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When the Signal Is Not from the Original Molecule To Be Detected: Chemical Transformation of *para*-Aminothiophenol on Ag during the SERS Measurement

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Abstract: Surface-enhanced Raman spectroscopy (SERS) has long been considered as a noninvasive technique that can obtain the fingerprint vibrational information of surface species. We demonstrated in this paper that a laser with a power level considered to be low in the traditional SERS measurement can already lead to a significant surface reaction. *para*-Aminothiophenol, an important probe molecule in SERS, was found to be oxidized to form 4,4′-dimercaptoazobenzene (DMAB) on a roughened silver surface during the SERS measurement. The assumption was confirmed experimentally by surface mass spectroscopy and SERS as well as electrochemistry of the synthesized DMAB, which agrees well with theoretical calculations. A defocusing method was used to avoid the laser induced surface reaction and perform reliable SERS characterization and identification, which can effectively avoid erroneous interpretation of the distorted experimental result.

To correlate the structure of molecules and interfaces with their functionalities, various methods including spectroscopic and microscopic ones, have been developed for a better understanding of systems.[1] As these methods usually rely on the interaction of an external excitation source, such as an electron and a photon, with the systems, a paradox often appears in an attempt to achieve higher sensitivity as well as temporal and spatial resolution: to avoid a change to the system, a small perturbation has to be used and the signal obtained will be weak; however, to achieve a higher sensitivity or resolution, a larger perturbation needs to be introduced, which may lead to a change in the structure of the species, and the signal obtained would not be from the species we are interested in.

Surface-enhanced Raman spectroscopy (SERS) can provide fingerprints of molecules with single-molecule sensitivity.[2] It has found wide application in chemistry, physics, material science, biosciences, and medical sciences and promoted our understanding of interfacial structures with the unprecedented interfacial sensitivity.[3] It has been considered a nondestructive method due to the use of a laser from visible to the near-infrared for excitation, as normal optical spectroscopies do. However, it has been often neglected that SERS needs metal nanostructures to boost the signal. The special physical properties (enhanced highly localized electromagnetic field or even heating effect) and the high chemical activity of metal nanostructures may result in some unexpected phenomena that may not occur in other spectroscopic methods. For example, the laser-induced deterioration of the sample to produce carbonaceous species, especially in the presence of O_2, has been reported.[4] Pettinger et al. proposed identifying the decomposition of a probe molecule to carbonaceous species and the dynamic processes of single-molecule events with two cathedral characteristic peaks of carbon species and the defined peaks with molecular signature, respectively.[5a,b] In addition, a strong heating effect arising from the strong localized surface plasmon resonance (LSPR) may lead to desorption of the molecule in the probed area and an undetectable SERS signal.[5c] Another case is that the molecule may transform to other species under the catalytic effect of metal nanoparticles and/or in the presence of oxygen, giving a rather stable SERS signal similar to that of the initial molecule. This case is more deceptive because the signal of the product can be taken as that of the initial molecule, which may lead to misinterpretation of the result.

para-Aminothiophenol (PATP) is an increasingly important probe molecule in SERS because of its strong interaction with Ag and Au, the intense SERS signal, and the significance in molecular electronics.[6] An early work on SERS of this molecule proposed that the photon-driven charge transfer (PDCT) process contributes to the SERS enhancement for PATP adsorbed on Ag, supported by the potential and wavelength dependent variation of the intensity of the bands at 1140, 1391, and 1440 cm^{-1}, assigned to the b_2 modes of the PATP molecule.[7a] This assignment has been widely accepted thereafter.[6−8] Their intensities have been widely used to estimate the SERS enhancement of some unique substrates.[8] The dynamic change in intensity and position of these bands has been used to demonstrate some interesting effects, for example the single-molecule nature of PATP in a molecular junction.[6] By comparing the intensity of these bands, PDCT enhancement of over 7 orders of magnitude has been obtained, compared to that of the normal value of less than 3 orders of magnitude.[7d]

We will demonstrate with PATP that a laser illumination considered low in conventional SERS can chemically transform PATP to 4,4′-dimercaptoazobenzene (DMAB). Surface mass spectroscopy (SMS) and SERS measurements on the synthesized DMAB convincingly support our proposal. It is DMAB rather than PATP that gives the "b_2 mode" signals. The method used to prevent the photoinduced reaction in SERS measurement can be borrowed to investigate some sensitive systems and avoid significant perturbation to the system. Our finding points out that the conclusion stemmed from PDCT of the PATP molecule in the literature should be reinterpreted.[7a−c]

