Received: 8 May 2011

Revised: 8 November 2011

(wileyonlinelibrary.com) DOI 10.1002/jrs.3143

Selective reduction of nitroaromatic compounds on silver nanoparticles by visible light

Lixin Xia,^a* Xinhu Hu,^b Mengtao Sun,^c* Jushi Li,^a Donghui Yang,^a Xiaofang Wang^a and Hongxing Xu^{c,d}

For the first time, we report experimentally and theoretically that nitroaromatic compounds, 2,4-dinitrobenzenethiol and 4-chloro-2nitrobenzenethiol, on silver sols can be selectively reduced to 2-amino-4-nitrobenzenethiol and 2-amino-4-chlorobenzenethiol simply by irradiating with a visible light in ambient conditions, and the selective photoreduction is a very facile process. The results of quantum chemical calculations are in good agreement with our experimental data. Copyright © 2012 John Wiley & Sons, Ltd.

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

Keywords: 2,4-dinitrobenzenethiol; 4-chloro-2-nitrobenzenethiol; silver colloids; surface-enhanced Raman scattering spectroscopy; selective photoreduction

Since the discovery of the photodecomposition of aromatic sulfides, pyridine, pyrazine, and benzaldehyde adsorbed on silver substrates using visible or near-ultraviolet radiation,^[1,2] the photoreactions of adsorbates on metal substrates have attracted considerable interest because of potential applications in many areas of science and technology, including optoelectronics, chemical and biosensors, drug delivery, microfabrication, and catalysis.^[3] Various types of photoreactions on metal substrates have subsequently appeared, including the photodecomposition of rhodamine 6 G,^[4] dimethyl cadmium,^[5] triazine,^[6] phthalazine,^[7] fluorobenzene,^[8] and methyl orange dye;^[9] the photodimerization pyridyl-substituted ethylenes,^[10] substituted stilbenes,^[11] of rhodanine,^[12] and 4-aminobenzenethiol (4-ABT);^[13-16] and the photoreduction of *N*-methylpyridinium and methyl viologen.^[17–19] Particularly, with the advent of more sensitive detection systems, nitrobenzene derivatives have also been proved to undergo photochemical reactions on rough silver surfaces, which used to be not recognized to be able to readily undergo such reactions. For instance, 4-nitrobenzoic acid (4-NBA)^[3,20] and 4-nitrobenzenethiol (4-NBT)^[21-23] adsorbed on rough silver were converted in ambient conditions to 4-aminobenzoic acid (4-ABA) and 4-ABT, respectively, by radiation with a visible laser. As another example of 4-NBA, azo dibenzoate has also been considered as the photoproduct.^[20,24,25] This is plausible because 4-ABA adsorbed on silver surface can also undergo hydrolysis and dimerization to form azo dibenzoate by an oxidative route when exposed to atmospheric moisture and laser light.^[26] In addition, which nitroaromatic compounds adsorbed silver substrates were reduced by other methods have been reported in sequence.[27-30] Thus, it would be very interesting to determine whether a selective reduction for nitroaromatic compounds could also take place on a metal surface under visible light radiation and how such reaction proceeds if it could occur. To reach such a goal, we synthesize first 2,4-DNBT and 4-C-2-NBT, and then attempt to obtain the SERS spectra of 2,4-DNBT and 4-C-2-NBT on silver sols to investigate if a selective photoreduction could take place in a manner similar to that for 4-NBA or 4-NBT; on the basis of the experiment data, we further see how such reaction proceeds and expect to get a deeper insight into the photoreaction mechanisms, which is still a matter of conjecture to this day. The synthesis strategy of 2,4-DNBT is shown in Scheme 1.

