# 減衰の大きな遷移金属系への高感度ギャップモードラマン分光の適用

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**実験方法**: (1) Ag substrate: Thick films of Ag ($t_{Ag}$=40 nm) evaporated on Si substrates were immersed into 1 mM p-mercaptobenzoic acid (PMBA) solution for 3 hr to form SAM (self-assembled monolayer) films. Ag nanoparticles (with a size of $r_{AgNP}$=30-40 nm) prepared by a citrate reduction method were immobilized on PMBA-SAM/Ag films by incubating in aqueous solutions containing 0.57 mM NaOH and 0.33 mM $BaCl_2$. Different SAM films of thiophenol (TP), cyclohexane thiol (CHT), 1-hexanthiol (1-HT) and 10-carboxy-1-decane thiol (CDT) were also prepared by immersing Ag films/Si into their ethanol solutions. SERS spectra of these SAM films on Ag substrates before and after the addition of AgNPs were measured using a He-Ne laser (632.8 nm, 7 mW) with p- and s-polarization.
(2) Pt and Fe substrates: SERS of the above SAM films were measured, while immobilizing AgNPs on Pt foil and Fe thin plate. Resonance conditions of a gap mode plasmon and spatial distribution of the local electric field were calculated for various metal substrates such as Ag, Au, Pt and Fe with AgNPs using a FDTD (Finite Difference Time Domain) method.
**結果と考察:** (1) Ag substrate/PMAB/AgNPs: FDTD calculations anticipated SERS enhancement of ~$10^{10}$ at 550-600 nm for Ag substrate/gap (1nm)/AgNP(r=30-40nm). Experimentally, we confirmed that Ag films ($t_{Ag}$=40 nm) without addition of AgNPs do not provide any SERS signal for PMBA-SAM films. In contrast, drastic enhancement of SERS signal was observed after immobilization of AgNPs on the same Ag film/Si samples, which was assured by electrostatic attractive force between dissociated $PMBA^-$ anion and negatively charged AgNPs via $Ba^{2+}$ cations. Indeed, fairly large surface coverage of AgNPs (40-50 AgNPs/$\mu m^2$) was confirmed on Ag films/Si substrates by SEM observations. By using the observed surface coverage of AgNPs and the area of hot spot to be r=5 nm ([5]), we obtained experimental SERS enhancement of $1.2\times10^9$ under each AgNP. Other thiols such as TP, CHT and 1-HT except CDT provided essentially similar SERS enhancement of $10^8$-$10^9$, indicating not only electrostatic interaction but also van der Waals interaction are relevant to immobilize AgNPs onto Ag film surfaces via these SAM films as evidenced by SEM observations. (2) Pt and Fe substrates: FDTD calculations predicted enormous SERS enhancement of $10^8$-$10^9$ under a gap mode resonance (550-750 nm) for these transition metal substrates and an AgNP (r=30-40 nm, and a gap size of 1 nm). Indeed, $PMBA^-$ anions with a help of $Ba^{2+}$ cations to immobilize AgNPs gave $1.7\times10^7$ of SERS enhancement. Similarly, SERS enhancement of $1.8\times10^8$ and $7.3\times10^8$ was observed for TP-SAM on Pt and Fe substrates, respectively.

Thus, we demonstrated a gap mode plasmon is promising to elucidate various adsorbates on Pt and Fe substrates as well as Ag. Also, we found that both of electrostatic force and van der Waals interaction are relevant for the efficient immobilization of AgNPs to utilize a gap mode resonance.

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## Gap Mode SERS for Largely Damping Transition Metals Enhanced Raman Scattering

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Theoretical calculations anticipated that Ag or Au nanoparticles (AgNPs, AuNPs) in the flocculates can be replaced by various metal substrates including transition metals with large damping such as Pt, Rh and Fe, while providing marked enhancement in SERS (Surface Enhanced Raman Scattering) similar to Ag and Au. However, detailed experimental conditions to utilize a gap mode have not been sufficiently elucidated such as how to immobilize metal nanoparticles via chemical species on metal substrates. Relating to this, we have studied flocculates of metal nanoparticles using various molecules, which link metal nanoparticles using electrostatic and chemical interaction. Here, we first employed various self-assembled monolayer films immobilizing AgNPs on Ag substrates. Then, Pt and Fe substrates were employed to confirm pronounced enhancement factor in a gap mode SERS.