



Short Communication

The oxidant and laser power-dependent plasmon-driven surface photocatalysis reaction of *p*-aminothiophenol dimerizing into *p,p'*-dimercaptoazobenzene on Au nanoparticles

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ABSTRACT

Recently, plasmon-driven surface photocatalysis (PDSPC) reactions have attracted more and more attention by means of surface-enhanced Raman scattering (SERS) because we can *in situ* monitor the reaction process and determine the final products and their quantities by the real-time SERS spectrum. In this work, self-assembly AuNPs with both high catalytic activity and strong SERS effect were used as a bifunctional platform for *in situ* monitoring of PDSPC reactions. *p*-Aminothiophenol (PATP), a famous model molecule, was selected as a probe molecule and FeCl₃ and NaClO were selected as oxidants. In this way, oxidation reaction of PATP dimerizing into *p,p'*-dimercaptoazobenzene (DMAB) has been investigated by SERS, and the results show that oxidant and laser power can alter the conversion rate of the reaction. This work provides a novel approach for controlling PDSPC reaction rate, which may be useful for understanding the mechanism of PDSPC reactions.

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1. Introduction

In recent years, plasmon-driven surface photocatalysis (PDSPC) reactions have attracted more and more attention by application of SERS because SERS can reveal the catalytic reaction process *in situ*, which has significant importance for mechanism study and reaction condition optimization [1–22]. PATP has been a model probe for studying the photocatalysis reactions on metallic NPs by SERS because of its unique SERS spectral feature. The oxidation of PATP into DMAB by PDSPC reaction has been extensively reported experimentally and theoretically [1–22]. The previous works demonstrate how to control the surface-catalyzed oxidation of PATP into DMAB by different experimental conditions, such as the substrate, wavelength, and reaction timescales and pH values [5,11,13–14,18–19]. The results show that conversion of PATP into DMAB is an oxidation reaction, where electron loss from PATP to environment leads to the formation of DMAB [2–3,20,23]. Accordingly, the presence of an oxidant is conducive to electron transfer, which will increase the rate of reaction. That being the case, an appropriate oxidant would speed up the formation of DMAB. In this work, we selected two commonly used reagents, FeCl₃ and NaClO as oxidants to control the conversion of PATP into DMAB. The impact of the excitation power on the reaction is also investigated. The results

show that the oxidants as well as the laser power both can alter the reaction rate.

2. Materials and methods

2.1. Reagents and instruments

Trisodium citrate, ferric chloride (FeCl₃) and sodium hypochlorite (NaClO) were bought from Beijing Chemical Reagent Company (China); hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl₄·4H₂O) were purchased from Kermel Chemical Reagent Co. Ltd., (Tianjin, China); PATP were obtained from J&K Chemical Company (China). All reagents are analytical grade and used without further purification. Deionized (DI) water (Millipore Milli-Q System, >18.2 MΩ/cm) was used throughout the experiment. Raman spectra were recorded with JY HR800 (HORIBA Jobin Yvon), equipped with a 50× objective (NA = 0.5) and Ar-Kr laser with 647 nm wavelength. Field-emission gun scanning electron microscope (SEM, Hitachi S-4800, 3 kV) were used to characterize the prepared samples.

2.2. Preparation of the gold nanoparticles (AuNPs) and SERS sample

AuNPs were synthesized by reduction of HAuCl₄ using trisodium citrate according to the previously reported method [24]. Briefly, a 100 mL of 0.01 M HAuCl₄ aqueous solution was heated to boiling under stirring. After adding 1.5 mL of 1% trisodium citrate solution, the

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mixed solution was boiling for about 30 min. After cooling to room temperature under stirring, the resulting AuNPs colloid with the size of 35 nm was stored in a refrigerator at 4 °C for further use.

To prepare the SERS substrate, small polished Si wafers were cleaned in a 3:7 solution of 30 wt% H₂O₂ and 30 wt% H₂SO₄ for 1 h. The wafers were then rinsed by DI water and dried, then put into a 1 wt% 3-aminopropyltriethoxysilane (APTES) solution. After aging over 10 h, the wafers were rinsed thoroughly by DI water and dried. Then the wafers were immersed into an AuNPs suspension for more than 1 h to allow assemble the AuNPs on Si wafers. After being rinsed with DI water to remove unattached AuNPs, the SERS-active substrates were obtained. For achieving the SERS spectra of PATP, the substrates were soaked in a PATP solution of ethanol for 30 min. After being rinsed with ethanol to remove free molecules, the sample was soaked in water for SERS measurement.

3. Results and discussions

Fig. 1 shows the typical SEM images of the as-prepared SERS substrate, which reveal that the average size of AuNPs is about 35 nm and the AuNPs are packed into a sub-monolayer. Some clusters were formed on the wafer where the AuNPs were in close proximity to their neighbors, which was beneficial for the creation of electromagnetic “hot spots” [25]. According to the EM enhancement mechanism, the AuNPs film must be highly SERS active.

