

# Critical Importance of a nanogap between metal nanoparticles and metal substrates in surface enhanced Raman scattering

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**Introduction.** Attainment of enormous enhancement with high reproducibility is critical for the utilization of SERS in quantitative analysis. Single molecule detection by Raman scattering has been investigated using a coupled localized surface plasmon (LSP) of adjacent metal nanostructures, by controlling the nanogap size and the adsorption of target molecules [1-2]. For this purpose, we have studied flocculates of silver and gold nanoparticles (AgNPs, and AuNPs), which are a few closely adjacent nanoparticles, providing various molecules with enormous SERS intensity in solutions [3-8]. In addition, theoretical calculations anticipated that AgNPs or AuNPs in flocculates can be replaced by various metals substrates including transition metals with large damping such as Pt, Rh and Fe, while providing marked enhancement in SERS similar to Ag and Au. Here, we report our recent results on SERS using a flocculation of metal nanoparticles (MNP) [3-8], a gap mode between metal substrates and MNP under external and attenuated total reflection (ATR) configurations.

**1. Flocculation-SERS.** Flocculates of AgNPs were formed using p-mercaptobenzoic acid (PMBA) to utilize a coupled localized surface plasmon on each AgNP. We found that electrostatic interaction between dissociated PMBA and counter ions, as well as van der Waals force between protonated PMBAs on AgNPs plays a crucial role in the flocculation. Dissociation of PMBA on AgNPs was determined not only by pH in solutions but also by surface coverage of PMBA. Mono- and divalent cations modified the  $\nu_{\text{COO}}$  band at  $\sim 1420 \text{ cm}^{-1}$  by  $20 \text{ cm}^{-1}$  indicating distinct interaction of the cations with dissociated carboxylate anions of PMBA on AgNPs.

**2. Gap mode-SERS under an external geometry.** Enormous and equivalent SERS enhancement of  $10^8$ - $10^9$  was observed for various thiol molecules such as PMBA, thiophenol, cyclohexane thiol and 1-hexanthiol adsorbed on Ag thick films with AgNPs ( $r=30$ - $40 \text{ nm}$ ) using a gap mode resonance, in accordance with those predicted by Finite Difference Time Domain (FDTD) calculations. Furthermore, SERS intensity of PMBA<sup>-</sup> anions adsorbed on a Pt substrate with a help of Ba<sup>2+</sup> cations to immobilize AgNPs was enhanced by  $1.7 \times 10^7$  as anticipated. Similarly, SERS enhancement of  $1.8 \times 10^8$  and  $7.3 \times 10^8$  was observed for TP-SAM adsorbed on Pt and Fe substrates, respectively.

**3. Gap mode plasmon under ATR configurations.** Immobilization of AgNPs on PATP-SAM/Ag film ( $t_{\text{Ag}}=45 \text{ nm}$ )/Dove prism provided additional SERS enhancement of 370 at a resonance angle of  $45.0^\circ$ . Attached AgNPs slightly increased the resonance angle of propagating surface plasmon (PSP) by  $\sim 2^\circ$ . Also AgNPs significantly broadened the reflectivity dip from  $1.5^\circ$  to  $3.2^\circ$  in FWHM. These features are probably due to increased scattering (out-coupling) of a PSP via AgNPs as anticipated by theoretical evaluations using Fresnel equations and effective medium theory. Overall SERS enhancement using both a PSP and a gap mode was  $2.1 \times 10^6$  as an averaged value over entire Ag films. By using surface coverage of AgNPs,  $\sim 4 \%$ , and a hot spot size of 5-6 nm at a nanogap, we estimated the enhancement of  $3.4 \times 10^9$  for adsorbed molecules under each AgNP. Details in FDTD simulations of reflectivity and spatial distribution of local electric field for the prism/Ag film/PATP/AgNPs with different coverage of AgNPs will also be presented.

**Acknowledgement.** This research was supported by KAKENHI (25286014 and 25600022) by JSPS.

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