Surface-Enhanced Raman Scattering of Benzyl Phenyl Sulfide in Silver Sol: Excitation-Wavelength-Dependent Surface-Induced Photoreaction

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Ag sol prepared by the citrate-reduction method is a promising surface-enhanced Raman scattering (SERS) substrate that can be activated not only by 514.5 nm radiation but also by 568 nm and 632.8 nm radiation. Using these facts, the SERS of benzyl phenyl sulfide (BPS) in silver sol is revisited to assess the excitation-wavelength dependence of the C−S bond scission of BPS on Ag to produce surface-bound benzenethiolate. The SERS spectral features clearly indicate that the C−S bond cleavage of BPS on Ag occurs far more favorably under green light at 514.5 nm than under red light at 632.8 nm. The laser power-dependence study suggests further that the photodissociation of BPS proceeds on Ag via an initial single-photon absorption process rather than a multiphoton absorption one.

Introduction

Noble metallic nanostructures exhibit a phenomenon known as surface-enhanced Raman scattering (SERS) in which the scattering cross sections are dramatically enhanced for molecules adsorbed thereon.[1] 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.[2–6] The CHEM enhancement mechanism, contributing an additional EF = $10^1–10^2$, 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.[7–9] Both mechanisms suggest the possibility of enhanced absorption and enhanced photochemistry for surface-adsorbed molecules.

Direct observation of a surface-enhanced photochemical reaction has indeed been reported.[10–24] Aromatic sulfides such as benzyl phenyl sulfide (BPS) and dibenzyl sulfide (DBS) adsorbed on silver undergo surface reactions involving facile cleavage of C−S bonds by 514.5 nm radiation.[15–19] These molecules are recently found not to undergo such reactions on a gold surface with visible light.[19,24] As another example, 4-nitrobenzoic acid (4-NBA) and 4-nitrobenzenethiol (4-NBT) adsorbed on silver are converted in ambient conditions to 4-aminobenzoic acid (4-ABA) and 4-aminobenzenethiol (4-ABT), respectively, upon irradiation with an argon ion laser (514.5 nm).[20–23,35] These surface-induced photoreactions can be used in the fabrication of patterned binary organic monolayers on silver substrates.[19,21]

In our earlier SERS experiments, Ag sol was prepared by reduction of Ag(NO₃) with borohydride.[16–18] The Ag sol thus prepared was aggregated well upon the addition of adsorbate

molecules. The aggregated Ag sol then showed large EF under the excitation of an argon ion laser at 514.5 nm, but the EF achievable by a He/Ne laser at 632.8 nm was, however, too small to observe the surface-bound species. It has thus remained unanswered whether surface-induced photoreaction will or will not occur for aromatic sulfides on Ag under the irradiation of a He/Ne laser. Recently, Maxwell et al.[25] reported that nanostructured thin films fabricated using Ag sols prepared by citrate reduction showed large EF of SERS not only under 514 nm radiation but also under 633 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, whereas the films with >100 nm particles are most efficient at 633 nm excitation. These suggest that Ag colloids prepared by the citrate-reduction procedure will be SERS-active not only under 514.5 nm radiation but also under 568 and 632.8 nm radiation. The SERS of BPS in silver sol is thus revisited to see the excitation-wavelength dependence of the C−S bond scission of BPS on Ag.

Experimental Section

The Ag sol was prepared by following the recipes of Lee and Meisel.[26] Namely, 45 mg of Ag(NO₃) (Aldrich) was initially dissolved in 250 mL of water, and the solution was brought to a boil. A solution of 1% sodium citrate (5 mL) was then added to the AgNO₃ solution under vigorous stirring, and boiling was continued for ∼30 min. The resulting Ag sol solution was stable for several weeks. To 1 mL of Ag sol solution was added 10^{-3} M aqueous solution of benzyl phenyl sulfide (BPS) dropwise to a final concentration of 10^{-5} M with a micropipet. The aggregation of Ag sol was facilitated by adding aqueous BaCl₂ to a final concentration of 10^{-4} M. When the grayish-yellow sol became bluish-green, aqueous poly(vinylpyrrolidone) (PVP, MW 360000) was added into the sol to a final concentration of ∼1 wt % as a colloid stabilizer. BPS was purchased from Aldrich and used as received. The chemicals otherwise specified were reagent grade, and ultrapure water, of resistivity greater

