Visible laser–induced photoreduction of silver 4-nitrobenzenethiolate revealed by Raman scattering spectroscopy

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We have investigated the photochemical characteristics of silver 4-nitrobenzenethiolate (Ag-4NBT) by means of Raman spectroscopy. When Ag-4NBT is irradiated with an argon ion laser at 514.5 nm, its Raman spectrum changes over time, resulting in the production of 4NBT-capped silver nanoparticles. The surface-enhanced Raman scattering (SERS) spectrum of 4NBT adsorbed on those Ag nanoparticles is subsequently converted to that of 4-aminobenzenethiol (4ABT). These surface-induced photoreduction characteristics were investigated by monitoring the growth of Raman peaks of 4ABT as a function of the laser exposure time. Water vapor or ambient conditions were more effective than vacuum conditions for the photoreduction of 4NBT to 4ABT. Nonetheless, the occurrence of photolysis even under vacuum conditions suggests that the benzene ring hydrogen atoms might be the H-atom source of the nitro-to-amine group conversion although in ambient conditions water or solvent molecules trapped inside the Ag–4NBT should be the primary H-atom source and facilitate the transfer of electrons, as well as the diffusion of Ag atoms to form highly SERS-active nanoaggregates. Copyright © 2009 John Wiley & Sons, Ltd.

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Introduction

Direct observation of a surface-enhanced photochemical reaction has been investigated by means of surface-enhanced Raman scattering (SERS) spectroscopy.[1−11] In particular, several SERS studies have been reported in the literature regarding the physicochemical properties of aromatic nitro molecules adsorbed on silver.[5−8] In most cases, 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 increase in intensity as a function of the laser illumination time, suggesting that the nitro molecules are subjected to photoreaction on the silver surface. For instance, the SERS spectral features of 4-nitrobenzenethiol (4NBT)[9,10] and 4-nitrobenzoic acid (4NBA)[11] on silver were found to be coincident with those of 4-aminobenzenethiol (4ABT) and 4-aminobenzoic acid (4ABA) on Ag, respectively. Much the same conclusion was derived not only from the X-ray photoelectron spectroscopy measurement but also from a coupling reaction conducted to form amide bonds.[9] By using such a photoreaction, we could prepare patterned binary monolayers on Ag with selectable surface chemical properties.[9] Site-specific chemical reactions and patterned crystal nucleation could subsequently be performed with those binary monolayers.

The source of hydrogen atoms in such surface-induced photoreduction of aromatic nitro molecules on silver has been claimed to be water or solvent molecules trapped inside the 4NBA and 4NBT monolayers rather than 4NBA and 4NBT themselves.[9,11] On the other hand, the reaction has been presumed to involve charge transfer from silver to the adsorbed aromatic nitro molecule.[11] It is well conceivable that if the energy difference between the Fermi level (EF) 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. The electron transfer step would then be a direct, optically induced charge transfer from the Fermi level to the low-lying lowest unoccupied molecular orbital of the adsorbate–silver complex.[9]

Silver thiolate (AgSR) and silver carboxylate (AgCO_2R) are one class of organic–inorganic heterostructured materials possessing a layered structure.[12−18] Upon heating, AgSR and AgCO_2R undergo dramatic structural changes, producing thiol or acid-derivatized Ag nanoparticles.[13,19−24] Ag nanostructures are also produced by irradiation with a visible laser, suggesting that AgSR and AgCO_2R can be used as a photoimaging material.[25,26] In this investigation, silver 4-nitrobenzenethiolate (Ag-4NBT) was chosen as one of the model silver thiolates possessing nitro functional groups. Ag-4NBT has two kinds of reaction sites: one is the silver ion and the other is the nitro group. The first concern of this work was to understand the photoreduction occurring under irradiation with visible lasers. The second concern was to clarify,
if the nitro-to-amine group conversion took place, the sources of hydrogen atoms to form amine groups. In fact, we confirmed that 4ABT-derivatized Ag nanoparticles are produced upon irradiation by an argon ion laser (at 514.5 nm) on Ag-4NBT. In addition, the photo-induced nitro-to-amine conversion is found to occur several times faster in ambient than in vacuum conditions. Therefore, the water or solvent molecules trapped inside the Ag-4NBT must be the primary H-source. Nonetheless, not only the occurrence of photolysis even in vacuum conditions but also the observation of the intense Raman background due to amorphous carbon formation dictated to include the possibility of benzene ring as the H-source to form amine groups by irradiation with a visible laser.

