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Is 4-nitrobenzenethiol converted to *p*,*p*′-dimercaptoazobenzene or 4-aminothiophenol by surface photochemistry reaction?

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For the first time, the experimental and theoretical evidence for the conversion of 4-nitrobenzenethiol (4-NBT) to *p*,*p*′-dimercaptoazobenzene (DMAB) in Ag and Cu sols by surface photochemistry reaction is obtained with surface-enhanced Raman scattering (SERS) spectroscopy. The SERS spectrum of 4-NBT in Cu sol is identical to that of DMAB produced from 4-aminothiophenol in Ag sol as reported in recent literature, thereby providing direct spectral evidence.

Supporting information may be found in the online version of this article.

Keywords: 4-nitrobenzenethiol; *p*,*p*′-dimercaptoazobenzene; 4-aminothiophenol; surface photochemistry reaction

Introduction

The surface-enhanced photochemical reaction of aromatic nitro molecules adsorbed on silver has been observed experimentally using surface-enhanced Raman scattering (SERS).[1–4] It is found that the SERS peaks of the original nitro molecules gradually lose intensity and some new peaks appear; which suggests that the nitro molecules are subjected to photoreaction on the silver surface.[4]

Recently, we have proved that the photochemical conversion of 4-aminothiophenol (PATP) to *p*,*p*′-dimercaptoazobenzene (DMAB) occurs during SERS experiments with enhancing Ag colloids.[5] The SERS spectra of a mixture of PATP with Ag colloids showed good agreement with the theoretically predicted spectra of DMAB and were significantly different from PATP spectra. This interpretation was further proven by surface mass spectrometry measurements.[6] The mass spectra clearly revealed the presence of DMAB in the sample.[6] All the Raman peaks were assigned as the symmetric ag vibrational modes, which are strongly enhanced by surface plasmons.[5,7] In this communication, we demonstrate that also a mixture of the nitro compounds related to PATP, i.e. 4-nitrobenzenethiol (4-NBT), yields very similar SERS spectra, which can be assigned to DMAB. Thus, also 4-NBT is converted surface photochemically to DMAB. This contradicts the interpretation of this spectrum published in Refs [4,8–13], where the surface photochemical reaction of 4-NBT to PATP has been postulated.

Experimental and Theoretical

SERS-active Ag and Cu colloids (their syntheses and characterization can be seen in Supporting Information) were used in SERS measurements. 4-NBT powder was used for normal Raman measurement. A solution of 4-NBT in water at 5×10^{-6} M mixed with Ag and Cu sols was introduced into capillary sample cells for SERS measurement. The SERS spectra were recorded by a Renishaw in Via Raman system. Lasers emitting at 632.8 and 514.5 nm were used as excitation sources; the laser power on the SERS sample was limited to 2 mW with a 50× objective. All quantum chemical calculations (see Supporting Information) were carried out with the Gaussian 09 suite.[14]

Results and Discussion

The measured normal Raman scattering (NRS) spectrum of 4-NBT powder (Fig. 1(a)) shows that there are three main strong Raman peaks at 1099, 1331 and 1574 cm^{-1}, which are well reproduced by theoretical simulations (Fig. 1(b)). Also, the theoretical result reveals that there are two near-degenerate Raman peaks around 1100 cm^{-1}. The visualization of these four vibrational modes of the NRS spectrum in Fig. 1(b) is given in Supporting Information. The Raman peak A in Fig. 1(b) is the S–C stretching vibration. The Raman peaks C and D in Fig. 1(b) are $\nu_s(NO_2)$ and the C=C stretching vibration of the benzenyl ring, respectively. Before the measurement of the SERS of 4-NBT, we first simulated the SERS of 4-NBT adsorbed on the Ag cluster (Fig. 1(c)). It is found that there