Silver sols were prepared using the Lee–Meisel method.^[31] (see supporting information). The final Ag particle concentration in the solution was estimated to be 3.5×10^{-11} mol L⁻¹. 2,4-DNBT and 4-C-2-NBT were prepared as low-concentration solutes in ethanol and added to the silver sols resulting in final concentrations of 2,4-DNBT and 4-C-2-NBT being around 1×10^{-6} mol L⁻¹. The mixture was incubated for 3 h to allow for efficient adsorption. Prior to the observation of photochemical reaction, field emission scanning electron microscopy (FESEM) was used to analyze the surface morphology and size distribution of the silver nanoparticles. According to measurements made with FESEM, most of the silver particles were approximately spherical in shape, with sizes ranging from 60 to 100 nm, and there was a portion of nanorods, which exhibited a mean diameter of about 60 nm and lengths ranging from 90 to 170 nm.

Direct observation of a surface-enhanced photochemical reaction has been investigated by means of surface-enhanced Raman scattering (SERS) spectroscopy.^[24–26] Here, we investigated the feasibility of a selective reduction by monitoring the SERS spectrum of 2,4-DNBT adsorbed on the silver surface under the visible

* Correspondence to: Lixin Xia, College of Chemistry, Liaoning University, 66 Chongshan Middle Road, Huanggu District, Shenyang 110036, China. E-mail: lixinxia@lnu.edu.cn

- a College of Chemistry, Liaoning University, Shenyang 110036, China
- b Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
- c Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
- d Division of Solid State Physics, Lund University, Lund 22100, Sweden

Mengtao Sun, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. E-mail: mtsun@aphy.iphy.ac.cn



Scheme 1. Synthesis of 2,4-DNBT.

light radiation at 632.8 nm in ambient air. The data acquisition time was 20 s. As shown in Fig. 1, the complete absence of the S–H stretching peak in the SERS spectrum, observable at 2546 cm⁻¹ for pure 2,4-DNBT, indicates that the 2,4-DNBT is chemisorbed onto the silver surface as thiolate after the S–H bond cleavage. It is noteworthy that a new set of peaks appears, for instance, at 1042, and 875 cm⁻¹. Referring to previous work,^[24–26] the band at 1042 cm⁻¹ is due to the in-plane C–H bending plus the C–S stretching modes plus N–H deformation vibrations; the band 875 cm⁻¹ results from the C–H bending plus N–H deformation modes. Moreover, the asymmetric and symmetric stretching vibration peaks of the original two-site nitro group at 1524 and 1306 cm⁻¹ disappear compared with the Raman spectrum of pure 2,4-DNBT. On the other hand, the SERS peak at 1346 cm⁻¹ that can be assigned to the symmetric stretching vibration of the four-site



Figure 1. (a) The normal Raman spectrum of pure 2,4-DNBT in its neat solid state and (b) the SERS spectrum of the 2,4-DNBT adsorbed on silver sols, which was irradiated with 632.8 nm laser light of 10 mW for 20 s.

nitro group^[21–23] still is prominent. These results indicates that only the two-site nitro group of 2,4-DNBT was subjected to photoreaction while the four-site nitro group was not subjected to change. Although other molecules such as nitroso-, hydroxylamine-, and azo compounds would also be produced by reduction of nitroaromatic molecules,^[32] no peak because of any such compound is identified at all in our SERS spectrum. The procedure for the selective photoreduction is depicted in Scheme 2.

To obtain insight into experimental SERS spectra shown above, the quantum chemical calculations (see supporting information) were performed with GAUSSIAN 09 suite.^[33] The assignment of Raman peaks at 1524, 1346, 1306, 1042, and 875 cm⁻¹ according to the calculations can be seen in Fig. 2. Our qualitatively calculated results support strongly the experimental observations.