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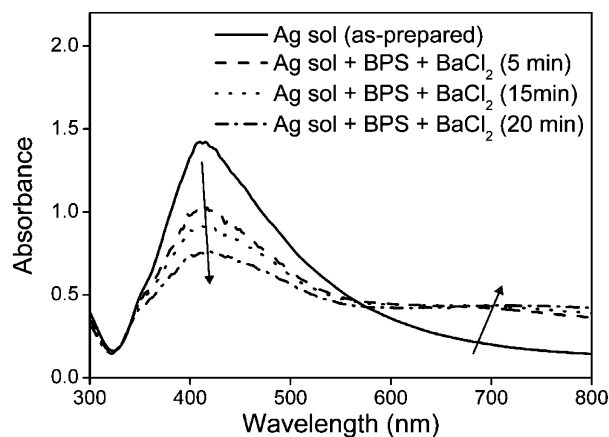
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Figure 1. Time-dependent UV/vis absorption spectra of Ag sol after the addition of BPS and BaCl₂ up to 10^{-5} and 10^{-4} M, respectively.

Figure 2. TEM images of Ag sols (a) before (i.e., as-prepared) and (b) after adding BPS and BaCl₂ up to 10^{-5} and 10^{-4} M, respectively. The inset in (a) shows the magnified image.

than 18.0 MΩ·cm (Millipore Milli-Q System), was used in making aqueous solutions.

Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer equipped with an integral microscope (Olympus BH2−UMA). The 514.5 nm line from a 20 mW Ar⁺ laser (Melles-Griot Model 351MA520) or the 568 nm line from a 20 mW Ar⁺/Kr⁺ laser (Melles-Griot Model 35KAP431) or the 632.8 nm line from a 17 mW He/Ne laser (Spectra Physics Model 127) was used for the excitation source of the Ag sol SERS experiment. Raman scattering was detected with 180° geometry with a Peltier cooled (−70 °C) charged-coupled device (CCD) camera (400 × 600 pixels). A glass capillary (KIMAX-51) with an outer diameter of 1.3−1.5 mm was used as a sampling device. The laser beam was focused onto a spot approximately 2 μm in diameter with an objective microscope on the order of ×20. When it was needed to minimize the laser-induced changes in the SERS spectra, sample solutions flowed at different flow rates through the glass capillary using a syringe pump (Sage Instrument Model 341). The data acquisition time was usually 90 s for the silver sols. 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, and the accuracy of the spectral measurement was estimated to be better than 1 cm⁻¹. The Raman spectrometer was interfaced with an IBM PC, and the spectral data were analyzed with Renishaw WiRE software v. 1.2 based on the GRAMS/32C suite program (Galactic).

To estimate the size of silver colloidal particles, we obtained transmission electron microscope (TEM) images with a JEM-200CX transmission electron microscope at 200 kV after placing a drop of the as-prepared sol or the sampling solution, that is, sol with BPS added and then PVP stabilized ready for SERS measurement, onto Ni/Cu grids. UV/vis spectra of the sol solutions were obtained with a SCINCO S-2130 spectrometer.

