Inhibiting plasmon catalyzed conversion of para-nitrothiophenol on monolayer film of Au nanoparticles probed by surface enhanced Raman spectroscopy

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HIGHLIGHTS

- The plasmon induced conversion of PNTP was dependent on the laser power, solvent and substrate structure.
- Water played the essential role in the plasmon catalyzed reaction of PNTP in ionic liquids.
- The introduction of coadsorption species resulted in the inhibition on dimerization of PNTP.
- The activity of plasmon catalyzed dimerization of PNTP was in the sequence of H_2O > methanol > *n*-hexane ≈ acetonitrile ≈ DMF.

GRAPHICAL ABSTRACT
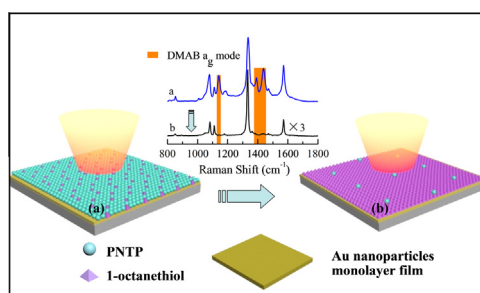
ABSTRACT

The plasmon catalyzed surface reaction has been attracted considerable attention due to its promising application in heterogeneous catalysis. This kind of plasmon catalysis played bilateral roles in driving the unconventional reactions or destructing the surface molecule layer. The acceleration or inhibition on this catalysis is still remained significant challenge. In this paper, monolayer film of Au nanoparticles was fabricated at air/water interface as substrates both for surface enhanced Raman spectroscopy (SERS) and plasmon catalyzed surface reaction. The influence from several issues, involving surfactants, coadsorption species, the solvent and water, were systemically investigated to probe the acceleration and inhibition on the plasmon catalysis reaction. The concentration and molecular weight of surfactant polyvinylpyrrolidone (PVP) exhibited significant influence in the reactive activity for the plasmon catalyzed dimerization of para-nitrothiophenol (PNTP) to p,p'-dimercaptoazobenzene (DMAB). A suitable molecular weight of 10,000 and concentration of 10 mg/mL were beneficial for improving the conversion efficiency of PNTP to DMAB. The higher molar ratio of coadsorbed 1-octanethiol and the aprotic solvents resulted in the inhibition of dimerization because 1-octanethiol occupied the surface sites to isolate the adsorbed PNTP molecules with a larger distance and lack of proton source. The plasmon catalysis occurred in ionic liquids suggested that water was essential for the dimerization of PNTP, in which it was used to accelerate the reaction rate and severed as the hydrogen source.

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Introduction

Since the first discovery of surface-enhanced Raman spectroscopy (SERS) in 1974, it has been successfully used in surface

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science, life, materials and relevant fields due to its extremely high surface sensitivity [1–3]. Although the exact description on mechanisms of SERS enhancement effect was still in debating, two dominate enhancement contributions were well accepted, that is, charge transfer (CT) and electromagnetic (EM) enhancements [4,5]. The former was mainly contributed by charge transfer between adsorbed molecules and metal surfaces driven by photon with an appropriate energy, while the latter was generally caused by surface plasmon resonance (SPR), in which the SPR provided the strong electromagnetic field to enhance the Raman signals of probe molecules. Thus, the SPR played the critical role in contributing SERS effect [6]. For example, due to the strong coupling effect of localized SPR, the enhancement factor of molecules adsorbed in the junction of adjacent Ag nanoparticles reached to 14–15 orders of magnitude, which made the single molecule detection possible [7]. Therefore, as extremely sensitive tool, SERS effectively detected the varying adsorbate even on the surface condition with a slight change. However, the laser played dual roles in the generation of SPR for SERS and inducing the surface catalyzed reaction. From the surface reaction point of view, the collective oscillation of metal conducting electrons could significantly enhance local electromagnetic field on a metal surface under the irradiation of a laser, thus improving the photochemical process in metal surface. Besides, it was reported that surface plasmon by relaxation promoted the formation of hot electron–hole pairs to drive surface catalyzed reaction [8]. And the heating effect caused by the non-radiative relaxation process also accelerated the surface reaction. Therefore, by integrating strongly plasmonic and catalytic metal nanoparticles, the laser induced catalytic activity was improved dramatically. Some unconventional reactions, including the reduction of CO_2, water splitting, dissociation of H_2 and decarboxylation, were achieved on the plasmonic nanostructures [9–12]. Most importantly, the plasmonic nanostructures promised to be a breakthrough for driving photon-assisted processes and offered the powerful tool to in situ probe the mechanism of the relevant surface processes at molecular level. So far, it has already received considerable attentions, particularly for the N–N coupling reaction from the nitro-/amino-aromatic compounds anchored on metal nanoparticles. For instance, Roth found the SERS signals of para-nitrobenzoic acid (PNBA) and para-aminobenzoic acid (PABA) on the silver surface were obviously different from their normal Raman signals. It was demonstrated that the PNBA and PABA were underwent a photochemical reaction and finally were transferred to aromatic azodibenzoate compounds [13,14]. The observation of similar SERS spectral feature from different molecules indicated the same products were formed by the laser induced surface reaction. Then the typical bands originated from azo compounds were observed from a series of anilines and aromatic nitro compounds [15]. Based on the above fact, one could assume that the SERS was not a non-destructive tool, and the explanation on the SERS feature became complex. Generally, these unusual SERS spectra from the products confused the researchers and the misunderstanding explanation was proposed. One typical example was the assignments of three enhanced Raman bands at 1143 cm^{-1}, 1390 cm^{-1} and 1432 cm^{-1} of para-aminothiophenol (PATP) adsorbed on Ag nanoparticles. Osawa et al. assigned these signals to the "b$_2$ modes" of PATP, which was well accepted and widely used to elaborate the chemical enhancement mechanism for a long period [16]. Ren and his co-workers demonstrated experimentally and theoretically that these vibrational modes originated from "a$_g$ modes" of p,p'-dimercaptoazobenzene (DMAB), which was produced from the coupling reaction of PATP. These bands were assigned to the C–N and N=N stretching vibration of DMAB [17]. They also investigated the catalytic oxidation which was mainly contributed to the activation of oxygen through the surface plasmon on metal nanoparticles [18]. What's more, by high

