

Highly-Sensitive Spectroscopic Analysis using Sodium Chloride and Related Salts

Masayuki Futamata

Graduate School of Science and Engineering, Saitama University

Summary

Addition of a trace quantity of cationic triphenyl methane (TPM⁺) dyes to isolated Ag nanoparticles in an aqueous solution yielded Ag flocculates composed of a few closely adjacent suspended nanoparticles. This change was evidenced by coupled LSP peaks emerged at 600-800 nm. However, neutral para-rosaniline molecules as well as neutral rhodamine 123 (R123) did not cause the Ag flocculation in contrast to their cations, indicating a crucial role of electrostatic interaction between cationic dyes and negatively charged Ag surfaces for the flocculation. Accordingly, cationic dye molecules are located in the nanogap between closely adjacent Ag nanoparticles which evoked enormous SERS intensity. The formation of the Ag flocculates was insensitive to steric hindrance by different amino groups in TPM dyes. This observation is consistent with dominant role of the electrostatic interaction. Nevertheless, distinct red shifts of fluorescence peaks were observed depending on the molecular structures such as coplanar and propeller phenyl rings, suggesting perturbed electronic states of TPM dyes upon adsorption through the amino groups.

Addition of neutral R123 molecules (10^{-7} M) to an as-prepared gold nanoparticles (AuNPs) suspension generated flocculates that are a small number of closely adjacent particles. Formation of AuNP flocculates were evidenced by the coupled localized plasmon peak at 720-750 nm. The AuNP flocculates provided pronounced SERS spectra of adsorbed neutral R123 molecules (SERS-A) as anticipated by FDTD (Finite Difference Time Domain) simulations. The observed SERS spectra are significantly different from those of cationic R123⁺ molecules (SERS-B), which electrostatically adsorbed on Cl⁻-treated AuNPs. The difference is not simply due to deprotonation but reflects a distinct difference in adsorption nature between neutral R123 and cationic R123⁺ molecules. Indeed neutral R123 molecules exclusively gave an Au-N stretching band at 202 cm⁻¹, showing the chemisorption on Au surfaces through lone pair electrons at the amino groups. The different adsorption nature is further evidenced by the observation that cationic R123⁺ molecules adsorbed on as-prepared AuNP flocculates gave both SERS-A and SERS-B spectra. Thus, the cationic R123⁺ molecules form the flocculates both by chemisorption and electrostatic adsorption owing to modest surface charge on as-prepared AuNPs.