Results and Discussion

As can be seen from the solid line in Figure 1, the UV/vis absorption maximum of the as-prepared Ag sol occurs at 412 nm, which must arise from the surface plasmon absorption of Ag nanoparticles. Upon the addition of BPS and BaCl₂ into the sol, a dramatic spectral change takes place. The position of the absorption maximum gradually red shifts, and then the spectrum becomes smooth over 500 nm, with a long tail extending up to ∼800 nm. These spectral changes can be attributed to the aggregation of Ag nanoparticles caused by the reduction of the
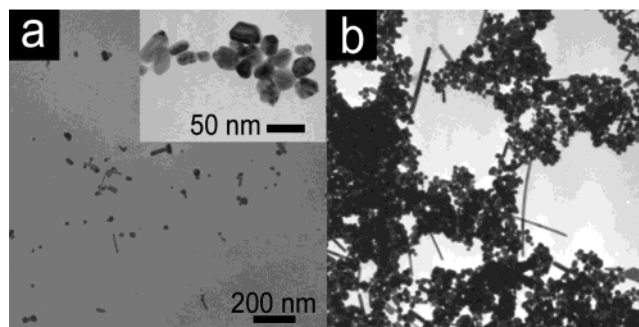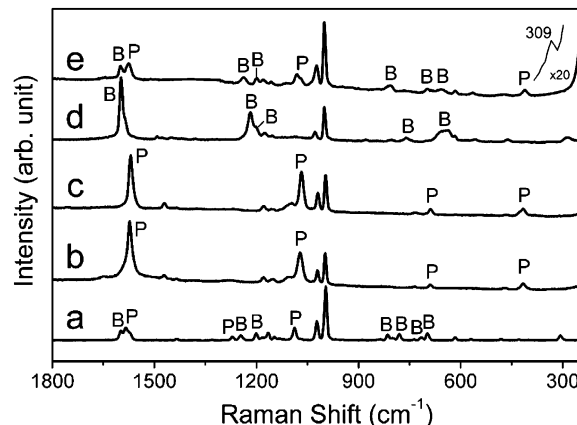

Figure 3. Raman spectra obtained using 514.5 nm radiation as an excitation source: (a) NR spectrum of BPS in neat state and (b) SERS spectrum of BPS in static Ag sol; SERS spectra of (c) benzenethiol and (d) benzyl mercaptan in Ag sol; (e) SERS spectrum of BPS in Ag sol in flowing conditions. Vibrational modes due to benzylthio and phenylthio (benzenethiolate) moieties are labeled as "B" and "P", respectively.

negative charge on the colloidal particles.[27,28] In other words, Ag particles in the aqueous colloidal dispersion bear a negative charge due to the adsorbed citrate. Aggregation is induced by the newly added adsorbates, which displace the adsorbed citrate ions, thus reducing the charge on the particles to the point where collisions occur as a result of diffusional motion. Recalling the EM enhancement mechanism,[2−6] the sol would then show SERS activity not only under the 514.5 nm radiation but also under the 632.8 nm radiation. In light of this, PVP was added to the sol as a colloid stabilizer when the sol exhibited a broadened absorbance over 500 through 800 nm. The PVP-stabilized sol was used as the sampling solution in the subsequent SERS measurements.

Figure 2a shows the TEM image of the as-prepared Ag sol. The particles are rather polydisperse, and their average diameter is estimated to be 35 ± 13 nm (see the inset in Figure 2a). Figure 2b shows the TEM image of a PVP-stabilized sampling solution, i.e., BPS, BaCl₂, and PVP-added Ag sol. It is seen that Ag particles are present in a highly aggregated state. The UV/vis absorption spectral feature in Figure 1 must then be closely associated with the presence of such aggregates.[29]

Figure 3a shows the normal Raman (NR) spectrum of BPS in the neat state, obtained using the 514.5 nm line of an Ar⁺ laser as the excitation source; vibrational modes due to benzylthio and phenylthio moieties are labeled in Figure 3 as "B" and "P", respectively. Figure 3b shows the SERS spectrum of BPS in Ag sol, obtained also using 514.5 nm radiation. Because the latter spectrum was obtained under static conditions,

TABLE 1: Vibrational Assignments for the SERS Peaks in Figure 3[a]

