The pH-Controlled Plasmon-Assisted Surface Photocatalysis Reaction of 4-Aminothiophenol to \( p,p' \)-Dimercaptoazobenzene on Au, Ag, and Cu Colloids

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ABSTRACT:

In this paper, we report experimentally and theoretically a surface photocatalysis reaction of 4-aminothiophenol (PATP) to \( p,p' \)-dimercaptoazobenzene (DMAB) on Au, Ag, and Cu colloids. Surface enhanced Raman scattering (SERS) spectra of PATP on Au and Cu colloids are significantly different from the normal Raman spectrum of PATP powder. Quantum chemical calculations reveal that PATP on Au and Cu colloids is converted to DMAB by a surface photocatalysis reaction, and all the strongly enhanced Raman peaks are the symmetric Ag vibrational mode by surface plasmon. The pH value effects on surface photocatalysis reaction were also investigated experimentally. It is found that plasmon-assisted surface photocatalysis reaction can be efficiently controlled by different pH values. The possibility of protonation of PATP adsorbed on Au and Ag nanoparticles at pH 3 is investigated theoretically. The molecular mechanism is proposed for controlling surface photocatalysis reaction by pH values.

I. INTRODUCTION

It has become an important scientific area for the interaction of laser radiation with molecules absorbed on metal surfaces. Initially the effect in this area focused on the phenomena of surface-enhanced Raman scattering (SERS).1–5 These experiments showed that the apparent cross section for Raman scattering of a molecule absorbed on a rough surface of silver enhanced by many orders of magnitude above its gas phase value. There are two widely accepted enhancement mechanisms, which are electromagnetic field enhancement and chemical enhancement (charge transfer between molecules and metal).4–10

Using SERS, recently surface photocatalysis reactions have been investigated theoretically and experimentally. Recently, we have proved the photochemical conversion of 4-aminothiophenol (PATP) to \( p,p' \)-dimercaptoazobenzene (DMAB) occurs during SERS experiments with enhancing Ag colloids.11 The SERS spectra of a mixture of PATP with Ag colloids showed good agreement with theoretically predicted spectra of DMAB and were significantly different from PATP spectra. This interpretation was further proven by surface mass spectrometry measurements.12 The mass spectra clearly confirmed the presence of DMAB in the sample.12 All of the Raman peaks are assigned as the symmetric Ag vibrational modes, which are strongly enhanced by surface plasmon.11,13 By means of time-dependent SERS, Canpean and co-workers also claimed catalytic coupling reaction PATP on polystyrene spheres decorated with gold nanoparticle.14 It is also confirmed experimentally that 4-nitrobenzenethiol can be converted to DMAB by surface photochemical reaction in Cu sol.15 Recently, it is found
that gold nanoparticles are a new class of visible light photocatalysts for synthesis of fine organic chemicals.\textsuperscript{16–18}

Recent reports show an increasing trend in applying SERS-based pH sensing probes in cellular and tissue studies,\textsuperscript{19–21} where SERS nanosensors act as a pH meter. Using SERS-based pH sensing, in this paper, we studied pH-controlled surface photocatalysis reaction of 4-aminothiophenol (PATP) to \( p, p^\prime \) -dimercaptoazobenzene (DMAB) on Au and Ag colloids. First, in the case of near neutral pH value, the surface photocatalysis reaction of PATP to DMAB on Au and Cu colloids is investigated experimentally and confirmed by quantum chemical calculations. Second is the pH-controlled surface photocatalysis reaction of PATP to DMAB on Au and Ag colloids. Lastly, the conclusions are derived that in the alkaline environment, such surface photocatalysis reaction also occurs, while the acidic condition does not favor this kind of photocatalysis reaction.

2. EXPERIMENTAL SECTION

The SERS active Au, Ag, and Cu colloids were synthesized, according to refs 22, 23, and 24, respectively. The scanning electron microscopy (SEM) images were obtained using a field emission (FE) microscope (Sirion, FEI) operating at an accelerating voltage of 10 kV. The SEM images (see Figure 1) show that most Au nanoparticles, Ag nanoparticles, and Cu micrometer-sized particles are hollow spheres with an average diameters of 25 nm, 80 nm, and 5\( \mu \)m, respectively.

PATP was purchased from Aldrich Chemical Co. and used without further treatment or purification. The solution of PATP in ethanol was introduced into capillary sample cells for normal Raman measurement. The solution of PATP in aqueous Au and Cu sols with 10\textsuperscript{-4} M concentrations was introduced into capillary sample cells for SERS measurement. The SERS spectra were recorded by a Renishaw inVia Raman system equipped with an integral microscope (LEICA, DMLM). The 632.8 nm radiation from the He–Ne laser was used as an excitation source. In our Raman experiment, the laser power used on the SERS sample was limited to 2 mW with a 50× objective. The appropriate holographic notch filter was set in the spectroscopy. The holographic grating (1800 grooves/mm) and the slit allowed for a spectra resolution of 1 cm\textsuperscript{-1}. The spectrometer was measured to be \( \pm 0.2 \) cm\textsuperscript{-1}. Raman scattering was detected using a Peltier-cooled CCD detector (576 × 384 pixels). For comparison, the pH value effects on SERS spectra were also measured experimentally, where HCl and NaOH were used to control pH = 3 and 10, respectively.

