Isomerization of \(p,p'\)-Diiodoazobenzene Controlled by the Surface Plasmon-Assisted Reaction

Yanqiu Yang,† Fei Teng,† Long Yu,† Yu Liu,† Peng Song,‡∗† and Lixin Xia†∗‡

†College of Chemistry and ‡School of Physics, Liaoning University, Shenyang 110036, China

ABSTRACT: Based on a SERS study, the plasmon-assisted coupling reaction of \(p\)-idoaniline (PIAN) to \(p,p'\)-diiodoazobenzene was investigated. This model plasmon-assisted reaction exhibits an outstanding SERS performance with the limit of detection as low as \(10^{-13}\) M. Under low concentrations, the control of the \(\text{cis} \rightarrow \text{trans}\) isomerization of \(p,p'\)-diiodoazobenzene was achieved by characterizing the Raman peak intensity at 1432 cm\(^{-1}\) of the coupling reaction catalytic product. We present the regulation strategy for the isomerization of azobenzene derivatives enabled here, through the controlled adjustment of reactant concentration, and expand the application of SERS technique.

1. INTRODUCTION

Azobenzene, as an important precursor in a chemical reaction, is used in the manufacture of commercial materials, including biphenyl dyes, rubber accelerators, etc. By introducing an azobenzene group into the polymer, the novel physicochemical properties can be realized. The isomerization of azobenzene, as a photochemical reaction converting azobenzene between the \(\text{cis} \rightarrow \text{trans}\) structures, has great effects on its potential application fields of optical information storage materials, nonlinear optical materials, liquid crystal materials, and biomolecular active light control. As such, the biological photoswitches have been proven to be regulated by the isomerization of azobenzene.3

The control of the isomerization of azobenzene has also attracted extensive attention. Previous studies have proven that the electric field is an effective way to regulate the isomerization of azobenzene.6,7 This inspires us to take surface plasmon resonance (SPR)8,9 as an excitation source to control this isomerization process since the plasmon effect can produce the enormous electromagnetic field on the surface of the rough metal electrode, which is currently used in enhancing the Raman signal in the surface enhancement Raman scattering (SERS) study.10

SERS has been recognized to be an effective method in investigating the intermolecular interactions and monitoring plasmon-assisted reactions.11−15 Since the discovery of plasmon-driven chemical reactions, there have been numerous reports on its mechanism and influencing factors.16−18 Note that characterization of the isomerized structure of azobenzene derivatives using the SERS technique has the advantages of fast response time,19−21 and \(10^{3} \sim 10^{8}\) times enhanced Raman signal intensity.22,23 Also, it has been proven that the outstanding SERS performance exhibits high sensitivity with the limit of detection as low as \(10^{-9}\) M.24 Most importantly, the mapping technique in SERS detection can be used to sweep multiple points in a randomly selected region, which avoids the contingency of the experiment, improves the experimental reproducibility, and provides an intuitive image in monitoring this isomerization reaction process.25,26

2. RESULTS AND DISCUSSION

Herein, we have selected \(p\)-idoaniline (PIAN), which will undergo plasmon-assisted coupling reactions when PIAN is absorbed on silver nanoparticles (NPs) under the irradiation of laser. Through regulating its concentration, the control of the isomerization of \(p,p'\)-diiodoazobenzene was achieved.27 As shown in Figure 1a, the surface roughness and size of the SERS substrate, that is, Ag NPs, were characterized using scanning electron microscopy (SEM). Clearly, the rough surface morphology of Ag NPs is spherical, which is expected to provide a sufficiently large number of “hot spots” for plasmon-driven chemical reactions and result in enough intensity of the surface plasmon resonance effect. The transmission electron microscopy (TEM) image (Figure 1b) shows that the Ag NPs are \(40\) nm in size and the PIAN is well-absorbed on the surface of Ag NPs, when the silver substrate was prepared by mixing with this SERS probe molecule.