BPS (NR) Figure 3a	BPS/Ag[b,c] Figure 3b	BT/Ag[d] Figure 3c	BZM/Ag[e] Figure 3d	BPS/Ag[c,f] Figure 3e	assignments[g]
306				309 vw, sh	CSC bending
401 vw	416	417		412	7a (P)
569 vw			557 vw	564 vw	16b (B)
615	613 vw	617 vw	617	616	6b (B, P)
			657	657	CS stretching (B)
694 sh	689	689			6a (P)
697					CS stretching (B)
715			702 sh	698	4 (B)
801 sh			802 vw	808	CH$_2$ rocking (B)
814			815 sh	815 sh	1 (B)
996	1001	1001	1000	1001	12 (B, P)
1023	1022	1023	1028	1023	18a (B, P)
1088	1073	1070		1082	1 (P)
1165	1156	1156	1155	1157	9b (B, P)
1182	1181	1180	1177	1179	9a (B, P)
1200			1201 sh	1202	13 (B)
1246			1219		CH$_2$ wagging (B)
				1237	CH$_2$ twisting (B)
1272					3 (P)
	1473	1475			19a (P)
1584	1575	1573		1576	8a (P)
			1586		
1599			1597	1599	8a (B)

[a] Units in cm^{-1}; BPS = benzyl phenyl sulfide; BT = benzenethiol; BZM = benzyl mercaptan; vw = very weak; sh = shoulder. [b] SERS spectrum of BPS in Ag sol in static conditions. [c] Assigned on the basis of refs 17 and 18. [d] Assigned on the basis of ref 31. [e] Assigned on the basis of ref 32. [f] SERS spectrum of BPS in Ag sol in flowing conditions. [g] Abbreviations: B = benzylthio moiety; P = phenylthio moiety.

surface-induced photoreaction should have occurred on silver to produce benzenethiolate and benzyl radical.[19,30] Indeed, all the characteristic peaks of the benzylthio moiety of BPS are completely missing in Figure 3b, and the actual spectrum is essentially the same as the SERS spectrum of benzenethiol shown in Figure 3c. The disappearance of bands due to the benzylthio moiety in Figure 3b can be evidenced further by comparison with the SERS spectrum of benzyl mercaptan shown in Figure 3d. If the sampling solution is flowed using a syringe pump, the surface-induced photoreaction is considerably reduced. Some of the bands in the SERS spectrum may be shifted from the corresponding bands in the NR spectrum, but the peaks due to both the phenylthio and benzylthio moieties are clearly identified in the SERS spectrum, as in Figure 3e, which is obtained by flowing the sol at a rate of 0.06 mL/s through a glass tube with a ~1 mm inner diameter; this indicates that the chemical species responsible for the SERS spectrum is adsorbed BPS. All of these spectral features observed with an Ar$^+$ laser at 514.5 nm are consistent with those in the earlier report.[17,18] The vibrational spectral assignments of the peaks in Figure 3 are summarized in Table 1.

The NR and SERS spectra of BPS as well as the SERS spectra of benzenethiol and benzyl mercaptan in Ag sol obtained using 568 nm radiation as an excitation source are collectively shown in Figure 4. The NR spectral pattern in Figure 4a is little different from that in Figure 3a. The SERS spectral feature of BPS in static Ag sol in Figure 4b is, however, quite different from its counterpart in Figure 3b obtained using 514.5 nm radiation as an excitation source. The SERS spectrum of BPS in Figure 4b differs also from that of benzenethiol in Figure 4c as well as from the SERS spectrum of benzyl mercaptan in Figure 4d. We have already confirmed that BPS is readily converted on Ag to benzenethiolate upon irradiation by an Ar$^+$ laser at 514.5 nm. The observation made herein suggests that BPS is not decomposed readily on Ag by the 568 nm radiation. In fact, assuming that the SERS spectrum obtained in flowing conditions, i.e., Figure 4e, is wholly due to unreacted BPS on
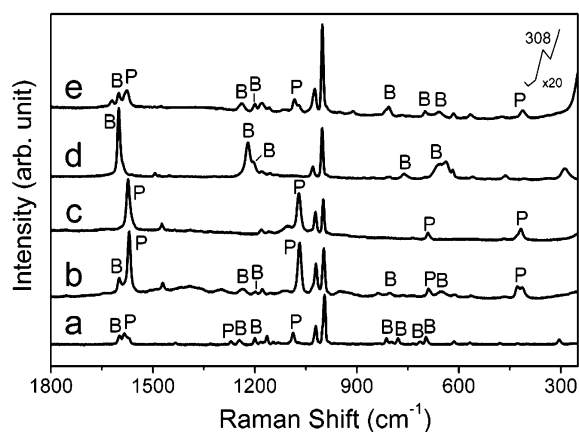

