No. 0812

Highly-Sensitive Raman Spectroscopy Using Sodium Chloride and Related Salts

Masayuki Futamata

Graduate School of Science and Engineering, Saitama University

Summary

To establish an ultimate Raman spectroscopy with single molecule sensitivity, we have studied the effect of sodium chloride salt, in particular the effect of various anion addition to silver nanoparticles, on which we recently found SERS and LSP resonances of cationic dye adsorbed Ag particles were activated by the particular anions. Among various anions, the Cl^-, Br^- and SCN^- anions activated SERS of the coadsorbed dye while substituting residual a-carbon. It also caused notable redshift of the fluorescence peak of dye suggesting electronic interaction between adsorbates and Ag surfaces. In contrast, CN^- and $S_2O_3^{2-}$ anions quenched the SERS according to their exclusive adsorption as evidenced by the CN (SERS) bands and XPS data. Furthermore, the activating anions provoked a marked blueshift of the coupled plasmon peak from 650 - 700 nm to 500 - 550 nm for a few closely -adjacent Ag particles, as well as for densely packed particles. This was expounded by slight increase of the gap size between the Ag particles by only 1nm on the basis of the theoretical simulations. It was ensured by the slight dissolution, oxidative etching, of the Ag particles. Consequently, negative charges on the Ag surface by partially remaining anions, and a slight increase of the gap size facilitated cationic dye molecules to adsorb on the nanoparticles, especially at the junction, providing pronounced SERS activity. We also found that specifically intense interaction between negatively charged Ag and R6G cationic dye evidenced by the formation of quite stable adjacent Ag nanoparticles in solution.