Previous studies have widely confirmed that, when the \(p\)-aminothiophenol (PATP) molecule adsorbed on the surface of the silver electrode, the surface plasmon-assisted coupling reaction of PATP to \(p,p'\)-dmercaptoazobenzene (DMAB) can be realized.15,28,29 Three unusually strong signals at 1140, 1390, and 1432 cm\(^{-1}\) in the detected SERS spectrum should be attributed to the \(-\text{N=N=}-\) Raman characteristic peaks of the product DMAB. In our experiment, the SERS mapping of \(10^{-3}\)
M PIAN and Ag NP mixed solution was first performed, and hundreds of data points were collected with a step size of 1 μm and laser power of 1%. The randomly selected mapping scan rectangular area is expressed as red in Figure 2b. From the mapping image demonstrating the Raman peak intensity corresponding to the specific wavelength, shown in Figure 2c, it can be clearly and visually found that there are obvious Raman peaks at 1140, 1390, and 1432 cm$^{-1}$. This indicates that the surface plasmon-assisted coupling reaction of PIAN underwent conversion to $p,p'$-diiodoazobenzene and the $\equiv N \equiv N$ bond is formed since these three characteristic vibrational modes should be attributed to those of the $\equiv N \equiv N$ bond in $p,p'$-diiodoazobenzene. Correspondingly, the three-dimensional Raman spectra of PIAN absorbed on Ag NPs at all the sampling points are shown in Figure 2d. The signal intensities of the Raman characteristic peaks at 1140 cm$^{-1}$ can reach $5.0 \times 10^3$, while the peaks at 1390 and 1432 cm$^{-1}$ almost run up to $1.5 \times 10^4$.

When we reduced the concentration of PIAN to $10^{-9}$ M, the surface plasmon-assisted coupling reaction from $p$-iodoaniline to $p,p'$-diiodoazobenzene can occur. As can be seen from Figure 3, though the corresponding intensity becomes weaker with the decrease in PIAN concentration, the characteristic Raman vibrational modes of the $\equiv N \equiv N$ bond in the product $p,p'$-diiodoazobenzene all appear the same. Note that the reduction in the signal intensity is different from the three Raman peaks. In detail, the reduction at 1390 cm$^{-1}$ is small, while the reduction at 1432 cm$^{-1}$ is more significant. When the concentration of PIAN was further reduced to $10^{-13}$ M, theoretically, this concentration should be unreactive. Generally, the red area (high signal intensity) at the corresponding wave number was significantly less, and it appeared that not every point participated in the reaction at this concentration. However, as shown in Figure 4, Raman peaks at 1140, 1390, and 1432 cm$^{-1}$ at some monitoring data points can also be observed. Similarly, the reduction at 1432 cm$^{-1}$ is particularly notable, as compared with that of 1390 cm$^{-1}$.

Until now, the thing that deserves our attention is, all as the characteristic Raman vibrational modes of the $\equiv N \equiv N$ bond in $p,p'$-diiodoazobenzene, why is the peak intensity at