Figure 4. Raman spectra obtained using 568 nm radiation as an excitation source: (a) NR spectrum of BPS in neat state and (b) SERS spectrum of BPS in static Ag sol; SERS spectra of (c) benzenethiol and (d) benzyl mercaptan in Ag sol; (e) SERS spectrum of BPS in Ag sol in flowing conditions. Vibrational modes due to benzylthio and phenylthio (benzenethiolate) moieties are labeled as "B" and "P", respectively.

Ag, the static sol SERS spectrum in Figure 4b has to be attributed to a mixture of ~34% BPS and ~66% benzenethiolate on Ag, on the basis of the relative peak intensities at 1600 cm^{-1} (B) and 1573 cm^{-1} (P). This illustrates clearly that the surface-induced photoreaction of BPS on Ag is strongly dependent on the wavelength of the excitation light.

The above observation suggests that BPS on Ag will be negligibly affected by the irradiation of a He/Ne laser at 632.8 nm. This can indeed be confirmed from the NR and SERS spectra of BPS, benzenethiol, and benzyl mercaptan in Figure 5, obtained using 632.8 nm radiation as an excitation source. The SERS spectral pattern in Figure 5b, which was obtained in static conditions, is almost the same as that in Figure 5e, which was obtained in flowing conditions. On the other hand, any characteristic benzenethiolate peaks are barely identified in Figure 5b, indicating the unfavorable photoreaction of BPS on
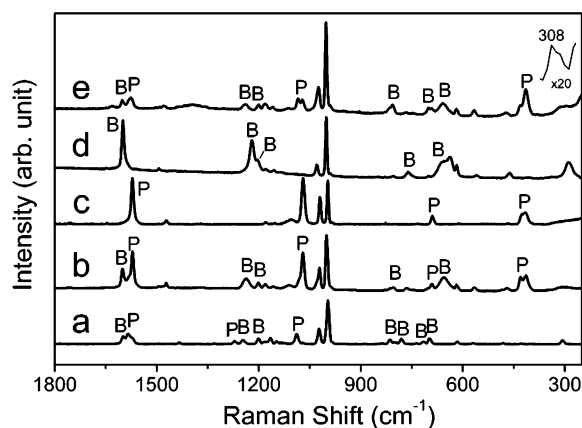
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Figure 5. Raman spectra obtained using 632.8 nm radiation as an excitation source; (a) NR spectrum of BPS in neat state and (b) SERS spectrum of BPS in static Ag sol; SERS spectra of (c) benzenethiol and (d) benzyl mercaptan in Ag sol; (e) SERS spectrum of BPS in Ag sol in flowing conditions. Vibrational modes due to benzylthio and phenylthio (benzenethiolate) moieties are labeled as "B" and "P", respectively.
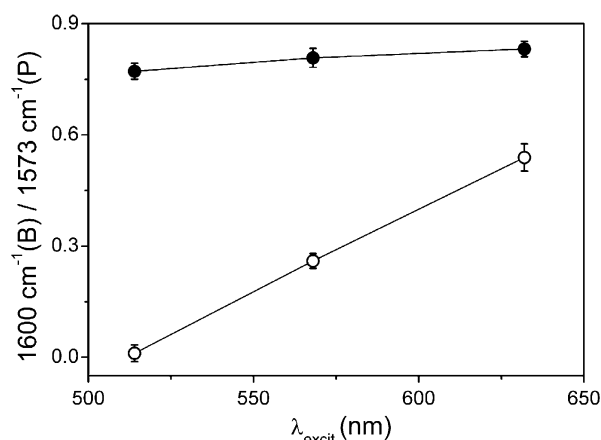

Figure 6. Relative peak intensities of representative vibrational modes of benzylthio and phenylthio moieties (i.e., 1600 cm^{-1} (B)/1573 cm^{-1} (P)) versus the excitation wavelength for the SERS spectra of BPS obtained in static condition (marked as "open circle") as well as in flowing condition (marked as "filled circle").