**Experimental**

Silver nitrate (99.8%), 4-nitrobenzenethiol (4NBT, 80%), 4-aminobenzenethiol (4ABT, 97%) and silver powder (μAg, >99.9 + %) with a nominal particle size of 2–3.5 μm were purchased from Aldrich and used as received. Unless specified, other chemicals were reagent grade. Highly pure water whose resistivity was greater than 18.0 MΩ·cm (Millipore Milli-Q System) was used throughout. To prepare Ag-4NBT, a methanolic solution of AgNO₃ (2 mmol, 20 ml) was added dropwise to an equimolar 1:1 mixture of 4NBT in methanol (20 ml). The mixture was stirred vigorously during preparation; the reaction was actually carried out in an Al foil-wrapped flask to minimize light exposure. After 2 h of vigorous stirring, the resulting orange colored solid was filtered, washed thoroughly with water and methanol, and finally dried in air. To confirm the source of hydrogen atoms in the photoreduction of Ag-4NBT, the residual water vapor or solvent molecules trapped inside Ag-4NBT salt were more thoroughly excluded at first by drying the sample at 150 °C for 48 h. Then the sample was placed in a capillary, dried again in vacuum about 10⁻² Torr, and finally sealed with a butane flame. For a comparative study, 4NBT and 4ABT were separately adsorbed onto μAg powders. Initially, 0.050 g of silver powder was placed in a small vial into which 1.5 ml of 1 mM ethanolic 4NBT or 4ABT was added. After 3 h, the liquid phase was decanted. The remaining solid powders were subsequently washed with excess ethanol and left to dry in a vacuum for 2 h.

Raman spectra were obtained using a Renishaw Raman system model 2000 spectrometer equipped with an integral microprobe (Olympus BH2-UMA). The 514.5 nm radiation from a 20-mW air-cooled argon laser (Melles-Griot Model 351MAS20) was used as the excitation source. Raman scattering was detected with 180° geometry using a Peltier-cooled (−70 °C) CCD camera (400 × 600 pixels). A glass capillary (KIMAX-51) with an outer diameter of 1.5–1.8 mm was used as a sampling device, but when it was needed to reduce photolysis, samples made into pellets were spun at 3000 rpm during the Raman spectral measurement. The data acquisition time was usually 30 s. The holographic grating (1800 grooves/mm) and the slit permitted a spectral resolution of 1 cm⁻¹. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm⁻¹. The Raman spectrometer was interfaced to an IBM-compatible PC, and the spectral data were analyzed using Renishaw WinR software, version 1.2, based on the GRAMS/32C suite program (Galactic Industries). Field emission scanning electron microscopy (FE-SEM) images were obtained with a JSM-6700F field emission scanning electron microscope operated at 10.0 kV. Transmission electron microscopy (TEM) images were acquired on a Hitachi H-7600 transmission electron microscope operated at 100 kV. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained with a TA Instrument 2050 thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of 10 °C/min.

**Computational**

On one hand, a two-dimensional (2D) correlation analysis was carried out for a series of Raman spectra of Ag-4NBT taken as a function of laser exposure time in ambient and vacuum conditions. On the other hand, a quantum mechanical calculation was carried out for an isolated Ag-4NBT molecule. Density functional theory (DFT) and time-dependent DFT with B3LYP exchange correlation functionals were adopted for the calculations of ground and excited state molecular properties, respectively. In order to properly describe heavy element, effective core potential SKJC basis set in combination with diffuse functions and one set of polarization functions was used, which is referred to as SKJC+(d). All calculations reported here were performed with the general atomic and molecular electronic structure system (GAMESS).

**Results and Discussion**

Figure 1 shows a typical FE-SEM image of the synthesized Ag-4NBT salt. Micrometer-sized platelets were identified. Bokhonov et al. reported that long-chain silver carboxylates are photocatalytically decomposed into silver nanoparticles under UV irradiation. Yonezawa et al. showed that a silver film composed of silver clusters could be obtained from the photolysis of silver alginates under UV irradiation. These reports suggest that silver carboxylates can be transformed to nanosized silver particles upon irradiation by UV light. It is indeterminate, however, whether Ag nanoparticles can also be produced by the irradiation of visible light onto Ag-4NBT. If Ag nanoparticles are produced by visible light irradiation, the organic moiety, i.e., 4NBT, may also be subjected to photochemical reaction. It can be expected from our recent SERS observations that the nitro-to-amine group conversion takes place for 4NBT on nanostructured silver by irradiation with an argon ion laser at 514.5 nm. In the earlier work, the photoconversion efficiency was found to be highly dependent on the extent of surface roughness, i.e., the atomic and nanoscale roughnesses, which are intimately associated with the chemical and electromagnetic enhancement sites in SERS, respectively. Separately, we also found earlier that the Ag nanoparticles physically in contact with the self-assembled monolayers (SAMs) of 4NBT on Au could induce the photolytic reduction of the 4NBT moiety simply by irradiation with 514.5 nm laser in ambient conditions. Based on these observations, we have examined the visible light response of Ag-4NBT by Raman spectroscopy.