In our previous study, we have found that the intensities of the "b_2 modes" of PATP depend on the laser power density and diminish at a lower value.[9] This power dependent behavior conflicts with the PDCT model that is a quasi-resonance enhanced Raman tuned by the wavelength of the laser and the potential and will not depend on the laser power.[7a] To find out the discrepancy, we followed the literature work of the potential dependent study of PATP on a roughened Ag electrode. To obtain a low power density without significantly affecting the signal, we carefully used a very low laser power density (8×10^2 mW/cm^2) by a defocusing strategy developed by our group[4e] to avoid the possible laser induced effect. We employed the fast expansion of the laser spot when the sample is away from the focal plane of a microscope objective of a high numerical aperture, which can significantly lower the power density. Simultaneously, we

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expanded the slit and/or hole of the Raman instrument to allow more light out of the focal plane to be collected to minimize the loss of the Raman signal. By bringing the focus ∼5 μm away from the sample, the power density was decreased to 1% of the original value, while the Raman signal still retained 80% of the maximum value. It significantly improved the signal-to-noise ratio especially under a very low power density. This method is advantageous over that by simply decreasing the laser power, by which the signal intensity will decrease proportionally.

During the experiment, the potential was varied from −0.1 to −0.8 V with a step of 0.1 V. Surprisingly, we obtained the spectral data with a different feature (Figure 1a) from that previously reported.[7a] The spectral feature is dominated by the bands at 1004, 1078, 1176, 1488, and 1595 cm^{-1} attributed to a_1 modes of PATP, and their intensities increase slightly when the potential shifts negatively.[7a] The spectral feature can be recovered when the potential was switched back to −0.1 V, indicating no obvious loss of PATP on Ag under this laser power density. We did not observe any signal related to the b_2 modes. When we increased the laser power density to 2×10^7 mW/cm^2 without changing the sampling position, we obtained very different spectral features with three new bands appearing at 1142, 1388, and 1432 cm^{-1} and a broadened one at ∼1595 cm^{-1}. The SERS signal of the former three bands, which had been assigned to b_2 modes responsible for the PDCT, changes quite significantly with the electrode potential at a similar trend to that reported by Osawa.[7a] This power dependent spectral variation is similar to our previous work of PATP adsorbed on Au nanoparticles,[9] which indicates that the appearance of the b_2 modes is not due to the PDCT process but may be ascribed to a process induced by a high-power laser.

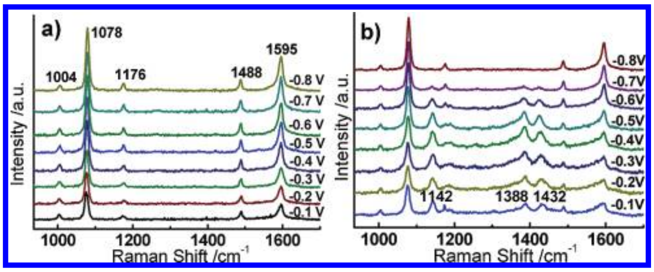

Figure 1. Potential dependent Raman spectra from a roughened Ag electrode preadsorbed with PATP in 0.1 M NaClO_4 illuminated with a laser at power densities of 8×10^2 mW/cm^2 (a) and 2×10^7 mW/cm^2 (b).

Our recent theoretical studies of SERS of PATP−Ag systems using various possible Ag clusters, binding sites, and configurations showed that the vibrational frequencies of the b_2 modes of PATP cannot be reproduced. Instead, the calculated Raman spectrum of DMAB, an oxidative coupling product of PATP, agrees magically with the spectral feature of PATP obtained at a high laser power. The three new bands having been observed in PATP with the assignment of "b_2 modes" correspond to the a_g modes of DMAB (see Supporting Information for detailed assignment of the Raman spectrum). This result suggests possible chemical transformation of PATP on the Ag surface to DMAB.[4d] This assumption is well supported by the following surface mass spectroscopic (SMS) measurement.

