Laser-Induced Photoreaction of Bis(4-nitrophenyl) Disulfide on Copper Revealed by Surface-Enhanced Raman Scattering

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Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering (SERS) in which the Raman scattering cross sections are dramatically enhanced for molecules adsorbed thereon.[1-4] Although the exact mechanism of SERS is still a matter of controversy, it is generally accepted that two enhancement mechanisms, one a long-range electromagnetic (EM) effect and the other a short-range chemical (CHEM) effect, are simultaneously operative. Both mechanisms suggest the possibility of the enhanced absorption and enhanced photochemistry for surface-adsorbed molecules.

Direct observation of a surface-enhanced photochemical reaction has been reported. Aromatic sulfides such as benzyl phenyl sulfide and dibenzyl sulfide adsorbed on silver undergo surface reactions involving facile cleavage of C–S bonds by 514.5 nm radiation.[5] As another example, 4-nitrobenzenethiol and 4-nitrobenzoic acid adsorbed on silver are converted in ambient conditions to 4-aminobenzenethiol and 4-aminobenzoic acid, respectively, upon the irradiation of an Ar^+ laser (514.5 nm).[6-8] These molecules are found, however, not to undergo such reactions on a gold surface with visible light.[9] This indicates that Ag substrates can act as moderate photoelectron emitters. In fact, the photoemission behavior of silver is known to be different in many aspects from that of other metals.[10]

Ever since the discovery of SERS phenomenon, SERS spectra from molecules on silver and gold substrates have been extensively studied. In contrast, copper substrate has received far less attention owing to its inherent instability towards oxidation. Given the potential applications of copper as an inexpensive raw material in the development of various nano- and optoelectronic devices, it is desired to explore the characteristics of any possible laser-induced photoreaction occurring on nanostructured copper substrates. Recently, we found that the copper foil etched in a dilute solution of HNO_3 is an efficient photoelectron emitter such that the SERS spectrum of 4-nitrobenzenethiol on copper is readily converted to that of 4-aminobenzenethiol under the 632.8 nm radiation from a He/Ne laser.[11] In this light, the SERS of bis(4-nitrophenyl) disulfide on copper has been investigated. The first concern of this investigation is whether S-S bond scission will occur for bis(4-nitrophenyl) disulfide during self-assembly adsorption process on copper surface. The second concern is to determine whether the nitro group will also be converted to amine on copper substrate. In fact, the conversion of bis(4-nitrophenyl) disulfide to 4-aminobenzenethiol by visible laser appeared to occur on copper, conforming again a remarkable photoelectron emitting characteristics of the nanostructured copper.

Experimental

Copper foil (0.05 mm thick), bis(4-nitrophenyl) disulfide, and 4-aminobenzenethiol, were purchased from Aldrich and used as received. Unless otherwise specified, other chemicals were reagent grade, and a highly pure water of resistivity greater than 18.0 MΩ·cm (Millipore Milli-Q System) was used when making aqueous solutions. The Cu foil was made to be SERS-active by immersing it in diluted (1:1) HNO_3 solution for ~30 s. For the self-assembly of bis(4-nitrophenyl) disulfide or 4-aminobenzenethiol onto Cu, the HNO_3-etched Cu foil was immersed in 1 mM ethanolic solution of the adsorbate for about 1 h. The stock solutions of adsorbate in ethanol were bubbled with nitrogen before use.

Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). The 632.8 nm line from a 17 mW He/Ne laser (Spectra Physics Model 127) or the 514.5 nm line from a 20 mW Ar^+ laser (Spectra Physics Model 163-C4210) were used as the excitation source. Raman scattering was detected with 180° geometry with a Peltier cooled (-70^{o}C) charge-coupled device (CCD) camera (400×600 pixels). The laser beam was focused onto a spot approximately 1 μm in diameter with an objective microscope with magnification of the order of 20×. The holographic grating (1800 grooves/mm) and the slit allowed the spectral resolution to be 1 cm^{-1}. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer.