Figure 2(a) and (b) shows the normal Raman (NR) spectra of pure 4NBT in its neat solid state and Ag-4NBT salt, respectively. During the measurement of the latter spectrum, a pelletized Ag-4NBT sample was spun at 3000 rpm in order to minimize any possible photoreaction. The NR spectrum of pure 4NBT was nearly the same as the Raman spectrum of Ag-4NBT salt taken under spinning condition, except that the S–H stretching band is seen at 2548 cm⁻¹ in the neat solid state spectrum but is completely missing in the Ag-4NBT salt spectrum.
The Raman spectral features of Ag-4NBT obtained in the static condition were significantly different from those obtained under spinning. In Fig. 3(b) are shown the Raman spectra of Ag-4NBT salt taken consecutively under exposure to an argon ion laser at 514.5 nm for 0–30 min; the sampling area was ∼1 µm² with the power at 0.2 mW. For comparison, the Raman spectrum taken under spinning conditions (the same as that in Fig. 2(b)) is reproduced in Fig. 3(a). Dramatic differences are identified in the spectral region of 1100–1500 cm⁻¹. As indicated using arrows in Fig. 3(b), several new peaks are emerging, for instance, at 1439, 1392, and 1145 cm⁻¹, while a peak at 1332 cm⁻¹ quickly weakens as the laser exposure time increases. Because the 1332 cm⁻¹ peak can be assigned to ν₇(NO₂), its decrease in intensity indicates that a certain photoreaction occurs at the nitro group of 4NBT. For reference, the SERS spectrum of 4-ABT adsorbed on µAg powders obtained also using an argon ion laser at 514.5 nm line is shown in Fig. 3(c). The peaks at 1572, 1439, 1392, and 1145 cm⁻¹ are due to the ν₈b, ν₁₉b, ν₃, and ν₉b modes of the 4ABT benzene ring, respectively, while the peak at 1078 cm⁻¹ is due to the ν₇a mode, related to the C–S bond stretching vibration. It is evident that the new peaks in Fig. 3(b) are caused by 4ABT, indicating that 4NBT in Ag-4NBT is converted to 4-ABT by the irradiation with 514.5 nm radiation. These observations suggest that Ag nanoparticles have indeed been produced from Ag-4NBT upon irradiation by the argon ion laser and that the nitro-to-amine group photoconversion has subsequently taken place on nanosized Ag particles.

To confirm the production of nanosized silver particles, a piece of pelletized Ag-4NBT that had been exposed to the 514.5 nm line of an argon ion laser for 10 s was immersed in a chloroform–methanol mixture, and then the mixture was shaken gently after which the decanted solution was dropped onto a copper grid for the TEM measurement. As can be seen in Fig. 4, nanosized silver particles...
are clearly observed. The sizes are polydisperse and the shapes are quite irregular. Some particles are also seen to be present in an aggregated state. These data confirm that the spectra in Fig. 3(b) must be the SERS spectra that have been derived from the photolysis of Ag-4NBT to give aggregated Ag nanoparticles followed by nitro-to-amine photoconversion on these particles.

Then, two particular questions are raised: namely, how the reaction proceeds and what the hydrogen source is. The detailed mechanism of the nitro-to-amine conversion on Ag is a matter of conjecture, but photoelectrons are known to be readily ejected from Ag even by a visible laser. It has been observed by Fedurco et al.\(^\text{44}\) that the surface roughening of Ag results in a drastic increase of the photocurrent for the wavelength close to the surface plasmon frequency. On the other hand, it is known that when photoreaction occurs for aromatic nitro molecules in a solution phase, a chemical species from which hydrogen atom(s) can be abstracted is needed.\(^\text{45}\) For a similar photoreaction to occur in air, water in ambient condition has been claimed to act as a hydrogen source.\(^\text{46}\) To confirm whether water is the hydrogen source in the photoreaction process of Ag-4NBT under the irradiation of an argon ion laser, a control experiment was carried out.