We recorded the SERS spectra of PATP adsorbed on the AuNPs using a 647 nm irradiation as the excitation source. As reported previously, the SERS peaks of PATP varied as a function of laser irradiation time (as shown in Fig. 2). The PATP molecule belongs to the symmetry group of C_{2v} when it adsorbed on the AuNPs. The recorded SERS spectrum at the beginning is dominated by the C—S stretching vibration at ~1080 cm⁻¹ and the C=C stretching vibration at ~1590 cm⁻¹, bands assignable to the totally symmetric (a₁) vibration modes of PATP. With the time, additional three new bands emerge, at ~1145, 1380 and 1435 cm⁻¹ due to the β(CH) and ν(N=N) of the DMAB, respectively [7,15–16]. These bands are assigned to the a_g modes, the characteristic bands of DMAB, so the intensity ratios of a_g mode bands to that of a₁ mode bands can be used to estimate the yield of DMAB. We selected the

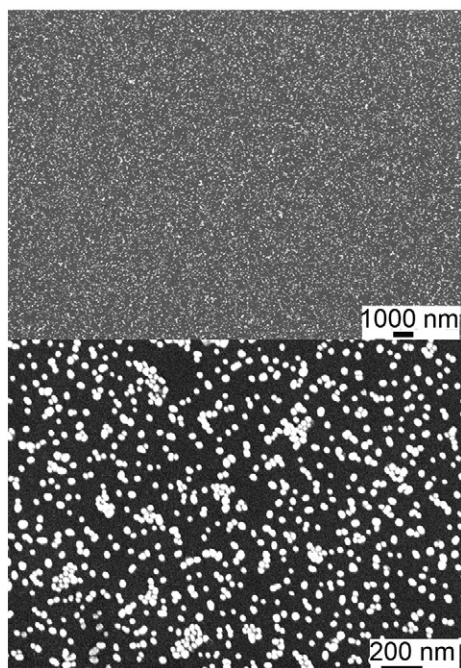


Fig. 1. (A) SEM images of the as-prepared Au nanoparticles' substrate and (B) the expanded image.

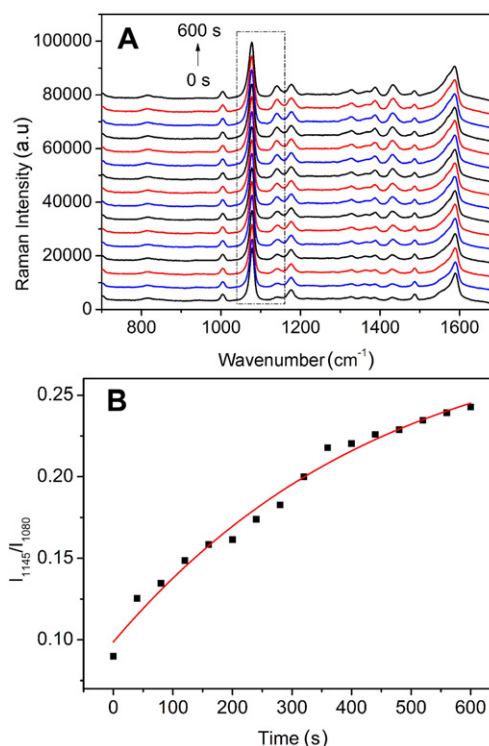


Fig. 2. (A) Time-dependent SERS spectra of PATP adsorbed on AuNPs measured when sample soaked in DI water, (B) variation of the 1145 cm⁻¹ band intensity with respect to that of the 1080 cm⁻¹ band.

band around 1145 cm⁻¹ as a characteristic band of the obtained DMAB. Fig. 2B shows the variation of the band at ~1145 cm⁻¹ with respect to the band at ~1080 cm⁻¹. The relative intensity is related to the amount of the received DMAB and the increase of the intensity shows the percentage of the DMAB increase with the aging time. Time-dependent SERS spectra of PATP on AuNPs substrate under continuous exposure to a 647 nm laser are shown in Fig. 2 and the ratio increases with time, indicating that some of the PATP molecules have been converted into DMAB. However, the intensity of the a_g band with respect to that of the a₁ band is relatively low. The ratio only increases up to ~0.24 when the irradiation time is up to 600 s. This indicates that the conversion of PATP to DMAB is relatively low in the absence of additional oxidant with the exception of O₂ in air.

The previous studies shown that the reaction that PATP adsorbed on plasmonic nanostructures converted into DMAB is strongly influenced by the solution pH [5,19], the irradiation wavelength [11,26], the irradiation power [11], the substrate materials [26], and the surrounding atmosphere [3,23]. As we know, PATP was converted into DMAB by an oxidation reaction. So the rate of conversion will be accelerated if the oxidants are present in the surrounding atmosphere because the resulting surface active oxygen atoms could enhance the surface catalytic efficiency. We chose FeCl₃ as oxidation agent. Firstly, AuNPs substrate was put into a PATP solution for 30 min. Then the sample was rinsed with ethanol. Finally, the sample was soaked in a 0.1 mM FeCl₃ solution for SERS measurement. We found that the Raman bands at 1000 cm⁻¹–1500 cm⁻¹ are dramatically increased compared to the sample soaked in deionized (DI) water, which could confirm the occurrence of the oxidation reaction with a larger conversion rate. As shown in Fig. 3, the a_g mode bands at ~1145, 1380 and 1435 cm⁻¹ emerge and the intensities become more and more intense with the time. Comparing to the ‘b₂’ mode signals of PATP achieved in the absence of the additional oxidant, the intensities of these bands achieved after addition of oxidant are more intense and the ratio is up to ~0.65 when the irradiation time is up to 600 s, showing the more PATP had been converted into DMAB. Considering that the previous study found that the low

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