---

**Figure 1.** (a) SEM image of Ag NPs. (b) TEM image of the Ag NP-absorbed $p$-iodoaniline molecule.

**Figure 2.** Mapping results of PIAN with $10^{-3}$ M based on the Ag SERS substrate. (a) Whole area under the microscope. (b) Selected mapping scan rectangular area. (c) 2D mapping image. (d) 3D Raman spectra.
1432 cm$^{-1}$ reduced more obviously? One main explanation is possible: the cis–trans configuration conversion of the azobenzene group in the product $p,p'$-diiodoazobenzene occurs due to the change in PIAN concentration. For further investigation, a series of PIAN concentrations were selected for SERS detecting, and the characteristic Raman peak change was specifically characterized in Figure 5. As can be seen from Figure 5a, when the PIAN concentration is higher, the emergence of all the three characteristic Raman peaks (1140, 1390, and 1432 cm$^{-1}$) is quite obvious. This indicates that the surface plasmon-assisted coupling reaction could be completely done under this concentration. In addition, our theoretical calculation results reveal that the product, that is, $p,p'$-diiodoazobenzene, is the trans structure, which is consistent with a previous study.32 The insets of the molecular structures in Figure 5a correspond to its theoretically optimized structure of PIAN and $p,p'$-diiodoazobenzene using the Gaussian 09 package. Furthermore, when the concentration of PIAN was reduced to $10^{-7}$ M, as can be seen from Figure 5b, the three characteristic Raman peaks remain. This coupling reaction could also be almost done under this concentration, from the mapping images almost displaying red in the selected sweep range (see the inset of Figure 5b), which originated from the fact that the Raman characteristic peak signal intensity of the product $p,p'$-diiodoazobenzene at 1432 cm$^{-1}$ is still strong. It should be noted that the peak intensity at 1432 cm$^{-1}$ is the most significantly reduced in the three characteristic Raman peaks, which indicates that the conversion of the azobenzene group from a trans to cis structure occurs. Because the previous study has proven the fact that when the $p,p'$-diiodoazobenzene
exists in its cis configuration, the Raman peak intensity at 1432 cm\(^{-1}\) is weak, while the peak intensity at 1390 cm\(^{-1}\) remains strong.\(^{31}\) This phenomenon becomes more and more obvious with the decrease in PIAN concentration. Figure 5c,d again shows that the coupling reaction can still be done, but not completely, under a very low concentration of PIAN. However, in this condition, the reaction product gradually turns into its cis structure of \(p,p’\)-diiodoazobenzene.

When the concentration of PIAN is low enough, the steric hindrance effect between the PIAN molecules will be counteracted. The special \(\pi-\pi\) and \(n-\pi\) interactions take effect between the azo group and benzene ring, causing the ring to distort along the \(-N\equiv N-\) bond.\(^{33}\) In detail, the \(\pi-\pi\) and \(n-\pi\) interactions will involve the rupture of the \(N\equiv N\) p-bond, which facilitates the free rotation along the \(N-N\) bond and results in the changes of the C–N–N–C dihedral angle, with the \(N-N-C\) angle remains fixed at \(\sim 120^\circ\).\(^ {34}\) The ortho hydrogen of the benzene ring can also be expected to interact with the lone pair electrons on the remote nitrogen.\(^ {35}\) All these factors facilitate the formation of its cis structure of \(p,p’\)-diiodoazobenzene.

3. CONCLUSIONS

In conclusion, this study demonstrated that the conversion between the cis–trans structures of \(p,p’\)-diiodoazobenzene can be induced by the concentration of the solution monitored using the SERS technique. Under higher concentrations, the molecule is its trans structure, while with the decrease in concentration, the cis–trans isomerization takes place, and the cis structure of \(p,p’\)-diiodoazobenzene appears. Generally, the concentration regulation and SERS characterization are very simple, which expands the application of SERS in monitoring the isomerization process of the molecules by characterizing the corresponding Raman peak changes.

4. EXPERIMENTAL AND COMPUTATIONAL METHODS

In our experiment, \(p\)-iodoaniline (PIAN, 98%) and sodium citrate analytical reagent (99%) were purchased from Sun Chemical Technology (Shanghai) Co., Ltd. A solution of \(10^{-3}-10^{-16}\) M PIAN was prepared using ethanol (99.8%) as a solvent. The substrates for the SERS measurement were prepared using sodium citrate to reduce silver nitrate.\(^ {36}\) Different concentrations of the PIAN solution were mixed with Ag NPs, dropped onto glass slides, and then dried in air. The Raman spectra ranged from 894.33–1687.17 cm\(^{-1}\) (center, 1300.00 cm\(^{-1}\)) using a 532 nm laser irradiation. Raman spectroscopy measurements were performed using a Renishaw inVia spectrometer. The Raman spectral mapping technique is an advanced semiautomatic technology that selects an area and automatically scans hundreds of data points in this area into spectra, integrating artificial color images based on the specified peak intensities. All measurements were conducted using a 50 \(\times\) 50 microscope objective (a spot size of \(\sim 2\) \(\mu\)m), 532 nm excitation wavelength, and laser power of 50%. Scanning and transmission electron microscopy images were obtained using a Hitachi Su8010 field emission scanning electron microscope (Japan) and a JEM-2100 ultrahigh resolution transmission electron microscope (Japan), respectively. The ground-state geometries of PIAN and \(p,p’\)-diiodoazobenzene were optimized using the Gaussian 09 package\(^ {37}\) with density functional theory (DFT), Becke’s