According to the TGA and its first-derivative traces as shown in Fig. 5, the decomposition of Ag-4NBT proceeds at around 310 °C and the actual mass loss amounts to 35%. The mass loss event is presumably associated with the formation of 4NBT-capped silver nanoparticles caused by the decomposition of Ag-4NBT. Consulting these TGA data, a minute amount of Ag-4NBT was dried at 150 °C for 48 h to remove any water or solvent molecules trapped inside the Ag-4NBT, and then placed in a capillary, drying further in vacuum (at \(10^{-2}\) Torr) for 24 h, after which the capillary was sealed off with a butane flame.

Figure 6(a) and (b) shows a series of Raman spectra taken as a function of laser exposure time for Ag-4NBT kept in ambient and vacuum conditions, respectively; when taking the spectra, the irradiation of an argon ion laser, a control experiment was carried out. As implied in the above discussion, photoproduction of SERS-active nanoaggregates from Ag-4NBT is a complex process consisting of photoreduction of Ag\(^+\) and diffusion. We presume that the photolysis of AgSR occurs via the production of organic radicals:

\[
\text{AgSR} \longrightarrow \text{Ag}^0 + \text{R} - \text{S} \longrightarrow \text{Ag}^0 + 1/2(\text{R} - \text{S} - \text{S} - \text{R}) \quad (1)
\]

The Ag atoms will then diffuse to one another to form Ag nanoaggregates. It is well known that organic disulfides are adsorbed very favorably onto Ag as monothioliates.\(^\text{48}\) This implies that \(\text{R} - \text{S} - \text{S} - \text{R}\) formed via photolysis will immediately adsorb onto Ag nanoaggregates as monothiolates, resulting in the appearance of an SERS spectrum of a thiol (RSH) on Ag. Presumably, it will take time is needed to see the distinct spectral changes. This would indicate on one hand that the photolysis itself has nothing to do with water or other solvents adversely trapped inside the salt. The present observation might also indicate that the hydrogen atoms in the photogenerated amine groups originated from the benzene ring of 4NBT on Ag. If so, it is very remarkable that C–H bond scission can take place even for aromatic rings by the irradiation with a visible laser. This does not necessarily mean that the photolysis of Ag-4NBT is free from the environment. We are attempting to synthesize fully deuterated Ag-4NBT to better clarify these problems.

Although the photolysis takes place even under vacuum conditions, the exact mechanism by which Ag nanoaggregates are formed from Ag-4NBT is a matter of conjecture. In the UV–vis spectrum of Ag-4NBT dispersed in ethanol, two broad bands were identified at 283 and 418 nm (data not shown). In the visible region, only a scattering background monotonically increasing toward short wavelengths was identified. In the UV–vis spectra of aliphatic thiol–silver complexes such as a 1:1 mercaptoethanol–silver (AgMET) complex, two absorption bands were observed similarly at 306 and 368 nm.\(^\text{47}\) This may suggest that the two UV–vis absorption bands of Ag-4NBT are associated with the Ag–S–C moiety. In this light, the irradiation with an UV laser would be required for the cleavage of the Ag–S bond. The production of neutral Ag from Ag-4NBT in this work might have then occurred via a multiphoton absorption process. A single photon dissociation process by an argon ion laser cannot be completely ignored, however, considering an ab initio quantum mechanical calculation. The highest molecular orbital (HOMO) of an isolated Ag-4NBT molecule is computed to be the p orbital of the S atom, while the lowest unoccupied molecular orbital (LUMO) is confined to Ag. A charge transfer transition from sulfur to silver may then be supposed to occur. When three Ag atoms are modeled to be bound to a single 4NBT moiety, the net charges of the Ag and S atoms are determined to be +0.522 and –0.380 e, respectively, in the ground state, but they become reduced to +0.250 and –0.231 e, respectively, in the first excited state. The ionic character of the Ag–S bond thus considerably diminishes upon an electronic excitation. The Ag–S bond is also enlarged by ~0.05 nm upon excitation, otherwise with no noticeable structural change. Most importantly, the first vertical electronic excitation energy is computed to be 2.616 eV, corresponding to 474 nm photon energy. The computed excitation energy is fairly close to the photon energy used as the excitation source in this work (514.5 nm). Referring to these quantum calculations, the 418-nm band observed in the UV–vis spectrum of Ag-4NBT may be assumed to be too broad to extend toward the wavelength of the laser light.

Consulting these TGA data, a minute amount of Ag-4NBT was dried at 150 °C for 24 h, after which the capillary was sealed off with a butane flame.