Ag by light with longer wavelengths. The infeasibility of the photoreaction at longer wavelengths can also be gleaned from the SERS spectral variations plotted collectively against the excitation laser wavelength. Figure 6 shows the relative peak intensities of two representative benzylthio and phenylthio vibrational bands, i.e., the peaks at 1600 cm^{-1} (B) and 1573 cm^{-1} (P), versus the excitation wavelength for the SERS spectra of BPS obtained in static conditions (marked as "open circle") as well as in flowing conditions (marked as "filled circle"); a value of "zero" corresponds to complete conversion of BPS to benzenethiolate on Ag. In fact, in static conditions, the intensity ratio steadily increases along with the increase in the excitation wavelength, whereas in flowing conditions, the ratio remains intact without variation. This clearly indicates that the photoreaction of BPS on Ag under green light must be far more effective than that under red light.

Although the surface-induced photoreaction of BPS on Ag occurs very effectively under green light, its detailed reaction mechanism is a matter of conjecture. The reaction may nonetheless be presumed to involve charge transfer from silver to the adsorbed molecule. 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
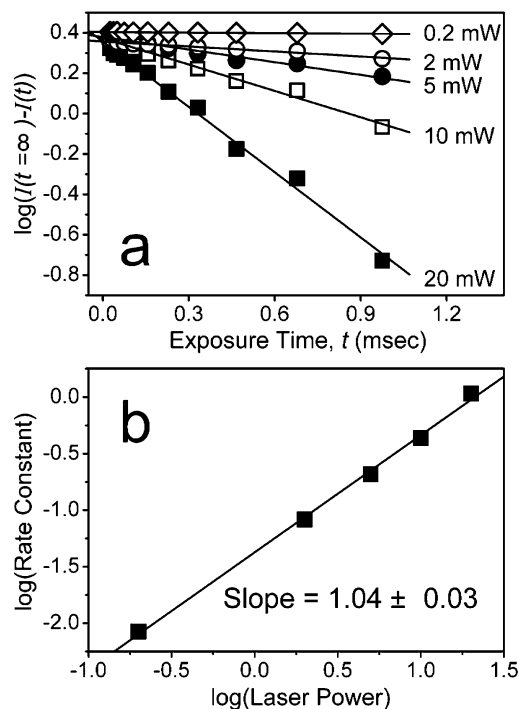

Figure 7. (a) Typical kinetic plot for the photodecomposition of BPS to benzenethiolate on Ag; $I(t)$ is the intensity of the product band at 1573 cm^{-1} after BPS-adsorbed Ag nanoparticles are irradiated with 514.5 nm radiation for time t by flowing through the sampling capillary at different rates. (b) Laser power dependence of C−S bond dissociation rate constant of BPS on Ag under 514.5 nm radiation.

excitation radiation, a resonant charge transfer from the metal to the excited state of the complex can take place.[7−9,33−36] The electron-transfer step would be a direct, optically induced charge transfer from the Fermi level to the lowest unoccupied molecular orbital of the adsorbate−silver complex. On the basis of these presumptions, we have conducted a series of power-dependence experiments at 514.5 nm to see whether such electron transfer proceeds via a single-photon absorption process or a multiphoton process. Figure 7a shows a kinetic plot for typical experimental results after background correction and normalization with respect to the peak (ν_{18a}) at 1023 cm^{-1}. Herein, $I(t=\infty)$ means the intensity of the product band at 1573 cm^{-1} due to benzenethiolate on Ag after prolonged irradiation whereas $I(t)$ is the intensity of the same band but measured at time t after the irradiation of the laser light at 514.5 nm; actually, the laser exposure time was controlled by changing the flow rate of the sample solution.[37] The surface concentration of the product seems to increase exponentially, attaining a plateau after prolonged exposure to the laser light. The decomposition of BPS on Ag is thus presumed to be a unimolecular first-order reaction. Recalling that the Raman intensity of the product (or reactant) band depends on its concentration,[1] a simple relationship between the SERS intensity of the product band and the exposure time t is given by

