Influence of Surface Functionalities of Self-Assembled Monolayers on the Adsorption of Gold Nanoparticles

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Surface-enhanced Raman scattering (SERS) has drawn a lot of attention due to extremely high sensitivity, which provides a wide range of applications including sensors,[1] single-molecule detection,[2,3] and cellular imaging.[4] Surface plasmon resonances of noble metal nanoparticles produce intense electromagnetic fields particularly at the interstitial sites of the nanostructures, enhancing the Raman scattering of molecules residing at the place.[5] Therefore, arranging nanostructures in close distances in a controlled fashion is a key to producing SERS. In this respect, a nanostructure that exploits self-assembled monolayers (SAMs) is one of the most attractive SERS-active platforms.[6]

SAMs are produced by the spontaneous assembly of thiolate molecules on gold surfaces.[7] Intermolecular van der Waals forces make SAMs a rugged and highly ordered structure. The surface properties of SAMs can be easily modified by changing the terminal groups of thiolate molecules. Adsorption of gold nanoparticles (AuNPs) on the surfaces of SAMs creates SERS hot spots between the nanoparticles and the gold surfaces.[8] The SERS behavior of such structures can be controlled at the molecular level simply by changing the molecules constituting the SAMs.[9]

For the fabrication and application of those AuNP-SAMs-Au structures, it is required to understand the nature of interactions between AuNPs and the surfaces of SAMs. The affinity of a few functional groups such as -SH and -NH₂ toward AuNPs has been reported.[10,11] However, no systematic studies have been done on the reactivity of various other functional groups. Here we explore the nature of interactions between the citrate-stabilized AuNPs and the surfaces of SAMs made up of -CH₃, -OCH₃, -NH₂, -NO₂, -OH, or -COOH functional groups. The SERS activity of the resulting structures is also compared.

For the experiments, we produce SAMs of phenyl rings with different functional groups on the surface by immersing cleaned gold substrates in a 10 mM ethanol solution of *p*-HSC₆H₄X (X= CH₃, OCH₃, NH₂, NO₂, OH, COOH) for 24 hours. The contact angle measurements (SEO Co., Phoenix 450) characterize the surface properties of SAMs.

AuNPs are prepared by reduction of HAuCl₄ using sodium citrate as reported previously.[12] High resolution transmission electron microscopy (JEOL, JEM3010) determines the size of AuNPs (29 nm). The AuNP solutions are used as prepared to maintain the acidic condition (pH 3.0) without aggregation.

To investigate the interactions of AuNPs with the surface functionality of SAMs, we immerse the SAMs on gold substrates into the AuNP solutions for 12 hours and measure the adsorption density using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F). Extending the immersion time to 24 hours did not change the results. Raman spectra of the SAM molecules interlaid between AuNPs and gold substrates are acquired by a Raman microscope (Kaiser, Raman MicroProbe). Diode laser (λ = 785 nm, 200 mW) is focused on the sample through a 100× objective and the resulting Raman scattering is collected by the same objective and delivered to a holographic spectrometer (f/1.8). All presented spectra are the average of 3 spectra each of which is obtained at an exposure time of 3 s.

Figure 1 shows that AuNPs are densely adsorbed onto the -CH₃, -OCH₃, and -NH₂ surfaces whereas the surface density of AuNPs on -NO₂, -OH, and -COOH is rather low. We believe that the electrostatic and van der Waals interactions play a major role in the adsorption of citrate-stabilized AuNPs. The interplay among AuNPs, organic functional groups, and solvent also counts. Notably, -CH₃ and -OCH₃ are hydrophobic while -OH and -COOH are strongly hydrophilic, as indicated by the measured contact angles presented in Fig. 1. Hydrophobic surfaces (-CH₃ and -OCH₃) favor the interactions with citrate-capped AuNPs rather than water solvent, leading to the dense adsorption. In contrast, hydrophilic -OH and -COOH surfaces prefer solvation by water, deterring AuNPs from approaching the surfaces, resulting in the sparse adsorption.
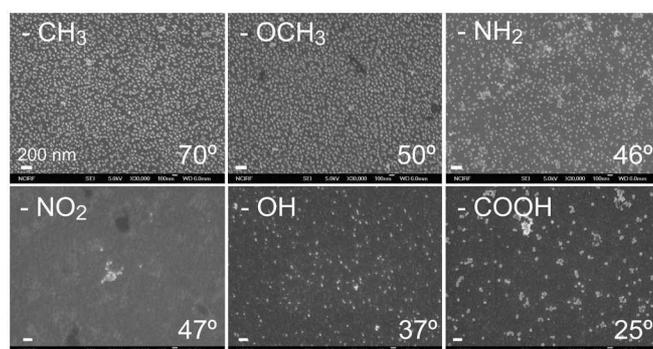