Figure 5. SERS signals of (a) \(10^{-3}\) M, (b) \(10^{-7}\) M, (c) \(10^{-9}\) M, and (d) \(10^{-11}\) M PIAN based on the Ag substrate under the irradiation of 532 nm. The insets in (a) correspond to the optimized structures of PIAN (bottom) and \(p,p’\)-diiodoazobenzene (top). The insets in (b)–(d) are the mapping images of the Raman intensity at 1432 cm\(^{-1}\).
three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP functional), and def2-SVP basis set.

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: songpeng@lnu.edu.cn (P.S.).
E-mail: lixinxia@lnu.edu.cn (L.X.).

**ORCID**
Peng Song: 0000-0003-3093-0068

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (21671089 and 21271095), the Scientific Research Fund of Liaoning Province (LT20170101, 20175040409), the Innovative Talent Support Program of Liaoning Province (grant no. LR2017062), the Liaoning Provincial Department of Education Project (grant no. LF2017110), and the Shenyang High-Level Innovative Talents Program (grant no. RC180227).

**REFERENCES**

(1) Moustafa, M. E.; McCready, M. S.; Puddephatt, R. J. Switching by Photochemical trans−cis Isomerization of Azobenzene Substituents in Organonitrogen Complexes. *Organometallics* 2012, 31, 6262−6269.

(2) Albunia, A. R.; Rizzo, P.; Coppola, M.; De Pascale, M.; Guerra, G. Azobenzene Isomerization in Polymer co-Crystalline Phases. *Polymer* 2012, 53, 2727−2735.

(3) Matharu, A. S.; Jeeva, S.; Ramanujam, P. S. Liquid Crystals for Holographic Optical Data storage. *Chem. Soc. Rev.* 2007, 36, 1868−1880.

(4) Masiero, S.; Lena, S.; Pieraccini, S.; Spada, G. P. The Direct Conversion of Light into Continuous Mechanical Energy by Photoreversible Self-Assembly: A Prototype of a Light-Powered Engine. *Angew. Chem. Int. Ed.* 2008, 47, 3184−3187.

(5) Zhang, F.; Zarin-Afsar, A.; Al-Abdul-Wahid, M. S.; Prosser, R. S.; Davidson, A. R.; Woolley, G. A. Structure-based Approach to the Photocontrol of Protein Folding. *J. Am. Chem. Soc.* 2009, 131, 2283−2289.

(6) Photochromism, Molecules and Systems; Dür, H., Boua-Laurent, H., Eds.; Elsevier: Amsterdam, 2003, p 165.

(7) Fanghanel, D.; Timpe, G.; Orthmann, V. Photochromic Compounds with N-N and C-N Chromophores in Organic Photochromes; El'tsov, A. V., Ed.; Springer: Boston, MA, 1990, p 105−175.

(8) Cui, L.; Wang, P.; Chen, X.; Fang, Y.; Zhang, Z.; Sun, M. Plasmon-dimerized Dimerization via S-S Chemical Bond in an Aqueous Environment. *Sci. Rep.* 2015, 4, 7221.

(9) Dong, B.; Fang, Y.; Chen, X.; Xu, H.; Sun, M. Substrate-, Wavelength-, and Time-Dependent Plasmon-Assisted Surface Catalysis Reaction of 4-Nitrobenzenethiol Dimerizing to p,p'-Dimercaptoazobenzene on Au, Ag, and Cu Films. *Langmuir* 2011, 27, 10677−10682.

(10) Mukherjee, B.; Leong, W. S.; Li, Y.; Gong, H.; Sun, L.; Shen, Z. X.; Simsek, E.; Thong, J. T. Raman Analysis of Gold on WSe2Single Crystal Film. *Mater. Res. Exp.* 2015, 2, No. 065009.

