

Surface-Enhanced Raman Scattering (SERS) from Azobenzene Self-Assembled “Sandwiches”

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A silver island film was thermally deposited on the top of an azobenzene self-assembled monolayer on gold, yielding a SERS-active system possessing a “sandwiched” structure of $\text{Ag}|R_1\text{-Azo-R}_2\text{S-|Au}$. For the first time, the positions of the Azo groups were controlled by using azobenzenealkanethiols with different terminal groups (R_1) or interchain spacers (R_2), to clarify the relationship between the SERS effect and the structural nature of the system. As will be shown, increases in distances of Azo groups from the gold substrate and from the silver film both cause the enhancement factor to decay exponentially, indicating that the enhancement correlates to both the gold substrate underneath and the silver islands above.

Introduction

Recently, a great deal of attention has been paid to the photoactive and electroactive self-assembled monolayers (SAMs) in both fundamental and applied studies.¹ Surface-enhanced Raman scattering (SERS) has been used to provide information to help in understanding the effect of the structure of SAMs on their physical, chemical, and biological properties. The SERS technique is attractive because it can deliver useful spectroscopic signals to characterize the conformational and environmental properties of functional molecules at a monolayer level in aqueous media.^{2–7} Several research groups are actively combining the unique features of SERS and SAMs for various applications such as providing information concerning the conformations of *n*-alkanethiol SAMs^{2–4,6,7} and bringing insight into the surface enhancement mechanism by molecular design of the SAMs' structure.⁵ Because the azobenzene group has a large Raman scattering cross section^{8–10} and azobenzenealkanethiols are shown to form stable and reproducible monolayers on gold surfaces,^{6,11} the azobenzene self-assembled monolayer becomes a unique system for the study of the generation of SERS and for the further elucidation of its mechanism.

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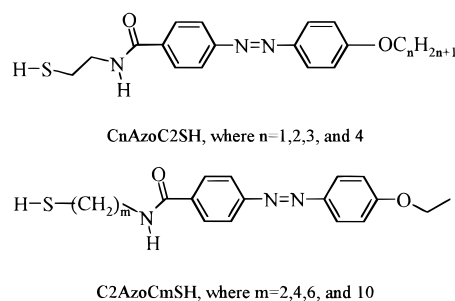
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Chart 1



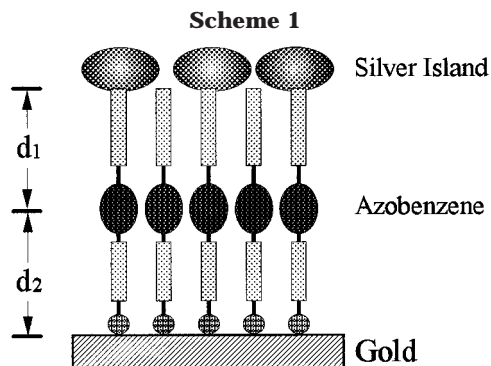
We have reported the electrochemical in-situ SERS investigation of azobenzene self-assembled monolayers and demonstrated the redox behavior between azobenzene and hydrazobenzene on gold electrode surfaces.^{7a} The azobenzene SAMs were also used to obtain the two-dimensional SERS maps of gold substrates prepared by different methods: electrochemical roughening and gold nanoparticle assembly.^{7b} Recently, Mirkin and his colleagues also performed SERS investigations of azobenzene-tethered SAMs,⁶ while Sun et al. carried out fundamental studies of the mechanism of SERS by using azobenzene SAMs.^{5c} In this letter, we report a novel azobenzene SERS-active system, which has a unique “sandwiched” structure, $\text{Ag}|R_1\text{-Azo-R}_2\text{S-|Au}$. The position of the azobenzene group was controlled precisely by molecular design of the azobenzenealkanethiols, which enables us to correlate the SERS intensity with the structural nature of the system studied.

Experimental Section

The azobenzenealkanethiol molecules ($\text{C}_n\text{AzoC}_m\text{SH}$) used in this study are shown in Chart 1. The synthesis and purification procedure have been reported in detail elsewhere.¹¹ All other chemicals were of reagent grade and used as received. Ultrapure water ($>17 \text{ M}\Omega\cdot\text{cm}$) was used throughout the experiments.