vacuum tip-enhanced Raman spectroscopy (HV-TERS), Sun et al. provided convincing spectroscopic evidence for the dimerization of PATP molecules to DMAB [19]. Very recently, Liu et al. investigated the factors that influenced the reaction for further understanding the plasmon catalysis mechanism. They found that the formation of DMAB was critically depended on the surface coverage of PATP, the aggregation state of nanoparticles, laser power, laser wavelength and the nature of metal nanoparticles [20,21]. The disappearance of DMAB signals at very low concentration of Ag nanoparticles indicated that DMAB was only formed between the PATP molecules adsorbed on the neighboring nanoparticles with a suitable distance. Sun et al. reported the direct experimental and theoretical evidences of the surface-catalyzed transformation from PATP to DMAB assisted by local surface plasmon [22]. Then systematic investigations have also supported the findings revealed by SERS spectroscopy [23,24].

Similarly, researchers originally considered PATP as the photochemical reaction product of para-nitrothiophenol (PNTP). Sun and co-workers demonstrated that the PNTP was actually converted to DMAB [25]. Since then, a series of studies have been carried out to investigate the plasmon induced reduction of PNTP from different aspects, such as the substrate, laser power, wavelength, timescale, and pH values [26,27]. In addition, Xu et al. controlled the plasmon-driven dimerization reaction of PNTP to DMAB by the incident laser intensity, tunneling current and bias voltage [28]. Deckert et al. developed a dual-wavelength tip-enhanced Raman spectroscopy approach to monitor the transformation process of PNTP to DMAB at nanoscale for obtaining the deeper insight in reaction mechanism [29]. Sun et al. controlled the plasmon-driven sequential reaction of para-nitrothioanisole (PNTA) via pH values in aqueous environment. They demonstrated that abundant H$^+$ in the aqueous environment could effectively capture hot electrons, reducing the hot electron concentration and hindering chemical reactions. While in an environment with abundant negative ions, hot electrons could be effectively increased, promoting plasmon-driven chemical reactions [30]. So far, most of the investigation was focused on the transformation of PNTP rather than the inhibition of the plasmon catalyzed reaction. Actually, the investigation on the inhibition was beneficial to obtain the deeper insight into the mechanism of the plasmon catalyzed reaction. Moreover, as a strong adsorbent, PNTP was adsorbed on a metal substrate strongly, forming a self-assembly monolayer. Generally, the formation of compact and uniform monolayer of functional organic molecules became one of the key steps during the fabrication of molecule-based optoelectronic devices, thus it was essential to take the photostability of monolayer into account [31]. However, the plasmon induced surface reaction was occurred quickly as PNTP was irradiated under a laser on metal nanoparticles. It resulted in the remarkable defect for fabrication and application of organic optoelectronic devices. Therefore, a few parameters, such as laser power, wavelength were controlled to inhibit the surface reaction [26]. Unfortunately, it was not effective, especially on the SERS substrates, such as Au, Ag, Cu [3,26]. Therefore, the appropriate strategy was highly desired in order to inhibit the surface plasmon catalyzed reaction, not only for the well understanding of surface reaction mechanisms, but also for avoiding the defect in the organic optoelectronic devices irradiated with a light.

In this paper, a compact and uniform monolayer film of Au nanoparticles was self-assembled at air/water interface as the substrate for the generation of surface plasmon resonance. The optimal conditions for converting PNTP to DMAB were then obtained based on SERS monitoring. The influence of concentration and molecular weight of the surfactant PVP on the conversion of PNTP to DMAB was explored. In order to inhibit the plasmon induced surface reaction, another molecule of 1-octanethiol was