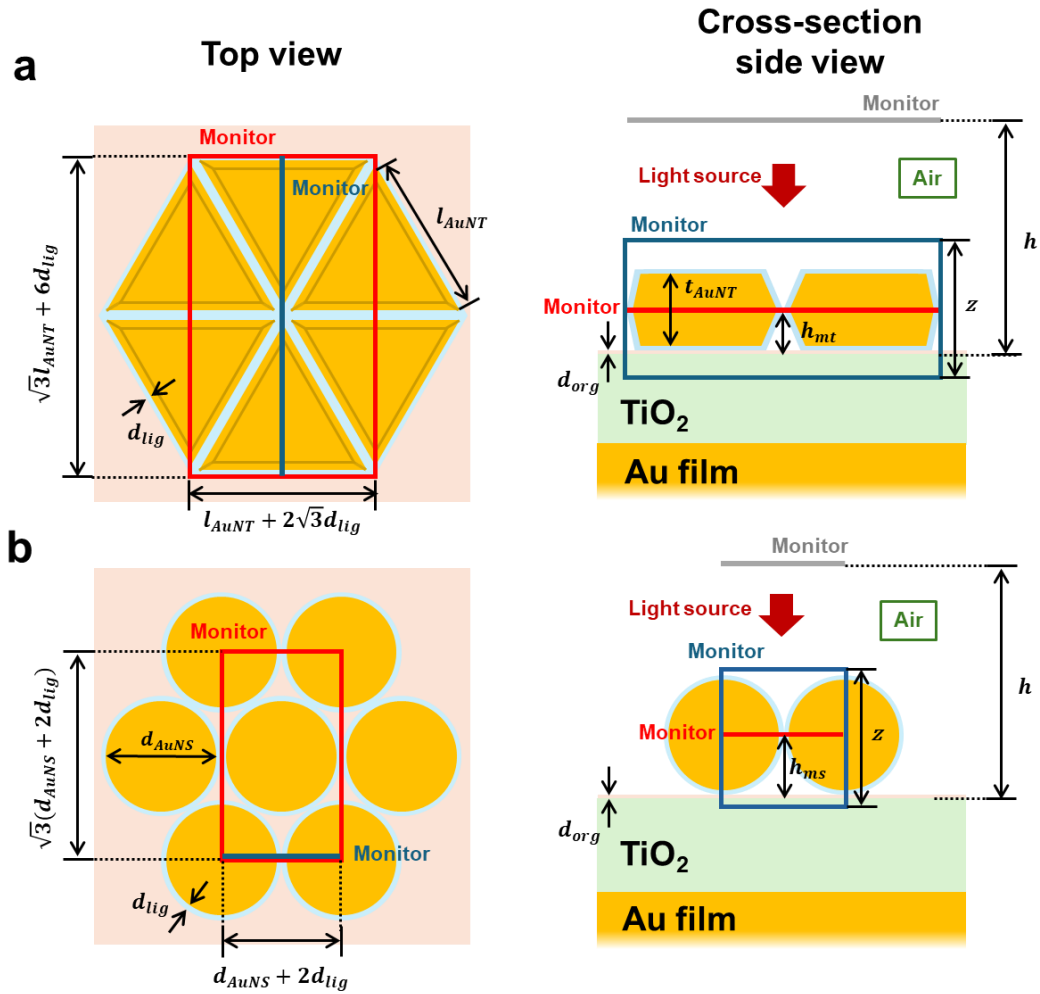


Figure 2-5. Details of FDTD models. (a) Top view (left) and cross-sectional side view at the blue monitor (right) of t-ATA structure. The edge length (l_{AuNT}) is 70 nm, and the thickness of AuNT (t_{AuNT}) is 30 nm. (b) Top view (left) and cross-sectional side view at the blue monitor (right) of s-ATA structure. The diameter (d_{AuNS}) is 45.6 nm. The thickness of the adhesion organic layer (d_{org}) and the surface ligand (d_{lig}) are 1 nm and 2 nm, respectively. For the monitors in both (a) t-ATA and (b) s-ATA structures, the blue monitors record the cross-sectional field distribution at side view. The height (z) is 70 nm. The red monitors record the cross-sectional field distribution at top view,

and the positions are set to be 18 nm for t-ATA (h_{mt}) and 25.8 nm for s-ATA (h_{ms}) from the TiO₂ surface. The gray monitors record the extinction spectra. Each has the same dimension as its corresponding red monitor below, and the positions (h) are set to be 300 nm from the TiO₂ surface.

2-3. Results and Discussion

2-3-1. Preparation of self-assembled AuNT and AuNS film on substrate

AuNTs were synthesized following a seed-mediated growth method. TEM images reveal that the AuNTs possess an average edge length of 70 nm (**Figures 2-6a, b**). The SEM image of the face-to-face assembled AuNTs shows an average thickness of about 28 nm (**Figures 2-6c, d**). Their extinction spectrum in dispersion exhibits a sharp peak around 660 nm, accompanied with a weaker shoulder at around 520 nm (**Figures 2-6e**). The particle volume is estimated to be 49575.5 nm³, considering the AuNTs are octahedrons according to reported models.^{84, 85} To investigate the effect of particle shape on modal coupling and the resulting SERS performance, AuNSs were prepared from the seed-mediated growth method without adding halide ions that induce anisotropic growth. The diameters of the AuNSs were controlled to be ~46 nm, corresponding to a particle volume comparable to that of the AuNTs (**Figures 2-7a, b**). Their extinction spectrum in dispersion shows a single plasmonic peak centered at ~533 nm (**Figure 2-7c**).

Next, self-assembled AuNT and AuNS films are prepared on substrates via Langmuir-Schaefer method. In both cases, the plasmonic peaks of the assembled films were broadened and red-shifted relative to their dispersed states, due to interparticle plasmonic coupling (**Figures 2-8a, b**). Notably, the AuNT film exhibited a broader plasmonic band with multiple shoulder peaks, which can be attributed to multiple resonance modes induced by its shape anisotropy. The SEM images indicate that both the AuNT and AuNS films formed closely packed monolayers, albeit with some defects and

voids (**Figures 2-8c, d, Figure 2-9**). The fast Fourier transform (FFT) patterns show significant regularity in the scale of laser spot size in the Raman measurement (**Figure 2-9**). SEM analysis revealed surface coverages of approximately 76% for the AuNT film and 72% for the AuNS film (**Figures 2-8c, d, Figure 2-9**), which is consistent with previously reported results.⁷⁵

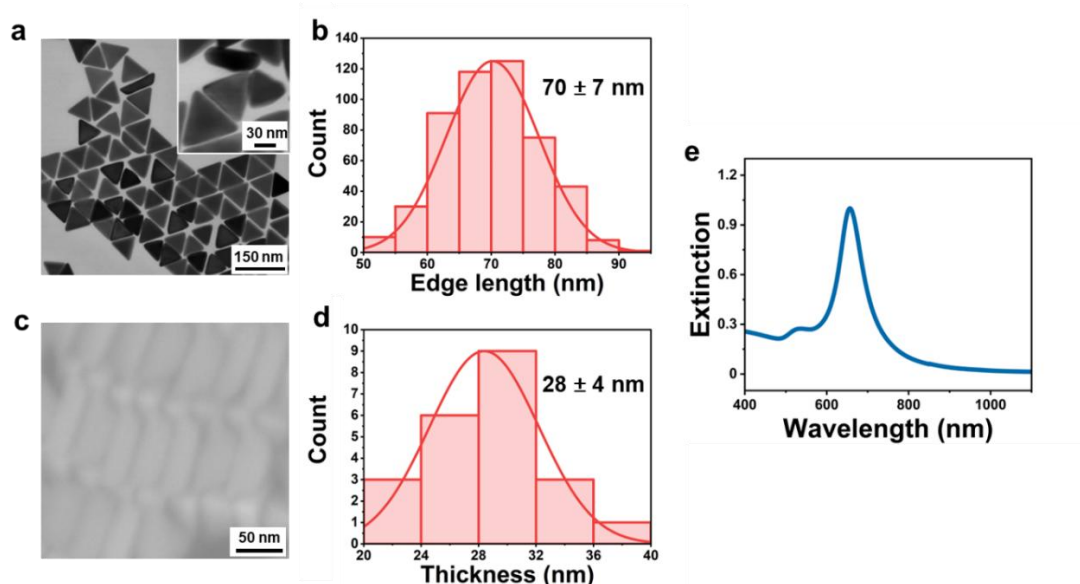


Figure 2-6. Characterization of AuNTs. (a) STEM image. (b) Distribution of edge length. The average edge length is determined to be 70 ± 7 nm (500 particles counted) particle counted). (c) SEM image of face-to-face assembly of AuNTs. (d) Distribution of thickness of AuNTs. The average edge thickness is determined to be 28 ± 4 nm (22 particles counted). (e) Extinction spectrum of dispersed AuNTs.

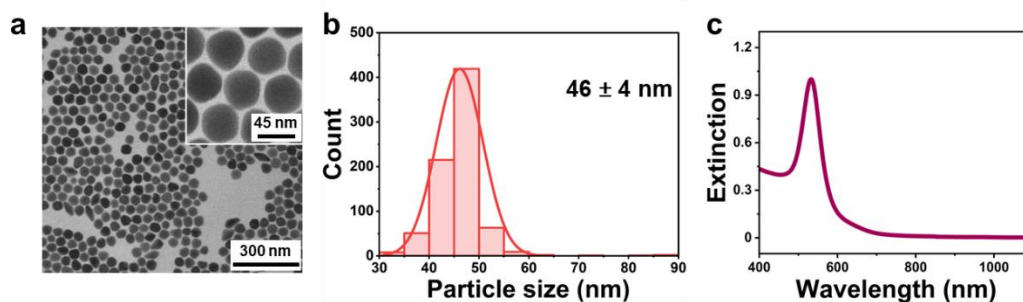


Figure 2-7. Characterization of AuNSs. (a) TEM image. (b) Size distribution. The average diameter is determined to be 46 ± 4 nm (770 particles counted). (c) Extinction spectrum of dispersed AuNS.

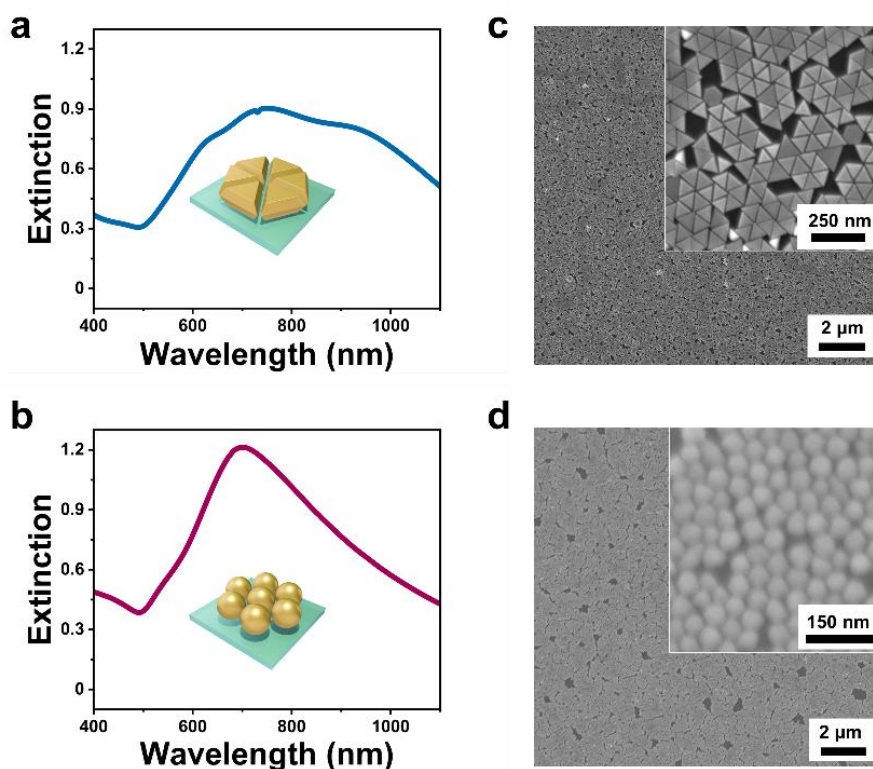


Figure 2-8. Characterization of AuNT and AuNS films. (a, b) Extinction spectra of nanoparticle-assembled films composed of (a) AuNTs and (b) AuNSs. (c, d) SEM images of (c) the AuNT film and (d) the AuNS film deposited on indium tin oxide (ITO) substrates.

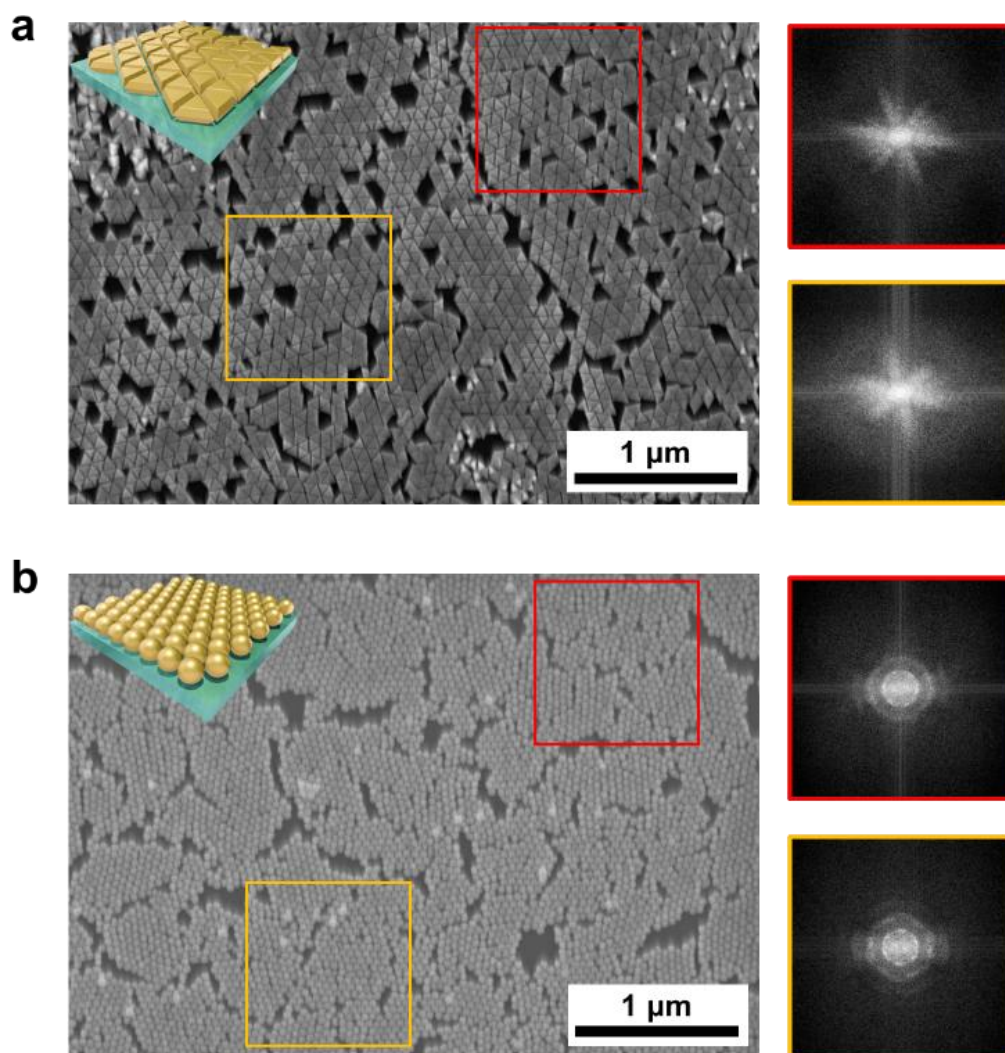


Figure 2-9. Large area SEM images of the self-assembled (a) AuNT film and (b) AuNS film on ITO substrates. The images on the right show the corresponding fast Fourier transform (FFT) patterns obtained from local regions of the SEM images.

2-3-2. Evaluation of the modal coupling between AuNP film and FP cavity

To examine the modal coupling with FP cavity, the AuNT and AuNS films were transferred onto TA substrates, forming t-ATA and s-ATA structures, respectively. By varying the TiO₂ thickness, the modal coupling behaviors on the t-ATA and s-ATA structures were evaluated based on their extinction spectra, which are calculated by the negative logarithm of the reflectance.

At thin TiO₂ thickness range, the TA structure exhibits quarter-wave cavity mode. At the TiO₂ thickness of 20 and 30 nm the cavity mode of TA structures overlaps with the inter-band transition of the bottom Au film. With the increase of the TiO₂ thickness, the wide and weak cavity mode red shift to the longer wavelength range (**Figure 2-10**), which consistent with the previous report.⁵⁸ With the AuNT and AuNS film on the top, the spectra exhibit a resonance feature within the wavelength range of 500–600 nm (**Figure 2-11**). For TiO₂ thickness of 20 nm and 30 nm, the spectra of t-ATA show an increasing trend at wavelengths longer than 900 nm (**Figure 2-11a**), whereas the spectra of s-ATA display distinct peaks in this region (**Figure 2-11b**), suggesting an optical influence from the bottom Au mirror. When the TiO₂ thickness exceeds 50 nm, the resonance peaks undergo a red shift accompanied by a decrease in intensity, indicating the diminished interactions between the top nanoparticle films and the bottom Au mirror.^{74, 89, 90}

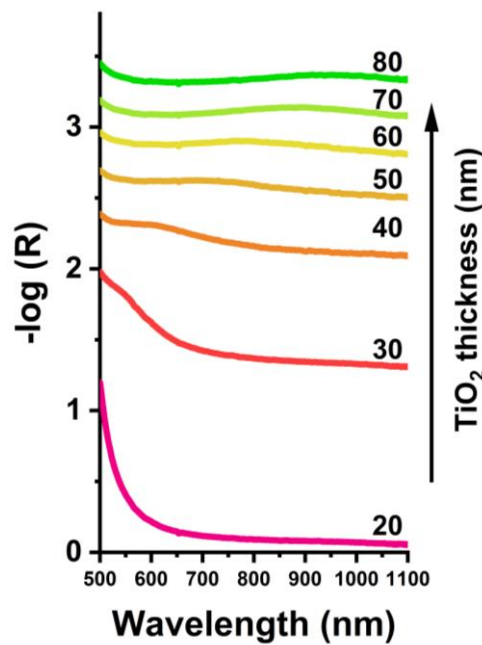


Figure 2-10. Extinction spectra of TA structures with 20–80 nm TiO_2 layers.

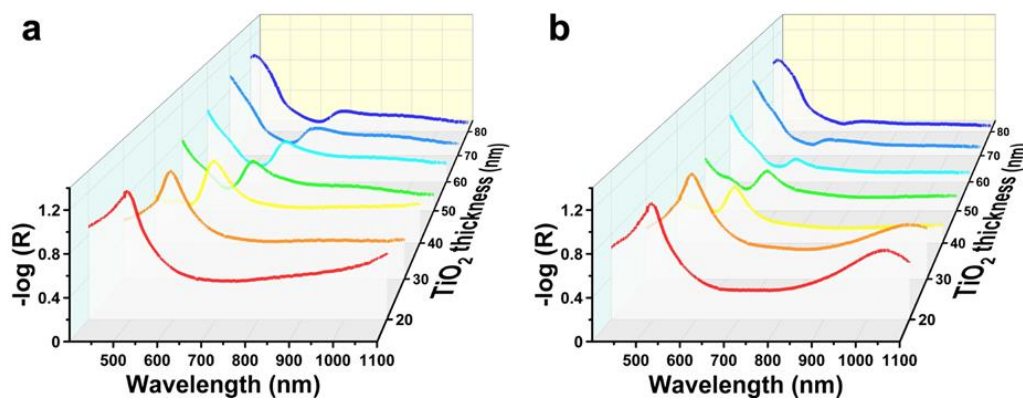


Figure 2-11. Extinction spectra of (a) t-ATA and (b) s-ATA structures with 20–80 nm TiO_2 layers.

At thick TiO_2 range (120–230 nm), the TA structures support clear second-order cavity modes (**Figure 2-12**).^{57, 58} In the spectral region above 500 nm, distinct peak splitting appeared both in t-ATA and s-ATA structures, indicating the mode hybridization that originates from LSPR-cavity mode coupling (**Figures 2-13**). The modal coupling strength is evaluated by fitting the dispersion curve with harmonic oscillation model.

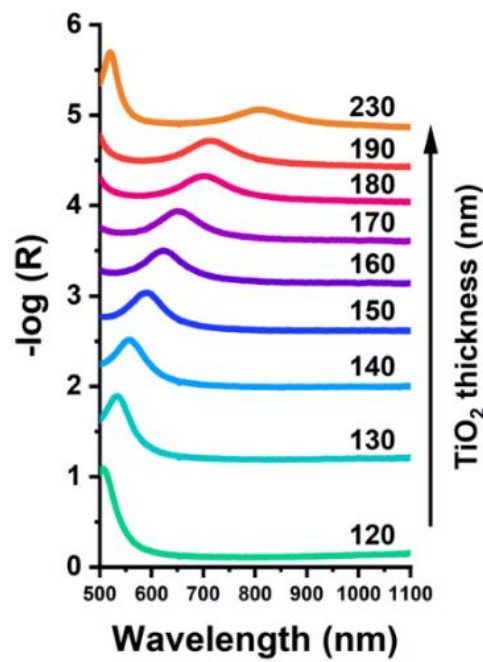


Figure 2-12. Cavity modes of TA substrates with 120–230 nm TiO_2 layers.