Construction of a sandwiched azobenzene self-assembled system consisted of two steps. The first one was to assemble

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azobenzenethiol molecules onto a gold substrate which was obtained by vacuum evaporation of high-purity gold (99.99%) onto a clean surface of glass already coated with chromium to improve adhesion, followed by immersing the "piranha solution"-cleaned gold substrates into a 1.0 mM CnAzoCmSH/C₂H₅OH solution for about 24 h to form the CnAzoCmSH SAMs. After removal of the SAM-covered gold substrates from the solution, the sample was washed with ethanol and water sequentially. The second step was to cover a silver island film (about 6 nm in thickness) by vacuum deposition of Ag to the surface of the above-prepared azobenzene SAMs on gold, yielding a sandwiched system with the structure of Ag|R₁-Azo-R₂S-Au (Scheme 1). To avoid significant structural change or deconstruction of the monolayer, the deposition was carried out under high vacuum (10⁻³ Pa), without heating the substrate, and the evaporation temperature for silver was kept as low as possible.

Raman measurements were performed with a Renishaw System 1000 Raman imaging microscope (Renishaw plc, U.K.) equipped with a 25 mW (632.8 nm) He-Ne laser (Model 127-25RP, Spectra-Physics) and a peltier-cooled CCD detector (576 pixels × 384 pixels). A 50× objective mounted on an Olympus BH-2 microscope was used to focus the laser beam into a spot of approximately 1 μm in diameter and to collect the backscattered light from the sample.

Results and Discussion

Figure 1 shows the typical Raman spectra of two series of sandwiched azobenzene self-assembled systems (Ag|R₁-Azo-R₂S-Au) in the range between 700 and 1800 cm⁻¹. Three major bands in the 1100–1700 cm⁻¹ region with good S/N ratio are observed. They can be attributed to the φ-N stretching ($\nu_{\phi-N=}$, ~1143 and ~1189 cm⁻¹), the Fermi resonance of the -N=N- stretching with out-of-plane bending of the C-H of the phenol rings ($\nu_{-N=N-}$, ~1402 and ~1456 cm⁻¹), and the benzene ring vibration (around 1601 cm⁻¹), respectively. All of the three vibrational bands mentioned above originate from the azobenzene moiety.⁵⁻¹⁰ Another important feature (figure not shown) in the recorded SERS spectra is the absence of the S-H stretching band (at ~2590 cm⁻¹ in the solid sample), which indicates the cleavage of the S-H bond and the formation of azobenzene SAMs on the gold surface.² Since the excitation wavelength at 632.8 nm is outside the electronic absorption band of the solid state of all CnAzoCmSH molecules and significant differences in the positions of characteristic bands and their relative intensities between these spectra and the normal Raman spectra from the parent molecules are observed, the spectra recorded and shown in Figure 1 are believed to result from the surface enhancement effect. Due to the highly oriented monolayer structure, the Raman label, that is, azobenzene, was well separated from both the gold and silver surfaces.^{6,11} In this sense, the chemical enhancement can be ruled out and the electromagnetic (EM) enhancement mechanism holds true for the present system.

To evaluate the magnitude of the enhancement factor (EF) for these azobenzene self-assembled "sandwiches",