(11) Li, J. F.; Ding, S. Y.; Yang, Z. L.; Bai, M. L.; Anema, J. R.; Wang, X.; Wang, A.; Wu, D. Y.; Ren, B.; Hou, S. M.; Wandlowski, T.; Tian, Z. Q. Extraordinary Enhancement of Raman Scattering from Pyridine on Single Crystal Au and Pt Electrodes by Shell-Isolated Au Nanoparticles. *J. Am. Chem. Soc.* 2011, 133, 15922−15925.

(12) Ni, Z. H.; Wang, H. M.; Luo, Z. Q.; Wang, Y. Y.; Yu, T.; Wu, Y. H.; Shen, Z. X. The Effect of Vacuum Annealing on Graphene. *J. Raman Spectrosc.* 2010, 41, 479−483.

(13) Zhang, M.; Zhao, L. B.; Luo, W. L.; Pang, R.; Zong, C.; Zhou, J. Z.; Ren, B.; Tian, Z. Q.; Wu, D. Y. Experimental and Theoretical Study on Isotropic Surface-Enhanced Raman Spectroscopy for the Surface Catalytic Coupling Reaction on Silver Electrodes. *J. Phys. Chem. C* 2016, 120, 11956−11965.

(14) Wong, C. P.; Liu, J.; Kasim, J.; See, A.; Shen, Z. X. Impact of Implantation and Annealing on Channel Strain of Transistors with Embedded Silicon-Germanium Source and Drain. *Jpn. J. Appl. Phys.* 2011, 50, 040208.

(15) Fang, Y.; Li, Y.; Xu, H.; Sun, M. Ascertaining p'-Dimercaptoazobenzene Produced from p-Aminothiophenol by Selective Catalytic Coupling Reaction on Silver Nanoparticles. *Langmuir* 2010, 26, 7737−7746.

(16) Cao, E.; Guo, X.; Zhang, L.; Shi, Y.; Lin, W.; Liu, X.; Fang, Y.; Zhou, L.; Sun, Y.; Song, Y.; Liang, W.; Sun, M. Electrooptical Synergy on Plasmon-Exciton-Codriven Surface reduction Reactions. *Adv. Mater. Interfaces* 2017, 4, 1700869.

(17) Lin, W.; Cao, Y.; Wang, P.; Sun, M. Unified Treatment for Plasmon−Exciton Co-driven Reduction and Oxidation Reactions. *Langmuir* 2017, 33, 12102−12107.

(18) Lin, W.; Cao, E.; Zhang, L.; Xu, X.; Song, Y.; Liang, W.; Sun, M. Electrically enhanced hot hole driven oxidation catalysis at the interface of a plasmon−exciton hybrid. *Nanoscale* 2018, 10, 5482−5488.

(19) Hakonen, A.; Andersson, P. O.; Schmidt, M. S.; Rindzevicius, T.; Käll, M. Explosive and Chemical Threat Detection by Surface-enhanced Raman Scattering: A Review. *Anal. Chim. Acta* 2015, 893, 1−13.

(20) Zheng, J.; He, L. Surface-enhanced Raman Spectroscopy for the Chemical Analysis of Food. *Compr. Rev. Food Sci. Food Saf.* 2014, 13, 317−328.

(21) Stiles, P. L.; Dieringer, J. A.; Shah, N. C.; Van Duyne, R. P. Surface-enhanced Raman spectroscopy. *Annu. Rev. Anal. Chem.* 2008, 1, 601−626.

(22) Otto, A.; Mrozek, I.; Grabhorn, H.; Akemann, W. Surface-enhanced Raman scattering. *J. Phys. Condens. Matter* 1992, 4, 1143−1212.

(23) Schatz, G. C.; Young, M. A.; Van Duyne, R. P. Electromagnetic Mechanism of SERS in Surface-Enhanced Raman Scattering; Kneipp, K., Moskovit, M., Kneipp, H., Eds.; Topics in Applied Physics; Springer: Berlin, Heidelberg, 2006, Vol. 103, pp 19−45.

