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Efficient immobilization of silver nanoparticles on metal substrates through various thiol molecules to utilize a gap mode in surface enhanced Raman scattering☆

Hiroki Suzuki, Hayato Chiba, Masayuki Futamata*

Saitama University, 338-8750 Saitama, Japan

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ABSTRACT

To utilize a gap mode in surface enhanced Raman scattering, we elucidated the interaction between adsorbed species and Ag nanoparticles (AgNPs). Various thiol molecules such as normal alkanethiols, thiols with a phenyl, cyclohexane or naphthalene ring on Ag films immobilized AgNPs through van der Waals force, and electrostatic interaction. Immobilized AgNPs provided enormous Raman enhancement by a factor of 10^7–10^{10} for thiol molecules at a nanogap, in consistent with that anticipated by finite difference time domain calculations. Only alkanethiols with a tert-methyl group and those with a carboxylic group did not immobilize any AgNPs probably owing to steric hindrance. A gap mode is relevant for a variety of metals even with large damping like Pt and Fe, indicating a crucial role of electric multipoles in AgNPs generated by a localized surface plasmon and induced mirror images in metal substrates for markedly enhanced electric field at a nanogap.

1. Introduction

Enormous enhancement with high reproducibility is critical to the utilization of surface enhanced Raman scattering (SERS) in quantitative analysis of target molecules. Single molecule detection by Raman scattering has been achieved using a coupled localized surface plasmon (LSP) of closely adjacent metal nanostructures [1,2]. We have formed flocculates, a few closely adjacent silver and gold nanoparticles (AgNPs, and AuNPs), and found that they show enormous SERS enhancement favored by controlling the interaction between metal nanoparticles (MNPs) and target molecules in solutions [3–5]. Theoretical calculations suggest that one of AgNPs or AuNPs in flocculates can be replaced with metal substrates [6], while providing enormous enhancement factors in SERS equivalent to those obtained in flocculates of AgNPs and AuNPs. Illumination of laser, with electric field oscillating in parallel with the metal surface normal, excites a gap mode in a geometry of sandwiching target molecules at a gap between MNPs and metal substrates. The gap mode can be explained as a coupling of an LSP in MNPs and a propagating surface plasmon (PSP) on metal substrates. Because the size of MNPs (e.g. 30–40 nm in our experiments) is much smaller than the wavelength of incident light (e.g. 632 nm), an excited LSP in MNPs produces an evanescent wave in close proximity to the particles in addition to a propagating wave. Part of the evanescent wave around a nanogap excites a PSP on metal substrates while conserving energy and momentum of an electromagnetic wave. Accordingly, oscillating charges in MNPs and metal substrates generated by these plasmons further interact each other to enhance electric field at a nanogap. In this plasmon-coupling mechanism, both metals constituting nanoparticles and substrates should have sufficiently small internal damping to suppress thermal dissipation of electromagnetic energy. Another explanation for the enhanced electric field at a nanogap is based on interaction between multipoles in MNPs, generated by an LSP excitation, and their mirror images induced in metal substrates through an evanescent wave. In this mechanism, metals with large damping factors, represented by imaginary part of a dielectric constant ($\varepsilon''_{\text{metal}}$), are also available. Anyhow, relevance of the gap mode to various transition metals [7,8] opens much wider applications of SERS not only to characterization of various chemical species on well-defined metal surfaces [9,24], but also to analysis of catalytic reaction on metal nanostructures [8,9]. Furthermore, an MNP can be attached to the tip of cantilevers or sharpened optical fiber probes for near-field Raman spectroscopy. Such an MNP attached probe most likely provides Raman images in a single molecule sensitivity and spatial resolution of a few nanometers [8,10,25]. However, we have

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* Corresponding author. Tel.: +81 48 858 3383; fax: +81 48 858 3383.
E-mail address: futamata@chem.saitama-u.ac.jp (M. Futamata).