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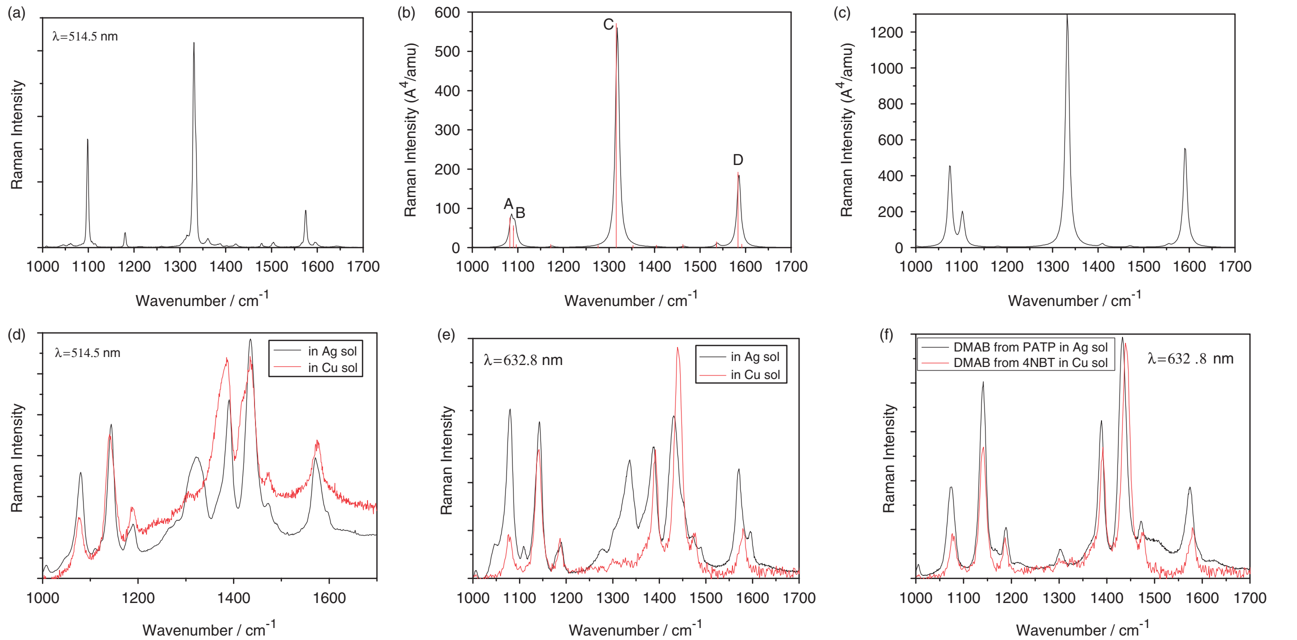

Figure 1. (a) The NRS spectrum of 4-NBT powder, (b) the simulated NRS spectrum of 4-NBT, (c) the simulated SERS of 4-NBT adsorbed on Ag_5 cluster, (d) and (e) the experimental SERS spectrum of DMAB produced from 4-NBT excited at 514.5 and 632.8 nm in Ag and Cu sols, respectively, (f) the experimental SERS of DMAB produced from PATP (taken from Refs [5,6]), and from 4-NBT by surface photochemistry reaction.

are three Raman peaks, and the profile of the SERS spectrum of 4-NBT is very similar to that of the isolated 4-NBT molecule in the powder in Fig. 1(a). Finally, the SERS spectra of 4-NBT in Ag and Cu sols were measured (Fig. 1(d) and (e)) at the incident wavelengths of 514.5 and 632.8 nm, respectively. It is found that the profile of experimental SERS spectra is different from the simulated SERS spectrum of 4-NBT. There are three additional strong Raman peaks at 1142, 1387 and 1432 cm^{-1} in Ag and Cu sols, as shown in Fig. 1(d) and (e). Note that the Raman peak at 1331 cm^{-1} disappears in Cu sol, while this Raman peak in Ag sol is still present.

To reveal the nature of experimental SERS spectra in Fig. 1(d) and (e), we compared Fig. 1(d) and (e) with the experimental SERS spectrum of DMAB produced from PATP by surface photochemistry reaction (taken from Refs [5,6]). According to Fig. 1(f), it is found that the experimental SERS spectrum of DMAB produced from PATP by surface photochemistry reaction (taken from Ref. [5]) is very similar to that in Fig. 1(d) and (e)), especially in the case of the Cu sol (they are almost identical). So, by surface photochemistry reaction, the same species has been produced from different molecules, i.e. that DMAB can not only be produced from PATP, but also from 4-NBT. The ag_{17} vibrational mode at 1432 cm^{-1} (in Fig. 1(d)–(f)) is the N═N stretching vibration of DMAB,[5,6] which reveals the formation of DMAB.

Note that the Raman peak at 1331 cm^{-1} of DMAB produced in Cu sol completely disappears, while this Raman peak of DMAB in Ag sol is still present. This shows that this surface photochemical reaction in Cu sol is a complete reaction, while a partial reaction occurs in the Ag sol as shown by the $v_s(NO_2)$ vibrational mode. This phenomenon reveals that Cu sol is a better substrate for such surface photochemical reaction.

Conclusion

The SERS spectra in Fig. 1(d) and (e) are the SERS spectra of DMAB produced from 4-NBT by surface photochemistry reaction. The Cu sol is a better substrate than the Ag sol for such surface photochemical reaction. DMAB can not only be produced from PATP but also from 4-NBT by surface photochemical reaction.

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Supporting information

Supporting information may be found in the online version of this article.

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