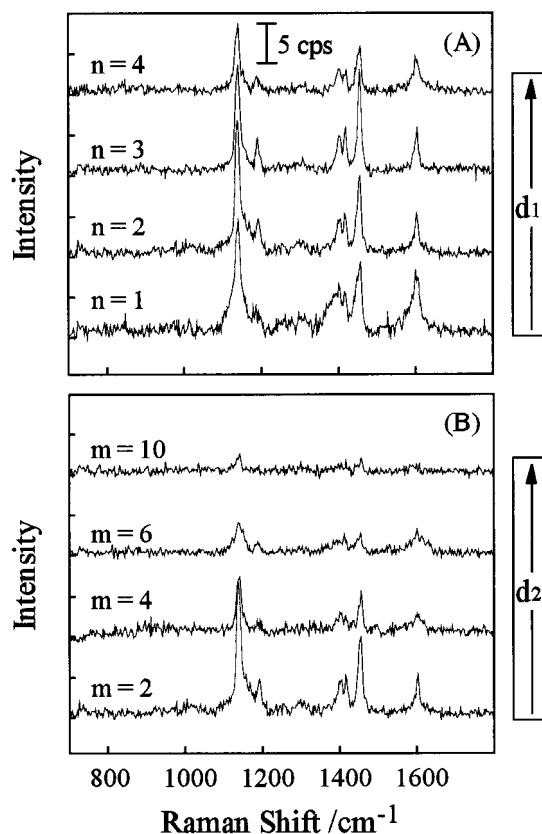


Figure 1. Representative SERS spectra of azobenzene self-assembled "sandwiches" (A) with different terminal groups in the SAMs (Ag|C_n-Azo-C₂S-Au), where $n = 1, 2, 3,$ and 4 ; (b) with different length of alkyl spacers in the SAMs (Ag|C₂-Azo-C_mS-Au), where $m = 2, 4, 6,$ and 10 .

we compared the measured SERS intensities to the calculated intensities of nonenhanced Raman scattering by using eq 1:

$$EF = (I_{\text{SERS}}/I_{\text{norm}})(N_{\text{bulk}}/N_{\text{surf}}) \quad (1)$$

where I_{SERS} , I_{norm} , N_{bulk} , and N_{surf} are the measured SERS intensity for a monolayer of scatterers, the measured intensity of nonenhanced or normal Raman scattering from a bulk sample, the number of molecules under laser illumination for the bulk sample, and the number of molecules in the SAM, respectively. I_{SERS} and I_{norm} were measured at 1143 cm⁻¹ ($\nu_{\phi-N=}$), while the N_{bulk} and N_{surf} values were calculated on the basis of the estimate of the concentration of surface species or bulk sample and the corresponding sampling areas. The surface concentration of the C2AzoC2SH SAM on gold has been previously determined to be 4.21×10^{-10} mol/cm².^{11a} Taking the sampling area (ca. 1 μm in diameter) into account, N_{surf} has a value of 3.30×10^{-18} mol. For the solid sample, the sampling volume is the product of the area of the laser spot (ca. 1 μm in diameter) and the penetration depth (~2 μm) of the focused laser beam. Assuming the density of bulk C2AzoC2SH is 1 g/cm³, N_{bulk} can be calculated to be 5.5×10^{-15} mol. Substituting values of those four variables into eq 1, EF is 560 ± 50 for the Ag|C₂-Azo-C₂S-Au system. This is larger than that obtained for phenyl SAMs on a Ag surface,^{5a} although it is still lower compared to the most frequently cited value of 10⁶ for pyridine absorbed on an electrochemically roughened Ag surface.¹² It should

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be noted that, besides the alkyl-spacer-induced distance effect^{5a,c} (to be further discussed in the following section), the experimental conditions such as the size and distribution of silver particles in the island film and the surface morphology of the gold substrates have not been well optimized according to the observed SERS intensities, by which a much higher EF might be expected.

To further understand the correlation between the positions of the Azo group within Ag|SAM|Au “sandwiches” and the corresponding Raman response, two series of azobenzenealkanethiols (Chart 1), $C_n\text{AzoC}_2\text{SH}$ (where $n = 1, 2, 3, \text{ and } 4$) and $C_2\text{AzoC}_m\text{SH}$ (where $m = 2, 4, 6, \text{ and } 10$), were used in our investigation. We denoted the distance between the Azo group and the silver island film as d_1 and the distance separating the Azo group from the gold substrate as d_2 , respectively (Scheme 1). Because azobenzene SAMs are highly oriented and closely packed and all these monolayers possess a similar perpendicular molecular orientation due to the interchain hydrogen bonding and the intermolecular aromatic interaction,^{11c,e} the distances between the Azo groups and the metal surfaces can be related to the number of methylene units present in the azobenzene thiol molecules.