To confirm the fact that the results described above is caused by the selective photoreduction of 2,4-DNBT or only by its incomplete photoreduction, the sample was radiated with the same laser line for various lengths of time from 10 to 50 s (Fig. 3). The changing spectra as a function of laser exposure time clearly reveal the appearance of a new molecule as described above. We assume that the SERS intensity is proportional to the quantity of the species adsorbed on the surface. Thus, the intensity of the SERS bands near 1453 and 1346 cm⁻¹ can be used to represent the amino and nitro group quantity of the photoproduct, respectively, and thus their changes in intensity reflect that a certain photoreaction occurs at the nitro groups of 2,4-DNBT. As indicated by the dot lines in Fig. 3, the intensity rates of $I(1453 \text{ cm}^{-1})/I(1346 \text{ cm}^{-1})$ are gradually heightened with the increase in the exposure time up to the 30 s point and reach a constant value after 30 s with the radiation, suggesting that the new band at 1453 cm⁻¹ results from the selective photoreduction of 2,4-DNBT rather than its incomplete photoreduction.

To examine the universality of the selective photoreduction, we also synthesized 4-C-2-NBT, and then obtained its SERS spectra under the same conditions as in the case of 2,4-DNBT. Concretely,



Scheme 2. Schematic representation of the procedure for the selective photoreduction of 2,4-DNBT on a silver surface under 632.8 nm laser radiation.



Figure 2. The calculated vibrational modes of 2,4-DNBT-Ag complex and pure 2,4-DNBT.

the purpose is to investigate that 4-C-2-NBT would undergo a selective reduction of the two-site nitro group similar to 2,4-DNBT or dehalogenation of the four-site chloro group in a manner similar to that for 4-chloro-benzenethiol and 4-bromo-benzenethiol.^[34] The synthesis strategy of 4-C-2-NBT is shown in Scheme 3.

Figure 4 shows the SERS spectrum of 4-C-2-NBT on silver sols and the normal Raman spectrum of pure 4-C-2-NBT using the 632.8 nm as the excitation. It was also observed that the S-H stretch at 2544 cm^{-1} in the normal Raman spectrum was missing in the SERS spectrum. This indicates that the 4-C-2-NBT is chemisorbed onto the silver surface through its sulfur atom, as likely the 2,4-DNBT. It is very clear that several new peaks appear in Fig. 4 (b) compared with the Raman spectrum of pure 4-C-2-NBT, for instance, at 1448 and 878 cm⁻¹. The band at 1448 cm⁻¹ can be attributed to the C–H bending plus the N–H deformation modes, and the peak at 878 cm⁻¹ results from the N–H deformation vibrations. Moreover, the asymmetric stretching vibration peak of the







Figure 4. (a) The normal Raman spectrum of pure 4-C-2-NBT in its neat solid state and (b)–(d) the time dependence of SERS spectra for 4-C-2-NBT adsorbed on silver sols, which was irradiated with 632.8 nm laser light for various lengths of time from 20 to 50 s.



Scheme 3. Synthesis of 4-C-2-NBT.



Figure 5. The calculated vibrational modes of 4-C-2-NBT-Ag complex and pure 4-C-2-NBT.



Figure 6. The normal Raman spectrum of pure simple in its neat solid state and the time dependence of SERS spectra for simple adsorbed on silver sols using 514.5 nm laser light of 10 mW for various lengths of time from 10 to 50 s. (a) 2,4-DNBT and (b) 4-C-2-NBT.

two-site nitro group at 1552 cm^{-1} disappears, and the relative intensity of the symmetric stretching vibration peak of the nitro group at 1333 cm^{-1} are dramatically weakened compared with



Figure 7. UV-Vis adsorption spectra of (a) 2,4-DNBT and (b) 4-C-2-NBT.

Wavelength / nm

the Raman spectrum of pure 4-C-2-NBT. These results indicate that the two-site nitro group of 4-C-2-NBT was subjected to photoreaction, although the extent of the photoreaction cannot be precisely evaluated. On the other hand, the SERS peak at $331 \, \mathrm{cm}^{-1}$ that can be assigned to the in-plane C–Cl deformation vibration still is prominent, and its relative intensity keeps a

constant value after a prolonged irradiation (50 s). These results suggest that no dehalogenation occurs, and further 4-C-2-NBT takes place a selective photoreduction. The calculated vibrational modes of 4-C-2-NBT–Ag cluster and pure 4-C-2-NBT are shown in Fig. 5, which are in good agreement with our experimental data.

