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# Highly-Sensitive Spectroscopic Analysis Using Sodium Chloride and Related Salts

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Summary

Attainment of enormous enhancement with high reproducibility is crucial and challenging for the utilization of SERS in quantitative analysis. Concerning this, we have succeeded in linking AgNPs by cationic rhodamine molecules, which yields SERS enhancement of ~$10^9$. Here, the flocculation is applied to DNA bases in addition to cationic and neutral rhodamine molecules on AuNPs to characterize their adsorbed state. The adsorption of DNA bases as well as rhodamine 6G (R6G) molecules induced flocculates of Au nanoparticles (AuNPs), a few closely adjacent AuNPs providing enormously enhanced Raman scattering. DNA bases chemisorb on Au surfaces via lone pair electrons at amino groups as evidenced by $\nu_{Au\text{-}N}$ stretching mode at ~220 $cm^{-1}$, whereas cationic R6G molecules physisorb using electrostatic interaction between positively charged amino groups and negatively charged Au surfaces.

The flocculation is also applied to PMBA molecules on AgNPs, which are often used in SERS study, to prove its relevance as a highly-sensitive analytical tool. We elucidate the dissociation of a carboxylic group in PMBA on AgNPs using SERS spectra as a function of pH and surface coverage of PMBA. The flocculates of Ag nanoparticles (AgNPs) were formed using p-mercaptobenzoic acid (PMBA) to utilize enhanced electric field in surface enhanced Raman scattering (SERS). Electrostatic interaction between dissociated PMBAs and hydrated counter ions like $Na^+$ and $H^+$, as well as van der Waals force between protonated PMBAs on neighboring AgNPs plays a crucial role in the flocculation of AgNPs. Also dissociation of PMBA on Ag surfaces is determined not only by pH in the solutions but also by the surface coverage of PMBA. Indeed, SERS spectra from both dissociated and protonated PMBA molecules were observed even in quite acidic solutions. In all of these experiments, NaCl addition to AuNP and AgNP is crucial to replace surface residuals such as citrate, a-carbon and metal oxide for efficient adsorption of target molecules or ions in solution. Consequently, NaCl addition to metal nanoparticles is quite useful to establish single molecule SERS, which is promising to characterize distinct hydration of various metal ions or to elucidate interaction of metal ions with biomolecules.