Figure 1A shows the SERS spectra of the sandwiched azobenzene self-assembled systems with different terminal groups (Ag|C_n-Azo-C₂S-Au, where $n = 1-4$). In this case, the distance between the Azo group and the silver island (d_1) varies, while the distance between the Azo group and the gold surface is kept constant. Therefore, the variation in the Raman intensity in this series of spectra suggests the dependence of Raman scattering intensities on d_1 . In Figure 1B are shown the SERS spectra of sandwiched azobenzene self-assembled systems with different interchain spacer groups (Ag|C₂-Azo-C_mS-Au, where $m = 2, 4, 6, \text{ and } 10$). In this case, the distance between the Azo group and the gold surface (d_2) is changed, while there is no difference in the distance between the Azo group and the silver island film. The variation in the Raman intensities of this series of SERS spectra reflects the dependence of Raman scattering intensities on d_2 . As d_1 increases from $n = 1$ to $n = 4$, the intensity in Figure 1A slightly increases initially and then decreases. In contrast, the Raman intensity apparently drops for increasing d_2 in Figure 1B. To show these changes more clearly, we chose two characteristic bands located at 1143 and 1456 cm⁻¹ for further comparison. They are excellent Raman markers for studying the distance dependence of the SERS intensity in our sandwiched systems because (1) their prominent intensities favor detection with a good S/N ratio, especially when distances are large, and (2) their relatively constant peak positions ensure these spectral bands to be identified unambiguously. The relative intensities at 1143 and 1456 cm⁻¹ as a function of d_1 or d_2 were plotted out as Figure 2, which directly demonstrated the behavior mentioned above. In addition, changes in Raman intensities for the two different wavelengths seem to follow the same trend. However, in Figure 2A the Raman intensities of the two wavelengths reached their maximum scattering at different d_1 values, probably resulting from the discrepancy in enhancement effects from the different orientations for these two vibrations.

It should be noted that the recorded SERS intensity relates not only to the enhancement factor (EF) but also to the surface concentration of the Raman label groups, which depends on the structure of the azobenzene thiol molecules used to form the monolayer.¹¹ To further evaluate the correlation between the position of the azobenzene group and the SERS response, the difference

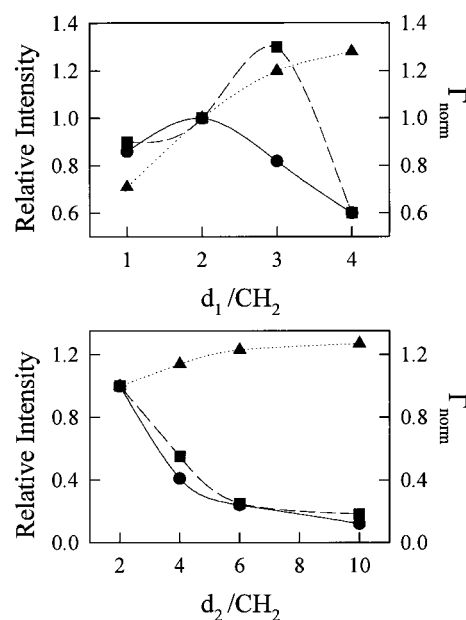


Figure 2. Relative SERS intensities of bands (1143 cm⁻¹: ● and 1456 cm⁻¹: ■) versus distances between (A, top) the Azo group and upper silver island film (d_1); (B, bottom) the Azo group and the underlying gold substrate (d_2). The relative surface concentrations (Γ_{norm} : ▲) of Azo groups in respective Azo SAMs were also shown after normalization to that of C2AzoC2SH.

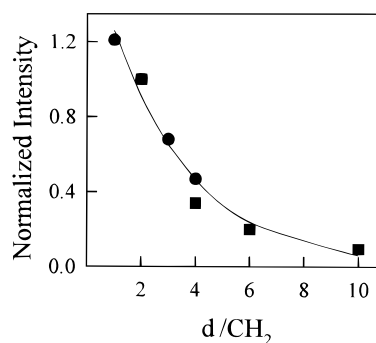


Figure 3. Normalized SERS intensities as a function of the number of CH₂ units in d_1 (●) (alkyl chain between Azo and silver film) and d_2 (■) (alkyl chain between Azo and gold), the solid line is a fit to all the experimental data points with an exponential decay.