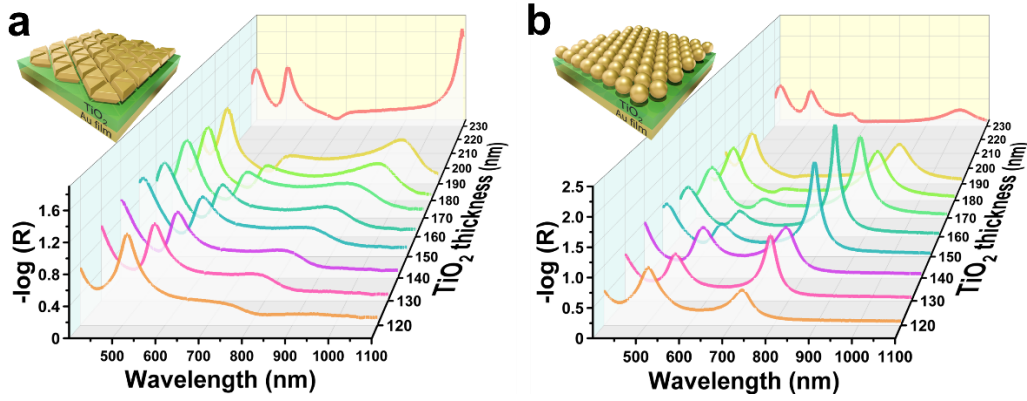


Figure 2-13. Modal coupling between AuNP films and TA structures. (a, b) Extinction spectra of (a) t-ATA and (b) s-ATA structures at TiO_2 thickness range of 120–230 nm.

To construct the dispersion curve, the wavelengths of the hybrid modes were converted to energies. Meanwhile, the presence of AuNP films on the top alters both the effective cavity length and the refractive indices, leading to a shift of cavity mode.⁷⁴ Therefore, the effective cavity modes were manually adjusted from the experimentally measured cavity modes from TA structures so that the UBs and LBs can consistent with the harmonic oscillation model. This adjustment corresponded to the energy shifts of -0.2 eV and -0.3 eV for the t-ATA and s-ATA, respectively (**Figure 2-14**). The line width of each hybrid mode is determined from Lorentz fitting in **Figure 2-15** and **Figure 2-16**, respectively. The splitting energies ($\hbar\Omega$) and the linewidths of the UBs (γ_{UB}) and LBs (γ_{LB}) satisfy $\hbar\Omega > \sqrt{\frac{\gamma_{UB}^2}{2} + \frac{\gamma_{LB}^2}{2}}$, indicating that the t-ATA and s-ATA structures are in the modal strong coupling condition.^{58, 67-69} Then, the hybrid mode energies are plotted as a function of the wavenumber of effective cavity modes, and the dispersion relations are fit using the harmonic oscillator model (**Figure 2-17**). The splitting energies of the t-ATA and the s-ATA structure were determined to be approximately 650 meV. When

compared with the LSPR mode energy of AuNT film ($\hbar\omega_0 \approx 1.69$ eV) and AuNS film ($\hbar\omega_0 \approx 1.95$ eV), the splitting energies correspond to $\sim 0.38 \hbar\omega_0$ and $\sim 0.34 \hbar\omega_0$, respectively. These results confirm that both t-ATA and s-ATA achieved modal ultrastrong coupling.

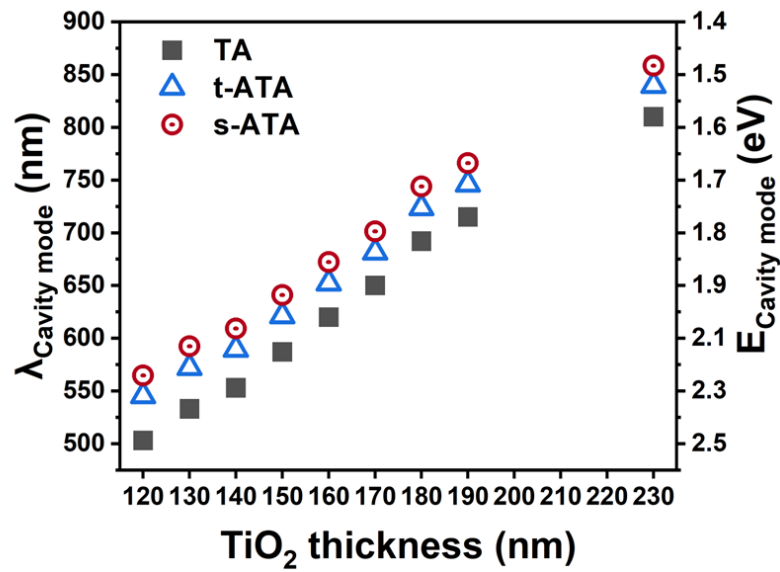


Figure 2-14. Estimated effective cavity modes in the t-ATA and s-ATA with 120–230 nm TiO₂ based on the measured cavity mode in **Figure 2-12**.

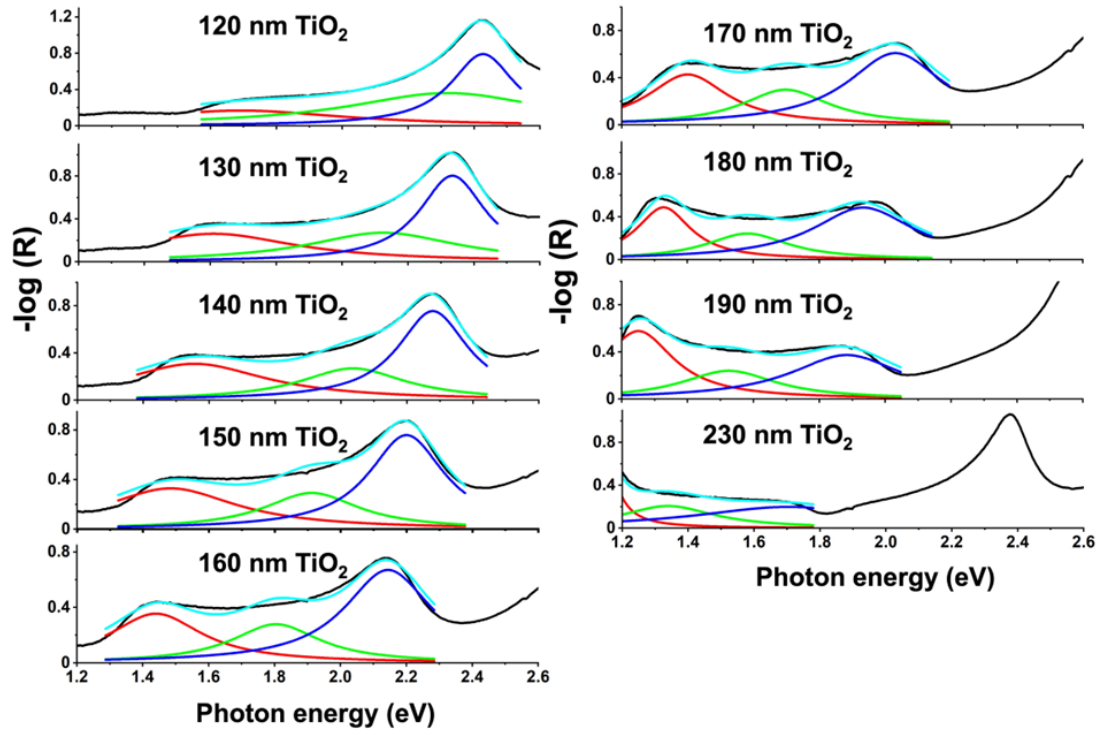


Figure 2-15. Lorentz fitting of absorption spectra of t-ATA structure at different TiO_2 thicknesses. The red lines and cyan lines indicate the lower polaritons and upper polaritons, respectively, and the green lines are attributed to the uncoupled cavity mode.

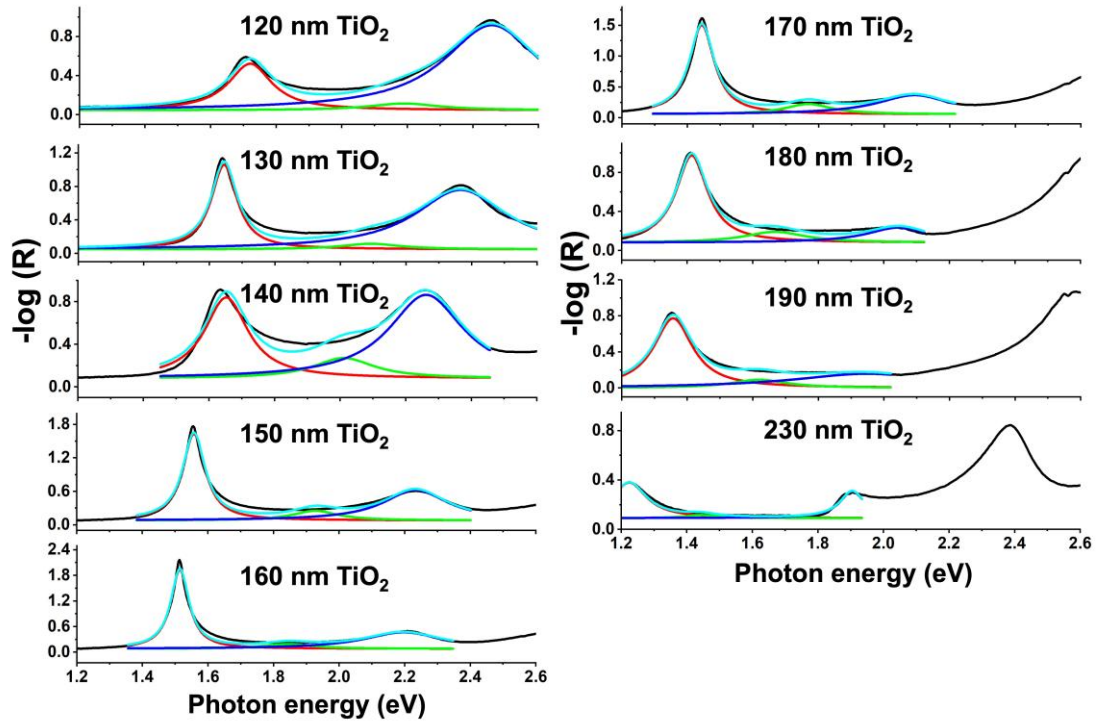


Figure 2-16. Lorentz fitting of absorption spectra of s-ATA structure at different TiO_2 thicknesses. The red lines and cyan lines indicate the lower polaritons and upper polaritons, respectively, and the green lines are attributed to the uncoupled cavity mode.

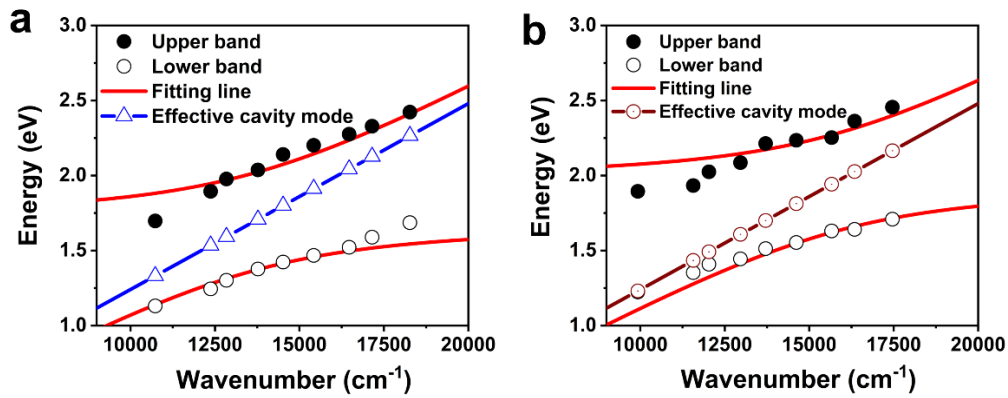


Figure 2-17. Dispersion curves of the hybrid modes for (a) t-ATA and (b) s-ATA with 120–230 nm TiO_2 .

According to the spectra of t-ATA and s-ATA structures, the resonance peaks of t-ATA appear at longer wavelengths than the s-ATA structures at the same TiO₂ thickness, which is a consequence of the red-shifted LSPR mode induced by the shape anisotropy of the AuNTs. Also, the different LSPR modes led to different TiO₂ thicknesses for tuning condition for the AuNT film and AuNS film, which correspond to 180 nm and 140 nm, respectively. In addition, the peak linewidths on t-ATA structures are broader than those of the s-ATA, indicating more complex modal coupling between multiple plasmon modes of the AuNT film and the cavity mode. These modal coupling behaviors are also consistent with previous reports,⁷⁴ and the larger peak splitting energies observed here can be attributed to the high surface coverage of the self-assembled AuNP film.

2-3-3. Validation of the modal coupling behavior by FDTD simulation

To verify the modal coupling behaviors across different TiO₂ thickness, the reflection spectra of TA, t-ATA and s-ATA structures were calculated using FDTD simulations, with the TiO₂ thickness varied from 20 to 230 nm at an interval of 10 nm.

The calculated spectra of TA structures are shown in **Figure 2-18**, where the cavity mode positions demonstrate periodic behavior with the increase of TiO₂ thickness. At TiO₂ thickness range of 20–80 nm, the calculated spectra show wide cavity modes that red shifts with the increase of the TiO₂ thickness (**Figure 2-18a**), which is consistent with the experiment result shown in **Figure 2-10**. When the TiO₂ thickness exceeds 80 nm, the second-order cavity modes appear at 500–600 nm, which red shift with the TiO₂ thickness increase. As shown in **Figure 2-18b**, the second-order cavity modes show narrow band width, and the peak positions are consistent with the experiment results (**Figure 2-12**). Meanwhile, when the thickness exceeds 190 nm, the third-order cavity modes appear at around 500 nm, while the second-order cavity modes reach the near-infrared region.

For t-ATA and s-ATA structures, the calculated spectra at TiO₂ thickness range of 20–110 nm and 120–230 nm are shown in **Figure 2-19** and **Figure 2-20**, respectively. The TiO₂ thickness-dependent modal behavior calculated by FDTD simulation also agreed well with the experimental results, the thickness range of 120–230 nm demonstrates the obvious peak splitting in both t-ATA and s-ATA structures (**Figure 2-20a, b**). The simulation results show minor deviations in peak positions as well as narrower band width compared with experimental results, which are likely due to imperfect nanoparticle assembly in the experimental samples. To evaluate the coupling strength of the simulation results, the dispersion curves were constructed by plotting the energies of the hybrid modes as a function of the wavenumber of the effective cavity mode (**Figure 2-20c, d**). The effective cavity mode is estimated from the simulated cavity modes with the energy shifts of -0.2 eV and -0.25 eV for the t-ATA and s-ATA, respectively. According to the curve fitting by harmonic oscillation model, the coupling strength for both t-ATA and s-ATA structure were estimated to be 650 meV, which also consistent with the experimental result (**Figure 2-17**).

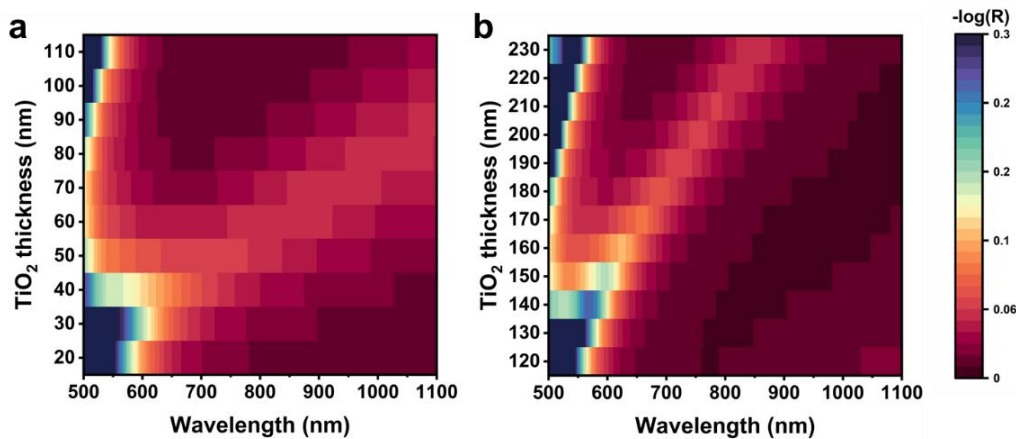


Figure 2-18. Simulated spectra of TA structures with TiO₂ layer at thicknesses range of (a) 20–110 nm and (b) 120–230 nm.

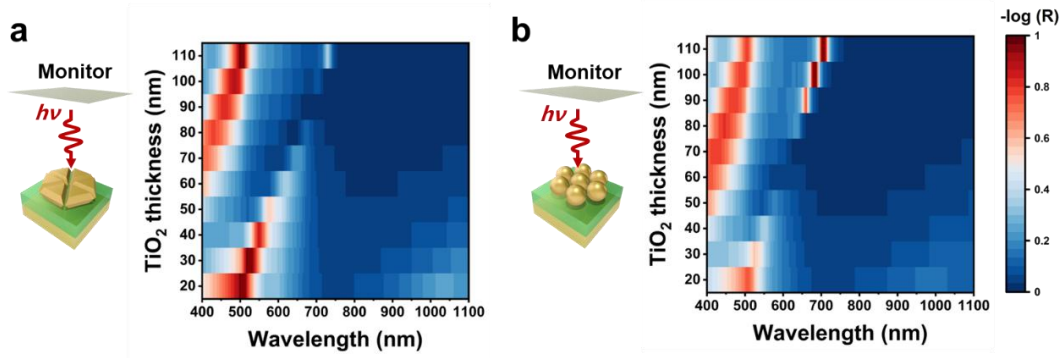


Figure 2-19. Dispersion curves of the simulated splitting extinction band for (a) t-ATA and (b) s-ATA with TiO_2 thicknesses ranging from 20 to 110 nm.

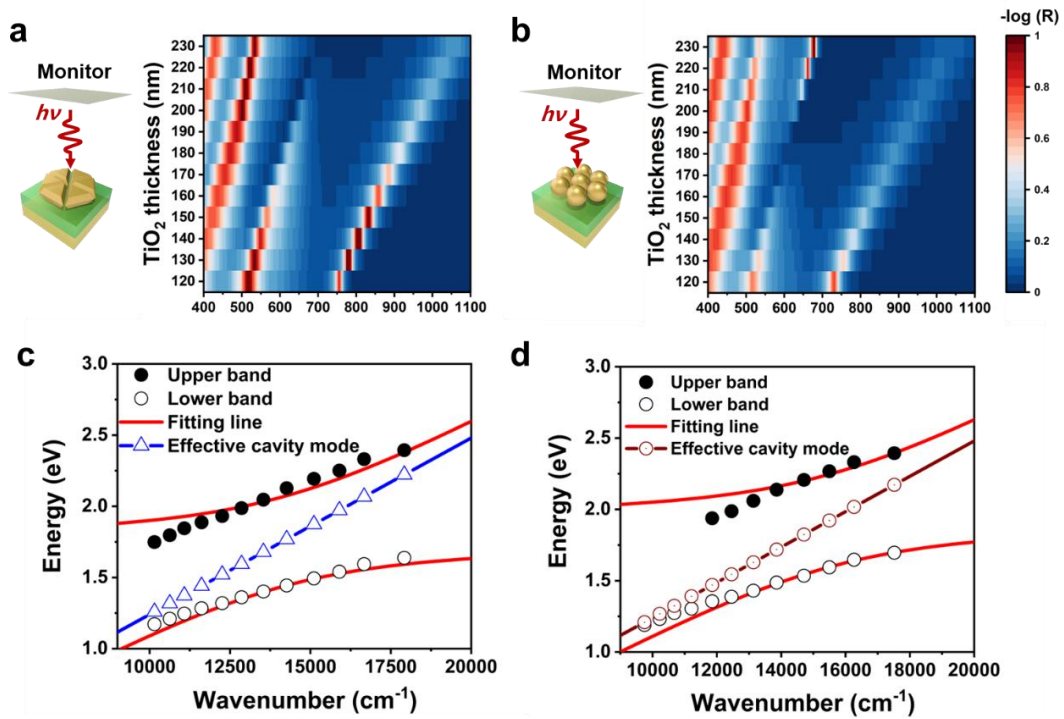


Figure 2-20. Dispersion curves of the simulated splitting extinction band for (a) t-ATA and (b) s-ATA with TiO_2 thicknesses ranging from 120 to 230 nm. The coupling strengths for both structures are estimated to be ~ 650 meV.

2-4. Conclusion

In this chapter, AuNTs and AuNSs with approximately equal particle volume were synthesized through a seed-mediated growth method. Densely packed AuNT and AuNS films with over 70% surface coverage were prepared using Langmuir-Schaefer technique and subsequently transferred on TA substrates, forming t-ATA and s-ATA structures. The modal coupling behavior in t-ATA and s-ATA structures were investigated both numerically and experimentally. Modal ultrastrong coupling was observed when the TiO_2 layer exceeds 120 nm, with the experiment and the simulation result shows good agreement. Compared with the AuNS with optimal particle volume, AuNTs exhibit multiplied LSPR modes at longer wavelength due to shape anisotropy, as a result, the hybrid modes of the t-ATA showed larger band width at each TiO_2 thickness with red-shifted peak position than that of s-ATA. The modal coupling strength reached 650 meV in both t-ATA and s-ATA structures, with the varied tuning conditions at the TiO_2 thickness of 180 nm and 140 nm, respectively. These findings highlight the particle shape effect on the modal ultrastrong coupling-induced resonance modification of the ATA structures, which provides useful information for design of nanophotonic devices that utilize the modal coupling in FP cavity.

Chapter 3

***Shape-dependent SERS performance of AuNP films
under modal ultrastrong coupling with FP cavities***

3-1. Introduction

The modal coupling with FP cavities led to the modification of the resonance characteristic of the plasmonic nanostructures through mode hybridization. Previous study on the SERS under modal coupling focused on ATA structure with small AuNP size (~ 15 nm in diameter) and thin TiO_2 layer (~ 30 nm).^{61, 62} The absorption bands under modal coupling displayed near-perfect light harvesting at specific wavelength ranges, which resulted in the boosted near field intensity and SERS signal.

In Chapter 2, relatively larger AuNPs than the previous studies, including AuNTs with edge length of 70 nm and AuNSs with 46 nm in diameter, were employed to form self-assembled nanoparticle films on TA substrates. The AuNTs and AuNSs have approximately the same particle volumes, and both demonstrated modal ultrastrong coupling at TiO_2 thicknesses more than 120 nm. Due to the multiplied LSPR modes on the AuNT film, the hybrid modes of the t-ATA at each TiO_2 thickness showed larger band width and red-shifted peak position than the s-ATA. The varied resonance properties caused by the shape effect result in different alignments with the fixed laser wavelength, which may partly account for the difference in the SERS response.

