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Substrate-Dependent Surface-Induced Photoreaction of Organic Monolayers on Silver

Sang Woo Han* and Kang Yeol Lee

Nanomaterials Laboratory, Department of Chemistry and Research Institute of Natural Sciences,
Gyeongsang National University, Jinju 660-701, Korea. *E-mail: swhan@gsnu.ac.kr

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Nano- to meso-scale structures to be employed in laboratory studies and commercial application may be realized by controlling chemical functionalities on a nanoscale. Site-selective alternations of surface chemistry provide a means of engineering surfaces that can be used in sensitive optoelectronic devices, sensors, and devices that mimic biological functions. Patterning of the self-assembled monolayers (SAMs) is an excellent strategy for preparing such templates that possess variable surface chemical properties.¹⁻³ Modification of organic monolayers is usually carried out either by utilizing the conventional optical methods using UV light as an excitation source¹ and other lithographic schemes based on state-of-the-art technologies.^{2,3}

Recently, non-destructive process by a surface-enhanced photochemical reaction has been reported.⁴⁻⁷ 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.⁴ As another example, 4-nitrobenzoic acid and 4-nitrobenzenethiol adsorbed on silver are converted in ambient conditions to 4-aminobenzoic acid and 4-aminobenzenethiol, respectively, upon irradiation with an argon ion laser (514.5 nm).⁵⁻⁷ These surface-induced photoreactions have been assumed to be associated with the charge transfer from silver to the adsorbed molecule.⁶ If the energy difference between the Fermi level (E_F) of the metal and the low-lying excited state of the charge-transfer complex (E_{CT}) matches the energy of the excitation radiation, a resonant charge transfer from the metal to the excited state of the complex will take place.⁸

Herein we aim to report a study on the substrate-dependence of the surface-induced photoreaction of organic monolayers on silver. Based on the fact that the mechanism of photoreactions should be charge transfer from silver surface to the adsorbate-silver charge-transfer complex, the reaction aspect distinctly depends on the type of substrate. We have chosen the 4-nitrobenzenethiol (4-NBT) SAMs as a model system, and investigated the photoreaction of the SAMs on the surfaces of Ag nanoparticles (AgNPs), micrometer-sized Ag powder, and Ag foil by using surface-enhanced Raman spectroscopy (SERS).

Experimental Section

4-NBT and pentanethiol were purchased from Aldrich. Other chemicals, unless specified, were reagent grade, and triply distilled water (resistivity greater than 18.0 M Ω -cm) was used when preparing aqueous solutions.

4-NBT capped silver nanoparticles were synthesized through the place exchange reaction of pentanethiol capped silver nanoparticles and 4-NBT.⁹ The pentanethiol capped Ag nanoparticles were prepared using a procedure from the literature.¹⁰ The pentanethiol capped Ag nanoparticles and 4-NBT (1 mM) were co-dissolved in 30 mL THF under constant stirring for a week. The solvent was then removed on a rotary evaporator and the remaining sample was washed thoroughly with diethyl ether to remove excess 4-NBT. For the adsorption of 4-NBT on powdered silver, 0.050 g of silver powder (nominal particle size of 2-3.5 μ m, > 99.9% purity, Aldrich) was placed in a clean small vial into which 0.5 mL of the ethanol solution of 4-NBT (1 mM) was added. After 1 h, the liquid phase was decanted. The remaining solid particles were washed with excess ethanol and left to dry in ambient air for 2 h. SAMs of 4-NBT on Ag foil were prepared by immersion of the silver substrate in 1 mM ethanolic solution of adsorbate for about 3 h. For surface-enhanced Raman scattering activity, Ag foil (Aldrich, 0.05 mm thick) was pre-roughened by immersing the substrate in diluted (1 : 1) HNO₃.^{4,6}

Raman spectra were obtained using a Renishaw Raman system 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). The 514.5 nm radiation from an air-cooled, 20 mW Ar⁺ laser (Spectra Physics model 163-C4210) was used as the excitation source. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 transmission electron microscope operating at 200 kV. The morphologies of the surfaces of powdered silver and silver foil were examined by using scanning probe microscopes (Digital Instruments Nanoscope IIIa and PSIA XE-100)

Results and Discussion

As mentioned in Introduction, several SERS studies have

been reported in the literature regarding the physicochemical properties of aromatic nitro molecules on silver.⁵⁻⁷ It has been observed that the SERS peaks of the original nitro molecules gradually lose intensities, and a new set of peaks appears. The new peaks rapidly increased in intensity as a function of the laser illumination time, suggesting that the nitro molecules were subjected to photoreaction on the silver surface. Based on these earlier observations, we have examined the SERS characteristics of 4-NBT on silver surfaces with different morphologies.