in the surface concentrations of azobenzene moieties in these “sandwiches” should be taken into account. As shown in Figure 2, the normalized surface concentration increases monotonically as a function of the number of methylene units for both d_1 and d_2 (Those data are taken from ref 11.) On the basis of the above consideration, we have normalized the Raman intensities of the 1143 cm⁻¹ band to the respective surface concentrations and plotted them against the number of methylene units (Figure 3). If the values of I_{norm} and N_{bulk} are roughly the same for different azobenzenealkanethiols, Figure 3 would also represent the dependence of EF values on the position of the azobenzene groups. It is clear in Figure 3 that the normalized SERS intensities decrease exponentially with increasing either d_1 or d_2 . Especially, the rates of decrease in both the d_1 and d_2 cases seem to be similar to each other, since their data can be well fitted with the same exponential decay (the solid line).

From the experimental findings in our studies, a few points can be noted. The first is the SERS activity of these “sandwiches”. The present investigation confirmed the

earlier results of Evans et al. to achieve a SERS effect by depositing an Ag island film on the previously prepared monolayers.³ Further, we could show the enhancement can be attributed not only to the overlying silver films but also to the gold substrate. Although we cannot observe a discernible Raman signal from the azobenzene monolayers on the thermally deposited gold substrates without the overlying silver film, the SERS spectra are sensitive to the distance between the Azo group and the gold surface (d_2) after the formation of the “sandwiches”.

Second, the “double dependence” behavior observed in this unique system suggests the mutual coupling of electromagnetic (EM) fields between two metal films within the “sandwiches”. It has been reported that the SERS signal decreases with increasing distance between the Raman label and the metal surface, which was modeled by the electromagnetic (EM) field enhancement theory.^{5,13,14} The fact that the EF values become smaller when the Raman labels are located further from both metal films enabled us to postulate a mutual coupling of electromagnetic waves of the EM fields from the two metal films. The local intensity of the EM field, contributed from both layers of metal, is stronger, presumably, than that of a regular SERS-active system with a Raman label attached to one metal surface. Moreover, the density of the EM field should be weaker in the middle but stronger near each metal terminal of the “sandwiches”.

Third, the similar decay rate of normalized SERS intensities can be understood with a symmetric distribution of the EM field between the two metal layers in these “sandwiches”. For electrochemically roughened metal surfaces or nanoparticle assemblies, the SERS responses are highly dependent on the nanostructures of the substrate, for example, particle or domain size and their distributions.^{15–17} The morphology of the thermally evaporated gold substrate is normally on a scale of several tens of nanometers, which is roughly in the same order as that for silver island films.^{7a,17} Another point which might be raised is the different wavelength dependent on the enhancement from gold and silver of the excitation laser. In terms of the electrodynamic resonance excitations, the

present wavelength (632.8 nm) is more favorable for gold rather than silver. This might partially account for the absolute low EF for the Ag|C₂-Azo-C₂S-Au system, since the separation between the azo group and gold is larger than that for silver. However, this will not affect the distance dependence we observed, since we were considering the trend of EF variations.

Further evaluation of the results obtained and comparison of our experimental data with theoretical models require further improvement in experimental techniques and development in theory, including the fine control of the surface morphology of the gold substrate, the specific nanostructures, the particle size and the shape distribution of the silver island film, and the construction of other novel sandwiched systems such as Au|SAM|Au and Au|SAM|Ag. All these studies are currently underway in our laboratory. Nevertheless, the present investigation enables us to get fundamental information for the characteristic SERS effect in the “sandwiched” self-assembled systems, emphasizing the importance of molecular design and self-assembly techniques to aid fabrication of functional molecular assemblies and understanding of their physical properties.

Conclusions

In this letter, we reported our first study on “sandwiched” azobenzene self-assembled systems. They were constructed by deposition of a silver island film onto the top of azobenzene SAMs on gold, and they showed significant Raman enhancement. Further, experimental results demonstrated that the SERS enhancement factor (EF) correlates to both the underlying gold substrate and the overlying silver island. It decreases as a function of both the distance between the Azo group and the underlying gold substrate and that between the Azo group and the upper silver island film. The present finding suggests that the Raman enhancement effect may correspond to the electromagnetic coupling effect between two metal layers in this novel SERS-active system.

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