In this chapter, the shape-dependent SERS properties of t-ATA and s-ATA structures were evaluated and compared (**Figure 3-1**). To clarify the positions of hotspots, the EM field distribution on the t-ATA and s-ATA under the different excitations and modal coupling states are examined by FDTD simulation. Next, the SERS performance toward different concentrations of 4-MBA were examined on t-ATA and s-ATA with varied TiO_2 thickness.

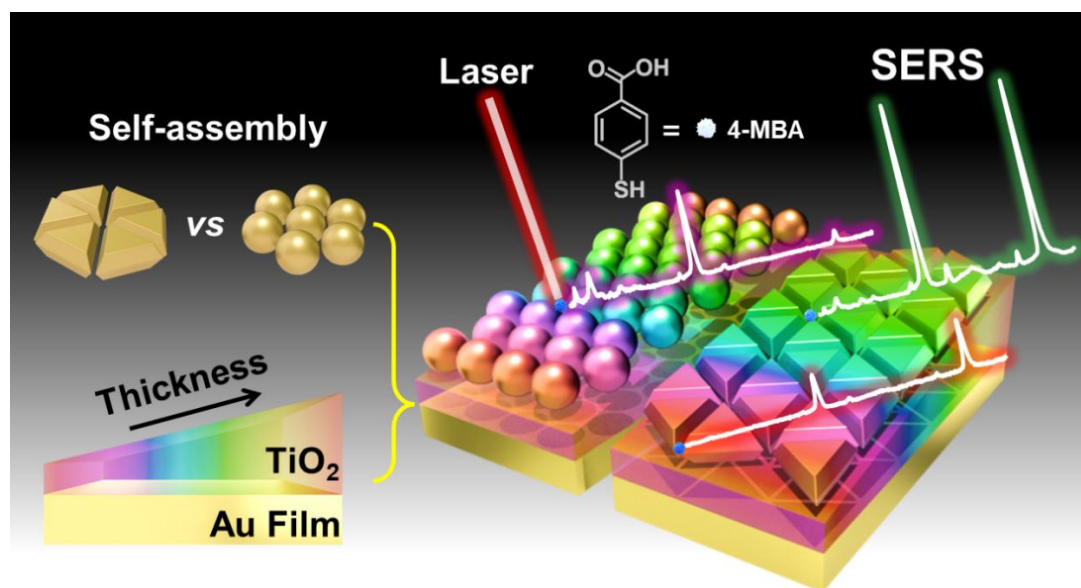


Figure 3-1. Schematic illustration of chapter 3. Investigation of SERS performance of AuNT and AuNS films under modal ultrastrong coupling conditions.

3-2. Experimental section

3-2-1. Chemical and apparatus

The chemical reagents and instruments used for preparation and characterization of self-assembled AuNS and AuNT films are described in Chapter 2 ([2-2-1](#)).

3-2-2. Preparation of self-assembled AuNP film on substrates

TA substrate is fabricated following the method described in Chapter 2 ([2-2-4](#)). TiO₂ substrate is fabricated by directly depositing TiO₂ on quartz substrate using ALD, the condition follows the ALD described in Chapter 2 ([2-2-4](#)). ITO substrate is purchased from GEOMATEC Co., Ltd. All the substrates were immersed in a 1 mM ethanolic solution of dodecylphosphonic acid for over 30 minutes, followed by annealing at 120 °C for 1 hour to obtain hydrophobic surfaces. The preparation of self-assembled AuNT and AuNS films on the substrates follows the method described in Chapter 2 ([2-2-5](#)).

3-2-3. FDTD simulation

FDTD simulation for analysis of the distribution of EM field and SERS EF are conducted using a model described in Chapter 2 ([2-2-7](#)).

3-2-4. SERS measurement

To prepare samples for SERS measurements, the substrates were immersed in ethanolic solutions of 4-mercaptobenzoic acid (4-MBA) at various concentrations overnight. After incubation, the substrates were rinsed with ethanol and Milli-Q water to remove non-specifically adsorbed 4-MBA molecules, then dried under a nitrogen stream. Raman measurements using a 785 nm laser were performed with a Raman microscope system (Renishaw, inVia Reflex) equipped with a 50× objective lens. For 633 nm excitation, a Raman microscope system (Horiba, HR-Evolution) with a 100× objective lens was used. Raman spectra were recorded over the range of 600–1700 cm^{-1} , with three accumulations per measurement.

3-3. Results and discussion

3-3-1. Field distribution under modal ultrastrong coupling

To clarify the optical hotspot positions, the EM-field enhancement ($|E_{loc}|^2/|E_0|^2$) on nanoparticle films under modal ultrastrong coupling conditions was investigated by FDTD simulations. The individual AuNT and AuNS model are set to be in identical particle volume. Considering the minimized interparticle distance in the presence of surface ligand, the edge-to-edge spacing in the AuNT film and the interparticle spacing in the AuNS film are fixed. Due to the peak variations at the strong coupling conditions caused by the different LSPR modes, the EM-field distributions of the t-ATA and s-ATA structures were analyzed under their respective tuning conditions, with TiO_2 thickness of

180 nm (**Figures 3-2a, b**) and 140 nm (**Figures 3-2c, d**), at the wavelengths corresponding to the two hybrid bands. The side- and top-view simulations of the particle assemblies revealed that the strongest local field enhancements occur at the interparticle gaps. Specifically, AuNT assemblies generate strong hotspots primarily at vertex-to-vertex and edge-to-edge gaps arising from the concentrated charge density induced by the anisotropic geometry (**Figures 3-2a, b**), whereas AuNS assemblies form comparatively moderate hotspots at point-to-point gaps (**Figures 3-2c, d**). It is worth noting that the spatial distribution of the enhanced fields remained largely consistent across different excitation wavelengths. Excitation at the LB wavelengths (911 nm for t-ATA and 778 nm for s-ATA) generates significantly broader and stronger field enhancements compared to excitation at the UB wavelengths.

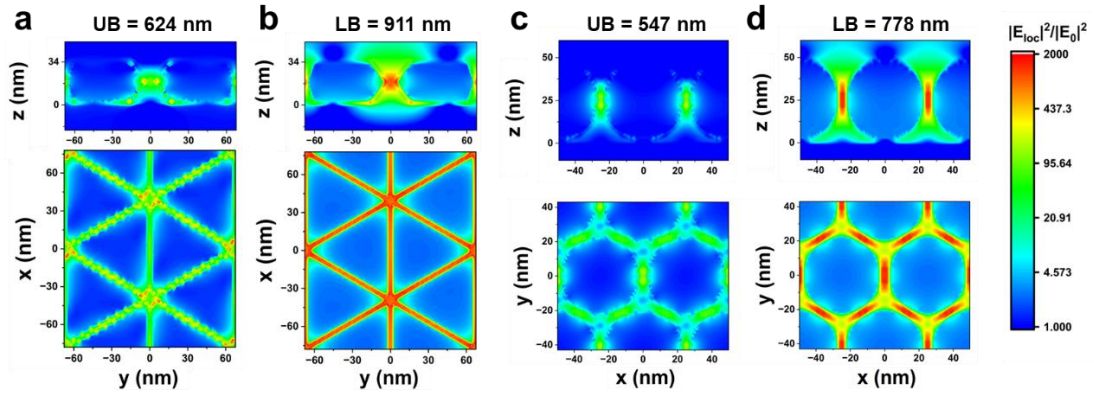


Figure 3-2. (a, b) Cross-sectional EM near-field distributions of t-ATA with a 180 nm TiO_2 layer under excitation at (a) 624 nm (UB) and (b) 911 nm (LB). (c, d) Cross-sectional EM near-field distributions of s-ATA with a 140 nm TiO_2 layer under excitation at (c) 547 nm (UB) and (d) 778 nm (LB).

In addition, the EM field distributions under the excitation of the LB wavelengths are further shown by histograms (**Figures 3-3a, b-i, -ii**) and 3D mappings (**Figures 3-3a, b-iii**). According to the field distributions in the corresponding cross-sectional planes, the

field intensity values exceeding 200 are mainly located within interparticle gaps (**Figures 3-3a, b-i**). In moderate field intensity range (200–1500), large number of pixels in t-ATA drop at the range of 650–1300, which correspond to the edge-to-edge regions (**Figures 3-3a-i, -iii**). For s-ATA, the distribution of pixels is dominated by the field intensity range of 200–500, with an additional cluster between 1000–1500, corresponding to the near-surface region of the sphere and the interstitial sites among three adjacent spheres (**Figures 3-3b-i, -iii**). In the high field intensity range (>1500), the t-ATA shows a sparse distribution in the 1500–2600 interval, associated with the minute regions around the triangle tips (**Figures 3-3a-ii, -iii**), where the Raman signal of analytes can be efficiently enhanced. In the case of s-ATA, all pixels remain below 1600, reflecting the hotspots at point-to-point gaps (**Figures 3-3b-ii, -iii**). Under appropriate excitations, the dense distribution of moderately enhanced EM fields in the s-ATA structure also holds potential to generate significant Raman signals. For further comparison between the t-ATA and s-ATA structures with identical TiO_2 thicknesses, the EM field distribution is also checked on t-ATA structure with 140 nm TiO_2 (**Figure 3-4**) and s-ATA structure with 180 nm TiO_2 (**Figure 3-5**) excited by the corresponding wavelengths at the UBs and LBs. The field distributions demonstrate that the LB resonance consistently yields the maximum field intensity with t-ATA generating stronger localized field enhancement, confirming that these features are inherent to the LB resonance rather than dependent on the specific tuning conditions. For SERS measurements, excitation lasers at 532, 633, and 785 nm are commonly used. Owing to the stronger field intensities excited at the wavelengths close to the LB, the 785 nm laser could be identified as optimal for SERS, since the Stokes-shifted wavelengths from 785 nm excitation would more easily align with the LB.

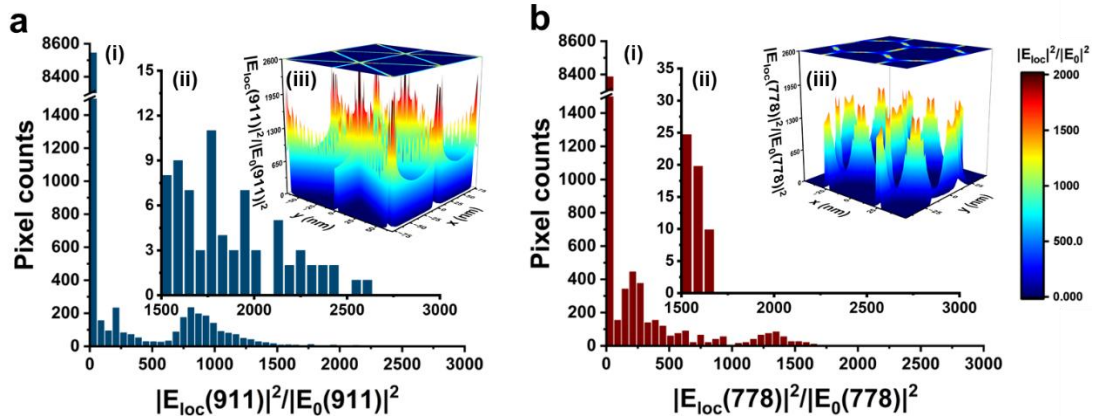


Figure 3-3. Statistical near-field distributions with the excitation at the LBs in the x-y cross-section plane for (a) t-ATA, 180 nm TiO₂ and (b) s-ATA, 140 nm TiO₂. (i, ii) Histograms showing pixel distributions across different field intensity ranges. (iii) 3D maps of near-field distributions. For comparison, the pixel count for s-ATA (g, i–ii) was scaled by a factor of 2.47 to match the unit area of t-ATA due to its smaller unit size.

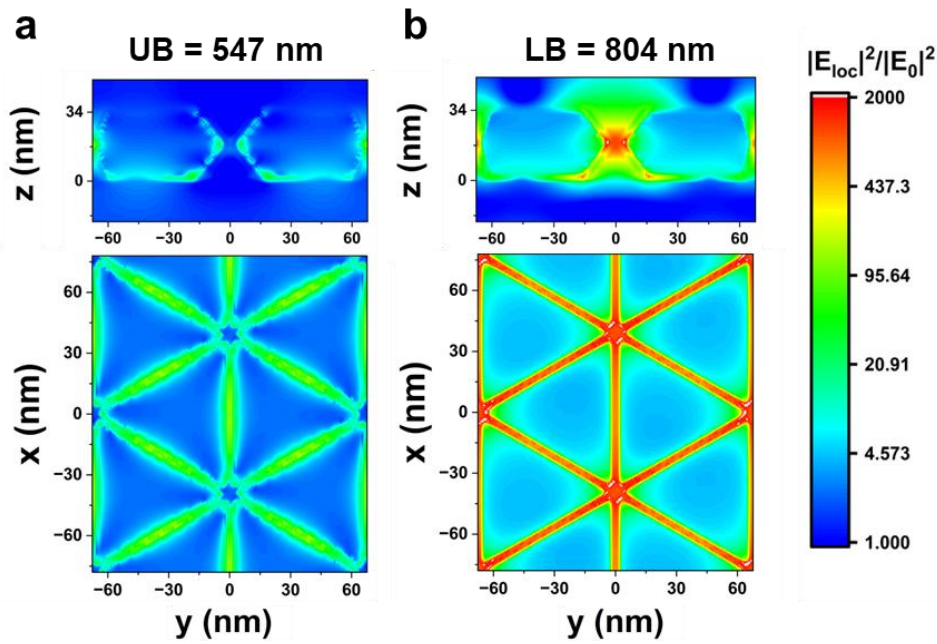


Figure 3-4. Cross-sectional near-field distributions of t-ATA with a 140 nm TiO₂ layer under excitation at (c) 547 nm (UB) and (d) 804 nm (LB).

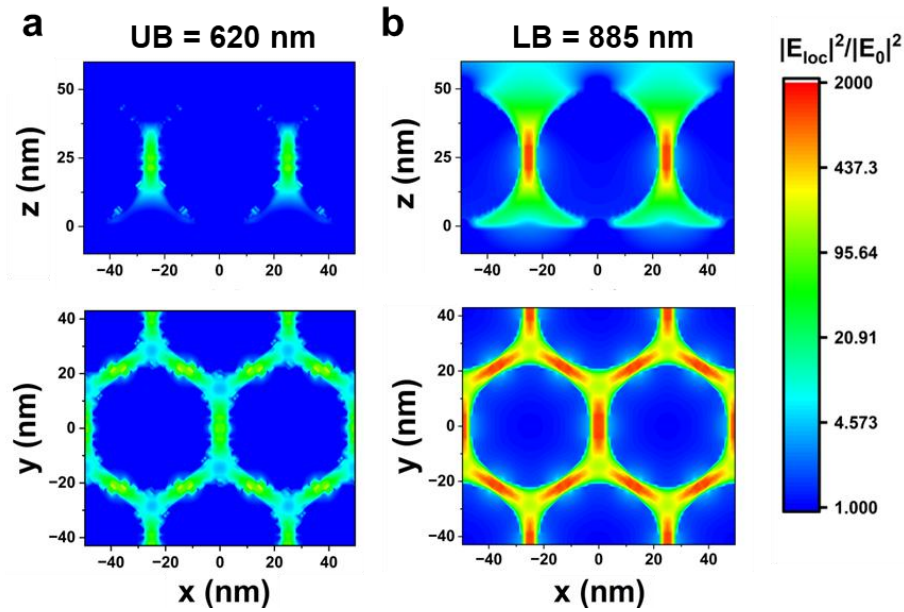


Figure 3-5. Cross-sectional near-field distributions of s-ATA with a 180 nm TiO₂ layer under excitation at (c) 620 nm (UB) and (d) 885 nm (LB).

3-3-2. SERS performance modulated by modal ultrastrong coupling

With the modified resonance properties under modal ultrastrong coupling conditions, the SERS performances of t-ATA and s-ATA structures were evaluated at varied TiO₂ thicknesses (**Figure 3-6**). 4-MBA was selected as the Raman reporter because its thiol group allows strong binding to the gold surface, while benzene ring provides distinct and intense vibrational modes suitable for SERS detection (**Figure 3-7**). The assignments of the Raman signals are listed in **Table 3-1**. The substrates were treated by an ethanolic solution of 4-MBA (10 mM).

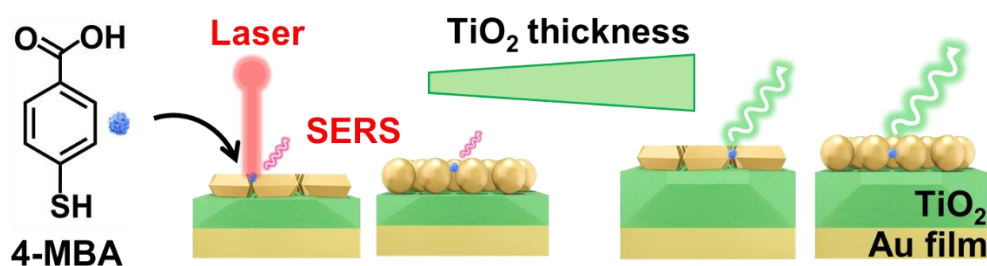


Figure 3-6. Schematic illustration of modulated SERS on t-ATA and s-ATA structures with varied TiO₂ thicknesses using 4-MBA as a Raman reporter.

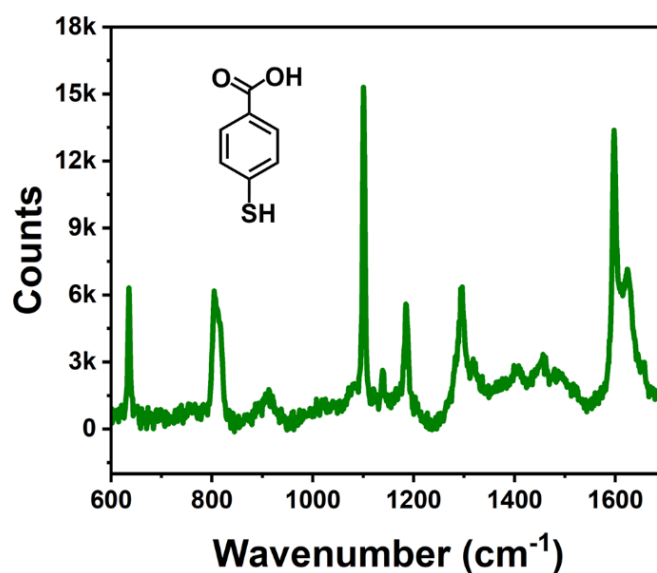


Figure 3-7. Raman spectrum of 4-MBA powder under 785 nm excitation. The exposure time was 10 s, the laser power was 50 mW, and the signal was accumulated over two acquisitions.

Table 3-1. Assignment of Raman signals for 4-MBA (785 nm)⁹¹⁻⁹³

Raman bulk (cm ⁻¹)	On nanoparticle film (cm ⁻¹)	Assignment
635	633	C–C–C ring in-plane bending
—	694	OCO bending, in-plane ring compression and C–S stretching
805	—	In-plane deformation, C–COOH stretching and COO ⁻ bending
910	—	S–H in-plane bending
1002	1003	in-plane ring breathing
1013	1017	Ring deformation
1100	1076	In-plane ring breathing + C–S stretching
1140	1146	C–C–C bending, C–S stretching and C- COOH stretching
1185	1174	C–H in-plane bending
1293	1276	C–H in-plane bending and C–C stretching
1399	1395	COO ⁻
1458	1480	C–H in-plane bending
1597	1583~1602	Symmetric ring breathing
1625	—	C=O stretching

Figures 3-8a, b-i show the SERS spectra of 4-MBA adsorbed on t-ATA (**Figure 3-8a-i**) and s-ATA (**Figure 3-8b-i**) substrates under the excitation of 785 nm. Two predominant SERS peaks were observed at 1076 cm^{-1} and 1589 cm^{-1} , corresponding to the in-plane ring breathing coupled with C–S stretching, and totally symmetric C=C stretching, respectively (**Table 3-1**). The SERS peak intensities on both t-ATA (**Figures 3-8a-ii**) and s-ATA (**Figures 3-8b-ii**) were plotted as bar graphs, which exhibit non-linear dependence on the TiO_2 thickness. The minimum intensities were observed at 120 nm, followed by an increase as the TiO_2 thickness increased, reaching a maximum at around 180 nm. Beyond this point, the SERS intensities at 230 nm decreased (**Figures 3-8a, b-ii**). It is worth noting that significant variations in the relative difference between the two dominant peaks emerged within the TiO_2 thickness range of 140–170 nm under the excitation of 785 nm laser. For the t-ATA structure, the intensity of the 1589 cm^{-1} peak dropped to approximately half of the 1076 cm^{-1} peak. While in the s-ATA structure, the 1589 cm^{-1} peak reduced to about one-quarter of the 1076 cm^{-1} peak but subsequently exceeds the 1076 cm^{-1} peak after 180 nm TiO_2 .