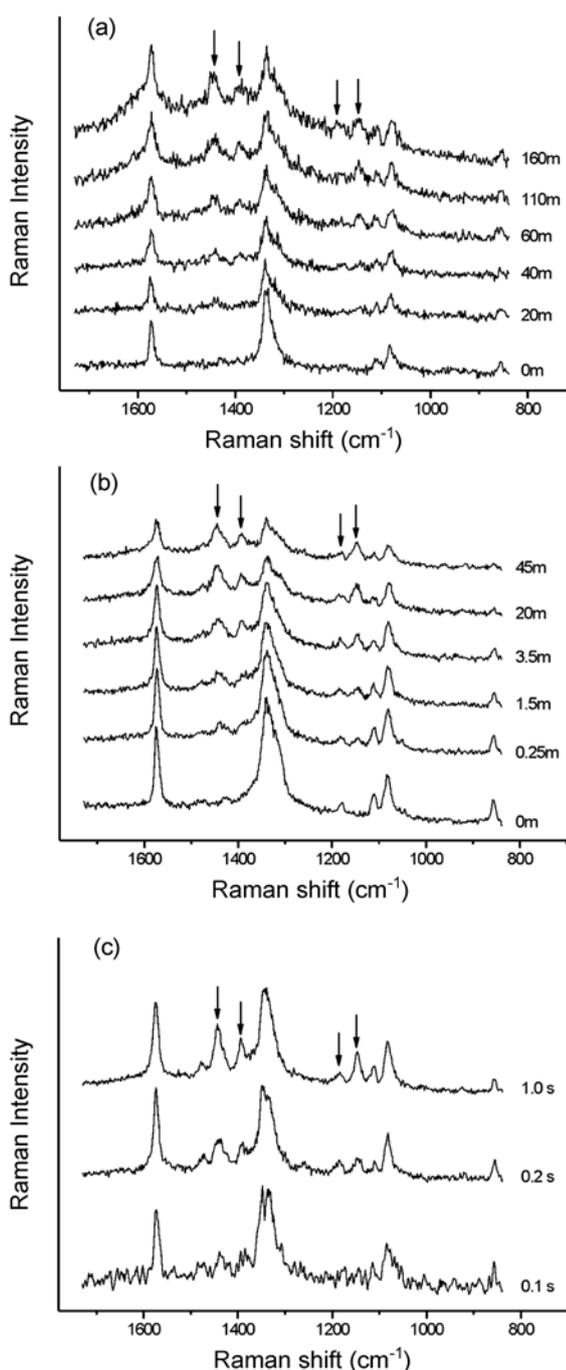


Figure 1. Time dependent SER spectra of 4-NBT on (a) AgNPs, (b) 2 μm -sized silver powder, and (c) Ag foil.

Figure 1(a) shows a series of Raman spectra of 4-NBT adsorbed on silver nanoparticles (AgNPs), taken as a function of time exposed to the 514.5 nm radiation from an Ar⁺ laser (actual power density: 0.2 W/cm²). Considering the monolayer coverage of 4-NBT molecules, the spectra must be SER spectra. It is evident that the SER spectral pattern changes as a function of the laser irradiation time. The most noticeable change is identified in the region of 1100-1500 cm⁻¹. As indicated by the arrows in Figure 1a, several new peaks appeared, for instance, at 1436, 1392, 1192, and 1143 cm⁻¹ with decrease of peaks related to 4-NBT such as one at 1356 cm⁻¹ assigned to the $\nu_s(\text{NO}_2)$ mode. This indicates that photoreaction has taken place for 4-NBT on the surface of AgNPs. Referring to the previous studies,⁵⁻⁷ the reaction product should be 4-aminobenzenethiol.

