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Adsorption of Aromatic Thiols on Gold Nanoparticle Surfaces Investigated by UV–vis Absorption Spectroscopy and Surface Enhanced Raman Scattering

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A UV–vis absorption spectroscopy and surface-enhanced Raman scattering (SERS) study shows that benzyl mercaptan was found to be adsorbed faster than thiophenol on gold nanoparticle surfaces at a low bulk concentration of $\approx 10^{-7}$ M, whereas they appeared to exhibit almost identical spectral behaviors at high concentration of $\approx 10^{-5}$ M.

Structural order has been one of major concerns in most applications of self-assembled thin films since the packing and orientation of adsorbates affect the surface chemistry of the monolayers.[1] In a theoretical work by Sellers et al.,[2] it was pointed out that SAMs of alkanethiolates on the 3-fold hollow sites should be energetically most favorable on Au(111) surfaces. A recent photoelectron diffraction study however indicated that methylthiolate should occupy atop sites, where the S–C bond axis was tilt by $\approx 50^\circ$ from the surface normal.[3] Aromatic-containing monolayers have a number of advantages due to their rigidity and conjugated nature,[4] and can be potentially utilized in molecular electronic devices. Compared with alkanethiols, relatively few studies have been performed on aromatic thiols. Aromatic thiols such as benzyl mercaptan (BM) and biphenylmethanethiol (BPMT) were reported to form closely-packed and highly-ordered monolayers on gold while a lower surface coverage was formed for thiophenol (TP) and biphenylthiol (BPT) by an infrared and electrochemical study.[5] A closely packed and ordered monolayer appeared to be fabricated by a presence of a methylene unit inserted between the phenyl ring and the sulfur head group.

Although colloidal dispersions of gold have been studied ever since the report by Faraday,[6] their physicochemical characterization were not performed systematically until lately.[7–9] Optical properties of gold particle aggregates have been extensively investigated by surface plasma resonance and transmission electron microscopy (TEM).[10] Surface plasmon resonance has been recently used to monitor analyte-surface binding interactions for chemical sensors.[11] For molecular assembly of alipathic thiols on gold nanoparticles, the extent of aggregation was estimated from a measure of the integrated extinction between 600 and 800 nm.[12]

Despite the equivocal selection rule and limited applicability to a few metals, surface enhanced Raman scattering (SERS) phenomena has become one of the most sensitive techniques to monitor the adsorbates on metal substrates at submonolayer coverage limit ever since its discovery by Fleishmann et al.[13] The analysis of spectral features has provided detailed information on interfacial structure, adsorption mechanism, and surface reactions.[14] In this letter the aggregation behaviors of aromatic thiols were examined by UV–vis absorption spectroscopy. The adsorption characteristics were further checked by SERS measurements. The purpose of this study is to better understand the aromatic thiol adsorbate–gold nanoparticle interactions.

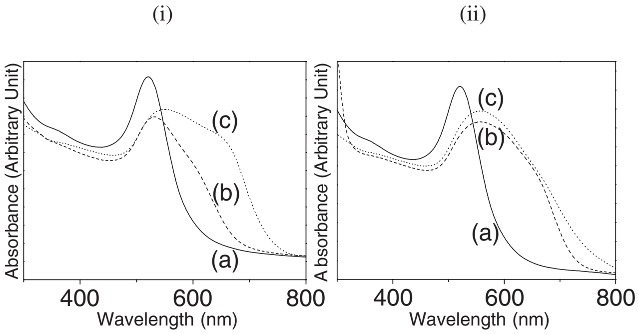

Figure 1. UV–vis absorption spectra of (a) non-aggregated, after the injection of (b) TP, and (c) BM for gold nanoparticles at (i) low ($\approx 10^{-7}$ M) and (ii) high concentration ($\approx 10^{-5}$ M) after ≈ 1 min from the injection of the adsorbates to the nanoparticle solution.

Figure 1a shows the UV–vis absorption spectra of gold particles. The $\lambda_{\max}$ value and full width at the half maximum were found at 520 and 86 nm, respectively, in agreement with the previous report.[10] The aggregation of aromatic thiol-covered gold particles by a self-assembly process could be checked by a red shift in a UV–vis absorption spectrum due to a decrease of inter-particle distances. Since the aggregation is induced by thiols at the initial stage of adsorption, the red-shift of UV–vis absorption spectrum may also indicate the formation of thiol-covered particles. At a low bulk concentration of $\approx 10^{-7}$ M, BM was found to aggregate faster than TP, whereas they appeared to exhibit almost identical behavior at high concentration of $\approx 10^{-5}$ M. It seems that a thermodynamic factor such as an energetically favorable monolayer formation should play a more significant role at low concentration, whereas a structural stability may be less important at high concentration since the self-assembly occurs fast.