The reason why two-site nitro groups of 2,4-DNBT and 4-C-2-NBT was subjected to photoreaction might be attributed to the close distance from the silver surface. The closer the distance of nitro groups from the silver surface was, the more possible it was for photoreaction to take place that was induced by a surface plasmon resonance effect. In other words, the oscillating electrons interact easily with the two-site nitro groups of 2,4-DNBT and 4-C-2-NBT because of closer distance. On the other hand, as can be seen in Figs 1, 3, and 4, the C-H vibrations of benzene ring were still retained after the photoreduction. This implies that water present under ambient conditions is the H-atom source for the selective photoreduction rather than the benzene ring hydrogen atoms of 2,4-DNBT or 4-C-2-NBT. It is believed that water was catalytically decomposed on the silver surface to provide H-atom,^[9] thus the two-site nitro group of 2,4-DNBT or 4-C-2-NBT is in a more favorable position to react with the H-atom than the four-site nitro or chloro group that is far from the Ag surface. That is not to say that the hydrogen atoms of the 2,4-DNBT or 4-C-2-NBT itself cannot be used as the H-atom source for the selective photoreduction but rather that water present under ambient conditions should be the primary H-atom source in our experiments in terms of the C-H vibrations of benzene ring reservation after photoreduction as shown in Figs 1, 3, and 4.^[3]

Our further interest was to investigate the selective photoreaction mechanisms. Therefore, we tried to record SERS spectra of the adsorbed 2,4-DNBT or 4-C-2-NBT with 514.5 nm excitation. It can be seen in Fig. 6 that the SERS spectra recorded with the 514.5 nm line are nearly the same as those obtained with 632.8 nm excitation relative to the normal Raman spectra. In other words, no frequency dependence of the selective photoreaction was observed for both 2,4-DNBT and 4-C-2-NBT. This is the usual understanding that a photoelectron is ejected more readily using a shorter-wavelength than a longer-wavelength laser, the present contradiction can be rationalized by assuming that the enhanced photoreaction at longer wavelength is deeply associated with charge transfer from the metal to the absorbed molecule, which showed via UV–Vis spectra (Fig. 7).

In summary, we have discovered the 2,4-DNBT and 4-C-2-NBT on silver sols were selectively reduced to 2-amino-4-nitro-benzenethiol and 2-amino-4-chlorobenzenethiol simply by irradiating with 632.8 or 514.5 nm laser in ambient conditions. After only 30 or 20 s of continuous laser illumination, the reactions are finished, suggesting that the selective photoreduction is a very facile process. To the best of our knowledge, this is the first report of visible light-induced selection reduction for nitroaromatic compounds on silver sols.

Acknowledgements

This work was supported by the Liaoning Natural Science Foundation, China (20092016), the Shenyang Natural Science Foundation, China (F10-230-4-00 and 090082), and the Liaoning University 211-Projects of the third period. Mengtao Sun thanks the National Natural Science Foundation of China (Grants

10874234, 90923003 and 20703064), the National Basic Research Project of China (Grant 2009CB930701).