For comparing relative photoreaction efficiency along the type of silver surfaces, we have also performed SERS measurements of 4-NBT on 2 μm -sized silver powder and HNO₃-etched Ag foil. These commercially available powdered silver and silver foil have been proven to be efficient substrates for the infrared and Raman spectroscopic characterization of molecular adsorbates.⁴⁻⁶ Figures 1b and 1c show series of SER spectra of 4-NBT adsorbed on silver powder and silver foil, respectively, taken as a function of time exposed to the 514.5 nm radiation (actual power density of laser irradiation and measuring conditions are same with the case of AgNPs). As shown in Figures 1b and 1c, the SER spectral patterns change as a function of the laser irradiation time. The overall changes of spectral features are almost same with those observed with AgNPs substrate, but the reaction time is dramatically different between three types of silver surfaces. To estimate the photoreaction extent of 4-NBT on the different substrates, the peak intensity of the band at 1436 cm⁻¹ is monitored as a function of laser irradiation time. The peak intensities of the band normalized with respect to the value obtained when the reaction plateaus are plotted in Figure 2. The pattern of the intensity variation was quite reproducible albeit that there

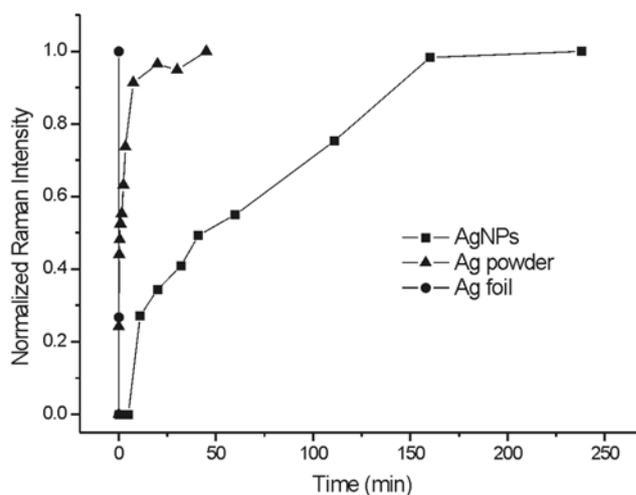


Figure 2. Normalized SER peak intensity of the band at 1436 cm⁻¹ vs duration of laser illumination time.

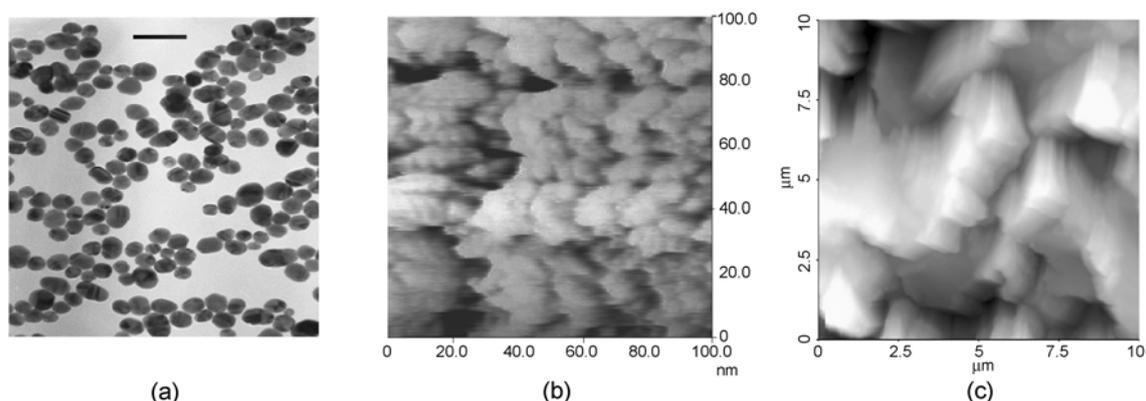


Figure 3. (a) TEM image of the AgNPs (Scale bar: 10 nm). (b) STM image of the 2 μm -sized silver powder. (c) AFM image of the HNO_3 -etched Ag film.

were some sample-to-sample fluctuations. It is seen that the photoreaction of 4-NBT takes place more readily on the surface of Ag powder than on that of AgNPs. The reaction plateaus after ~ 20 min in the case of SAMs on the 2 μm -sized silver powder while it takes about 3 hrs when the 4-NBT adsorbed at the surface of the AgNPs. It is noticeable that the photoreaction occurred on the silver foil is remarkably fast: the reaction of 4-NBT on the Ag foil completed within 1 second. The observed different reaction kinetics can be ascribed to different charge transfer efficiency between substrates. In fact, we have also obtained same results with other nitro compounds, *e.g.*, 4-nitrobenzoic acid (data not shown). This means that our results can be generally applicable for the similar situation.

Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering in which the scattering cross sections are dramatically enhanced for molecules adsorbed thereon.¹¹ It is believed that two enhancement mechanisms, one a long-range electromagnetic (EM) effect and the other a short-range chemical (CHEM) effect, are simultaneously operative. The EM mechanism, contributing a factor of 10^4 to the overall enhancement factor (EF), is based on the amplified electromagnetic field generated upon optical excitation of surface plasmon resonance of nanoscale surface roughness features in the 10-100 nm range.^{12,13} The CHEM enhancement mechanism, contributing an additional EF of 10^1 - 10^2 , is associated with the electronic coupling of molecules adsorbed on certain surface sites in atomic-scale roughness (such as atomic clusters, terraces, and steps) with the surface, leading to a situation similar to resonance Raman scattering.^{14,15} Both mechanisms suggest the possibility of enhanced absorption and enhanced photochemistry for surface-adsorbed molecules. Considering the fact that the mechanism of the surface-induced photoreactions should be charge transfer from silver to the adsorbed molecule,^{6,8} the observed experimental results for the relative photoreaction efficiency upon the type of Ag surfaces can be explained by the above enhancement mechanism. Since the electron transfer step is supposed to be a direct, optically induced charge transfer

from the Fermi level of the silver to the low-lying LUMO of the adsorbate-silver complex, the photoreaction will readily take place on a substrate with a morphology that can guarantee large enhancement of electromagnetic field and/or formation of efficient charge transfer complex.

In fact, for the EM mechanism to operate, certain degrees of surface roughness are required; the chemical enhancement may also be more effective on atomically rough surfaces than on smooth surfaces. Recently, Maxwell *et al.*¹⁶ reported that nanostructured thin films fabricated using Ag sols prepared by citrate reduction showed large EF of SERS under 514 nm radiation. By the size fractionation of colloidal nanoparticles, they found further that the films containing 80-100 nm Ag particles exhibit the highest enhancement efficiency at 514 nm excitation. On these grounds, we have taken microscopy images of the silver substrates used in the present work. Figure 3a shows a typical TEM image of AgNPs. The particles have spherical shape with average size of ~ 4 nm. The μm -size silver substrates are obviously too large for occurrence of the EM field enhancement associated with localized surface plasmons.¹⁷ Since much smaller microstructures were expected to be responsible for the photoreaction of 4-NBT on powdered silver, we have attempted to see the atomic scale roughness of the silver powder by scanning tunneling microscopy (STM). Figure 3b shows the STM image for the 2 μm -sized silver powder. As shown in the image, the surface of powdered silver appears to consist of a few tens of nanometer-sized protrudes. We have also examined the microscopic morphology of the HNO_3 -etched Ag foil that showed the highest photoreaction efficiency. Close inspection of atomic force microscopy (AFM) images of the silver foil (Figure 3c) indicates that the surface comprises domains with the size of around 100 nm. Referring the fact that the highest EM field and chemical enhancement can be acquired with the 80-100 nm Ag, the observed microscopic features of silver substrates are well correlated with the results of photoreaction experiments. In fact, there is also a possibility for the change of charge transfer kinetics caused by the changes in the energetics of both/either the

Fermi level of the Ag and/or the LUMO level of the adsorbate. It could be possible, depends on the size of the surface nanostructures, those energy levels would be shifted, results in the significant changes in the electronic coupling between metal and adsorbate. To clarify this issue, more thorough spectroscopic and microscopic studies will be conducted by fine-tuning the surface roughness of silver substrates.

Conclusions

We have obtained SERS spectra of 4-NBT adsorbed on different silver surfaces to examine the substrate dependence of the surface-induced photoreaction on silver. The photoreaction of 4-NBT takes place more readily on the surface of Ag powder than on that of nanoparticles. Highest photoreaction efficiency can be realized by using Ag foil as a substrate. This may reflect that silver foil can function as an efficient photoelectron emitter. The aspect of reaction can be well correlated with microscopic roughness features of silver substrates. Our future work will be directed toward the investigation of extent of surface-induced photoreaction upon controlling the shape of nanostructures present on Ag substrates.

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