Aggregation of Au nanoparticles by aromatic thiols is followed by the appearance of features between 600 and 800 nm in the UV–vis absorbance spectrum. The extent of aggregation (flocculation) was estimated from a measure of the integrated extinction between 600 and 800 nm versus time.[12] Measured flocculation was found to increase as time elapsed, and reached a maximum after a certain point of ≈ 5 min for a full-monolayer coverage. The ratio of the remaining Au nanoparticles could be estimated by subtracting the flocculation from the initial absorbance. Figure 2 shows an increase of flocculated Au nanoparticles by BM and TP. This result exhibits that the flocculation process for BM would occur faster than that for TP. Assuming the first order decay for the initial status of aggregation, the rate

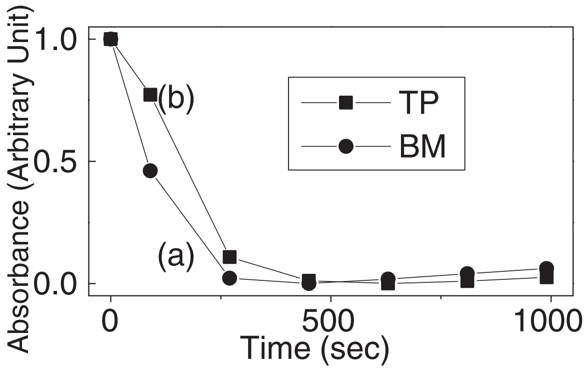

Figure 2. Decrease of non-aggregated gold nanoparticles versus time for (a) BM and (b) TP.

of flocculation for BM and TP, k_{BM} and k_{TP} could be approximately determined as 0.014 and 0.010 s^{-1}, respectively. This result suggests that BM should aggregate faster by a factor of $\approx$1.4 than TP under the experimental condition. The energy difference ΔG between BM and TP on Au nanoparticles could be roughly estimated by using the formula $k_{\mathrm{BM}}/k_{\mathrm{TP}} \propto \exp(\Delta G/RT)$, where R is the gas constant. This yields to $\Delta G \approx 0.83\,\mathrm{kJ/mol}$ at room temperature.

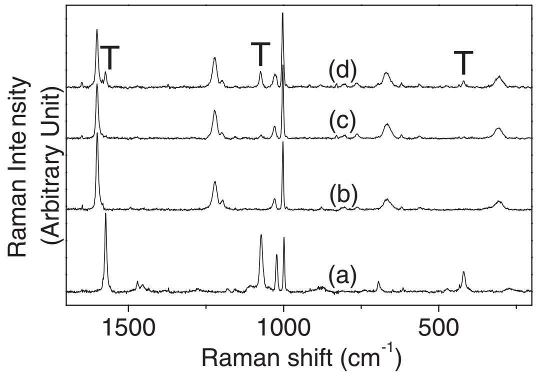

Figure 3. Surface enhanced Raman scattering of (a) thiophenol, (b) benzyl mercaptan, 1:1 mixture of thiophenol and benzyl mercaptan at (c) low and (d) high concentrations. T: thiophenol peak.

In order to further investigate the adsorption characteristics, SERS of TP, BM, and their 1:1 mixture was performed on gold nanoparticle surfaces at different concentrations. Figures 3c and 3d have shown the Au SERS spectra of 1:1 mixture of TP and BM at low and high bulk concentrations, respectively. At a low bulk concentration of $\approx 10^{-5}$ M, most peaks were ascribed to those of BM. The TP peaks labeled "T" could be observed clearly only at the higher bulk concentration. These results support a faster adsorption capability of BM on Au than that of TP. The SERS enhancements for the vibrational bands of BM were usually found to be higher than those of TP. Although not observed under the present experimental condition due to a rather longer data acquisition time for Raman than that of UV–vis spectra and the different Raman enhancement factor of each vibrational band, it is admitted that the SERS spectra should also depend on the elapsed time. Despite its polycrystalline nature,[15] a predominant (111) plane of gold nanopartpartcle surfaces was assumed to be useful for the present adsorption study. Since SERS selection rules do not provide a precise interpretation of band intensities, other spectroscopic techniques have been currently applied to reach a more consistent conclusion. Thermodynamic, electrochemical, and theoretical studies shall also be useful to explain the difference in the adsorption characteristics of aromatic thiols on Au surfaces.

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18 Colloidal nanoparticles were prepared following the procedures reported in the previous literature.[16] The concentration of the Au nanoparticles was estimated to be approximately $\approx 10^{-9}$ M. The TEM images were obtained with a Tecnai F20 Philips transmission electron microscope after placing a drop of colloidal solution on a carbon-coated copper grid. By counting at least 150 gold particles from TEM images, the statistical analysis revealed a size distribution of standard deviation in diameters, $\sigma \approx 8.6\%$ for 15.2 ($\pm$1.3) nm particles. The Au particles appeared to have a relatively homogeneous size distribution ($\sigma < 15\%$).[17] Raman measurements were described in the previous report.[15] A concentric ethanolic solution of aromatic thiols was diluted into the aqueous gold nanoparticle solution. To 1 mL of the Au nanoparticle solution, a 0.05 M ethanolic solution of aromatic thiols was added dropwise to a final concentration of 10^{-5}–10^{-7} M. UV–vis absorption spectra of the colloidal solutions were obtained with a Shimadzu UV-1601PC spectrophotometer at room temperature ($\approx$20 °C). The UV–vis absorption bandwidths were measured as twice the distance from the low-energy side of the absorption band to the maximum position at half the maximum intensity.

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