プラズモニックナノ構造の SiO₂コーティングによるホットエレク トロン遮断

Blocking Hot Electron Emission by SiO₂ Coating Plasmonic Nanostructures

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The transformation of *para*-aminothiophenol (PATP) to dimercaptoazobenzene (DMAB) is widely believed to be due to the emission of hot electrons from the plasmonic nanostructures,¹ which are generated during the decay of the surface plasmons (LSPPs). Our aim here is to separate the catalytic activity of plasmonic nanostructures from their SERS activity by using a 5 nm thick silicon dioxide (SiO₂) layer. This layer blocks hot electrons from reaching the PATP molecules but lets the electromagnetic field penetrate, allowing us to measure the SERS of the monomer without triggering a chemical reaction. The SERS measurement was performed at 633 nm on two-dimensional gold nanoparticle (2D AuNP) arrays covered with/without thin SiO₂.

The fabrication method for a 2D AuNP array formed at the oil/water interface is summarized in Ref. 2. The glass slide was pulled up from the solution using a dip-coater (SDI, ND-0407-S3: Kagawa University, 20 μ m/s), and thereby the AuNP array was transferred to the glass surface. The SERS substrate was coated with SiO₂ of 5 nm thickness (SiO₂/AuNP/glass) by using a dual ion beam sputtering system (Hashinotech, 10W-IBS: Kagawa University) under a pressure of 6.0×10^4 Pa. Extinction spectra of AuNP solutions and the SERS substrates were measured by an absorption photometer (Shimadzu, UV-2400PC and SolidSpec-3700: Kagawa University).

The SERS substrate was washed with deionized water and ethanol alternately and dried before SERS measurement. 10 μ L of 1 mM PATP in ethanol solution was cast and dried on the SERS substrate and covered with SiO₂. We performed the SERS measurement of PATP on each SERS substrate using a micro-Raman spectrometer (Renishaw inVia Raman Microscope: University of Cambridge). The wavelength of the excitation laser was 632.8 nm (He-Ne laser), and the output power was 2.31 mW. The objective lens with numerical aperture (NA) of 0.40 and magnification of x20 focused the excitation laser (spot diameter: 1.93 mm) and collected Raman scattering from the sample. The exposure time was 1 s.

The SERS spectrum of PATP on the bare 2D AuNP array (PATP/AuNPs/glass) is shown in Fig. 1 (800 W/mm², 633 nm laser). Strong Raman peaks are observed at 1074, 1138, 1389, 1434 and 1577 cm⁻¹ with a broad background ranging from 1200-1700 cm⁻¹. These lines indicate that PATP has reacted to give DMAB.

We note that the laser intensity used ($\sim 800 \text{ W/mm}^2$) is much larger than reported to be required to trigger the chemical reaction of PATP to DMAB ($\sim 20 \text{ W/mm}^2$) in order to make sure that the reaction occurs.¹

In order to stop the chemical reaction from occurring we deposit a 5 nm thick SiO₂ layer between the 2D AuNP array and the analyte layer (PATP/SiO₂/AuNP/Sub.). We observe that the three peaks of DMAB disappear, and the only Raman peaks are found at 1078, 1280 and 1582 cm⁻¹, which are similar to the normal Raman spectrum (NRS) of PATP, although the laser power is larger than the threshold for the chemical transformation by more than 50 times. Our results clearly show Raman peaks from PATP even when using the SiO₂ spacer between the 2D AuNP array and the PATP layer - the electromagnetic fields can penetrate the spacer layer and still leads to sizable SERS enhancements.

References

N. Takeyasu, et al. J. Phys. Chem. C **120**, 12163 (2016).
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Figure 1. Raman spectra of PATP, measured on AuNPs array with/without SiO_2 coating. NRS of PATP is also shown.