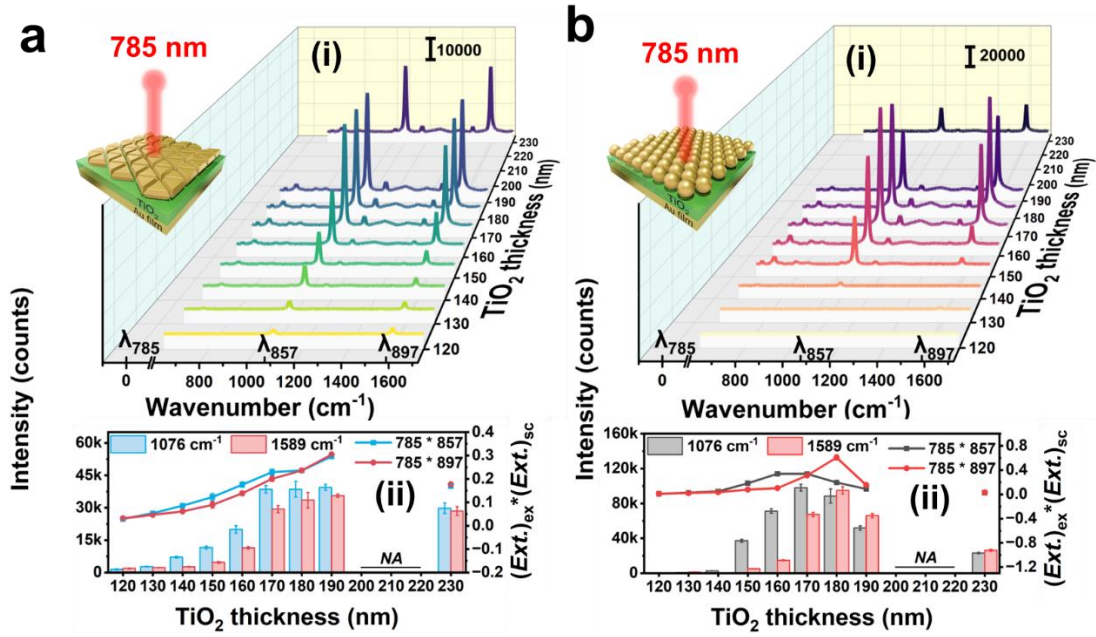


Figure 3-8. SERS performance of (a) t-ATA and (b) s-ATA under excitation of 785 nm (Laser power: 5 mW; exposure time: 1s; accumulations: 3). (i) SERS spectra. (ii) Comparison of SERS peak intensities with the corresponding extinction products. The bars correspond to the intensities of SERS peaks at 1078 cm⁻¹ and 1589 cm⁻¹ (left y-axis), and the lines with markers indicate the products of the extinctions at the excitation of 785 ((Ext.)_{ex}) and the Stokes-shifted-wavelengths ((Ext.)_{sc}) for the corresponding SERS peak (right y-axis). NA inserted in the graphs denote that no samples were made for these thicknesses.

These non-linear variations in the relative intensities of individual SERS peaks can be attributed to peak splitting induced by modal strong coupling, which alters the resonant extinction characteristics of the substrate. This altered resonance leads to selective enhancement of SERS signals corresponding to specific Stokes shifts. The correlation between the SERS enhancement factor (EF) and the localized field intensity is described by the following equation:

$$EF \propto \frac{|E_{loc}(\lambda_{ex})|^2 \times |E_{loc}(\lambda_{sc})|^2}{|E_0(\lambda_{ex})|^2 \times |E_0(\lambda_{sc})|^2}$$

where $E_{loc}(\lambda_{ex})$, $E_{loc}(\lambda_{sc})$ represent the local electric field strengths at the excitation and scattered (Stokes-shifted) wavelengths, respectively, and $E_0(\lambda_{ex})$, $E_0(\lambda_{sc})$ are the

incident electric field strength.^{34, 35} Additionally, previous study has shown a positive correlation between SERS intensity and the optical extinction of the substrate.⁹⁴ The extinction spectra of the t-ATA and s-ATA structures after treatment with 10 mM 4-MBA are shown in **Figures 3-9**. Slight peak shifts and broadening were observed, which could be attributed to the altered chemical interface damping (CID) caused by the dense modification of 4-MBA on the particle surfaces,^{95, 96} replacing the original surface ligand.⁹⁷ Based on the correlation among the EF, electric field intensity, and extinction, the products of the extinctions at the excitation (785 nm) and the SERS peaks-corresponded Stokes-shifted wavelengths (857 nm for 1076 cm^{-1} and 897 nm for 1589 cm^{-1}) are plotted in **Figure 3-8(ii)** as scatter line plots. These extinction products exhibited good agreement with the corresponding SERS intensities. It is noteworthy that the extinction products for the 1589 cm^{-1} peak are more significantly lower than those for the 1076 cm^{-1} peak within the TiO_2 thickness range of 140–170 nm compared to other TiO_2 thicknesses. This trend is also consistent with the relative differences in intensities observed between the two corresponding SERS peaks. The s-ATA structures exhibited a larger difference in SERS signal intensity, which corresponds to the greater extinction disparity at the corresponding wavelengths (**Figure 3-10**). At a TiO_2 thickness of 170 nm, the extinction difference between the two Raman peaks decreased, resulting in reduced signal intensity ratios for both types of nanoparticle films. When the TiO_2 thickness is more than 180 nm, a significant reversal in the extinction difference is observed for s-ATA structure, consistent with the inversion of the relative SERS intensities.

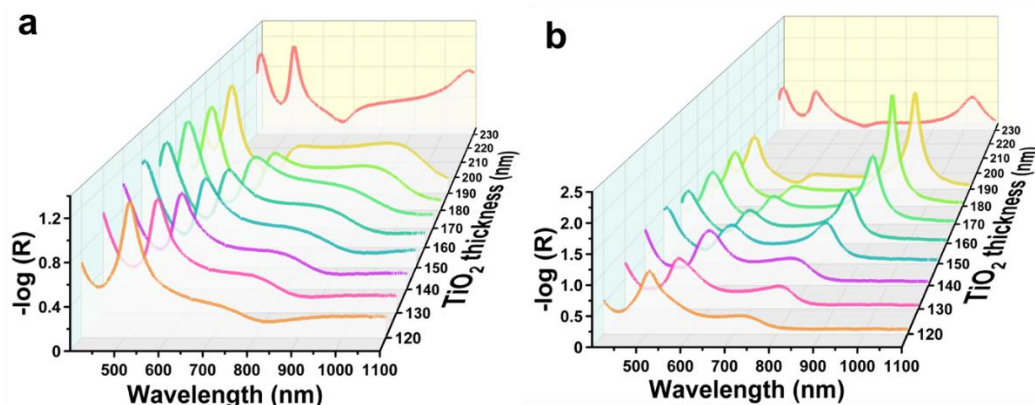


Figure 3-9. Absorption spectra of (a) the t-ATA and (b) the s-ATA with varied TiO_2 thicknesses after overnight treatment with a 10 mM ethanolic solution of 4-MBA.

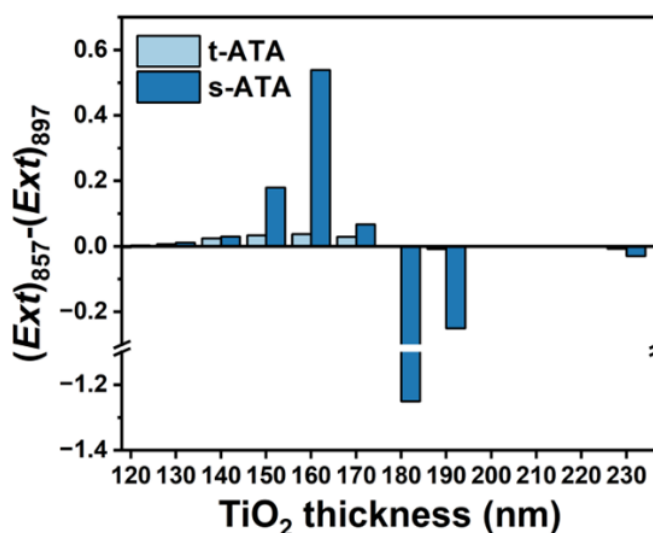


Figure 3-10. Absorption difference corresponded to the SERS peaks at 1076 cm^{-1} and 1589 cm^{-1} under excitation at 785 nm.

To further confirm the modulation of each SERS peak by mode splitting, the SERS of 4-MBA on the t-ATA structures were also checked under the excitation of 633 nm (**Figure 3-11**). The SERS spectra also demonstrate two predominant peaks with almost the same Stokes shifts as those under 785 nm excitation (**Figures 3-11a, b-i**). The

maximum intensities were observed at 170 nm and 140 nm for t-ATA and s-ATA, respectively, while the minimum intensities were at 230 nm (**Figures 3-11a, b-ii**). The products of the extinctions at the excitation (633 nm) and the SERS peaks-corresponded Stokes-shifted wavelengths (697 nm for 1076 cm^{-1} and 703 nm for 1589 cm^{-1}) are plotted in **Figures 3-11a, b-ii**. The signal intensities from both t-ATA and s-ATA structures followed the same trend as the extinction products across different TiO_2 thicknesses. Furthermore, the relative extinction of products corresponding to the two SERS peaks, which remained nearly constant across all thicknesses (**Figures 3-12**) and consistent with the stable intensity ratios observed in **Figures 3-11**.

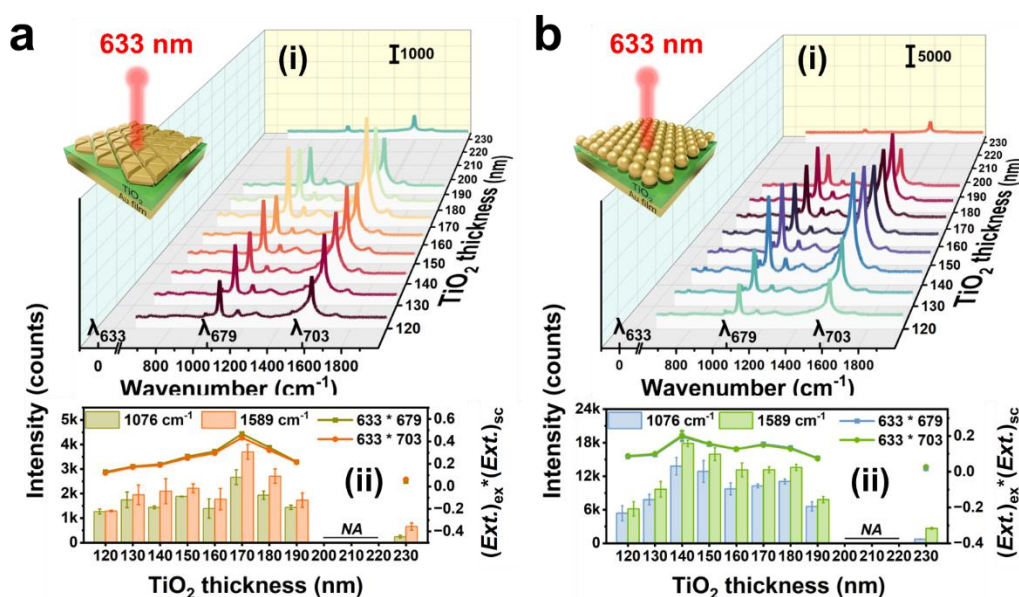


Figure 3-11. SERS performance of (a) t-ATA and (b) s-ATA under excitation of 633 nm (Laser power: 1 mW; exposure time: 1s; accumulations: 3). (i) SERS spectra. (ii) Comparison of SERS peak intensities with the corresponding extinction products. The bars correspond to the intensities of SERS peaks at 1078 cm^{-1} and 1589 cm^{-1} (left y-axis), and the lines with markers indicate the products of the extinctions at the excitation of 633 ((Ext.)_{ex}) and the Stokes-shifted-wavelengths ((Ext.)_{sc}) for the corresponding SERS peak (right y-axis). NA inserted in the graphs denote that no samples were made for these thicknesses.

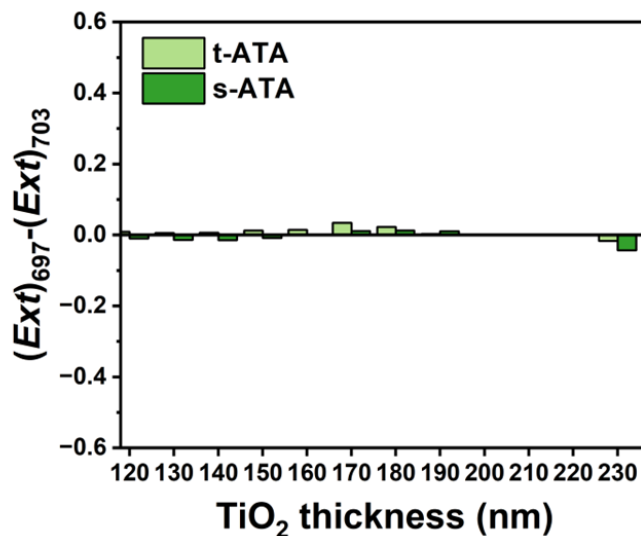


Figure 3-12. Absorption difference corresponded to the SERS peaks at 1076 cm^{-1} and 1589 cm^{-1} under excitation at 633 nm .

3-3-3. Comparison with the control substrate

Given the high refractive index of TiO_2 , the TiO_2 film alone can support a weak cavity mode (**Figure 3-13**). To elucidate which part of the FP cavity modulates the SERS performance of the AuNP films, control experiments were conducted using ITO and TiO_2 substrates (**Figure 3-14**). The AuNT films and AuNS films on ITO substrates, denoted as t-A/ITO and s-A/ITO, respectively, were used to assess the intrinsic SERS response of the AuNT and AuNS films without cavity effects. For systematic comparison, the t-ATA and s-ATA structures with 130 nm, 150 nm, 170 nm, 190 nm, and 230 nm TiO_2 layers are also compared to the corresponding control TiO_2 substrates with identical thicknesses but without the bottom Au films (t-AT and s-AT).

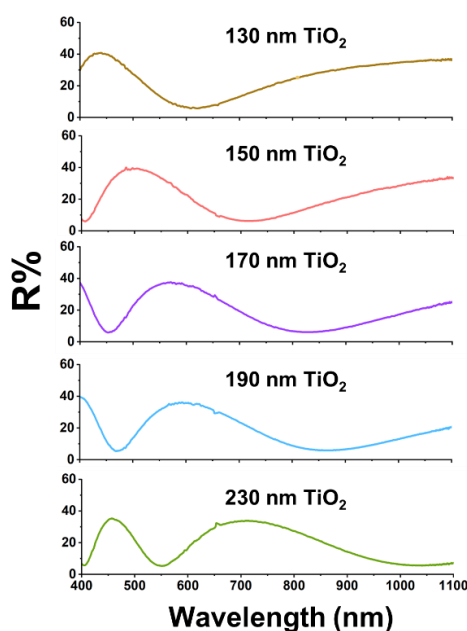


Figure 3-13. Reflection spectra of TiO_2 layers on quartz substrates with varied thicknesses.

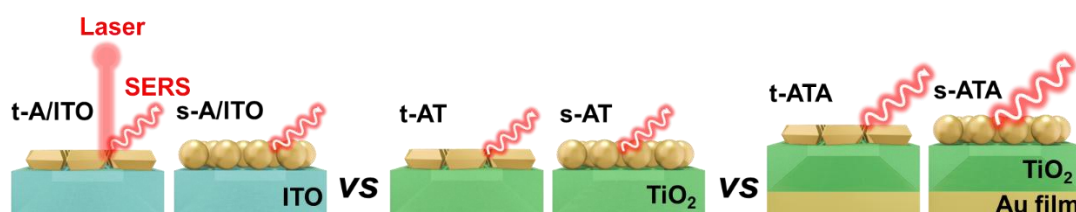


Figure 3-14. Schematic illustration of the experimental setup for comparison of SERS performance of AuNT or AuNS films on ITO, TiO_2 , and TA substrates.

The comparison of SERS spectra under 785 nm and 633 nm excitation is shown in **Figures 3-15**, and the intensities of the two main SERS peaks (1076 cm^{-1} and 1589 cm^{-1}) are summarized as bar graphs in **Figure 3-16**. For identical nanoparticle film, the difference in the SERS intensities on ITO and TiO_2 substrates is negligible under the same excitation wavelength. This observation is further supported by simulated near-field spectra at the vertex-cross sections on the t-A/ITO and s-A/ITO (**Figure 3-17a**), t-AT (**Figure 3-17b**) and s-AT (**Figure 3-17c**) structures. The nearfield intensities of t-A/ITO

and s-A/ITO are in the same order of magnitude as t-AT and s-AT structures, suggesting that the TiO₂ layer alone does not substantially influence field enhancement on either AuNT films or AuNS films.

When comparing the FP cavities with the TiO₂ substrates, a thickness-dependent effect is observed on both AuNT and AuNS films. Under the excitation of 785 nm, the SERS signal intensities on t-ATA and s-ATA structures with TiO₂ thickness of 130 nm and 150 nm are significantly lower and comparable with the corresponding t-AT and s-AT substrates, respectively. However, for TiO₂ thickness of 170–230 nm, the TA structures lead to significant SERS enhancements (**Figures 3-16a, b**). In specific, the AuNT film achieved approximately 2.7-fold enhancement at the t-ATA structures with a 190 nm TiO₂ layer (**Figure 3-16a**), which is close to the tuning condition with the wide LB overlaps the excitation and the Stokes-shifted wavelengths (**Figure 3-9a**). While for the AuNS film, the s-ATA structure yields around 5.1-fold signal enhancement with 170 nm TiO₂ (**Figure 3-16b**), where the strong LB band and the Stokes-shifted wavelengths were aligned owing to the modified peak position under an off-resonantly tuned condition (**Figure 3-9b**). Under the excitation of 633 nm, the strongest signal enhancements, by factors of 4.3 and 2.5, were observed at the TiO₂ thickness of 170 nm and 150 nm for t-ATA (**Figure 3-16c**) and s-ATA (**Figure 3-16d**) structures, respectively. The two thicknesses are sub-optimally tuned conditions of the respective structures, where the upper bands coincide the laser wavelength and the Stokes-shifted wavelengths (**Figure 3-9**). In contrast, at a TiO₂ thickness of 230 nm, the SERS signal intensity decreases compared to the control s-AT and t-AT substrates, which can be attributed to the mismatch between the resonance mode of the substrate and the excitation wavelength (**Figure 3-16c, d**). Furthermore, according to the typical field distribution checked on t-

A/ITO and t-A/ITO structures, the positions of hotspots also remain consistent with that on TA substrates (**Figure 3-18**). These comparative results provide additional evidence of the excitation wavelength-dependent modulation of SERS performance of AuNP films enabled by the modified spectra under the modal ultrastrong coupling with FP cavity.

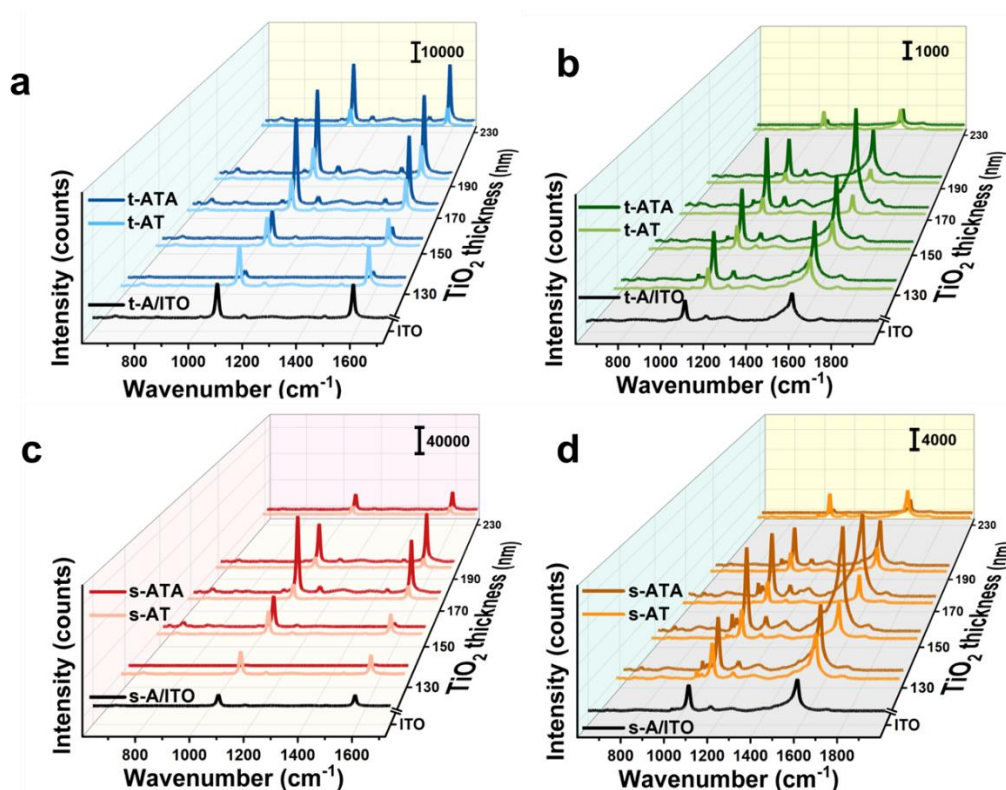


Figure 3-15. SERS spectra of AuNP films on ITO, TiO₂, and TA. (a, b) AuNT films and (c, d) AuNS films under the excitations of (a, c) 785 nm (laser power: 5 mW; exposure time: 1s; accumulations: 3) and (b, d) 633 nm (laser power: 1 mW; exposure time: 1s; accumulations: 3). The substrates were treated with a 10 mM ethanolic solution of 4-MBA.