Supporting information

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

References

- [1] G. M. Goncher, G. B. Harris, J. Chem. Phys. 1982, 77, 3767.
- [2] C. J. Sandroff, D. R. Herschbach, J. Phys. Chem. 1982, 86, 3277.
- [3] H. S. Han, S. W. Han, C. H. Kim, K. Kim, *Langmuir* **2000**, *16*, 1149.
- [4] S. Garoff, D. A. Weitz, M. S. Alvarez, Chem. Phys. Lett. 1982, 92, 283.
- [5] C. J. Chen, R. M. Osgood, Phys. Rev. Lett. **1983**, 50, 1705.
- [6] R. A. Wolkow, M. J. Moskovits, J. Chem. Phys. 1987, 87, 5858.
- [7] J. S. Suh, N. H. Jang, D. H. Jeong, M. J. Moskovits, J. Phys. Chem. 1996, 100, 805.
- [8] D. P. DiLella, R. R. Smardzewski, S. Guha, P. A. Lund, Surf. Sci. 1985, 158, 295.
- [9] P. Wang, B. Huang, Z. Lou, X. Zhang, X. Qin, Y. Dai, Z. Zheng, X. Wang, Chem. Eur. J. 2010, 16, 538.
- [10] J. J. McMahon, T. P. Dougherty, J. D. Riley, G. T. Babcock, R. L. Carter, Surf. Sci. 1985, 158, 381.
- [11] M. O. Wolf, M. A. Fox, *Langmuir* **1996**, *12*, 955.
- [12] S. Jabeen, T. J. Dines, R. Withnall, S. A. Leharne, B. Z. Chowdhry, *Phys. Chem. Chem. Phys.* **2009**, *11*, 7476.
- [13] Y. R. Fang, Y. Z Li, H. X. Xu, M. T. Sun, Langmuir 2010, 26, 7737.
- [14] Y. F. Huang, H. P. Zhu, G. K. Liu, D. Y. Wu, B. Ren, Z. Q. Tian, J. Am. Chem. Soc. 2010, 132, 9244.
- [15] Y. Z. Huang, Y. R. Fang, Z. L. Yang, M. T. Sun, J. Phys. Chem. C 2010, 114, 18263.
- [16] M. T. Sun, Y. Huang, L. Xia, X. Chen, H. Xu, J. Phys. Chem. C 2011, 115, 9629.
- [17] K. A. Bunding, R. A. Durst, M. I. Bell, J. Electroanal. Chem. 1983, 150, 437.
- [18] H. Feilchenfeld, G. Chumanov, T. M. Cotton, J. Phys. Chem. 1996,
- 100, 4937.
- [19] T. H. Lu, R. L. Birke, J. R. Lombardi, Langmuir 1986, 2, 305.
- [20] S. Sun, R. L. Birke, J. R. Lombardi, K. P. Leung, A. Z. Genack, J. Phys. Chem. 1988, 92, 5965.
- [21] S. W. Han, I. Lee, K. Kim, Langmuir 2002, 18, 182.
- [22] S. J. Lee, K. Kim, Chem. Phys. Lett. 2003, 378, 122.
- [23] K. Kim, Y. M. Lee, H. B. Lee, Y. Park, T. Y. Bae, Y. M. Jung, C. H. Choi, K. S. Shin, J. Raman Spectrosc. 2010, 41, 187.
- [24] P. G. Roth, R. S. Venkatachalam, F. J. Boerio, J. Chem. Phys. 1986, 85, 1150.
- [25] H. Bercegol, F. Boerio, J. Phys. Chem. 1995, 99, 8763.
- [26] R. S. Venkatachalam, F. J. Berio, P. G. Roth, J. Raman Spectrosc. 1988, 19, 281.
- [27] Y. U. Seo, S. J. Lee, K. Kim, Chem. Commun. 2004, 664.
- [28] G. Maduraiveeran, R. Ramaraj, Anal. Chem. 2009, 81, 7552.
- [29] Y. Mikami, A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, chem. Letter. 2010, 39, 223.
- [30] J. N. Solanki, Z. Venkata, Ind. Eng. Chem. Res. 2011, 50, 7338.
- [31] P. C. Lee, D. Meisel, J. Phys. Chem. 1982, 86, 3391.
- [32] H. Zhu, X. Ke, X. Yang, S. Sarina, H. Liu, Angew. Chem. Int. Ed. 2010, 49, 9657.
- [33] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, M. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, **2009**.
- [34] R. L. Garrell, C. Szafranski, W. Tanner, SPIE Raman Luminescence Spectroscopies Technol. II 1990, 1336, 264.