3. THEORETICAL CALCULATIONS

All of the quantum chemical calculations were done with the Gaussian 09 suite.\textsuperscript{25} The ground state geometry of PATP (see Figure 2a) was optimized with density functional theory (DFT),\textsuperscript{26} PW91PW91 functional\textsuperscript{27} and 6-311+g(2d,p) functional. With the optimized ground state geometry, the normal Raman scattering (NRS) spectrum of PATP was calculated at the same level of theory. The molecular structure of DMAB can be seen from Figure 2b. The models of PATP–Au\textsubscript{5} complex, PATP–Ag\textsubscript{5} complex, PATP–Cu\textsubscript{5} complex, Au\textsubscript{5}–DMAB–Au\textsubscript{5} junction and Au\textsubscript{5}–DMAB–Au\textsubscript{5} (see Figure 2c–f) were employed to study the electronic structures and SERS spectra. The ground-state geometries were optimized using DFT, PW91PW91 functional, 6-31G-(D) basis set for C, N, S, and H and LANL2DZ basis set\textsuperscript{28} for Au, Ag, and Cu. With the optimized ground state geometries, the SERS spectra were simulated with the same functional and basis set. The calculated Raman frequencies were scaled to 0.99. With the optimized ground state geometries, optical absorption spectra of PATP–Au\textsubscript{5} complex, PATP–Ag\textsubscript{5} complex,
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4. RESULTS AND DISCUSSION

We first measured the NRS spectrum of PATP in ethanol, which can be seen in Figure 3a. The simulated NRS spectrum of PATP can be seen in Figure 3b. Experimental and theoretical NRS spectra of PATP revealed that there are five Raman peaks. Before the SERS experiment, we simulated the Raman spectra of PATP adsorbed on Au and Cu nanoparticles, where the Au5 and Cu5 clusters were used in the quantum chemical calculations. Panels c and d of Figure 3 indicate that the SERS spectra of PATP on Au and Cu sols should be similar with those of the isolated PATP. The experimental SERS spectra (see Figure 3e,f) present that they are significantly different from the NRS spectrum of isolated PATP. There are three strongly enhanced SERS peaks around 1135, 1384, and 1428 cm⁻¹ in Au sol (and 1150, 1380, and 1422 cm⁻¹ in Cu sol). The small differences in Raman peaks (several nanometers) for the same vibrational modes in different sols result in different substrate effect. Our previous experimental reports and theoretical calculations revealed that they should be symmetric Ag₁₂, Ag₁₆, and Ag₁₇ vibrational modes of DMAB. Especially, Ag₁₇ vibrational mode is the −N=N− stretching mode of DMAB. Therefore our experimental results...
demonstrate that surface photocatalysis reaction of PATP to DMAB can occur in Au and Cu sols. Note that PATP cannot be converted to DMAB on flat Au film by surface photocatalysis reaction.13

To further confirm that the experimental SERS spectra in panels e and f of Figure 3 are the SERS spectra of DMAB produced from PATP by surface photocatalysis reaction, we calculated the SERS spectra of \( \text{Au}_{5} \text{DMAB} \) and \( \text{Cu}_{5} \text{DMAB} \) complexes.
Cu5—DMAB—Cu5 junctions, respectively. It is found that these three Raman peaks that appeared in SERS experiment are also, as expected, strongly enhanced. The symmetric Ag12, Ag16, and Ag17 vibrational mode for SERS of DMAB in Au and Cu sol can be seen from Figure 4, and Ag17 is the –N≡N– stretching mode. The above-mentioned theoretical simulations strongly support experimental results.

Table 1. Electronic Transition Energies of Au5—DMAB—Au5 and Cu5—DMAB—Cu5 Junctions, Where f Is Oscillator Strength

<table>
<thead>
<tr>
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<th>Au5—DMAB—Au5 junction</th>
<th>Cu5—DMAB—Cu5 junction</th>
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<tr>
<td>nm</td>
<td>f</td>
<td>nm</td>
</tr>
<tr>
<td>S1</td>
<td>447.53</td>
<td>0.0000</td>
</tr>
<tr>
<td>S2</td>
<td>360.87</td>
<td>0.0056</td>
</tr>
<tr>
<td>S3</td>
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<tr>
<td>S4</td>
<td>347.05</td>
<td>0.0000</td>
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<tr>
<td>S5</td>
<td>346.93</td>
<td>0.0843</td>
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<tr>
<td>S6</td>
<td>330.60</td>
<td>1.6262</td>
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<tr>
<td>S7</td>
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<tr>
<td>S8</td>
<td>315.84</td>
<td>0.2045</td>
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<tr>
<td>S9</td>
<td>307.74</td>
<td>0.0000</td>
</tr>
<tr>
<td>S10</td>
<td>307.74</td>
<td>0.0002</td>
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Table 2. Calculated Static Polarizabilities of PATP, Au5—DMAB—Au5 Junction and Cu5—DMAB—Cu5 Junction