Figure 1. FE-SEM images of AuNPs adsorbed on the SAMs with a terminal group indicated in each figure. The measured contact angles of each SAMs are also included in the lower right corner of each image for comparison with the adsorption density.
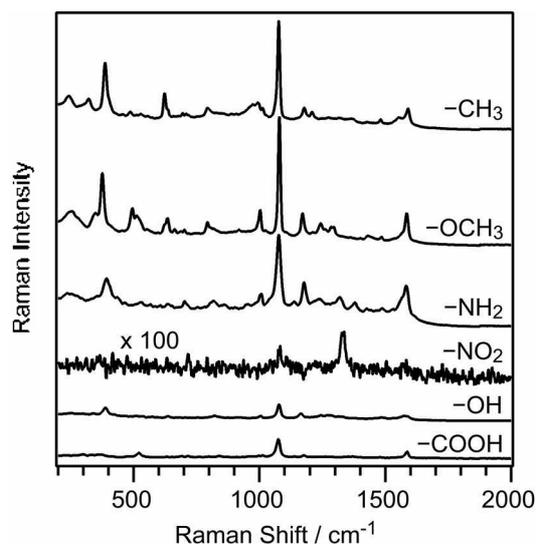
Figure 2. Raman spectra of the AuNP-SAMs-Au structures shown in Fig. 1. All spectra are displayed in the same scale to compare the intensity except for -NO₂ which is magnified by a factor of 100.

Figure 3. The relation between the number density of AuNPs and the SERS intensity. The number density of the adsorbed AuNPs is measured by random sampling of 1 μm^2 areas at 7 different locations on each FE-SEM image. The Raman intensity is the average of 4 spectral intensities of the 1078 cm^{-1} C-S stretching band.

The -NH₂ and -NO₂ surfaces show distinctively different affinity toward AuNPs despite similar hydrophobicity. It appears that the electrostatic interactions play an important role in these two cases. The -NH₂ surfaces remain protonated under our experimental conditions[13] while the -NO₂ surfaces possess partially negative charges from the resonance structure. Electrostatic attraction or repulsion between the charged surfaces and citrate-anion-capped AuNPs makes a difference in the adsorption propensity.

Figure 2 presents the Raman spectra obtained for the structures shown in Fig. 1. The Raman intensity is much stronger for the SAMs with -CH₃, -OCH₃, and -NH₂ surfaces to which a large number of AuNPs are adsorbed than for the SAMs with -NO₂, -OH, and -COOH terminal groups with scarce AuNPs adsorbed. The SERS intensity is dependent on the number of hot spots as well as the intrinsic Raman scattering cross-sections of the molecules. Since the Raman scattering mostly arises from the phenyl groups, the intrinsic Raman scattering cross-sections are nearly the same for all the investigated molecules. Therefore, the difference in the Raman intensity we observe is most likely from the number of hot sites determined by the number of adsorbed AuNPs.

The relation between the number density of AuNPs adsorbed and the SERS intensity is presented in Fig. 3. The Raman intensity of the 1078 cm^{-1} C-S stretching band[20] which appears in all spectra in common is roughly proportional to the number of AuNPs adsorbed, confirming that SERS indeed occurs at the SAMs interlaid between the AuNPs and the gold substrates.

In conclusion, we fabricated the SERS-active sandwich structures, AuNPs-SAMs-Au. The surface functionalities of SAMs determine the adsorption probabilities of AuNPs. The
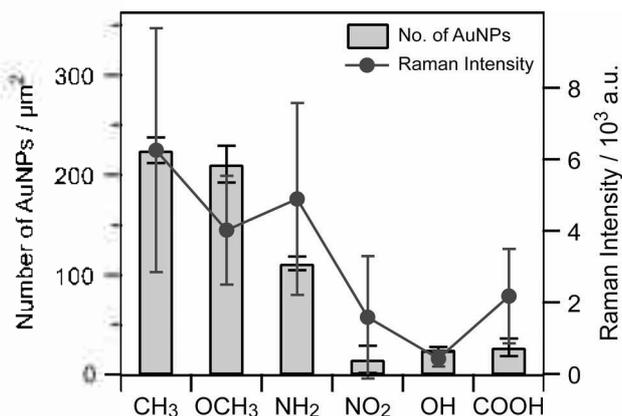
AuNPs are uniformly well-adsorbed on the hydrophobic surfaces made up of -CH₃ or -OCH₃ while they rarely bind to hydrophilic surfaces such as -OH and -COOH. Electrostatic interactions also play an important role in the adsorption of AuNPs on the -NH₂ and -NO₂ surfaces. The SERS intensity is stronger for high density of AuNPs on SAMs, confirming that SERS occurs between the AuNPs and the Au substrates.

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13. The pKa value of anilinium is 4.60.