学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

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)

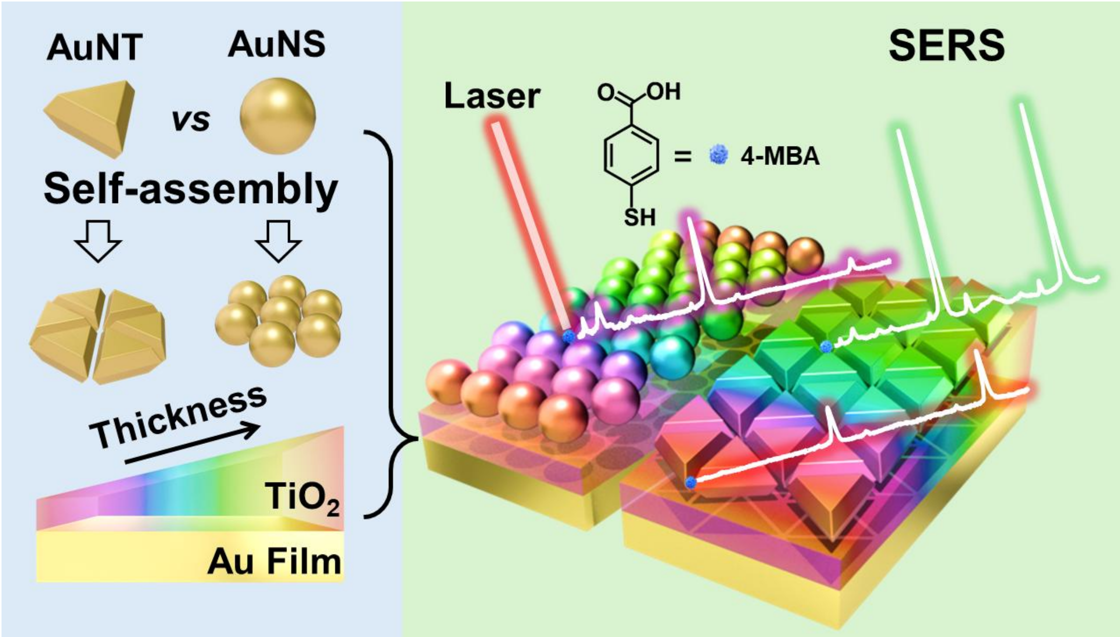
Biomolecules, including nucleic acids, proteins, lipids, carbohydrates and metabolites, are essential structural and regulatory components of living organisms. Their concentrations, structures and interactions dynamically change in response to the physiological and environmental conditions. Therefore, efficient detection of biomolecules are important in diverse fields such as biotechnology, food safety, environment monitoring, and early-stage medical diagnostics. Among wide variety of detection techniques, surface-enhanced Raman scattering (SERS) involves the inelastic scattering signal of molecule vibration mode amplified in strong electromagnetic field, which offers advantage of finger-printing signal with high sensitivity that enables single-molecule detection. Plasmonic nanostructures have emerged as a series of SERS platforms due to their efficient confinement of electromagnetic field via localized surface plasmon resonance (LSPR). Gold nanoparticles is a class of popular plasmonic structure, and their LSPR properties can be conveniently tailored by their size, shape, interparticle distances and dielectric environments. Once the gold nanoparticles approach to each other, the plasmon coupling induces the electromagnetic field enhancement at interparticle gaps, forming optical hotspots. Moreover, gold nanoparticles afford the advantage of high chemical stability than the silver counterparts. Through Langnuir techniques, gold nanoparticle film are formed by self-assembly at the air-water interface, which exhibits maximized packing density in large area. The resultant minimized interparticle distance is essential for improving hotspots, as well as the reproducibility of SERS signal on them. Besides optimizing the particle assembly, the SERS properties of gold nanoparticles can be further improved through integration with Fabry-Pérot (FP) cavity. With proper design, the LSPR of gold nanoparticles and the resonance mode of FP cavity would couple, namely, modal coupling. The model coupling modifies the resonance of the gold nanoparticle/ FP cavity structure, offering opportunities for tailoring and enhancing their SERS performance. Previous SERS study under modal coupling conditions focused on small gold nanoparticles placed on specific FP cavities. However, the effect of modal coupling on the SERS performances of gold nanoparticle films remains to be fully elucidated. Notably, anisotropic nanoparticles have received less attention regarding their modal coupling with FP cavities, despite their diverse surface properties and superior plasmonic performance compared to isotropic counterparts. In this thesis, I systematically investigated and compared the SERS performance of gold nanoparticle films composed of gold nanotriangles (AuNT) or gold nanospheres (AuNS) under the modal coupling with a semi-opened FP cavity structure, with a focus on the effect of particle shape.

In Chapter 1, I discuss the importance of biomolecule detection. The fundamentals of SERS, the advantages of SERS-based detection techniques utilizing gold nanoparticles, and optimization of their SERS properties by interfacial assembly are described, followed by the review of further-improved gold nanoparticle-based SERS platforms assisted by FP cavities.

In Chapter 2, I evaluate and compare the modal coupling behavior between self-assembled gold nanoparticle films and FP cavities composed of TiO_2 layer on Au mirror (TA). AuNT and AuNS with identical particle volume were prepared. Densely packed AuNT and AuNS films were fabricated on TA substrates utilizing Langmuir-Schaefer method, forming the AuNT film on TA (t-ATA) and AuNS film on TA (s-ATA) structures. Modal ultrastrong coupling behaviors was examined by varying the TiO_2 thickness, in conjunction with experimental measurements and finite-difference time-domain (FDTD) simulations.

In Chapter 3, I compare the SERS performances of the t-ATA and s-ATA structures at different TiO_2 thicknesses using 4-MBA as the reporter. The particle shape effect on SERS performance under the modal ultra strong coupling conditions are discussed at different excitation wavelengths and 4-MBA concentrations.

In Chapter 4, I summarize the thesis. This work provides comprehensive understanding of the modal coupling between gold nanoparticle films and FP cavities and its impact on SERS performance. The results offer valuable design guidelines for engineering SERS platforms optimized either for ultrasensitive detection or for controllable signal output depending on application needs.


AuNT
AuNS
vs
Self-assembly
Thickness
TiO2
Au Film
SERS
Laser
O
OH
SH
= 4-MBA