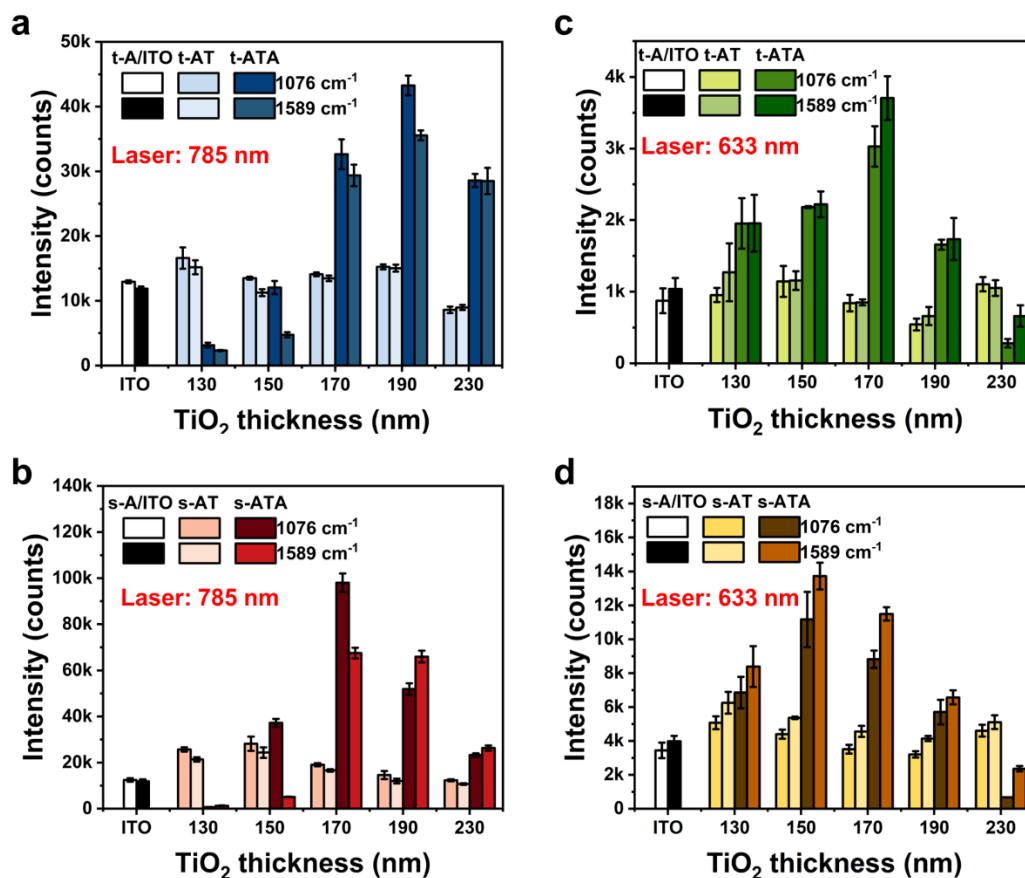


Figure 3-16. Comparison of SERS performance of AuNP films on ITO, TiO_2 , and TA substrates. (a-d) Bar graphs of SERS intensities at 1076 cm^{-1} and 1589 cm^{-1} on (a, c) AuNT films and (b, d) AuNS films under the excitations of (a, b) 785 nm (Laser power: 5 mW; exposure time: 1s; accumulations: 3) and (c, d) 633 nm (Laser power: 1 mW; exposure time: 1s; accumulations: 3). The substrates were treated with a 10 mM ethanolic solution of 4-MBA.

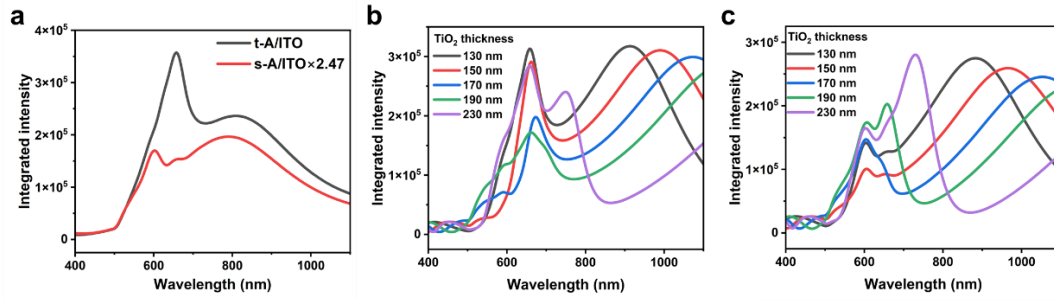


Figure 3-17. FDTD simulation of the near-field spectra of (a) t-A/ITO and s-A/ITO, (b) s-AT and (c) t-AT substrates. Due to the smaller single unit size of the AuNS film in the simulation, the integrated field intensities are scaled by 2.47 to match the unit area of the AuNT film. The thickness of ITO was set to 150 nm, and its refractive index was set to 1.8.⁹⁸

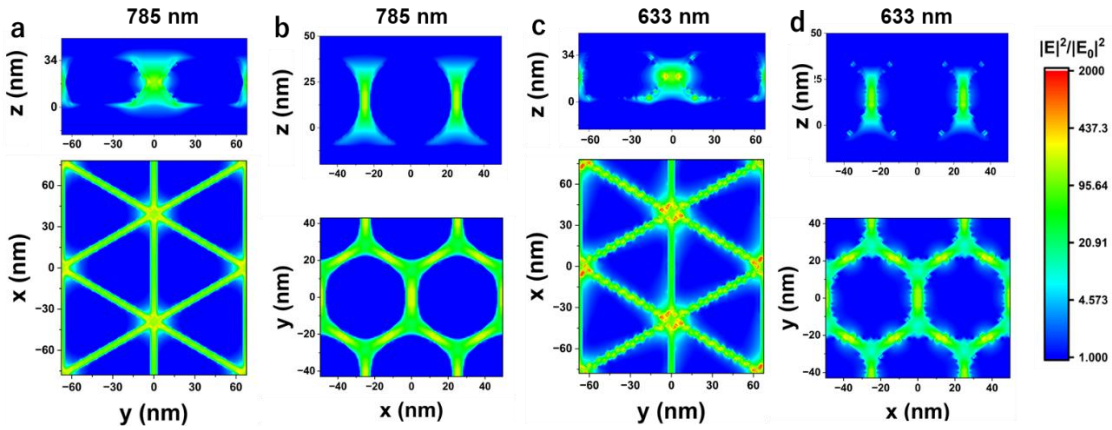


Figure 3-18. FDTD simulation of the cross-sectional EM near-field distributions of (a, c) t-A/ITO and (b, d) s-A/ITO under the excitation of 785 nm and 633 nm. The thickness of ITO was set to 150 nm, and its refractive index was set to 1.8.⁹⁸

3-3-4. Shape-dependent SERS performance under modal ultrastrong coupling

To gain deeper insight into the impact of particle shape on the modal ultrastrong coupling-modulated SERS performance, the AuNT and AuNS films were further compared under various 4-MBA adsorption conditions. After treatment with 4-MBA in various concentrations, the SERS spectra were collected on different substrates under the excitation of 785 nm, including t-ATA (Figure 3-19), s-ATA (Figure 3-20), t-AT and t-

A/ITO (**Figure 3-21**), as well as s-AT and s-A/ITO (**Figure 3-22**). Meanwhile, the intensities of the two characteristic Raman peaks (1076 cm^{-1} and 1589 cm^{-1}) are summarized, where variation trends of signal intensity with TiO_2 thickness remain consistent across different 4-MBA concentrations on both AuNT films (**Figures 3-19e, 3-21e**) and AuNS films (**Figures 3-20, 3-22e**). According to the spectra, the SERS peaks the surface ligands can be found before treatment with 4-MBA. After treatment with 10^{-8} M 4-MBA, characteristic peaks of 4-MBA appear and co-exist with the ligand signals. After treatment with 4-MBA solutions with the concentration higher than 10^{-6} M , the spectra display dual peak of 4-MBA. Notably, pronounced differences between the two film types emerged at 10^{-8} M regardless of the underlying substrate types (**Figures 3-19b, 3-20b, 3-21b, 3-22b**). Therefore, I focused on the comparison at 10^{-8} M . Four representative substrates were selected: TA substrates with 180 nm, 140 nm, and 120 nm TiO_2 layers, and ITO substrate. TA substrates with 180 nm and 140 nm TiO_2 layers correspond to the tuning conditions of modal ultrastrong coupling for t-ATA (**Figure 2-11a**) and s-ATA (**Figure 2-11b**), respectively. Under 785 nm excitation and across all the 4-MBA concentrations, the TA substrates with 180 nm and 120 nm TiO_2 layers correspond to the maximum and minimum SERS intensities for both t-ATA (**Figures 3-8a, 3-19e**) and s-ATA (**Figures 3-8b, 3-20e**), respectively. The ITO substrate is chosen as a typical control substrate. The SERS intensities after the treatment with different concentrations of 4-MBA on these four representative substrates are more intuitively shown in **Figure 3-23**. The signal intensities on both AuNT and AuNS films reached saturation above 10^{-6} M .

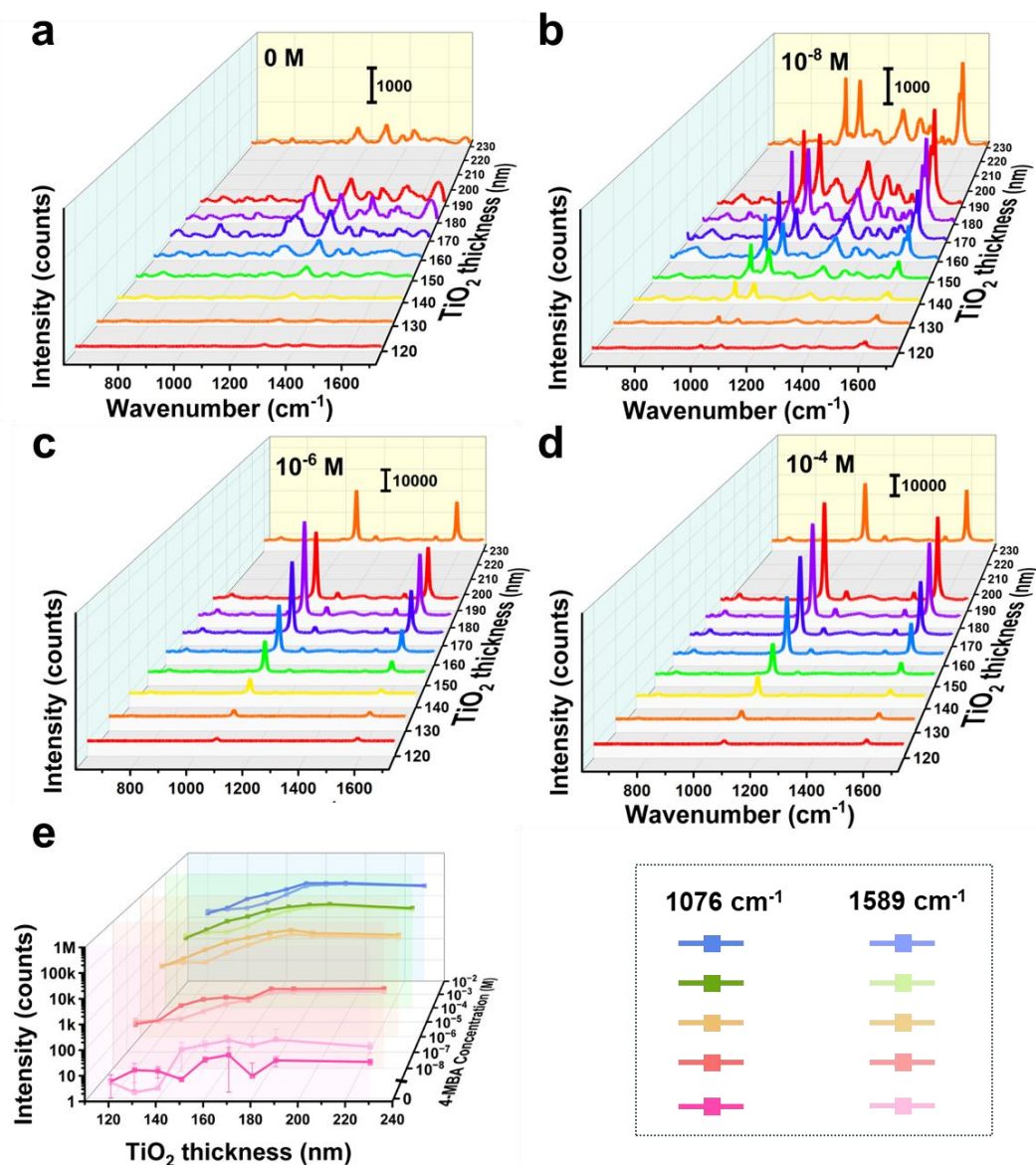


Figure 3-19. (a-d) SERS spectra measured at t-ATA structures with varied TiO_2 thicknesses: (a) before treatment, and after treatment with (b) 10^{-8} , (c) 10^{-6} , and (d) 10^{-4} M 4-MBA. The spectra in (a) and (b) were measured using 25 mW for 3 s and normalized to the equivalent of 5 mW/1s based on the intensity ratio shown in **Figure 3-24**. The spectra in (c) and (d) were measured using 5 mW for 1 s. All spectra were accumulated 3 times. (e) SERS intensity of 4-MBA across various concentrations on t-ATA structures with different TiO_2 thicknesses.

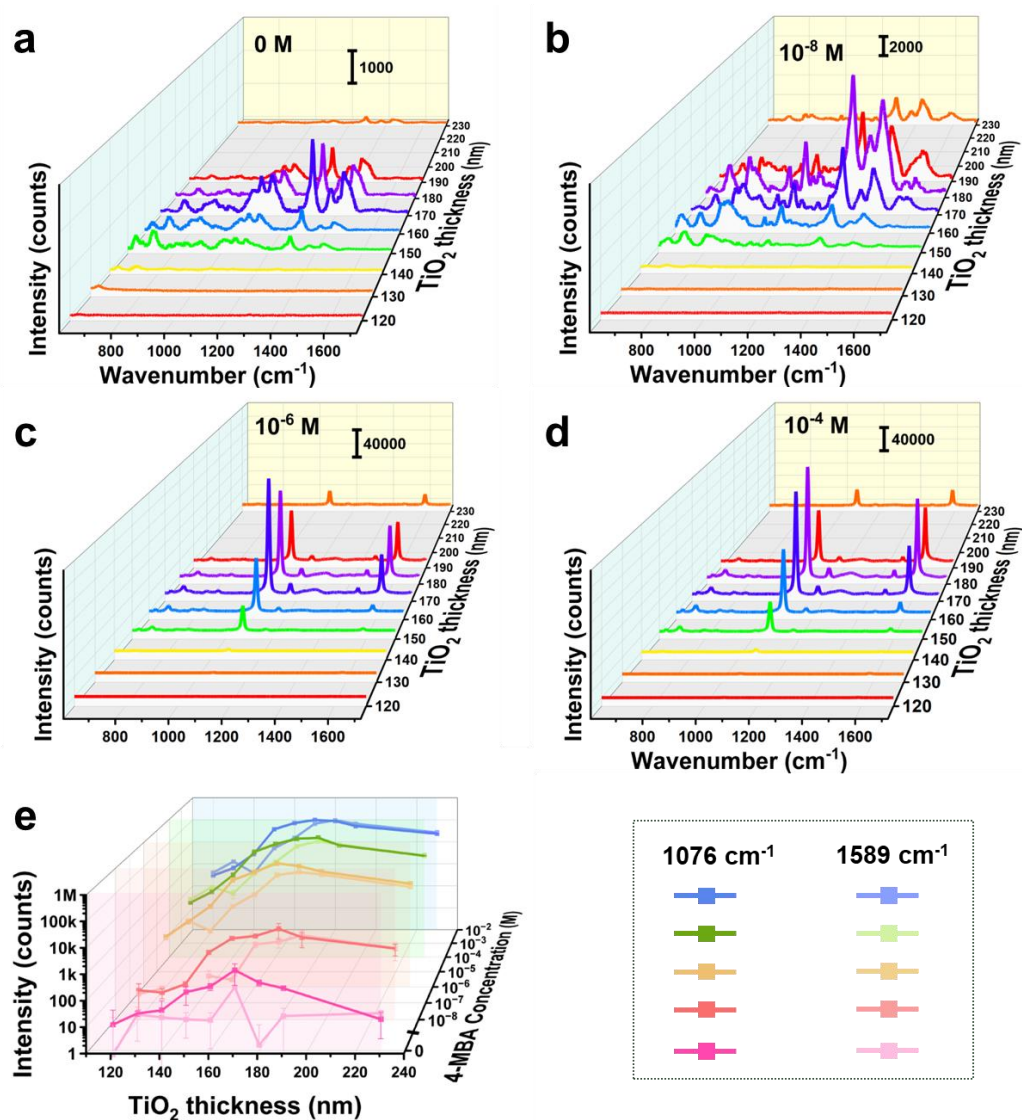


Figure 3-20. (a-d) SERS spectra measured at s-ATA structures with varied TiO_2 thicknesses (a) before treatment, and after treatment with (b) 10^{-8} , (c) 10^{-6} , (d) 10^{-4} M 4-MBA. All spectra were measured under a laser setting of 5 mW for 1 s with 3 times of accumulation. (e) SERS intensity of 4-MBA at various concentrations on s-ATA structures with different TiO_2 thicknesses.

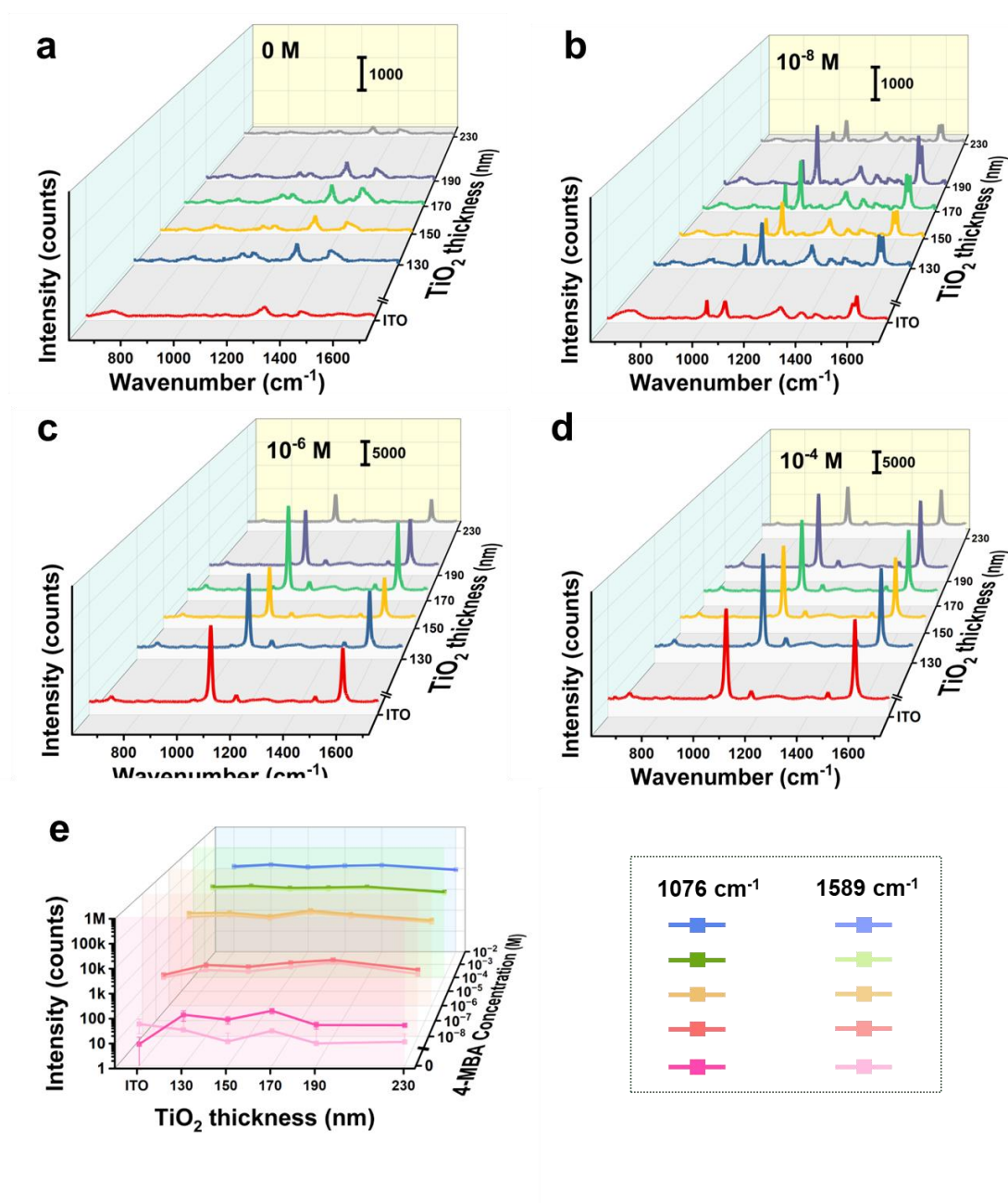


Figure 3-21. SERS spectra of 4-MBA at various concentrations on AuNT films on ITO or TiO_2 substrates with different TiO_2 thicknesses: (a) before treatment, and after treatment with (b) 10^{-8} , (c) 10^{-6} , (d) 10^{-4} M 4-MBA. All spectra were measured under a laser setting of 5 mW for 1 s with 3 times of accumulation. (e) SERS intensity of 4-MBA at various concentrations on t-A/ITO and t-AT structures with different TiO_2 thicknesses.