The SMS measurement was made over the PATP adsorbed Ag electrode after having been illuminated with a high-power laser. PATP-adsorbed and blank roughened Ag electrodes were used as controls. The first sample shows a molecular ion peak at an m/z of 245.5 is assignable to "$\text{H}+\text{S}-\text{Ph}-\text{N}=\text{N}-\text{Ph}-\text{S}$" fragment (Figure 2a(i)), while a peak at an m/z of 164 is assignable to "$\text{K}+\text{S}-\text{Ph}-\text{NH}_2$". We did not observe the 245.5 peak in Figure 2a (ii and iii) serving as controls. Therefore, the SMS result convincingly demonstrates the formation of DMAB from PATP under the illumination of the high-power laser.

Nonetheless, it would be more persuasive if we can directly obtain the SERS of DMAB and PATP. We synthesized the commercially unavailable DMAB (see Supporting Information for detailed synthesizing procedures, ^{1}H and ^{13}C NMR spectra, and IR spectra of DMAB). We then compared the SERS features of DMAB with that obtained from the PATP system; see Figure 2b. For clarity, we used a higher laser power to produce more transformed species. The two spectra show essentially identical spectral features, which convincingly demonstrates that they are from the same species.

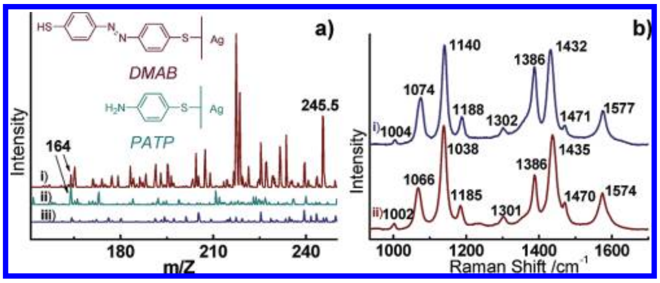

Figure 2. (a) DESI-MS spectra of PATP adsorbed roughened Ag electrodes illuminated with laser (i) and without any irradiation (ii) and a roughened Ag free of PATP (iii). (b) The Raman spectrum of PATP (i) and DMAB (ii) on the roughened Ag electrode excited by a laser at a power density of ca. 1×10^8 mW/cm^2.

Up to now, we have demonstrated the adsorbed PATP will be transformed to DMAB under a high-power laser and the Raman signals of the "b_2 modes" are actually contributed by the a_g mode of DMAB. Then, one may naturally wonder how to understand the potential dependent variation of the Raman intensity of the "b_2 modes" and the wavelength dependent shift of the potential at maximum intensity. Especially the latter has been used as persuading evidence for the presence of the PDCT process. A potential dependent SERS measurement of DMAB adsorbed on the roughened Ag surface will be indispensable.

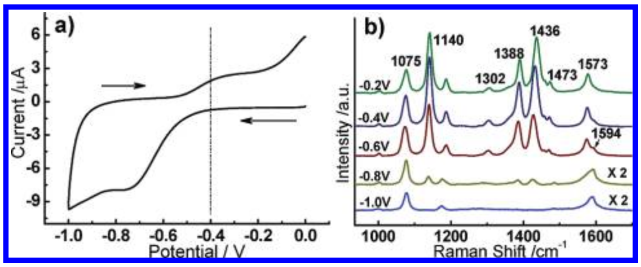

Figure 3. (a) Cyclic voltammogram of DMAB adsorbed on a roughened Ag, with a scan rate of 10 mV/s. (b) Potential dependent Raman spectra excited by a laser at a power density of 8×10^2 mW/cm^2.

Figure 3a exhibits the cyclic voltammogram (CV) of DMAB adsorbed on a roughened Ag electrode. A cathodic process clearly occurs at potentials more negative than −0.4 V and reaches the maximum at approximately −0.7 V. Further negative movement of the potential will lead to a hydrogen evolution reaction starting at −0.82 V. The potential dependent SERS result is shown in Figure 3b. The intensities of the 1140, 1388, and 1438 cm^{-1} bands change quite dramatically with the potential from −0.2 to −1.0 V, with an abrupt decrease at −0.8 V. A new band at 1594 cm^{-1} appears at −0.6 V, which corresponds to the a_1 mode of PATP, whereas the intensity of the 1075 cm^{-1} band does not vary much with the potential due to the overlap of the bands of PATP and DMAB. At -1.0 V, the spectrum remains the feature of PATP as in Figure 1a, which indicates the DMAB has been completely reduced to PATP.