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experimental limitations to utilize a nanogap of metal nanostructures, not only in highly sensitive Raman spectroscopy but also in the application to nanoparticle devices [26–29]. For instance, self-organization of MNPs has been theoretically simulated on the basis of van der Waals and double layer interaction [30–32], which are macroscopic analyses without using detailed information on attached molecules on MNPs. Also, only proteins [33] or small molecules with particular functional groups, like phthalocyaninato [34], bifunctional halogen-bonding [35], and dithiol groups [36], have been employed to form self-organized MNPs on substrates using robust intermolecular interactions. Further systematic study in immobilization and organization of MNPs on metal or dielectric substrates via various molecules, while elucidating microscopic interaction between them, is prerequisite to yield sufficiently large surface coverage of MNPs, and thereby nanogap area with enormous Raman enhancement. For this purpose, we investigated an efficient way of immobilizing AgNPs on thiol-SAMs with various end groups such as methyl, carboxyl, and amino groups on different metal substrates such as Ag, Pt, and Fe. Also, it is not always obvious why huge enhancement similar to that on Ag substrates is obtained on transition metals with large damping factors like Pt and Fe. Our motivation in the present work is to solve these issues, while separating the contribution of a coupling of an LSP in MNPs and a PSP of metal substrates from that of an image dipole or multipoles induced in metal substrates using finite difference time domain (FDTD) calculations [11].

2. Experimental setup

Silver nanoparticles were prepared by chemical reduction using trisodium citrate [4,5]. Sulfuric acid, sodium hydroxide, and various thiol molecules were purchased from Wako Pure Chemicals, and used without further purifications. Ag films (45 nm in thickness (t)) were evaporated on Si substrates at 10^{-6} T, on which Ti films (t = 5 nm) were pre-deposited to improve adhesion of Ag films. First, Ag film/Ti/Si substrates were immersed in ethanol solutions of various thiols (1 mM) for 2 h to form thiol-SAM films, followed by thorough rinsing with pure ethanol, which is critical to exclude the effect of flocculation of AgNPs in Raman measurements. Next, restricted amount of AgNP suspension (~100 μL) was dropped on the substrates and hold for 2 h in a closed petri dish. Before this process, surface residuals on AgNPs such as citrate anions were replaced with Cl^- to suppress steric hindrance for adsorption of AgNPs on thiols. We also investigated the effect of deprotonation of a carboxy group in p-mercaptobenzoic acid (PMBA) on the adsorption of AgNPs, by adjusting pH in solution during the formation of thiol-SAM and immobilization of AgNPs. Unbound AgNPs were removed from the substrates by rinsing them repeatedly with pure water. After drying by N_2 gas blow or a spin coater, SERS spectra were measured for AgNP/thiol-SAM/Ag film/Si substrates under an external geometry (at an angle of incidence of 65° with p-polarization) using a modified Renishaw micro-Raman spectrometer equipped with a He–Ne laser (632.8 nm and <1 μW/μm^2). Scanning electron microscope (SEM), Hitachi S-4100, was used to evaluate the surface coverage of AgNPs, ρ_{AgNP} (particles/μm^2), immobilized on metal substrates. As blank experiments, we attempted to immobilize AgNPs on Ag substrates without using thiols. A SERS enhancement factor was estimated by comparing Raman signal intensity of thiol molecules at a nanogap and that for neat powder or liquid measured by the same laser, optics, and a spectrometer. An FDTD method was used to evaluate a gap mode resonance, and local electric field at a nanogap between AgNP and metal substrates such as Ag, Pt, Fe, Ti, Pd and Al with distinct dielectric constants [12,13].