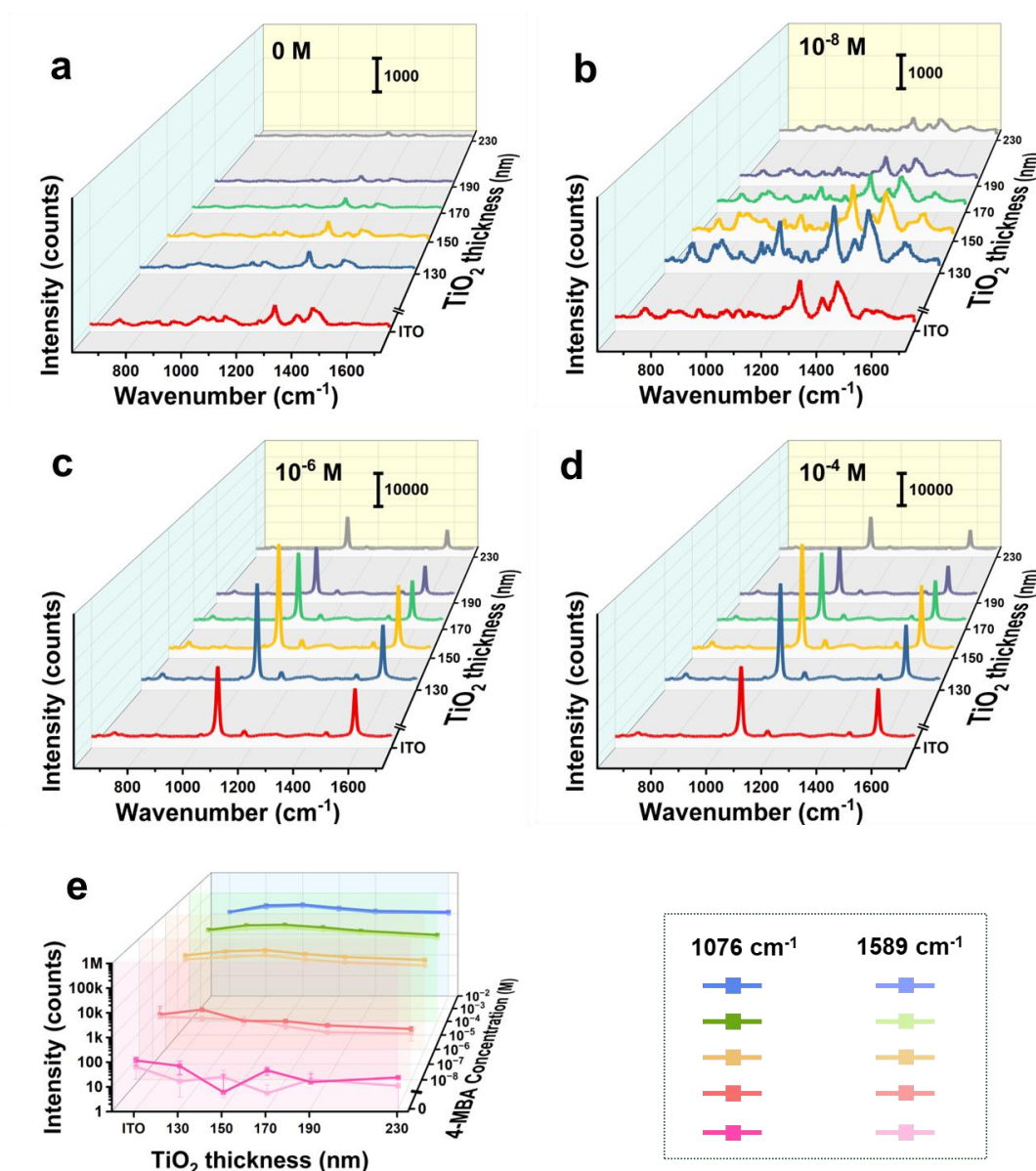


Figure 3-22. SERS spectra of 4-MBA at various concentrations on AuNS films on ITO or TiO_2 substrates with different TiO_2 thicknesses: (a) before treatment, and after treatment with (b) 10^{-8} , (c) 10^{-6} , (d) 10^{-4} M 4-MBA. All spectra were measured under a laser setting of 5 mW for 1 s with 3 times of accumulation. (e) SERS intensity of 4-MBA at various concentrations on s-A/ITO and s-AT structures with different TiO_2 thicknesses.

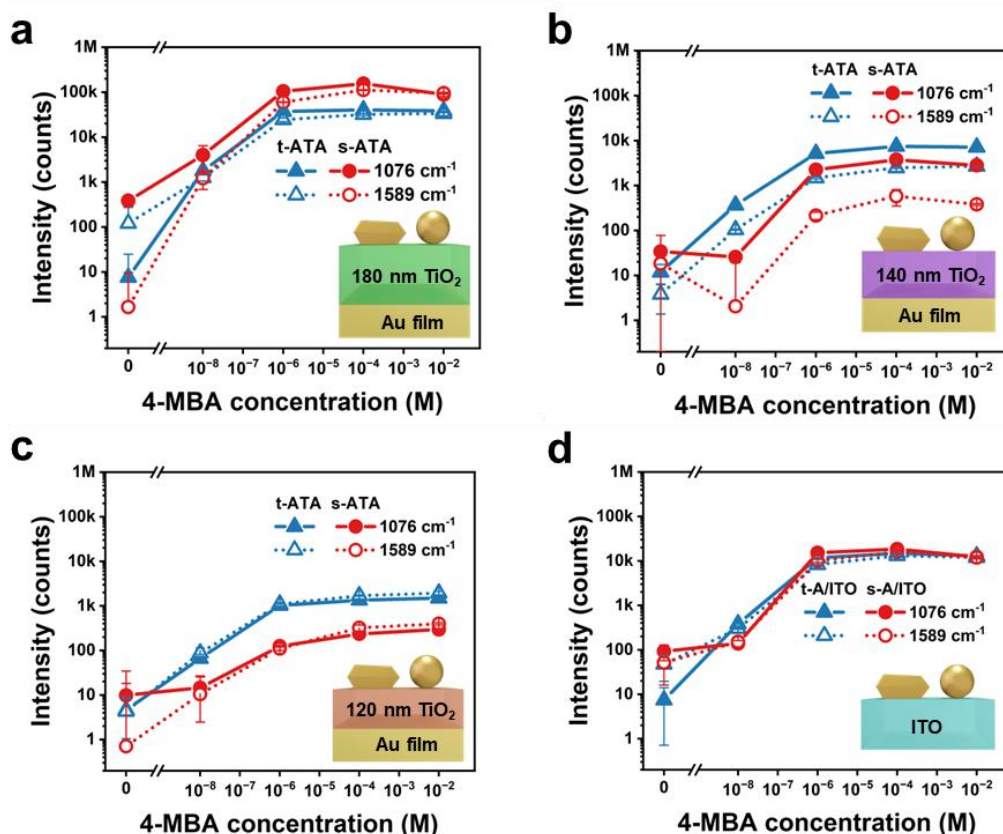


Figure 3-23. SERS intensity of 4-MBA at AuNT and AuNS films on TA substrate with (a) 180 nm TiO_2 , (b) 140 nm TiO_2 , (c) 120 nm TiO_2 , and (d) ITO substrates after treatment with 0- 10^{-2} M 4-MBA taken from **Figures 3-19e, 3-20e, 3-21e and 3-22e**. The intensities were obtained under the excitation of 785 nm laser with the setting of 5 mW for 1 s except for t-ATA and t-A/ITO structures before treatment (0 M) and after the treatment by 10^{-8} M, which were measured under the setting of 25 mW/3 s (converted to 5 mW/1 s equivalent). The conversion factor was obtained by measuring the same sample under the two conditions, see **Figure 3-24**.

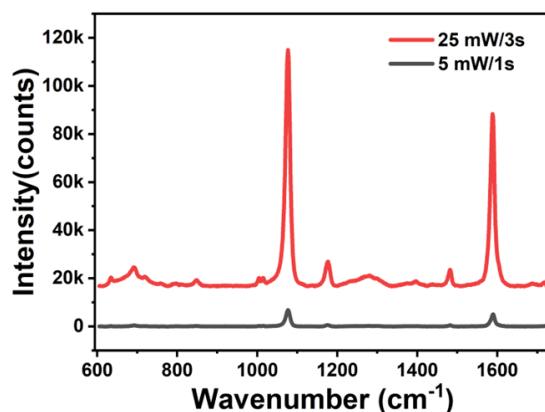


Figure 3-24. SERS spectra of the same substrate measured two different conditions: 25 mW for 3 s and 5 mW for 1 s, respectively, with three accumulations each. The signal intensity ratio is ~ 14 . The substrate consists of an AuNT film on a 30 nm TiO_2 layer treated by 10^{-6} M 4-MBA.

The SERS spectra on AuNT films and AuNS films after the treatment with 10^{-8} M 4-MBA are compared in **Figure 3-25**. Additional peaks around $\sim 1000\text{ cm}^{-1}$ and 1602 cm^{-1} were observed, particularly for the AuNT films, which are attributed to alternative ring-breathing modes of 4-MBA (**Figures 3-25, -i**). These peaks are likely to result from changes in the molecular adsorption orientation.^{99, 100} Nevertheless, clear characteristic peaks of 4-MBA remained detectable on the AuNT films regardless of substrate types, whereas those on the AuNS films were less distinguishable. Specifically, on the TA substrate with a 180 nm TiO_2 layer, although the absolute intensity of the 4-MBA characteristic peaks was similar between the AuNS and AuNT films, the AuNS-based SERS spectra exhibited stronger ligand-derived signals and more background interference (**Figure 3-25a-i, Table 3-2**). On the TA substrate with 140 and 120 nm TiO_2 , 4-MBA signals were undetectable on the AuNS films (**Figures 3-25b, c-i**). On the ITO substrate, the AuNS film showed markedly weaker 4-MBA signals and relatively stronger

ligand signals compared to AuNT films (**Figure 3-25d-i**). The qualities of the 4-MBA signals were evaluated by the intensity ratios of the characteristic SERS peaks (1076 cm^{-1} and 1589 cm^{-1}) to the peak that derive from surface ligand (1297 cm^{-1}) (**Figures 3-25a-d, -ii**). The AuNT films exhibited more than three-fold higher intensity ratios compared to the AuNS films, suggesting that the AuNT films support more prominent SERS signal of 4-MBA even though the concentration is as low as 10^{-8} M .

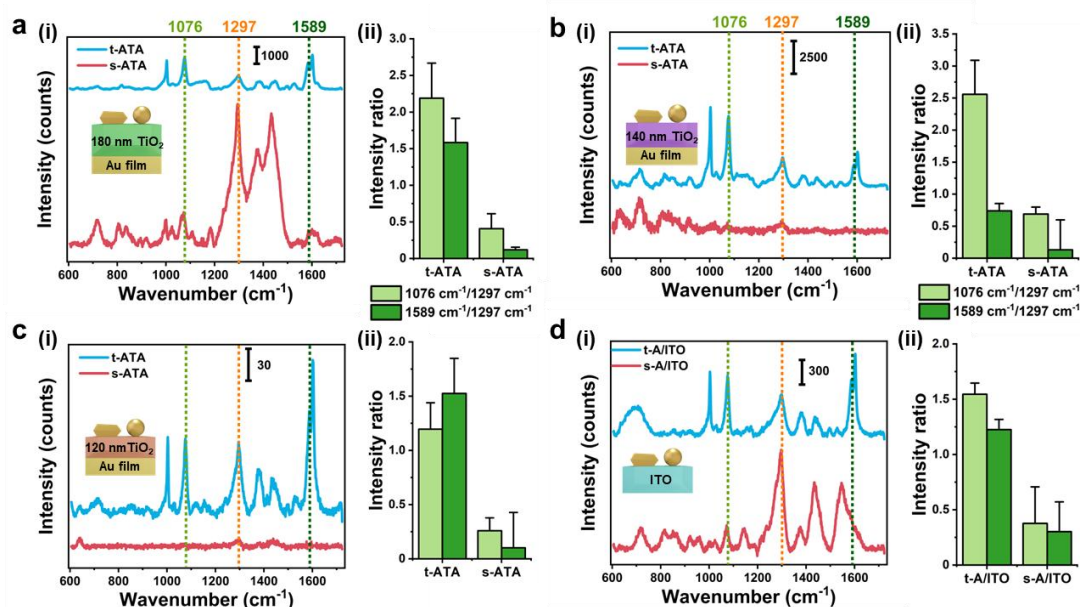


Figure 3-25. Comparison of SERS performance of AuNT and AuNS films on TA substrate with (a) 180 nm TiO₂, (b) 140 nm TiO₂, (c) 120 nm TiO₂, and (d) ITO substrates after treatment with 10^{-8} M 4-MBA concentrations. (i) SERS spectra of 4-MBA. The SERS spectra on s-ATA were measured under the setting of 5 mW/1 s, and the SERS spectra on t-ATA are obtained under the setting of 25 mW/3 s (converted to 5 mW/1 s equivalent). The conversion factor was obtained by measuring the same sample under the two conditions, see **Figure 3-24**. (ii) Bar graphs showing intensity ratios of the characteristic peaks (1076 cm^{-1} and 1589 cm^{-1}) relative to the ligand signal at 1297 cm^{-1} . All the SERS signals were measured 3 times of accumulation.

Table 3-2. Assignment of SERS signals for surface ligands (785 nm)^{101, 102}

Raman peak (cm ⁻¹)	Assignment
720	C–S stretching
920	Skelton deformation
1162	CH ₂ wag
1297	CH ₂ twist
1371	C–CH ₃ bending
1435	CH ₂ bending

Besides the matching between the excitation wavelength and the extinction, the effect of particle shape also contributes to the observed differences in SERS performance. **Figure 3-26** presents the surface properties of AuNT (**Figure 3-26a**) and AuNS (**Figure 3-26b**) and their effects on the distribution of 4-MBA on nanoparticle surface under varying adsorption conditions. As anisotropic nanoparticles, AuNT exhibit more complex surface characteristics than AuNS. The sharp tips of AuNTs possess high surface curvature and consequently lower local ligand density, which reduces steric hindrance and facilitates the penetration and adsorption of 4-MBA molecules (**Figure 3-26a-i**).¹⁰³⁻
¹⁰⁸ In contrast, their flat facets are densely covered with ligands, thereby limiting molecular access (**Figure 3-26a-ii**). Due to this different accessibility, when the 4-MBA concentration is low, the 4-MBA would preferentially attach on the tips due to the relatively low steric hindrance from the ligands (**Figure 3-26a-iii**). When the 4-MBA is abundant, the excess 4-MBA will be loaded on the top surface once the limited area in hotspots is saturated (**Figure 3-26a-iv**). AuNSs, on the other hand, feature relatively

uniform surface curvature, offering no preferential sites for 4-MBA adsorption (**Figure 3-26b-i**). When the 4-MBA concentration is low, the 4-MBA would randomly bind on the surface without any bias (**Figure 3-26b-ii**). When the 4-MBA concentration is high, the relatively low surface curvature allows more molecule loading on the hotspots (**Figure 3-26b-iii**).

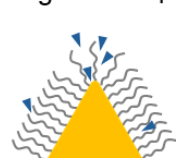
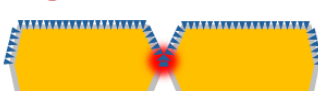
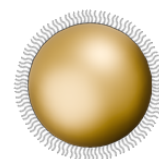
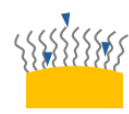
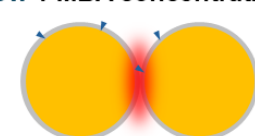
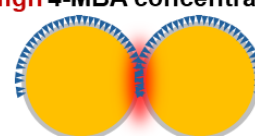
Shape	Surface properties	Analyte distribution
a 	~ Ligand ▲ 4-MBA (i) 	(iii) Low 4-MBA concentration  Preferential binding to hotspots
	(ii) 	(iv) High 4-MBA concentration  Limited loading capacity at hotspots
b 	~ Ligand ▲ 4-MBA (i)  Uniform surface curvature	(ii) Low 4-MBA concentration  No binding bias
		(iii) High 4-MBA concentration  Higher loading capacity at hotspots

Figure 3-26. Schematic of inferred distribution of 4-MBA on (a) AuNT and (b) AuNS at different adsorption conditions. The red areas denote the locations of hotspots. (a-i) Accessibility of 4-MBA on the tips of AuNT. (a-ii) Accessibility of 4-MBA on the flat surfaces of AuNT. (a-iii) Distribution of 4-MBA on AuNT film when 4-MBA concentration is low. (a-iv) Distribution of 4-MBA on AuNT film when 4-MBA is abundant. (b-i) Accessibility of 4-MBA on AuNS. (b-ii) Distribution of 4-MBA on AuNS film when 4-MBA concentration is low. (b-iii) Distribution of 4-MBA on AuNS film when 4-MBA is abundant.

To further clarify this effect in view of the EM field enhancement, the enhancement factor (EF) distributions for the 1076 cm^{-1} characteristic Raman peak were calculated for each substrate. These calculations were based on the products of the field intensities at the excitation wavelength $|E_{loc}(785)|^2/|E_0(785)|^2$ and the Raman scattering wavelength $|E_{loc}(857)|^2/|E_0(857)|^2$ (**Figures 3-27, 3-28**). In specific, for t-ATA with a 180 nm TiO_2 layer, the histograms reveal that most pixels exhibit low EF value (**Figure 3-27a-i**), while a small number of pixels reach exceptionally high EF values (**Figure 3-27a-ii**), which originate from the nanoparticle tips as visualized in the 3D schematic (**Figure 3-27a-iii**). In contrast, the s-ATA structure shows no pixels exceeding an EF of 400000 (**Figure 3-27b-ii**), and a substantial portion of the pixels fall into a moderate EF range (**Figure 3-27b-iii**). Similar trends were observed for the TA substrates with 140 nm (**Figures 3-27c, d**), 120 nm TiO_2 layer (**Figures 3-28a, b**) and the ITO substrate (**Figure 3-28c-d**), both exhibiting significantly reduced EF values on s-ATA or s-A/ITO structures compared with the t-ATA or t-A/ITO structures. These findings suggest that, with limited amount of 4-MBA, the tip-favored adsorption and localized hotspots of AuNTs enable better SERS performance. In contrast, at relatively high concentrations such as 10^{-6} M , the broader distribution of moderate EF regions in AuNS films more effectively excites 4-MBA molecules, resulting in strong overall SERS signals when the excitation overlaps the extinction bands, consistent with the experimental results (**Figure 3-8**).

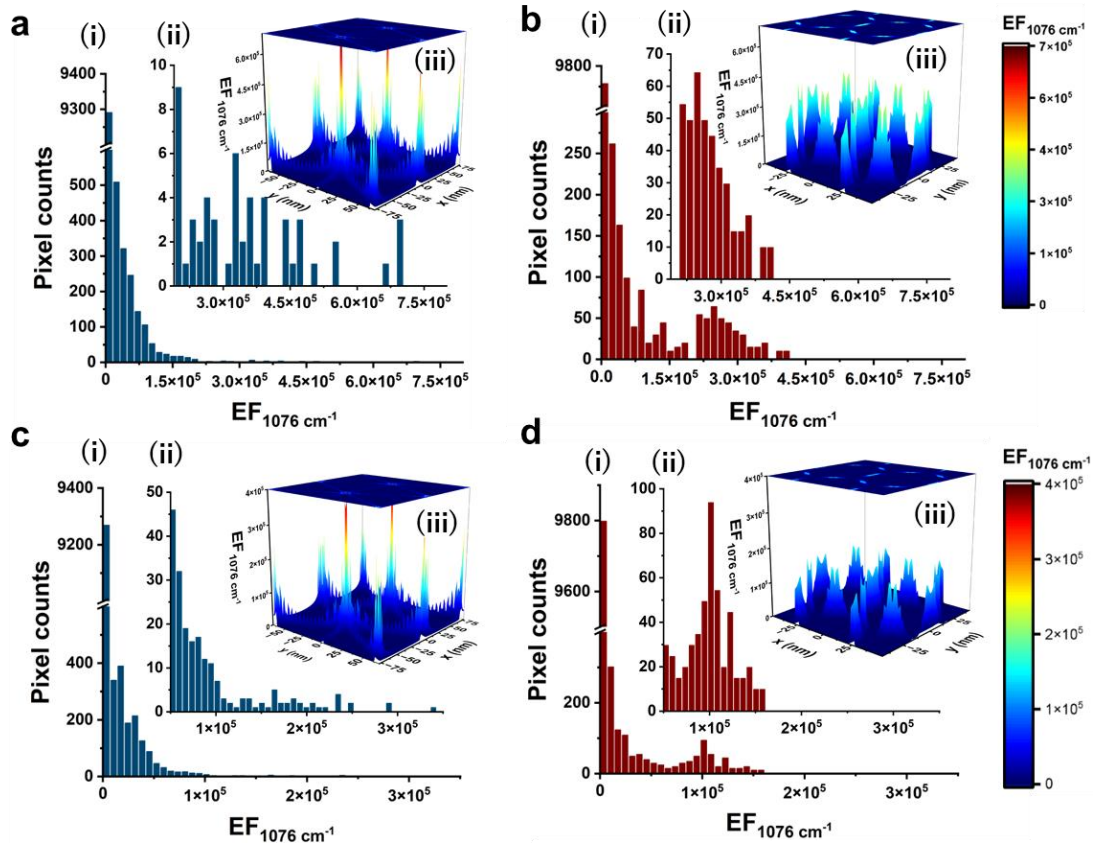


Figure 3-27. Distribution of enhancement factor (EF) at 1076 cm^{-1} at x-y cross-section plane for (a, c) t-ATA and (b, d) s-ATA structures with (a, b) 180 nm and (c, d) 140 nm TiO_2 . (i, ii) Histograms showing pixel distributions across different EF ranges. (iii) 3D map of field distributions. Due to the smaller single unit size of s-ATA (b, d, i-ii), the pixel count is scaled by 2.47 to match the unit area of t-ATA.

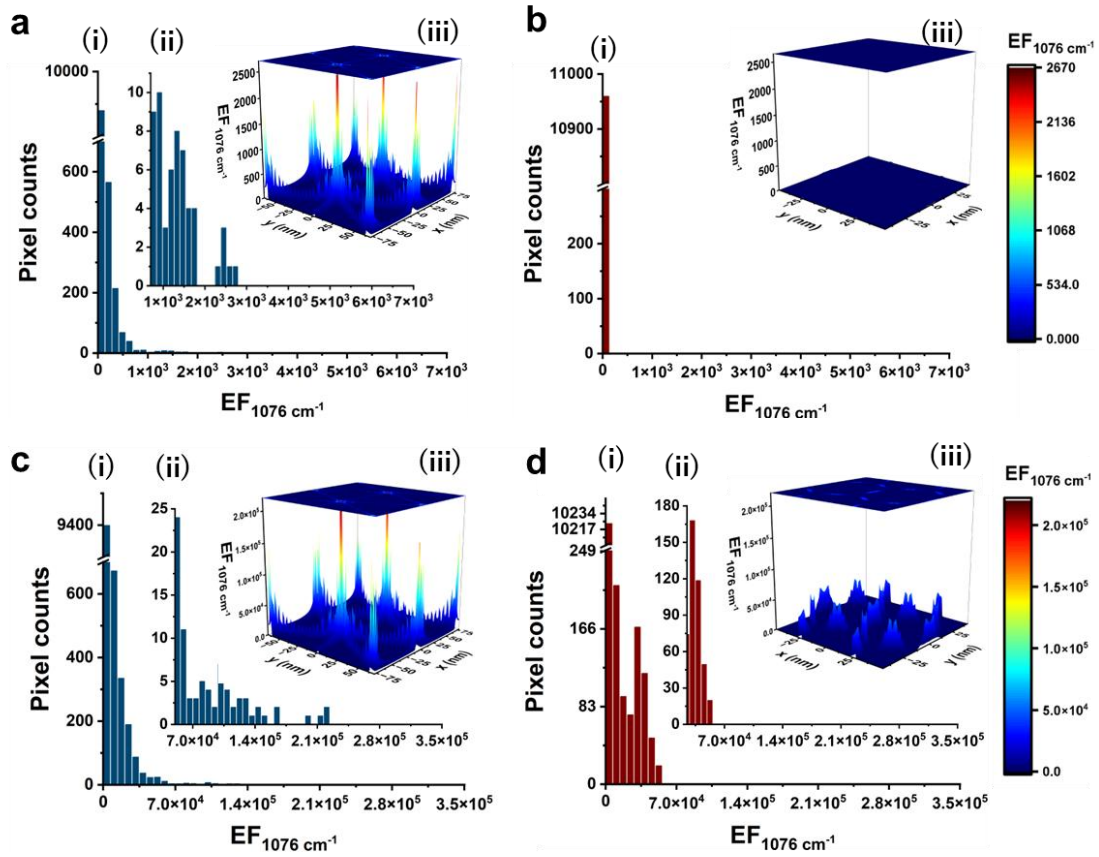


Figure 3-28. Distribution of enhancement factor (EF) at 1076 cm⁻¹ at x-y cross-section plane for (a, c) AuNT film and (b, d) AuNS film on different substrates: (a, b) TA substrate with 120 nm TiO₂, (c, d) ITO substrates. (i, ii) Histograms showing pixel distributions across different EF ranges. (iii) 3D map of field distributions. Due to the smaller single unit size of s-ATA (b, d, i-ii), the pixel count is scaled by 2.47 to match the unit area of t-ATA.