Figure 5. TGA (full line) and its first derivative traces (dotted line) of Ag-4NBT.
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Figure 6. A series of Raman spectra of Ag-4NBT taken as a function of laser exposure time in (a) ambient and (b) vacuum conditions; the power of the 514.5 nm radiation at the sampling position was $\sim 0.2$ mW, with the spectral acquisition time was 30 s.

A certain amount of time to form Ag nanoaggregates that are large enough to show strong SERS effects. The rate of surface diffusion may then be an important factor to see intense SERS spectra.

We also applied two-dimensional (2D) correlation analysis\(^{[27]}\) for the series of Raman spectra of Ag-4NBT taken as a function of laser exposure time in ambient and vacuum conditions (shown in Fig. 6(a) and (b), respectively) to establish the sequence between the photoproduction of neutral Ag and the nitro-to-amine group photoconversion. Unfortunately, the sequence between the formation of Ag and the photoreduction of nitro group could not be resolved from the synchronous and asynchronous 2D correlation spectra for 1000–1800 cm\(^{-1}\) regions generated from a series of Raman spectra of Fig. 6 (data not shown). As long as Ag-4NBT was under spinning, neither the decrease of the NO\(_2\) stretching peak nor the appearance of the 4ABT peaks took place, suggesting that Ag-4NBT did not convert directly to Ag-4ABT to produce, subsequently, 4ABT-adsorbed Ag nanoparticles. Upon irradiation by an argon ion laser, Ag-4NBT would then be subjected to two almost simultaneous photoprocesses, namely the formation of Ag nanoparticles followed by nitro-to-amine conversion.

Looking at the spectral changes in Fig. 6, the nitro-to-amine conversion appears to occur several times faster in ambient conditions than in vacuum. This may be more evident in Fig. 7 in which are shown the relative intensities of the b\(_2\)-type modes of 4ABT as well as the \(v_s(NO_2)\) mode of 4NBT as a function of the laser exposure time. Presumably, the thin water layers that must be present (in ambient condition) inside Ag-4NBT might play crucial roles not only as a diffusion medium for the Ag-to-SAM electron transfer but also as a source of hydrogen atoms in the nitro-to-amine conversion of 4NBT on Ag. It would then be informative to recall a few recent reports on the visible light-induced formation of Ag nanoparticles.\(^{[49,50]}\)

Canameras et al.\(^{[49]}\) reported the preparation method of immobilized Ag nanoparticles as SERS substrates by photoreduction of Ag\(^+\) using an argon ion laser (514.5 nm) coupled with a micro-Raman system. Ag nanoparticles were formed in the AgNO\(_3\)(aq)/glass interface exclusively in the absence of other reagents. Abid et al.\(^{[50]}\) also reported a fabrication method of silver nanoparticles by direct laser irradiation (operating at 500 nm with a pulse duration of 6 ns and a repetition rate of 10 Hz) in aqueous solution containing only a silver salt and surfactants. Although not definitive, the formation of silver nanoparticles in these cases is presumed to occur through the photolysis of water as well as the formation of radicals in the solution. Near the focal point, the energy density would be high enough for multiphoton processes to take place. The solvated electrons and the hydrogen radicals must then be effective reducing agents.

As shown in Fig. 7, the Raman intensities do not follow the usual simple exponential decay or growth. At the early stages of exposure time, however, the decay time, defined as the time the Raman intensity reduced to 1/e of the initial value, could be determined to be 3.3 and 19 min for \(v_s(NO_2)\) mode in ambient and
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References


Conclusions

We have observed the visible laser-induced transformation of Ag-4NBT salt into 4-ABT-adsorbed Ag nanoaggregates. Specifically, the Raman spectrum of Ag-4NBT changed over time under exposure to the 514.5 nm radiation of an argon ion laser, eventually becoming the same as the SERS spectrum of 4ABT on Ag substrate. This observation suggests that Ag nanoparticles have been produced from Ag-4NBT upon irradiation by an argon ion laser and that the nitro-to-amine group photoconversion has taken place on nanosized Ag particles. These photolysis reactions occur several times faster in ambient than in vacuum conditions. Any water possibly present and/or solvent molecules present under ambient conditions must be the primary H-atoms source and have played certain roles in the photolysis of Ag-4NBT, but what is invaluable was the observation that a similar photolysis has taken place as well in vacuum, thus leading to conclude that the benzene ring hydrogen atoms of 4NBT might also be the H-atoms source for the nitro-to-amine group conversion.