Results and Discussion

Figure 1a and 1b show the normal Raman spectrum of neat bis(4-nitrophenyl) disulfide and its SERS spectrum on copper substrate, respectively, both of which were obtained using a He/Ne laser at 632.8 nm as an excitation source; the power at the sampling position was ~1 mW. These two spectra exhibit quite different spectral patterns with each other. Although a few peaks related to the benzene ring modes appear nearly at the same position, the complete absence of the S–S stretching peak in the SERS spectrum, weakly observable at 553 cm^{-1} for pure bis(4-nitrophenyl) disulfide (reported at 542 cm^{-1} for di-

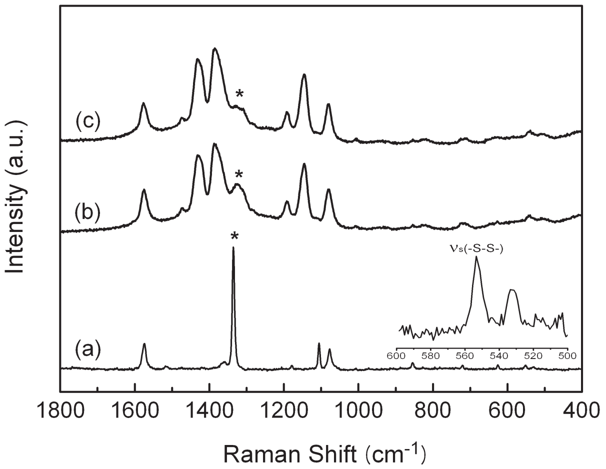

Figure 1. (a) Normal Raman spectrum of bis(4-nitrophenyl) disulfide in neat solid state. SERS spectra of bis(4-nitrophenyl) disulfide adsorbed on HNO_3-etched Cu (b) measured immediately and (c) after 5 min. All spectra were obtained using a He/Ne laser at 632.8 nm as the excitation source. The stars (*) indicate the $\nu_s(NO_2)$ peak. The inset spectrum shows the S-S stretching peak of pure bis(4-nitrophenyl) disulfide.

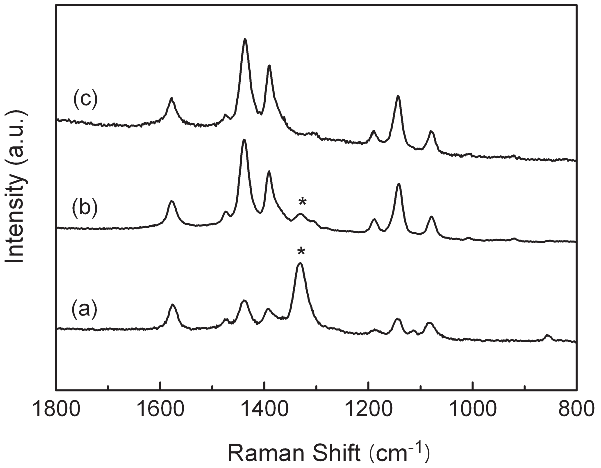

Figure 2. SERS spectra of bis(4-nitrophenyl) disulfide adsorbed on HNO_3-etched Cu measured using (a) a slightly defocused and (b) a focused laser beam. (c) SERS spectrum of 4-aminobenzenethiol adsorbed on HNO_3-etched Cu for comparison. All spectra were obtained using an Ar^+ laser at 514.5 nm as the excitation source. The stars (*) indicate the $\nu_s(NO_2)$ peak.

phenyl disulfide[12]), indicates that bis(4-nitrophenyl) disulfide is adsorbed on Cu as thiolate after the S-S bond cleavage. Sandroff and Herschbach[12] used SERS to study diphenyl disulfide adsorbed onto Ag films and found that the S-S bond cleaved under mild conditions. They cast a film of the disulfide onto an Ag film, and the SERS spectrum that they obtained was identical to that observed for the mercaptide on silver. From this observation they concluded that the disulfide adsorbs onto film as the monomer. More recently, Noh *et al.*[13] compared the S-S bond dissociation energies of various disulfides by means of a density functional theory (DFT) calculation. They found that the dissociation energy of diphenyl disulfide is lower (~15 kcal/mol) than that of dialkyl disulfide. The latter difference suggests that the S-S bond in diphenyl disulfide is much easier to cleave than that in dialkyl disulfide during their self-assembly onto metal substrates. Similarly, the S-S bond of bis(4-nitrophenyl) disulfide is assumed to cleave while adsorbing onto the copper surface.