(24) Lin, J.; Shang, Y.; Li, X.; Yu, J.; Wang, X.; Guo, L. Ultrasensitive SERS Detection by Defect Engineering on Single Cu2O Superstructure Particle. *Adv. Mater.* 2017, 29, 1604797.

(25) Wang, P.; Pang, S.; Pearson, B.; Chuyo, Y.; McLandshoroborough, L.; Fan, M.; He, L. Rapid Concentration Detection and Differentiation of Bacteria in Skimmed Milk Using Surface Enhanced Raman Scattering Mapping on 4-mercaptophenylboronic Acid Functionalized Silver Dendrites. *Anal. Bioanal. Chem.* 2017, 409, 2229−2238.

(26) Wu, S.; Liu, Y.; Ma, C.; Wang, J.; Zhang, Y.; Song, P.; Xia, L. Effect of Intermolecular Distance on Surface-Plasmon-Assisted Catalysis. *Langmuir* 2018, 34, 7240−7247.

(27) Luo, W. L.; Su, Y. Q.; Tian, X. D.; Zhao, L. B.; Wu, D. Y.; Tian, Z. Q. Reaction of p-Chloronitrobenzene Adsorbed on Silver Nanoparticles. *Acta Phys.-Chim. Sin.* 2012, 28, 2767−2773.

(28) Wu, D. Y.; Liu, X. M.; Huang, Y. F.; Ren, B.; Xu, X.; Tian, Z. Q. Surface Catalytic Coupling Reaction of p-Mercaptoaniline Linking to Silver Nanostructures Responsible for Abnormal SERS Enhancement: A DFT Study. *J. Phys. Chem. C* 2009, 113, 18212−18222.

(29) Huang, Y. F.; Zhu, H. P.; Liu, G. K.; Wu, D. Y.; Ren, B.; Tian, Z. Q. When the Signal is not from the Original Molecule to be Detected: Chemical Transformation of para-aminothiophenol on Ag during the SERS Measurement. *J. Am. Chem. Soc.* 2010, 132, 9244−9246.

(30) Xu, P.; Kang, L.; Mack, N. H.; Schanze, K. S.; Han, X.; Wang, H. L. Mechanistic Understanding of Surface Plasmon Assisted Catalysis on a Single Particle: Cyclic Redox of 4-Aminothiophenol. *Sci. Rep.* 2013, 3, 2997.
(31) Liu, X.; Tang, L.; Niessner, R.; Ying, Y.; Haisch, C. Nitrite-Triggered Surface Plasmon-Assisted Catalytic Conversion of $p$-Aminothiophenol to $p, p'$-Dimercaptoazobenzene on Gold Nanoparticle: Surface-Enhanced Raman Scattering Investigation and Potential for Nitrite Detection. *Anal. Chem.* 2014, 87, 499−506.

(32) Yang, X. M.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. Examination of the Photoreaction of $p$-Nitrobenzoic Acid on Electrochemically Roughened Silver Using Surface-enhanced Raman Imaging (SERI). *J. Phys. Chem. B* 1998, 102, 4933−4943.

(33) Barker, I. K.; Fawcett, V.; Long, D. A. Solvent Dependence of the Resonance Raman Spectra of Azobenzene, 4-aminobenzene, 4-methylaminobenzene and 4-dimethylaminoazobenzene. *J. Raman Spectrosc.* 1987, 18, 71−75.

(34) Bandara, H. D.; Burdette, S. C. Photoisomerization in different classes of azobenzene. *Chem. Soc. Rev.* 2012, 41, 1809−1825.

(35) Forber, C. L.; Kelusky, E. C.; Bunce, N. J.; Zerner, M. C. Electronic spectra of cis- and trans-azobenzenes: consequences of ortho substitution. *J. Am. Chem. Soc.* 1985, 107, 5884−5890.

(36) Chen, B.; Jiao, X.; Chen, D. Size-controlled and Size-designed Synthesis of Nano/Submicrometer Ag Particles. *Cryst. Growth Des.* 2010, 10, 3378−3386.

(37) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2013.