Collectively, these results demonstrate that t-ATA provides higher sensitivity due to the tip structure, which is less affected by the underlying FP cavity owing to the broader hybrid band generated by the multiple modal strong coupling. In contrast, the SERS signal on AuNS films can be more effectively enhanced when the excitation and resonance are well-aligned. Each of SERS peaks on the s-ATA is easily influenced by varying the TiO₂ thickness due to the sharp resonance LB peaks. In addition, tailoring the spectra under modal ultrastrong coupling conditions to control the resonance proves to be an effective

strategy for optimizing the SERS performance of the AuNP films. These insights provide valuable design guidelines for FP cavity-assisted SERS platforms: AuNT films, owing to their sharp-tip geometry, are well-suited for highly sensitive SERS sensors.⁷⁵ Meanwhile, AuNS films, with their strong and tunable modal coupling, are more appropriate for SERS applications involving abundant reporter molecules, such as information storage,³⁵ anticounterfeiting,¹⁰⁹ and related technologies.

3-4. Conclusion

In this chapter, the SERS performances of t-ATA and s-ATA structures were systematically investigated. The SERS enhancements on AuNT film and the AuNS film were affected by the resonance with the excitation due to the greatly modified spectra under the modal ultrastrong coupling conditions. FDTD simulation reveals that the hotspots in AuNT films and AuNS films are located at the tip-to-tip vertices and interparticle gaps, respectively. Their spatial distribution remains unchanged under different modal coupling states or excitation wavelengths although the field intensity varies. When the excitation and the LB aligned, the strongest field enhancement was observed. Using 4-MBA as a probe molecule, both t-ATA and s-ATA structures exhibited distinct SERS responses with abundantly absorbed 4-MBA. The SERS signal on t-ATA and s-ATA can be either suppressed or enhanced at specific TiO_2 thicknesses due to the spectral overlap with excitation. The signal enhancement on t-ATA and s-ATA achieved 2.7-fold and 5.1-fold, respectively. The enhancement on t-ATA is less affected by the TiO_2 thickness than the s-ATA due to the wider LB band that overlaps with the excitation of 785 nm. When the substrates are treated with 4-MBA in low concentration, the SERS spectra on AuNT films exhibited clearer characteristic peaks of 4-MBA than the AuNS films, which might be attributed to the tip-preferential adsorption. I believe the findings in the shape-dependent SERS performance of nanoparticle films under modal ultrastrong coupling conditions could provide useful information for rational design of SERS substrates.

Chapter 4

General conclusion

In this thesis, I investigated the shape-dependent SERS performance of self-assembled AuNP films modulated by modal ultrastrong coupling with FP cavities. The findings highlight the critical role of nanoparticle shape in tailoring plasmonic-cavity hybrid systems.

In chapter 2, the modal coupling between self-assembled AuNT and AuNS films with FP cavity were systematically investigated. AuNT and AuNS films with comparable particle volumes were fabricated on semi-open FP cavities via Langmuir-Schaefer method. By varying the TiO₂ thickness, the modal coupling between the nanoparticle films and FP cavities and compared. Both systems exhibited similar modal coupling behaviors, with resonance positions varying depending on particle shape. Notably, modal ultrastrong coupling was achieved at larger TiO₂ thicknesses, with a peak splitting energy of approximately 650 meV. The calculated spectra of t-ATA and s-ATA structures by FDTD simulation confirmed this modal ultrastrong coupling behavior, which demonstrated similar splitting energies with the corresponding experimental results.

In chapter 3, FDTD simulations revealed shape- and wavelength-dependent near-field enhancements, with the strongest enhancement occurring at the lower branch. SERS measurements demonstrated that the extinction intensities, which are tailorable through modal coupling, directly influenced the SERS output. By integrating with the TA structure with optimized TiO₂ thickness, the SERS signals on AuNT film and AuNS film can be enhanced up to 2.7-fold and 5.1-fold, respectively. AuNT films exhibited superior sensitivity that was less affected by TiO₂ thickness, attributed to broad extinction at the LB, while shape-dependent ligand coverage is likely to facilitate the analyte adsorption at hotspots. In contrast, AuNS films showed higher SERS signal enhancement under

sufficient analyte concentrations, which is susceptible to the TiO₂ thickness change due to the sharp hybrid peak associated with a relatively single mode.

In summary, I systematically studied the shape-dependent SERS performance of self-assembled gold nanoparticle films under modal ultrastrong coupling conditions with FP cavities. The results provide valuable design guidelines for engineering SERS platforms optimized either for ultrasensitive detection or for controllable signal output depending on application needs. In addition to the well-documented strategies that enhance hotspots through engineering nanostructures and hierarchical assemblies,¹¹⁰⁻¹¹⁵ the FP cavity-assisted approach in this thesis enables convenient and highly reproducible modulation of the resonance condition by simply adjusting the cavity thickness, while modal ultrastrong coupling further amplifies the contribution of existing hotspots in the gold nanoparticle film. Thus, the present platform can be readily integrated with more sophisticated nanostructures reported in recent high-performance SERS substrates, offering an additional degree of freedom for resonance control. Furthermore, by exploiting particle shape anisotropy, regio-selective functionalization of nanoparticles enables the analytes to be guided into the hotspots, thereby allowing the FP cavity-assisted nanoparticle film to be further developed for sensitive biomolecule detection.

References

- (1) Tang, T.-C.; An, B.; Huang, Y.; Vasikaran, S.; Wang, Y.; Jiang, X.; Lu, T. K.; Zhong, C., Materials design by synthetic biology. *Nat. Rev. Mater.* **2021**, *6* (4), 332-350.
- (2) Flynn, C. D.; Chang, D.; Mahmud, A.; Yousefi, H.; Das, J.; Riordan, K. T.; Sargent, E. H.; Kelley, S. O., Biomolecular sensors for advanced physiological monitoring. *Nat. Rev. Bioeng.* **2023**, *1* (8), 560-575.
- (3) Aman, R.; Mahas, A.; Mahfouz, M., Nucleic Acid Detection Using CRISPR/Cas Biosensing Technologies. *ACS Synth. Biol.* **2020**, *9* (6), 1226-1233.
- (4) Su, Z.; Li, T.; Wu, D.; Wu, Y.; Li, G., Recent Progress on Single-Molecule Detection Technologies for Food Safety. *J. Agric. Food. Chem.* **2022**, *70* (2), 458-469.
- (5) Williams, A.; Aguilar, M. R.; Pattiya Arachchillage, K. G. G.; Chandra, S.; Rangan, S.; Ghosal Gupta, S.; Artes Vivancos, J. M., Biosensors for Public Health and Environmental Monitoring: The Case for Sustainable Biosensing. *ACS Sustain. Chem. Eng.* **2024**, *12* (28), 10296-10312.
- (6) Haghayegh, F.; Norouziyazad, A.; Haghani, E.; Feygin, A. A.; Rahimi, R. H.; Ghavamabadi, H. A.; Sadighbayan, D.; Madhoun, F.; Papagelis, M.; Felfeli, T.; Salahandish, R., Revolutionary Point-of-Care Wearable Diagnostics for Early Disease Detection and Biomarker Discovery through Intelligent Technologies. *Adv. Sci.* **2024**, *11* (36), 2400595.
- (7) Liu, H.; Lei, Y., A critical review: Recent advances in “digital” biomolecule detection with single copy sensitivity. *Biosens. Bioelectron.* **2021**, *177*, 112901.
- (8) Hu, J.; Yan, X.; Chris Le, X., Label-free detection of biomolecules using inductively coupled plasma mass spectrometry (ICP-MS). *Anal. Bioanal. Chem.* **2024**, *416* (11), 2625-2640.
- (9) Cardoso, A. G.; Viltres, H.; Ortega, G. A.; Phung, V.; Grewal, R.; Mozaffari, H.; Ahmed, S. R.; Rajabzadeh, A. R.; Srinivasan, S., Electrochemical sensing of analytes in saliva: Challenges, progress, and perspectives. *TrAC, Trends Anal. Chem.* **2023**, *160*, 116965.
- (10) Castle, L. M.; Schuh, D. A.; Reynolds, E. E.; Furst, A. L., Electrochemical Sensors to Detect Bacterial Foodborne Pathogens. *ACS Sensors* **2021**, *6* (5), 1717-1730.
- (11) Gonçalves, M. S. T., Fluorescent Labeling of Biomolecules with Organic Probes. *Chem. Rev.* **2009**, *109* (1), 190-212.
- (12) Wu, N.; Bo, C.; Guo, S., Luminescent Ln-MOFs for Chemical Sensing Application on Biomolecules. *ACS Sensors* **2024**, *9* (9), 4402-4424.

- (13) Jin, Z.; Yim, W.; Retout, M.; Housel, E.; Zhong, W.; Zhou, J.; Strano, M. S.; Jokerst, J. V., Colorimetric sensing for translational applications: from colorants to mechanisms. *Chem. Soc. Rev.* **2024**, *53* (15), 7681-7741.
- (14) Roda, B.; Deo, S. K.; O'Connor, G.; Moraskie, M.; Giordani, S.; Marassi, V.; Roda, A.; Daunert, S., Shining light on biosensors: Chemiluminescence and bioluminescence in enabling technologies. *TrAC, Trends Anal. Chem.* **2024**, *180*, 117975.
- (15) Cialla-May, D.; Bonifacio, A.; Bocklitz, T.; Markin, A.; Markina, N.; Fornasaro, S.; Dwivedi, A.; Dib, T.; Farnesi, E.; Liu, C.; Ghosh, A.; Popp, J., Biomedical SERS – the current state and future trends. *Chem. Soc. Rev.* **2024**, *53* (18), 8957-8979.
- (16) Shen, Y.; Tissot, A.; Serre, C., Recent progress on MOF-based optical sensors for VOC sensing. *Chem. Sci.* **2022**, *13* (47), 13978-14007.
- (17) Karawdeniya, B. I.; Damry, A. M.; Murugappan, K.; Manjunath, S.; Bandara, Y. M. N. D. Y.; Jackson, C. J.; Tricoli, A.; Neshev, D., Surface Functionalization and Texturing of Optical Metasurfaces for Sensing Applications. *Chem. Rev.* **2022**, *122* (19), 14990-15030.
- (18) Liu, Q.; Zheng, J.; Xie, A.; Chen, M.; Gong, R.-Y.; Sheng, Y.; Chen, H.-L.; Qi, C.-B., Exosome, a Rising Biomarkers in Liquid Biopsy: Advances of Label-Free and Label Strategy for Diagnosis of Cancer. *Crit. Rev. Anal. Chem.* **2025**, *55* (6), 1136-1147.
- (19) Stanley, C. V.; Xiao, Y.; Ling, T.; Li, D.-S.; Chen, P., Opto-digital molecular analytics. *Chem. Soc. Rev.* **2025**, *54* (7), 3557-3577.
- (20) Hariri, A. A.; Cartwright, A. P.; Dory, C.; Gidi, Y.; Yee, S.; Thompson, I. A. P.; Fu, K. X.; Yang, K.; Wu, D.; Maganzini, N.; Feagin, T.; Young, B. E.; Afshar, B. H.; Eisenstein, M.; Digonnet, M. J. F.; Vuckovic, J.; Soh, H. T., Modular Aptamer Switches for the Continuous Optical Detection of Small-Molecule Analytes in Complex Media. *Adv. Mater.* **2024**, *36* (1), 2304410.
- (21) Kabashin, A. V.; Kravets, V. G.; Grigorenko, A. N., Label-free optical biosensing: going beyond the limits. *Chem. Soc. Rev.* **2023**, *52* (18), 6554-6585.
- (22) Liu, L.; Zhang, T.; Wu, Z.; Zhang, F.; Wang, Y.; Wang, X.; Zhang, Z.; Li, C.; Lv, X.; Chen, D.; Jiao, S.; Wu, J.; Li, Y., Universal Method for Label-Free Detection of Pathogens and Biomolecules by Surface-Enhanced Raman Spectroscopy Based on Gold Nanoparticles. *Anal. Chem.* **2023**, *95* (8), 4050-4058.
- (23) Syahir, A.; Usui, K.; Tomizaki, K.-y.; Kajikawa, K.; Mihara, H., Label and Label-Free Detection Techniques for Protein Microarrays. *Microarrays* **2015**, *4* (2), 228-244.
- (24) Ma, H.; Pan, S.-Q.; Wang, W.-L.; Yue, X.; Xi, X.-H.; Yan, S.; Wu, D.-Y.; Wang, X.; Liu, G.; Ren, B., Surface-Enhanced Raman Spectroscopy: Current Understanding, Challenges, and Opportunities. *ACS Nano* **2024**, *18* (22), 14000-14019.

- (25) M.B, B.; Rhakho, N.; Jena, S. R.; Yadav, S.; Altaee, A.; Saxena, M.; Samal, A. K., Detection of PFAS via surface-enhanced Raman scattering: Challenges and future perspectives. *Sustain. Chem. Environ.* **2023**, *3*, 100031.
- (26) Langer, J.; Jimenez de Aberasturi, D.; Aizpurua, J.; Alvarez-Puebla, R. A.; Auguie, B.; Baumberg, J. J.; Bazan, G. C.; Bell, S. E. J.; Boisen, A.; Brolo, A. G.; Choo, J.; Cialla-May, D.; Deckert, V.; Fabris, L.; Faulds, K.; García de Abajo, F. J.; Goodacre, R.; Graham, D.; Haes, A. J.; Haynes, C. L.; Huck, C.; Itoh, T.; Käll, M.; Kneipp, J.; Kotov, N. A.; Kuang, H.; Le Ru, E. C.; Lee, H. K.; Li, J.-F.; Ling, X. Y.; Maier, S. A.; Mayerhöfer, T.; Moskovits, M.; Murakoshi, K.; Nam, J.-M.; Nie, S.; Ozaki, Y.; Pastoriza-Santos, I.; Perez-Juste, J.; Popp, J.; Pucci, A.; Reich, S.; Ren, B.; Schatz, G. C.; Shegai, T.; Schlücker, S.; Tay, L.-L.; Thomas, K. G.; Tian, Z.-Q.; Van Duyne, R. P.; Vo-Dinh, T.; Wang, Y.; Willets, K. A.; Xu, C.; Xu, H.; Xu, Y.; Yamamoto, Y. S.; Zhao, B.; Liz-Marzán, L. M., Present and Future of Surface-Enhanced Raman Scattering. *ACS Nano* **2020**, *14* (1), 28-117.
- (27) Lin, L. L.; Alvarez-Puebla, R.; Liz-Marzán, L. M.; Trau, M.; Wang, J.; Fabris, L.; Wang, X.; Liu, G.; Xu, S.; Han, X. X.; Yang, L.; Shen, A.; Yang, S.; Xu, Y.; Li, C.; Huang, J.; Liu, S.-C.; Huang, J.-A.; Srivastava, I.; Li, M.; Tian, L.; Nguyen, L. B. T.; Bi, X.; Cialla-May, D.; Matousek, P.; Stone, N.; Carney, R. P.; Ji, W.; Song, W.; Chen, Z.; Phang, I. Y.; Henriksen-Lacey, M.; Chen, H.; Wu, Z.; Guo, H.; Ma, H.; Ustinov, G.; Luo, S.; Mosca, S.; Gardner, B.; Long, Y.-T.; Popp, J.; Ren, B.; Nie, S.; Zhao, B.; Ling, X. Y.; Ye, J., Surface-Enhanced Raman Spectroscopy for Biomedical Applications: Recent Advances and Future Challenges. *ACS Appl. Mater. Interfaces* **2025**, *17* (11), 16287-16379.
- (28) Kim, Y.-i.; Jeong, S.; Jun, B.-H.; Lee, Y.-S.; Lee, Y.-S.; Jeong, D. H.; Lee, D. S., Endoscopic imaging using surface-enhanced Raman scattering. *Eur. J. Nanomed.* **2017**, *9* (3-4), 91-104.
- (29) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J., Raman spectra of pyridine adsorbed at a silver electrode. *Chem. Phys. Lett.* **1974**, *26* (2), 163-166.
- (30) Stiles, P. L.; Dieringer, J. A.; Shah, N. C.; Van Duyne, R. P., Surface-Enhanced Raman Spectroscopy. *Annu. Rev. Anal. Chem.* **2008**, *1*, 601-626.
- (31) Jeanmaire, D. L.; Van Duyne, R. P., Surface raman spectroelectrochemistry: Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. *J. Electroanal. Chem. Interf. Electrochem.* **1977**, *84* (1), 1-20.
- (32) Ding, S.-Y.; You, E.-M.; Tian, Z.-Q.; Moskovits, M., Electromagnetic theories of surface-enhanced Raman spectroscopy. *Chem. Soc. Rev.* **2017**, *46* (13), 4042-4076.

- (33) Ghosh, S. K.; Pal, T., Interparticle Coupling Effect on the Surface Plasmon Resonance of Gold Nanoparticles: From Theory to Applications. *Chem. Rev.* **2007**, *107* (11), 4797-4862.
- (34) Balčytis, A.; Nishijima, Y.; Krishnamoorthy, S.; Kuchmizhak, A.; Stoddart, P. R.; Petruškevičius, R.; Juodkazis, S., From Fundamental toward Applied SERS: Shared Principles and Divergent Approaches. *Adv. Opt. Mater.* **2018**, *6* (16), 1800292.
- (35) Kim, T.; Lee, J.; Yu, E.-S.; Lee, S.; Woo, H.; Kwak, J.; Chung, S.; Choi, I.; Ryu, Y.-S., Fabry–Perot Cavity Control for Tunable Raman Scattering. *Small* **2023**, *19* (29), 2207003.
- (36) Khan, M. A. R.; Al Mamun, M. S.; Habib, M. A.; Islam, A. B. M. N.; Mahiuddin, M.; Karim, K. M. R.; Naime, J.; Saha, P.; Dey, S. K.; Ara, M. H., A review on gold nanoparticles: Biological synthesis, characterizations, and analytical applications. *Results in Chem.* **2022**, *4*, 100478.
- (37) Biswas, A.; Bayer, I. S.; Biris, A. S.; Wang, T.; Dervishi, E.; Faupel, F., Advances in top–down and bottom–up surface nanofabrication: Techniques, applications & future prospects. *Adv. Colloid Interface Sci.* **2012**, *170* (1), 2-27.
- (38) Vinnacombe-Willson, G. A.; Conti, Y.; Stefancu, A.; Weiss, P. S.; Cortés, E.; Scarabelli, L., Direct Bottom-Up In Situ Growth: A Paradigm Shift for Studies in Wet-Chemical Synthesis of Gold Nanoparticles. *Chem. Rev.* **2023**, *123* (13), 8488-8529.
- (39) Blanco-Formoso, M.; Pazos-Perez, N.; Alvarez-Puebla, R. A., Fabrication and SERS properties of complex and organized nanoparticle plasmonic clusters stable in solution. *Nanoscale* **2020**, *12* (28), 14948-14956.
- (40) Lane, L. A.; Qian, X.; Nie, S., SERS Nanoparticles in Medicine: From Label-Free Detection to Spectroscopic Tagging. *Chem. Rev.* **2015**, *115* (19), 10489-10529.
- (41) Guo, Q.; Xu, M.; Yuan, Y.; Gu, R.; Yao, J., Self-Assembled Large-Scale Monolayer of Au Nanoparticles at the Air/Water Interface Used as a SERS Substrate. *Langmuir* **2016**, *32* (18), 4530-4537.
- (42) Matricardi, C.; Hanske, C.; Garcia-Pomar, J. L.; Langer, J.; Mihi, A.; Liz-Marzán, L. M., Gold Nanoparticle Plasmonic Superlattices as Surface-Enhanced Raman Spectroscopy Substrates. *ACS Nano* **2018**, *12* (8), 8531-8539.
- (43) Jambhulkar, S.; Ravichandran, D.; Zhu, Y.; Thippanna, V.; Ramanathan, A.; Patil, D.; Fonseca, N.; Thummalapalli, S. V.; Sundaravadivelan, B.; Sun, A.; Xu, W.; Yang, S.; Kannan, A. M.; Golan, Y.; Lancaster, J.; Chen, L.; Joyee, E. B.; Song, K., Nanoparticle Assembly: From Self-Organization to Controlled Micropatterning for Enhanced Functionalities. *Small* **2024**, *20* (6), 2306394.