On the basis of the above result, we can propose the scenario of the interfacial processes of PATP in an electrochemical system under illumination of a high-power laser. During the electrochemical SERS measurement, the neighboring PATP molecules are first oxidized to form the surface DMAB at relatively positive potentials (Figure 4a). This assumption is supported by the oxidative formation of azo species from aniline group molecules in the presence of Au/TiO$_2$.[10] Similarly, it has been reported that *p*-aminobenzoic acid could react to form azo molecules on the SERS-active Ag surface.[4a] As the intensities of the a_g modes of DMAB at 1140, 1388, and 1438 cm^{-1} are significantly stronger than those of the a_1 modes of PATP, even if a small amount of PATP is transformed to DMAB (Figure 4a), they can already produce observable signal in the SERS spectra (Figure 4c and d). On the other hand, DMAB can also give a_g bands at similar positions to those of a_1 modes of PATP (1075 and 1594 cm^{-1}) with comparable signal intensity but with a slight shift in frequency. This results in broadened bands but an essentially constant integrated peak intensity. Therefore, the obtained SERS signals are a combination of DMAB and PATP. The so-formed DMAB can be reduced to PATP at negative potentials, evidenced by the decreasing SERS intensity of the 1140, 1388, and 1438 cm^{-1} bands. At very negative potentials (e.g., -0.8 V), DMAB can be completely reduced to PATP, showing only a spectral feature of PATP, similar to that obtained under the illumination of low-power-density laser (Figure 4b). Therefore, as shown in Figure 4, a high-power laser leads to the formation of DMAB and the electrochemical reduction eliminates DMAB. The combination of these two effects gives the bell-shaped potential dependent SERS intensity bands observed in the literature.[7a] As the electromagnetic field strength and the SERS enhancement critically depends on the LSPR position of the SERS substrate and the excitation laser line, the green and blue laser can more efficiently excite the LSPR of Ag substrates. Therefore, we deem that PATP can be transformed to DMAB much faster, i.e., at a more positive potential in the experiment.

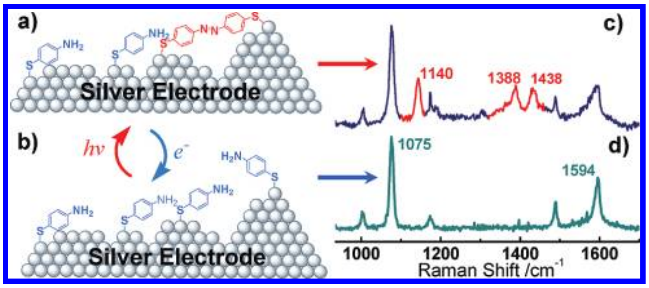

Figure 4. Transformation of DMAB (a, c) from PATP (b, d) adsorbed on Ag in the electrochemical SERS measurement.

In summary, we have demonstrated that the laser used for the SERS excitation, considered to be low in conventional SERS measurements, can significantly induce the surface reaction of probed species. We have shown that it is not the PDCT but the chemical transformation of PATP to 4,4′-dimercaptoazobenzene (DMAB) that leads to the appearance of "b_2 mode" peaks supported by the presence of the DMAB fragment in SMS measurement and the high similarity in the electrochemical SERS behavior between synthesized DMAB and PATP. The "b_2 mode" bands in fact originate from the a_g modes of DMAB. The evidence used to support the PDCT was reinterpreted by a combination of laser induced formation and electrochemical reduction of DMAB. On the basis of this result, we will understand that misinterpretation of some results is unavoidable sometimes due to the limitation of experimental conditions. However, if the conclusion made from the misinterpreted result is used to support the conclusion that needs further delicate work, then harmful effect should not be neglected, especially when the molecule involved is important, for example PATP, as shown in this work. This study clearly demonstrates the importance of strictly controlling the experimental conditions during the characterization or identification to avoid a strong disturbance to the system. Only in this manner can we be sure of the correctness of the data so that the potential for erroneous interpretation of the distorted experimental results is minimized and the true nature of the system can be revealed. This is particularly important in SERS, where absorption and scattering occur simultaneously in the nanoparticles supporting SERS. Especially when the excitation line is coincident with the LSPR position of the substrate, the local heating effect of nanoparticles may significantly induce the surface reaction or alter the surface processes, which may be the main reason for the chemical transformation observed in this study. However, if the heating effect is correctly used, it may open up a new and important direction of LSPR activated surface reactions.[11]

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Supporting Information Available: The experimental procedures, the characterization and vibrational assignment of DMAB, and the discussion on the adsorption configuration of DMAB. This material is available free of charge via the Internet at http://pubs.acs.org.

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