In the Raman spectrum (Figure 1a), the predominant Raman peak at 1335 cm^{-1} can be assigned to the symmetric stretching vibration of the nitro group ($\nu_s(NO_2)$) of bis(4-nitrophenyl) disulfide. In its SERS spectrum (Figure 1b), however, more enhanced peaks are observed around 1431, 1388, and 1140 cm^{-1}. Interestingly, these bands can all be attributed to 4-aminobenzenethiol (*vide infra*).[14] Their apparent enhancement has been ascribed in the literature to the charge-transfer (CT) from metal to the adsorbed molecule.[14-16] In particular in the potential dependent experiment, the intensity of the peak at ~1430 cm^{-1} varied as a function of the applied potential, in agreement with the CT mechanism, while the C-S stretching band at ~1080 cm^{-1} was almost insensitive to the potential change since the band (a_1-type) was enhanced only via the EM mechanism. Figure 1c shows the SERS spectrum of bis(4-nitrophenyl) disulfide adsorbed on Cu acquired after the exposure of the He/Ne laser light for 5 min. The stars (*) in Figure 1 indicate the $\nu_s(NO_2)$ peak. We noticed that upon increasing the irradiation time, the $\nu_s(NO_2)$ peak at ~1340 cm^{-1} gradually decreases.

To gain more insight into the laser-induced photoreaction, the SERS spectra were also measured using the 514.5 nm radiation as the excitation source. The SERS spectrum shown in Figure 2a was taken using a slightly defocused laser beam to minimize laser-induced changes, while the SERS spectrum of Figure 2b was taken using a focused laser beam at the same wavelength; the power at the sampling position was again ~1 mW. Any spectral change observable using the 514.5 nm radiation was much the same as that observed already by the 632.8 nm excitation. The SERS spectral pattern is obviously affected by the size of the laser beam. As indicated by the stars (*) in Figure 2, the $\nu_s(NO_2)$ peak at ~1340 cm^{-1} gradually decreases and several new peaks are emerging, for instance, at 1430, 1387, and 1144 cm^{-1}, each of which can be assigned to the ring 19b ($\nu_{CC}+\delta_{CH}$), 3 ($\nu_{CC}+\delta_{CH}$), and 9b (δ_{CH}) modes of 4-aminobenzenethiol, respectively (*vide supra*).[14,17] The SERS spectrum of 4-aminobenzenethiol adsorbed on HNO_3-etched Cu foil is also shown together in Figure 2c for comparison.

The overall processes of adsorption and consecutive laser-induced photoreaction of bis(4-nitrophenyl) disulfide on Cu surface are schematically drawn in Figure 3. Initially, bis(4-nitrophenyl) disulfide molecules adsorb on Cu as 4-nitrobenzenethiolates involving a facile cleavage of their S-S bonds. 4-Nitrobenzenethiolates on Cu are then subjected to laser-induced photoreaction to convert to 4-aminobenzenethiolates by either a He/Ne laser at 632.8 nm or an Ar ion laser at 514.5 nm. The nitro-to-amine conversion is, in fact, a reductive reaction, necessitating photoelectrons. It is then remarkable that the HNO_3-etched copper foil must be an efficient photoelectron emitter even under the 632.8 nm radiation. Recalling the earlier report that the surface roughening of silver not only causes a dramatic enhancement of photoyields at the wavelength close to the surface plasmon frequency but also leads to an extension of the photoresponse toward longer wavelengths,[18] the present observation may not be unrealistic.

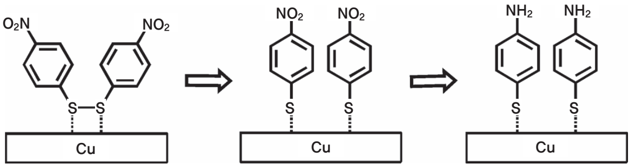

Figure 3. A schematic diagram showing the laser-induced photoreaction of bis(4-nitrophenyl) disulfide on Cu surface. Self-assembly adsorption process of bis(4-nitrophenyl) disulfide and subsequent nitro to amine conversion on copper substrate by visible laser during the SERS measurements.

It is nonetheless remarkable that the photoelectrons generated from an etched Cu substrate are more powerful than those from an Ag substrate at least under the irradiation of 632.8 nm radiation.

Conclusions

We have shown that the SERS spectrum of bis(4-nitrophenyl) disulfide on copper is readily converted to that of 4-aminobenzenethiol by the irradiation of either an Ar^+ laser or a He/Ne laser. That is, the disulfide adsorbate was adsorbed initially on copper as thiolate by the S-S bond scission, and the nitro-to-amine conversion took place by the laser-induced photoreduction. The most remarkable observation was that the photoelectrons generated from an etched copper foil are more powerful than those from an Ag substrate at least under the irradiation of the 632.8 nm radiation. We accordingly expect that both the higher SERS activity and the noticeable photoelectron emission characteristics of the copper nanostructures are invaluable for the development of copper-based nano- and opto-electronic devices.

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