$$I \propto I_0 \exp(-kt) \tag{1}$$

where I_0 is the initial intensity of the reactant. The rate constant k, in general, depends on the laser power p, as $k = ap^n$, where n is the apparent number of laser photons required to initiate the photoreaction and a is a wavelength-dependent constant proportional to the absorption cross-section.[13,14] The dissociation rate constant is then estimated from the slope of the initial increasing part of the plot. A similar experiment was conducted

at different laser powers, i.e., 0.2, 2, 5, 10, and 20 mW. Figure 7b shows the laser power dependence of the photodissociation rate constant obtained. The slope of the log−log plot of the rate constant versus the laser power is determined to be 1.04 ± 0.03, implying that the photodissociation of BPS proceeds on Ag via an initial one-photon absorption step rather then via a two-photon (or more) absorption step. Even though the participation of a multiphoton process cannot be completely ruled out, it seems that the single-photon absorption step is the dominant mechanism in this case. The C−S bond scission of BPS on silver is thus thought to occur via the absorption of a visible photon that is in resonance with the low-energy tail of the broadened absorption band of the adsorbed species, which is deeply associated with the Fermi level of the metal as well as the low-lying excited state of the charge-transfer complex.

We have recently discovered that Ag nanoparticles physically in contact with organic films can induce, simply by irradiating with visible laser (e.g., at 514.5 nm) in ambient conditions, the photolytic reduction of the organic moiety, indicative of the usefulness of Ag nanoparticles acting as moderate photoelectron emitters.[22] It may then not be unreasonable that BPS can be decomposed to benzenethiolate on Ag even by the 568 nm radiation. We separately recorded the SERS spectrum of BPS in Au sol (obtained by citrate reduction) and concluded that BPS was hardly subjected to photodecomposition on Au by the 568 nm radiation (data not shown). This suggests that photo-decomposition via a single-photon absorption step is unfavorable on Au at least using a visible laser as an excitation source. Au nanoparticles seem also not to be an efficient photoelectron emitter, unlike with Ag nanoparticles.

In fact, the photoemission behavior of Ag is known to be different in many aspects from that of other metals.[38] The most remarkable difference regards the effect of surface roughening, which in the case of silver not only causes a dramatic enhancement of the photoyield for the wavelength close to the surface plasmon frequency but also leads to an important extension of the photoresponse toward longer wavelengths. Surface chemisorbed molecules such as pyridine and methyl-amine have also been found effective for the enhancement of photoemission of a roughened Ag film by lowering its work function from 4.3 to 2.5−2.8 eV.[39] This implies that the surface plasmon-mediated photoemission of Ag can effectively occur at the visible light excitation, e.g., 514.5 nm (∼2.5 eV). In this connection, it is well conceivable that the condition of surface plasmon resonance can be satisfied with visible light by the adsorbate-induced aggregation of Ag nanoparticles. In particular, when the Ag nanoparticles are appropriately aggregated to show a large EM effect, the photoelectron ejection efficiency will reach such a level as to induce chemical reduction of nearby functional groups. In the case of Au, its oxidation potential is significantly lower than that of Ag so that a noticeable photoemission can hardly occur with visible light excitation. With higher energy excitation, for instance, at 266 nm, photo-reactions of organic molecules readily occur even on the surface of gold, however.[19]

In summary, SERS spectra of BPS were obtained in silver sol to examine the excitation-wavelength dependence of their surface-induced photoreaction on silver. The C−S bond cleavage of BPS on Ag to produce benzenethiolate was confirmed to be very effective under green light at 514.5 nm. Although the photoreaction under red light at 632.8 nm seemed infeasible, the conversion of BPS to benzenethiolate took place moderately by up to ∼66% upon irradiation by laser light at 568 nm. This may reflect one of the characteristics of silver, enabling it to

function as an efficient photoelectron emitter. A separate laser power-dependence study suggested that the photodissociation of BPS on Ag should proceed via an initial single-photon absorption process rather than via a multiphoton absorption one.

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