Surface-enhanced Raman Scattering Substrate under Modal Strong Coupling between Nanocavity and Plasmons of Gold Nanoparticles Loaded by Self-assembly Method

([1]*Research Institute for Electronic Science, Hokkaido University*, [2]*Creative Research Institution, Hokkaido University,* [3]*Center for Emergent Functional Matter Science, National Chiao Tung University, Taiwan*) ○Yoshiki Suganami[1], Tomoya Oshikiri[1], Hideyuki Mitomo[1], Xu Shi[2], Yasutaka Matsuo[1], Kuniharu Ijiro[1], Hiroaki Misawa[1,3]

Keywords: Surface-enhanced Raman scattering; Localized surface plasmon resonance; Modal strong coupling; Self-assembly

Recently, we found that the localized surface plasmon resonance of gold nanoparticles (Au-NPs) coupled with the Fabry-Pérot (FP) nanocavity improves the surface-enhanced Raman scattering (SERS) properties[1]. In this study, we have fabricated the modal strong coupling structure with large coupling strength composed of a high number density of Au-NPs on FP nanocavity using self-assembly methods and investigated their SERS properties because it is known that the strong coupling strength in the light-matter coupling system is proportional to the square root of the number density of oscillators[2].

An FP nanocavity was fabricated by depositing 100 nm of gold on a SiO_2 substrate using a sputtering method, followed by the deposition of 31 nm of TiO_2 using an atomic layer deposition method. A self-assembled monolayer of Au-NPs was formed on the water surface by dropping a chloroform solution of Au-NPs modified with dodecanethiol (DDT) ligand into ultrapure water. The Au-NPs monolayer was then transferred onto the TiO_2 surface to fabricate the DDT-modified Au-NPs/TiO_2/Au film (DDT-ATA) structure. Finally, the ozone cleaning process was performed to remove DDT molecules on DDT-ATA. From the SEM images, the surface coverage ratios with Au-NPs on the surface of DDT-ATA were calculated to be 48 %. The absorption spectra of DDT-ATA split into two peaks due to the hybrid modes associated with the modal strong coupling formation, and the splitting energy was calculated to be 670 meV from the dispersion curve. This value was almost twice the conventional ATA, whose coverage ratio was ca. 30%. In addition, the SERS performance of DDT-ATA substrate was investigated by using crystal violet as a prove molecule with an excitation wavelength of 785 nm. The Raman intensity of DDT-ATA substrate was 14-times higher than that of Au-NPs/TiO_2 substrate without FP nanocavity.

1) X. Zang, X. Shi, T. Oshikiri, K. Ueno, Y. Sunaba, K. Sasaki, and H. Misawa, *J. Phys. Chem. C* **2021**, 125, 19880.

2) M. Suzuki, K. Nishiyama, N. Kani, X. Yu, K. Uzumi, M. Funahashi, F. Shimokawa, S. Nakanishi, and N. Tsurumachi, *Appl. Phys. Lett.* **2019**, 114, 191108.