- (44) Song, L.; Huang, Y.; Nie, Z.; Chen, T., Macroscopic two-dimensional monolayer films of gold nanoparticles: fabrication strategies, surface engineering and functional applications. *Nanoscale* **2020**, *12* (14), 7433-7460.
- (45) Tim, B.; Kotkowiak, M.; Kowalska, N.; Nowicka, A. B.; Lewandowski, W., Influence of Gold Nanoparticle Assembly in Langmuir–Schaefer Monolayers on the Surface-Enhanced Spectroscopy Response of a Nanoplatfrom. *J. Phys. Chem. C* **2023**, *127* (32), 15978-15987.
- (46) Swierczewski, M.; Bürgi, T., Langmuir and Langmuir–Blodgett Films of Gold and Silver Nanoparticles. *Langmuir* **2023**, *39* (6), 2135-2151.
- (47) Sun, Z.; Umar, A.; Zeng, J.; Luo, X.; Song, L.; Zhang, Z.; Chen, Z.; Li, J.; Su, F.; Huang, Y., Highly Pure Gold Nanotriangles with almost 100% Yield for Surface-Enhanced Raman Scattering. *ACS Appl. Nano Mater.* **2022**, *5* (1), 1220-1231.
- (48) Lee, Y. H.; Lee, C. K.; Tan, B.; Rui Tan, J. M.; Phang, I. Y.; Ling, X. Y., Using the Langmuir–Schaefer technique to fabricate large-area dense SERS-active Au nanoprism monolayer films. *Nanoscale* **2013**, *5* (14), 6404-6412.
- (49) Scarabelli, L.; Coronado-Puchau, M.; Giner-Casares, J. J.; Langer, J.; Liz-Marzán, L. M., Monodisperse Gold Nanotriangles: Size Control, Large-Scale Self-Assembly, and Performance in Surface-Enhanced Raman Scattering. *ACS Nano* **2014**, *8* (6), 5833-5842.
- (50) Hugall, J. T.; Singh, A.; van Hulst, N. F., Plasmonic Cavity Coupling. *ACS Photonics* **2018**, *5* (1), 43-53.
- (51) Chen, J.; Song, G.; Cong, S.; Zhao, Z., Resonant-Cavity-Enhanced Electrochromic Materials and Devices. *Adv. Mater.* **2023**, *35* (47), 2300179.
- (52) Cui, Y.; He, Y.; Jin, Y.; Ding, F.; Yang, L.; Ye, Y.; Zhong, S.; Lin, Y.; He, S., Plasmonic and metamaterial structures as electromagnetic absorbers. *Laser Photonics Rev.* **2014**, *8* (4), 495-520.
- (53) Yu, J.; Ohtera, Y.; Yamada, H., Scattering-parameter model analysis of side-coupled plasmonic Fabry–Perot waveguide filters. *Appl. Phys. A* **2018**, *124* (7), 516.
- (54) Ding, T., Controllable tuning of Fabry–Perot cavities via laser printing. *J. Mater. Chem. C* **2020**, *8* (31), 10825-10830.
- (55) Huang, C.-P.; Chan, C.-T., Deep subwavelength Fabry-Perot resonances. *EPJ Appl. Metamater.* **2014**, *1*.
- (56) Guo, Y.; Jiang, S.; Chen, X.; Mattei, M.; Dieringer, J. A.; Cirraldo, J. P.; Van Duyne, R. P., Using a Fabry–Perot Cavity to Augment the Enhancement Factor for Surface-Enhanced Raman Spectroscopy and Tip-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2018**, *122* (26), 14865-14871.

- (57) Liu, Y.-E.; Shi, X.; Yokoyama, T.; Inoue, S.; Sunaba, Y.; Oshikiri, T.; Sun, Q.; Tamura, M.; Ishihara, H.; Sasaki, K.; Misawa, H., Quantum-Coherence-Enhanced Hot-Electron Injection under Modal Strong Coupling. *ACS Nano* **2023**, *17* (9), 8315-8323.
- (58) Shi, X.; Ueno, K.; Oshikiri, T.; Sun, Q.; Sasaki, K.; Misawa, H., Enhanced water splitting under modal strong coupling conditions. *Nat. Nanotechnol.* **2018**, *13* (10), 953-958.
- (59) Oshikiri, T.; Hayakawa, T.; Niinomi, H.; Nakagawa, M., Strong Light Confinement by a Plasmon-Coupled Parabolic Nanoresonator Array. *J. Phys. Chem. C* **2024**, *128* (12), 5271-5279.
- (60) Garcia, A. A. R.; Mao, C.-A.; Cheng, W.-H., Realization of ultrastrong coupling between LSPR and Fabry–Pérot mode via self-assembly of Au-NPs on p-NiO/Au film. *Nanophotonics* **2024**, *13* (14), 2501-2512.
- (61) Zang, X.; Shi, X.; Oshikiri, T.; Ueno, K.; Sunaba, Y.; Sasaki, K.; Misawa, H., Highly Sensitive and Spatially Homogeneous Surface-Enhanced Raman Scattering Substrate under Plasmon–Nanocavity Coupling. *J. Phys. Chem. C* **2021**, *125* (36), 19880-19886.
- (62) Suganami, Y.; Oshikiri, T.; Mitomo, H.; Sasaki, K.; Liu, Y.-E.; Shi, X.; Matsuo, Y.; Ijio, K.; Misawa, H., Spatially Uniform and Quantitative Surface-Enhanced Raman Scattering under Modal Ultrastrong Coupling Beyond Nanostructure Homogeneity Limits. *ACS Nano* **2024**.
- (63) Suganami, Y.; Oshikiri, T.; Shi, X.; Misawa, H., Water Oxidation under Modal Ultrastrong Coupling Conditions Using Gold/Silver Alloy Nanoparticles and Fabry–Pérot Nanocavities. *Angew. Chem. Int. Ed.* **2021**, *60* (34), 18438-18442.
- (64) Ebbesen, T. W., Hybrid Light–Matter States in a Molecular and Material Science Perspective. *Acc. Chem. Res.* **2016**, *49* (11), 2403-2412.
- (65) Kitajima, Y.; Sakamoto, H.; Ueno, K., Coupled plasmonic systems: controlling the plasmon dynamics and spectral modulations for molecular detection. *Nanoscale* **2021**, *13* (10), 5187-5201.
- (66) Berghuis, A. M.; Serpenti, V.; Ramezani, M.; Wang, S.; Gómez Rivas, J., Light–Matter Coupling Strength Controlled by the Orientation of Organic Crystals in Plasmonic Cavities. *J. Phys. Chem. C* **2020**, *124* (22), 12030-12038.
- (67) Houdré, R.; Gibernon, J. L.; Pellandini, P.; Stanley, R. P.; Oesterle, U.; Weisbuch, C.; O’Gorman, J.; Roycroft, B.; Illegems, M., Saturation of the strong-coupling regime in a semiconductor microcavity: Free-carrier bleaching of cavity polaritons. *Phys. Rev. B* **1995**, *52* (11), 7810-7813.

- (68) Frisk Kockum, A.; Miranowicz, A.; De Liberato, S.; Savasta, S.; Nori, F., Ultrastrong coupling between light and matter. *Nat. Rev. Phys.* **2019**, *1* (1), 19-40.
- (69) Suganami, Y.; Oshikiri, T.; Mitomo, H.; Sasaki, K.; Liu, Y.-E.; Shi, X.; Matsuo, Y.; Ijro, K.; Misawa, H., Spatially Uniform and Quantitative Surface-Enhanced Raman Scattering under Modal Ultrastrong Coupling Beyond Nanostructure Homogeneity Limits. *ACS Nano* **2024**, *18* (6), 4993-5002.
- (70) Gao, W.; Li, X.; Bamba, M.; Kono, J., Continuous transition between weak and ultrastrong coupling through exceptional points in carbon nanotube microcavity exciton–polaritons. *Nat. Photonics* **2018**, *12* (6), 362-367.
- (71) Baranov, D. G.; Munkhbat, B.; Zhukova, E.; Bisht, A.; Canales, A.; Rousseaux, B.; Johansson, G.; Antosiewicz, T. J.; Shegai, T., Ultrastrong coupling between nanoparticle plasmons and cavity photons at ambient conditions. *Nat. Commun.* **2020**, *11* (1), 2715.
- (72) Bonin, G. O.; Barrow, S. J.; Connell, T. U.; Roberts, A.; Chesman, A. S. R.; Gómez, D. E., Self-Assembly of Plasmonic Near-Perfect Absorbers of Light: The Effect of Particle Size. *J. Phys. Chem. Lett.* **2020**, *11* (19), 8378-8385.
- (73) Li, G.-C.; Zhang, Q.; Maier, S. A.; Lei, D., Plasmonic particle-on-film nanocavities: a versatile platform for plasmon-enhanced spectroscopy and photochemistry. *Nanophotonics* **2018**, *7* (12), 1865-1889.
- (74) Sun, Z.; Fang, Y., Fabry-Pérot Interference Cavity Length Tuned by Plasmonic Nanoparticle Metasurface for Nanophotonic Device Design. *ACS Appl. Nano Mater.* **2020**, *3* (11), 10732-10738.
- (75) Gao, T.; Yachi, T.; Shi, X.; Sato, R.; Sato, C.; Yonamine, Y.; Kanie, K.; Misawa, H.; Ijro, K.; Mitomo, H., Ultrasensitive Surface-Enhanced Raman Scattering Platform for Protein Detection via Active Delivery to Nanogaps as a Hotspot. *ACS Nano* **2024**, *18* (32), 21593-21606.
- (76) Cao, E.; Shi, X.; Oshikiri, T.; Liu, Y.-E.; Sun, Q.; Sasaki, K.; Misawa, H., Improving Charge Transfer under Strong Coupling Conditions via Interfacial Modulation. *ACS Photonics* **2024**, *11* (3), 1205-1212.
- (77) Cao, Y.; Oshikiri, T.; Shi, X.; Ueno, K.; Li, J.; Misawa, H., Efficient Hot-Electron Transfer under Modal Strong Coupling Conditions with Sacrificial Electron Donors. *ChemNanoMat* **2019**, *5* (8), 1008-1014.
- (78) Zang, X.; Shi, X.; Suganami, Y.; Liu, Y.-E.; Oshikiri, T.; Misawa, H., Investigation of Enhanced Water Oxidation under Plasmon–Nanocavity Strong Coupling Using In Situ Electrochemical Surface-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2023**, *127* (31), 15087-15095.

- (79) Zhao, S.; Fusco, Z.; Beck, F. J., Strong and tunable absorption in coupled nanoparticle–cavity systems for plasmonically enhanced hot electron devices. *Optica* **2022**, *9* (9), 1084-1093.
- (80) Yu, X.; Wang, Z.; Cui, H.; Wu, X.; Chai, W.; Wei, J.; Chen, Y.; Zhang, Z., A review on gold nanotriangles: synthesis, self-assembly and their applications. *Molecules* **2022**, *27* (24), 8766.
- (81) Losquin, A.; Zagonel, L. F.; Myroshnychenko, V.; Rodríguez-González, B.; Tencé, M.; Scarabelli, L.; Förstner, J.; Liz-Marzán, L. M.; García de Abajo, F. J.; Stéphan, O.; Kociak, M., Unveiling Nanometer Scale Extinction and Scattering Phenomena through Combined Electron Energy Loss Spectroscopy and Cathodoluminescence Measurements. *Nano Lett.* **2015**, *15* (2), 1229-1237.
- (82) Mitomo, H.; Takeuchi, C.; Sugiyama, R.; Tamada, K.; Ijro, K., Thermo-Responsive Silver Nanocube Assembled Films. *Bull. Chem. Soc. Jpn.* **2022**, *95* (5), 771-773.
- (83) Scarabelli, L.; Liz-Marzán, L. M., An Extended Protocol for the Synthesis of Monodisperse Gold Nanotriangles. *ACS Nano* **2021**, *15* (12), 18600-18607.
- (84) González-Rubio, G.; Scarabelli, L.; Guerrero-Martínez, A.; Liz-Marzán, L. M., Surfactant-Assisted Symmetry Breaking in Colloidal Gold Nanocrystal Growth. *ChemNanoMat* **2020**, *6* (5), 698-707.
- (85) Im, S. W.; Jo, E.; Kim, R. M.; Han, J. H.; Nam, K. T., 32-Symmetric Chiral Gold Nanoplates with Near-Infrared Circular Dichroism. *Adv. Opt. Mater.* **2023**, *11* (18), 2300037.
- (86) Xiong, K.; Mitomo, H.; Su, X.; Shi, Y.; Yonamine, Y.; Sato, S.-i.; Ijro, K., Molecular configuration-mediated thermo-responsiveness in oligo(ethylene glycol) derivatives attached on gold nanoparticles. *Nanoscale Adv.* **2021**, *3* (13), 3762-3769.
- (87) Polyanskiy, M. N., Refractiveindex.info database of optical constants. *Sci. Data* **2024**, *11* (1), 94.
- (88) Johnson, P. B.; Christy, R. W., Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, *6* (12), 4370-4379.
- (89) Chen, Z.; Feng, K.; Chen, Z.; Shen, J.; Li, H.; Dong, J., The impact of LSP–SPP coupling on the electric field enhancement of a composite SERS substrate consisting of an Au 2D sinusoidal grating and Ag colloidal nanoparticles. *Opt. Commun.* **2022**, *508*, 127797.
- (90) Le, F.; Lwin, N. Z.; Steele, J. M.; Käll, M.; Halas, N. J.; Nordlander, P., Plasmons in the Metallic Nanoparticle–Film System as a Tunable Impurity Problem. *Nano Lett.* **2005**, *5* (10), 2009-2013.

- (91) Chen, L.; Sun, H.; Zhao, Y.; Zhang, Y.; Wang, Y.; Liu, Y.; Zhang, X.; Jiang, Y.; Hua, Z.; Yang, J., Plasmonic-induced SERS enhancement of shell-dependent Ag@Cu₂O core-shell nanoparticles. *RSC Adv.* **2017**, 7 (27), 16553-16560.
- (92) Li, R.; Lv, H.; Zhang, X.; Liu, P.; Chen, L.; Cheng, J.; Zhao, B., Vibrational spectroscopy and density functional theory study of 4-mercaptobenzoic acid. *Spectrochim. Acta - A: Mol. Biomol. Spectrosc.* **2015**, 148, 369-374.
- (93) Williams, A.; Flynn, K. J.; Xia, Z.; Dunstan, P. R., Multivariate spectral analysis of pH SERS probes for improved sensing capabilities. *J. Raman Spectrosc.* **2016**, 47 (7), 819-827.
- (94) Yokota, Y.; Ueno, K.; Misawa, H., Essential nanogap effects on surface-enhanced Raman scattering signals from closely spaced gold nanoparticles. *Chem. Commun.* **2011**, 47 (12), 3505-3507.
- (95) Lee, S. A.; Link, S., Chemical Interface Damping of Surface Plasmon Resonances. *Acc. Chem. Res.* **2021**, 54 (8), 1950-1960.
- (96) Zhu, S.; Zhao, Q.; Fu, H.; Zhang, H.; Bao, H.; Le, Z.; Bao, X.; Liu, X.; Zhang, T.; Li, Y.; Cai, W., Chemical Interface Damping-Induced Attenuation of Surface Plasmon-Enhanced Raman Spectroscopy. *ACS Photonics* **2022**, 9 (9), 3000-3011.
- (97) Xiong, K.; Nagayama, M.; Ijio, K.; Mitomo, H., Fair surface modification with mixed alkanethiols on gold nanoparticles through minimal unfair ligand exchange. *Nanoscale Adv.* **2024**, 6 (18), 4583-4590.
- (98) Villar, I. D.; Zamarreño, C. R.; Hernaez, M.; Arregui, F. J.; Matias, I. R., Generation of Lossy Mode Resonances With Absorbing Thin-Films. *J. Lightwave Technol.* **2010**, 28 (23), 3351-3357.
- (99) Lai, Y.-H.; Chen, S.-W.; Hayashi, M.; Shiu, Y.-J.; Huang, C.-C.; Chuang, W.-T.; Su, C.-J.; Jeng, H.-C.; Chang, J.-W.; Lee, Y.-C.; Su, A.-C.; Mou, C.-Y.; Jeng, U. S., Mesostuctured Arrays of Nanometer-spaced Gold Nanoparticles for Ultrahigh Number Density of SERS Hot Spots. *Adv. Funct. Mater.* **2014**, 24 (17), 2544-2552.
- (100) Chen, T.; Wang, H.; Chen, G.; Wang, Y.; Feng, Y.; Teo, W. S.; Wu, T.; Chen, H., Hotspot-Induced Transformation of Surface-Enhanced Raman Scattering Fingerprints. *ACS Nano* **2010**, 4 (6), 3087-3094.
- (101) Foucault, R.; Birke, R. L.; Lombardi, J. R., SERS of Surfactants in Monolayer and Multibilayer Forms on an Electrified Ag Surface. *Langmuir* **2003**, 19 (21), 8818-8827.
- (102) Joo, T. H.; Kim, K.; Kim, M. S., Surface-enhanced Raman scattering (SERS) of 1-propanethiol in silver sol. *J. Phys. Chem.* **1986**, 90 (22), 5816-5819.

- (103) Wang, G.; Akiyama, Y.; Kanayama, N.; Takarada, T.; Maeda, M., Directed Assembly of Gold Nanorods by Terminal-Base Pairing of Surface-Grafted DNA. *Small* **2017**, *13* (44), 1702137.
- (104) Wang, G.; Zhang, Y.; Liang, X.; Takarada, T.; Maeda, M., Regioselective DNA modification and directed self-assembly of triangular gold nanoplates. *Nanomaterials* **2019**, *9* (4), 581.
- (105) Kim, Y.; Ji, S.; Nam, J.-M., A Chemist's View on Electronic and Steric Effects of Surface Ligands on Plasmonic Metal Nanostructures. *Acc. Chem. Res.* **2023**, *56* (16), 2139-2150.
- (106) Jia, H.; Li, F.; Chow, T. H.; Liu, X.; Zhang, H.; Lu, Y.; Wang, J.; Zhang, C.-y., Construction of Spatially Separated Gold Nanocrystal/Cuprous Oxide Architecture for Plasmon-Driven CO₂ Reduction. *Nano Lett.* **2022**, *22* (17), 7268-7274.
- (107) Kim, A.; Zhou, S.; Yao, L.; Ni, S.; Luo, B.; Sing, C. E.; Chen, Q., Tip-Patched Nanoprisms from Formation of Ligand Islands. *J. Am. Chem. Soc.* **2019**, *141* (30), 11796-11800.
- (108) Kim, A.; Vo, T.; An, H.; Banerjee, P.; Yao, L.; Zhou, S.; Kim, C.; Milliron, D. J.; Glotzer, S. C.; Chen, Q., Symmetry-breaking in patch formation on triangular gold nanoparticles by asymmetric polymer grafting. *Nat. Commun.* **2022**, *13* (1), 6774.
- (109) Zheng, M.; Shen, Y.; Zheng, L.; She, X.; Jin, C., Transfer-Printing Hydrogel-Based Platform for Moisture-Driven Dynamic Display and Optical Anti-Counterfeiting. *ACS Appl. Mater. Interfaces* **2023**, *15* (38), 45239-45248.
- (110) Lee, S.; Dang, H.; Moon, J.-I.; Kim, K.; Joung, Y.; Park, S.; Yu, Q.; Chen, J.; Lu, M.; Chen, L.; Joo, S.-W.; Choo, J., SERS-based microdevices for use as in vitro diagnostic biosensors. *Chem. Soc. Rev.* **2024**, *53* (11), 5394-5427.
- (111) Han, Y. W.; Ku, M.; Lee, S.; Jung, Y. S., Exceptionally Adaptable and Versatile SERS Platforms Enabled by Three-Dimensionally Transfer-Printed Nanowire Pattern Arrays. *Acc. Mater. Res.* **2025**, *6* (9), 1052-1064.
- (112) Ebrahimi, F.; Kumari, A.; Dellinger, K., Integration of Nanoengineering with Artificial Intelligence and Machine Learning in Surface-Enhanced Raman Spectroscopy (SERS) for the Development of Advanced Biosensing Platforms. *Adv. Sensor Res.* **2025**, *4* (2), 2400155.
- (113) Fang, G.; Lin, X.; Wu, J.; Xu, W.; Hasi, W.; Dong, B., Porous Nanoframe Based Plasmonic Structure With High-Density Hotspots for the Quantitative Detection of Gaseous Benzaldehyde. *Small* **2025**, *21* (7), 2408670.
- (114) Wang, T.; Zhu, K.; Wei, J.; Zhao, Y.; Xu, Z.; Zong, S.; Wu, L.; Yang, K.; Wang, H.; Wang, Z., A 3D Nanofiltration Array for Direct Plasma EV Purification with Label-

Free SERS Detection toward Accurate Clinical Breast Cancer Staging. *ACS Sensors* **2025**, *10* (9), 6840-6848.

(115) Lin, S.; Dong, M.; Li, C.; Lin, X.; Cong, Y.; Xu, W.; Bao, Z.; Dong, B., Machine Learning-assisted Ultrasensitive SERS Immunoassays Across Wide Concentration Ranges Toward Clinical Ovarian Cancer Diagnosis. *Adv. Funct. Mater.* **2025**, *35* (51), e09813.

List of academic presentations

1. The 15th Asia-Pacific Conference on Near-field Optics (APNFO 15)@Bali, Indonesia (August 18th–21st, 2025)
“Shape-dependent Surface-enhanced Raman Scattering on Self-assembled Gold Nanoparticle Films under Modal Ultrastrong Coupling with a Fabry-Pérot Cavity”
(Poster, August 19th) Poster award
○Zhiyu He, Xu Shi, Keiji Sasaki, Hiroaki Misawa, Kuniharu Ijiri, Hideyuki Mitomo
2. The 25th RIES-HOKUDAI International Symposium @Hokkaido University, Sapporo (November 26th–27th, 2025)
The 2025 RIES–CEFMS (Research Institute for Electronic Science – Center for Emerging Functional Matter Science) @Hokkaido University
(November 28th, 2025)
“Shape-Dependent Surface-Enhanced Raman Scattering Modulated by Modal Ultrastrong Coupling with Fabry-Pérot Cavities”
(Poster, November 27th–28th)
○Zhiyu He, Xu Shi, Keiji Sasaki, Hiroaki Misawa, Kuniharu Ijiri, Hideyuki Mitomo

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