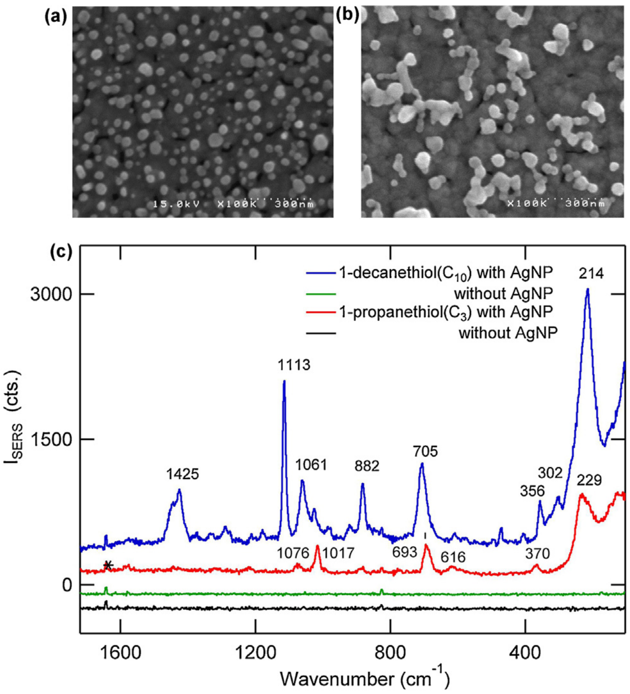

Fig. 1. SEM images (a and b) and SERS spectra (c) of C_n normal alkanethiol-SAM adsorbed on Ag films before and after immobilization of AgNPs, here n = 3 (a and c), 10 (b and c). White spots in SEM images in this and in the following figures represent AgNPs, which are immobilized on Ag films (t = 45 nm), evaporated on Si substrates, via thiol molecules.

3. Results and discussion

3.1. AgNPs/thiols/Ag film/(Ti)/Si substrate

Silver films (45 nm) were evaporated on a Ti-coated Si substrate, on which various thiol-SAM films of normal and branched alkanethiols, thiols with aromatic rings, and those with carboxyl groups were formed to immobilize AgNPs. Indeed, normal alkanethiols with different chain lengths between C_3 (1-propanethiol) and C_{10} (1-decanethiol) attached many AgNPs between 28 and 208 particles/μm^2 (Fig. 1a and b and Table 1). Here the number of immobilized AgNPs gradually decreased with increasing the length of an alkyl chain such as 208 particles/μm^2 for C_3, 85 particles/μm^2 for C_6, 59 particles/μm^2 for C_8, and 28 particles/μm^2 for C_{10} normal alkanethiols. Also, thiophenol (TP), 1-cyclrohexanethiol (CHT), 1-naphthalenethiol (NPT) immobilized 263–78 particle/μm^2 irrespective of their distinct structures containing aromatic, cyclohexane, benzene and naphthalene rings (Fig. 2a and Table 1). A carboxylic group bound to benzenethiol in PMBA immobilized AgNPs of 75 particle/μm^2 at pH = 11, sufficiently higher than $pK_a = 5.8$ to deprotonate and to interact with Ba^{2+} cations (Fig. 3a and Table 1). In this case, ion pairs of Ag substrates $-S-\phi-COO^-\cdots Ba^{2+}\cdots{}^-OOC-\phi-S-$AgNP were formed to immobilize AgNPs. In contrast, a modest number of AgNPs, 8 particles/μm^2, were immobilized via PMBA without controlling pH (Fig. 3b). In contrast to PMBA, 5-carboxyl-penthanethiol and 10-carboxyl-decanethiol immobilized only the faint number of AgNPs even under pH control (Table 1). Carboxy alkanethiols possess much weaker interaction with AgNPs compared with normal alkanethiols. Also, a smaller number of AgNPs were immobilized by branched alkanethiols compared with normal thiols. For instance, 2-methyl-1-propanethiol (2M1PT) immobilized 34 particle/μm^2 (Table 1), which is smaller than 208 particles/μm^2 for 1PT and close to 28 particle/μm^2 (Table 1) for 1-decanethiol (1DT) with a much longer chain. Moreover, tertially-butylthiol (tert-BT) and