<table>
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<tr>
<th></th>
<th>xx</th>
<th>yy</th>
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<tr>
<td>PATP</td>
<td>153.377</td>
<td>100.904</td>
<td>63.505</td>
</tr>
<tr>
<td>Au5—DMAB—Au5 junction</td>
<td>1221.991</td>
<td>573.792</td>
<td>430.347</td>
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<tr>
<td>Cu5—DMAB—Cu5 junction</td>
<td>1108.688</td>
<td>511.572</td>
<td>413.491</td>
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</table>

Figure 4. (a) Ag12 of DMAB in Au5—DMAB—Au5 junction, (b) Ag12 of DMAB in Cu5—DMAB—Cu5 junction, (c) Ag16 of DMAB in Au5—DMAB—Au5 junction, (d) Ag16 of DMAB in Cu5—DMAB—Cu5 junction, (e) Ag17 of DMAB in Au5—DMAB—Au5 junction, and (f) Ag17 of DMAB in Cu5—DMAB—Cu5 junction.

Figure 5. The distribution of the local electromagnetic field enhancement at 632.8 nm in junctions of Au nanoparticle dimer (diameter 20 nm) with a nanogap of 3 nm. A color bar in logarithmic scale for electric enhancement is shown.
The electronic transitions of Au₅/DMAB/C₀ and Cu₅/DMAB/C₀ junctions were studied with the TD-DFT method. The calculated results are listed in Table 1, which shows that they are the SERS spectra, not surface enhanced resonance Raman scattering (SERRS) spectra, since S₁ values are 447 and 441 nm, respectively. Theoretical results also exhibit that 0.373 and 0.021 e transferred to Au and Cu clusters, respectively, due to the interaction between molecule and metals. The charge transfer (between molecule and metal) results in the increase of the polarizabilities (see Table 2), which leads to the strongly enhancement of SERS spectra.

To study the local surface plasmon resonance effect on SERS, the near field distribution of an electromagnetic field is investigated with FDTD. Figure 5 shows that the SPR is localized in the nanogap and the strongest enhancement is at the center of the gap. The electromagnetic enhancement is |M|² = 3.3 × 10⁵, where |M| = |E_{local}/E_{in}|, and E_{local} and E_{in} are local and incident electric fields, respectively. The SERS enhancement is |M|⁴ = 1.0 × 10⁹.

Figure 6. (a) SERS spectrum of DMAB in Au sol (pH = 10), (b) SERS spectrum of DMAB in Ag sol (pH = 10), (c) SERS spectrum of PATP in Au sol (pH = 3), (d) SERS spectrum of PATP in Ag sol (pH = 3), (e) calculated SERS spectrum of PATP–Au₅ complex, (f) calculated SERS spectrum of PATP–Ag₅ complex, (g) calculated SERS spectrum of protonated PATP–Au₅ complex, and (h) calculated SERS spectrum of protonated PATP–Ag₅ complex.
The pH value dependent SERS spectra were also measured. For pH = 10 in Au and Ag sol, we found that the Raman peaks for Ag_{12}, Ag_{16}, and Ag_{17} vibrational modes are strongly enhanced (Figure 6a,b), which confirmed experimentally that the surface photocatalysis reaction of DMAB produced from PATP occurred. For pH = 3 in Au and Ag sol (Figure 6c,d), we found that the Raman peaks for Ag_{12}, Ag_{16}, and Ag_{17} vibrational modes are absent, and by comparing with Figure 6e,f, they are similar to the simulated SERS spectra of PATP adsorbed on Au and Ag nanoparticles (their vibrational modes can be seen in panels c–f of Figures 7), which do not appear in Figure 6d. So, PATP adsorbed on Ag nanoparticles was not protonated for pH = 3.

The molecular mechanism is proposed for controlling surface photocatalysis reaction by pH. In the neutral and alkaline condition, the PATP can be oxidized to DMAB on supported Au and Ag nanoparticles by surface plasmon resonance effect induced by laser. In the neutral and alkaline conditions, PATP first can be easily deprotonated, then the deprotonated PATP is oxidized to DMAB. While in the acidic condition, PATP is hard to be oxidized, because of abundant H^{+} in solution.

5. CONCLUSION

The pH-controlled plasmon-assisted surface photocatalysis reaction of PATP to DMAB on Au, Ag, and Cu colloids has been investigated experimentally and theoretically. It is found that plasmon-assisted surface photocatalysis reaction can be efficiently controlled by different pH values. When pH = 3, the surface photocatalysis reaction cannot occur; however under neutral and alkaline conditions (pH = 7 and 10), such a reaction does take place. By comparison of the experimental and calculated results, it is revealed that PATP was not protonated in Au and Ag sols, when pH = 3.

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REFERENCES

(11) Fang, Y. R.; Li, Y. Z.; Xu, H. X.; Sun, M. T. Langmuir 2010, 26, 7737.
(21) Pallaro, A.; Braun, G. B.; Reich, N. O.; Moskovits, M. Small 2010, 6, 618.
(32) FDTD Solutions, version 7.5; Numerical Solutions, Inc.: Vancouver, BC, Canada, 2009.