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pH-Dependent plasmonic catalysis of 4-nitrobenzenethiol in aqueous environment

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ABSTRACT

Plasmon-driven chemical reaction of 4-nitrobenzenethiol (4-NBT) dimerizing to p,p′-dimercaptoazobenzene (DMAB) has been successfully monitored under different pH solutions. The experimental results indicated that the chemical reactions were dependent on the pH values, and they proceeded more completely under acidic conditions than those under neutral and alkaline conditions. Furthermore, the rate of the chemical reactions was effectively controlled by exposure time and incident laser power. The stable pH dependence demonstrated the plasmon-driven chemical reactions of 4-NBT to DMAB are sensitive to the surrounding environment, and have wider applications.

1. Introduction

Azobenzene compounds are high-value and important chemicals widely used in chemical industry as dyes, food additives, and drugs [1]. They are synthesized either by oxidation of anilines or by reduction of nitroaromatics. In 2008, an environmentally friendly gold-nanoparticle-catalyzed synthetic method was proposed to selectively form azobenzene compounds from aromatic anilines [2]. It was reported that DMAB, an azobenzene derivative, can be produced from the selective catalytic coupling reaction of typical aromatic compounds PATP or 4-NBT on rough noble metal surfaces [3,4].

Recently, a novel application of plasmonics on chemical reactions has been widely investigated, such as photochemical isomerization [5], photodissociation [6,7], and catalytic reactions [8–19]. In this paper, we focused on plasmon-driven surface-catalyzed reactions. In plasmon-driven chemical reactions, plasmonic nanostructures are used to enhance the surface-catalyzed reactions [20,21]. Because they generate a significantly enhanced local electromagnetic field caused by local surface plasmon polaritons (SPPs), and noble metal nanoparticles exhibit high catalytic activity in many catalytic reactions [22,23]. Extensive experimental and theoretical studies have demonstrated that the plasmon-driven chemical reactions of both PATP and 4-NBT can be selectively dimmerized to DMAB when absorbed on plasmonic nanostructures [24–27]. The reactions are strongly influenced by the reaction timescales, substrate materials, laser wavelength and power, and the surrounding atmosphere [28–30]. In particular, the plasmon-driven oxidation reaction of PATP to DMAB could be effectively controlled by pH values [31–34], which would occur under neutral and alkaline condition, while not happen under acidic condition. However, how to control the plasmon-driven chemical reaction of 4-NBT to DMAB by different pH values, is still not clear.

With the help of surface plasmon, two 4-NBT molecules dimerize to a DMAB molecule, and can this plasmon catalyzed reaction be controlled by pH values? If possible, the dependence of pH on the catalytic reaction of 4-NBT to DMAB can be similar to that of PATP to DMAB? If not, the reactions can occur under all pH conditions, which need fewer constraints and then present a wider application. Herein, the dynamic process of the plasmon-driven conversion of 4-NBT into DMAB has been monitored via time-dependent and laser power-dependent surface-enhanced Raman scattering (SERS) spectra. Above all, we demonstrated the plasmon-driven catalytic reaction of 4-NBT to DMAB is dependent of pH values.

2. Experimental

The SRES active Ag colloid was prepared by sodium citrate reduction of $AgNO_3$ [35]. 30 mg $AgNO_3$ was dissolved in 150 mL deionized water. This solution was well-sealed and brought to heat with the microwave oven (595 W) for three minutes. Then 4 mL sodium citrate solution

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(1%) was added. After stirring enough, the mixed solution was heated in the microwave oven for 5 min, and then made it cool at room temperature. The final Ag nanoparticles were mixed with 4-NBT ethanol solution (1×10^{-5} M) for 24 h, and were introduced into capillary, sealing the both ends up, for SERS measurement. On the other hand, the pH value effects on the plasmon-driven chemical reaction were also investigated. Diluted HCl and NaOH solution were added to the mixed solution, to control pH = 3 and 10, respectively.

The surface morphology of Ag nanoparticles was characterized by SEM (Hitachi S-4800). Fig. 1a shows the SEM image of the coupling of Ag nanoparticles, and Fig. 1b is the SEM image of Ag nanoparticles mixed with 4-NBT molecule. Combining Fig. 1a and b, it was found that there were many three-dimensional (3D) nanogaps ("hot spots") in Fig. 1b. 3D hot spots can produce stronger localized surface plasmon resonance (LSPR) than 2D roughened substrate, thus further enhancing the plasmon-driven catalytic reactions. Furthermore, we measured the extinction spectra of Ag solutions and Ag solutions mixed with 4-NBT ethanol solutions (1×10^{-5} M) in the same volume under different pH values using absorption spectroscopy (HP8453, USA) (see Fig. 2a). From the extinction spectra, it was found that the absorption peak of Ag nanoparticles is about 410 nm, and there is a red shift of SPR peak of Ag nanoparticles after being mixed with 4-NBT molecule. We suggested this shift presumably resulted from the interaction of 4-NBT molecule and Ag nanoparticles and the effect of ethanol solvent.

The normal Raman spectrum of 4-NBT and SERS spectra of 4-NBT on the Ag nanoparticles were measured with the Renishaw invia spectrometer, and a 632.8 nm He–Ne laser (3.28 mW) was used as the exciting light. The all spectra were recorded with an accumulation time of 10 s.

3. Results and discussion

Fig. 2b shows the normal Raman spectra of 4-NBT powder, and there are three strong Raman peaks at 1100 cm^{-1}, 1332 cm^{-1}, 1576 cm^{-1}. Additionally, the strongest Raman peak at 1332 cm^{-1} is attributed to $v_s(NO_2)$ [26]. The SERS spectra of 4-NBT absorbed on the Ag nanoparticles were measured under 100% laser power (~3.28 mW) under neutral condition (see Fig. 3a). When laser irradiated at the first time of 10 s, it was found that the SERS spectrum was nearly identical to the Raman spectrum of 4-NBT powder (see Fig. 2b). However, as the exposure time increasing to 50 s, there occurred three weak peak at 1143 cm^{-1}, 1390 cm^{-1}, 1439 cm^{-1} (the red dash line in Fig. 3a), which were slightly different from the Raman spectrum of 4-NBT powder. With the exposure time adding to 100 s, a very significant difference was observed. As the previously reported [4], the appearance of Raman peaks at 1390 cm^{-1}, 1439 cm^{-1} were related to –N = N– stretching vibration of DMAB, which demonstrated the formation of DMAB. Further, as the laser irradiation time increased, the intensity of Raman peak at 1439 cm^{-1} continued to enhance. Until 200 s, the intensity of the Raman peak at 1439 cm^{-1} exceeded that at 1332 cm^{-1}, but the Raman peak of $v_s(NO_2)$ of 4-NBT at 1332 cm^{-1} had not disappeared completely, even though the exposure time further added. Therefore, the varying Raman peaks provided direct and strong evidence for the plasmon-driven chemical reaction of DMAB produced from 4-NBT. Meanwhile, the time-varying Raman intensity demonstrated this reaction is time-dependent.

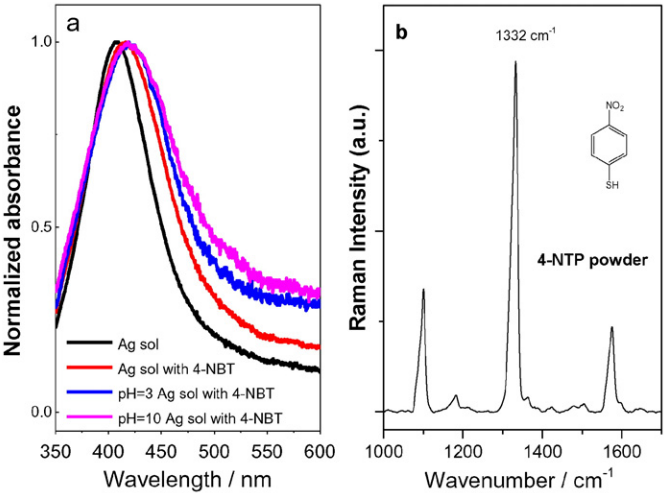

Fig. 2. (a) The extinction spectra of Ag sol and 4-NBT in Ag sol mixed with 4-NBT molecule under different pH values, and (b) normal Raman spectrum of 4-NBT powder.

The same work was done under alkaline condition. All measurements were at the same exposure time and incident laser power (100%). Fig. 3b (the red lines) showed an increasing intensity of Raman peaks centered at 1143 cm^{-1}, 1390 cm^{-1}, 1439 cm^{-1}, which clearly distinguished from the spectrum in Fig. 3b, indicating an increased extent of DMAB formation. We concluded that the plasmon-driven catalytic reaction of DMAB from 4-NBT also could occur under alkaline condition, and the reaction was time-dependent.

The above studies have suggested that the plasmon-driven chemical reaction of 4-NBT to DMAB could occur under neutral and alkaline condition. Then, will it occur in acidic environment? Therefore, we studied this reaction under acidic condition using the same method. Fig. 3c illustrated that the plasmon-driven catalytic reaction of 4-NBT to DMAB had not happened before 50 s. As the exposure time added to 50 s, the reaction begun to occur, and the intensity of Raman peak at 1439 cm^{-1} had exceeded that at 1332 cm^{-1} (see Fig. 3c). When the radiation time increased to 200 s, the yield of DMAB kept growing. Until 350 s, the extent of this reaction came to the maximum. It can conclude that the plasmon-driven catalytic reaction of 4-NBT to DMAB can take place under acidic condition, and was time-dependent, having similar behaviors as those under neutral and alkaline condition. It was worth mentioning that the reactions were more completely at pH = 3 than those under other two pH environments (see the spectra of 350 s in Fig. 3a, b and c).

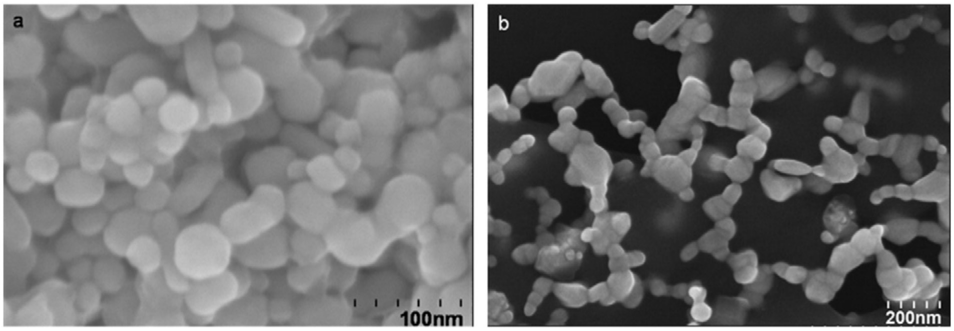

Fig. 1. (a) The SEM imaging of Ag nanoparticles without 4-NBT molecule, and (b) the morphology of Ag nanoparticles mixed with 4-NBT molecule.