Chemical Physics Letters 639 (2015) 47–51

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Selective plasmon driven surface catalysis in metal triangular nanoplate-molecule-film sandwich structure

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ARTICLE INFO

Article history:
Received 5 July 2015
In final form 1 September 2015
Available online 7 September 2015

ABSTRACT

Combined with surface enhanced Raman scattering (SERS) and finite difference time-domain (FDTD) method, the plasmon-driven surface catalytic (PDSC) reaction of *p,p′*-dimercaptoazobenzene (DMAB) produced from 4-nitrobenzenethiol (4NBT) or P-aminothiophenol (PATP) in Au triangular nanoplate-molecule-film sandwich structure is investigated. The disparity of SERS spectra at different positions on Au triangular nanoplate indicates that the surface catalysis is selective performed at some particular regions, which change along with the polarization direction of the incident laser. Furthermore, this selective surface catalysis phenomenon has also been confirmed by the simulated electric field distribution using FDTD method. Our results enlarge the metal nanostructure of PDSC reactions and provide a useful help to study the SERS and surface catalysis.

1. Introduction

As a highly active research field, plasmonics which could manipulate light in nanoscale has attracted great attentions in recent years [1–3]. Collective electrons oscillation on metal surface excited by photons is defined as surface plasmon polaritions (SPPs) [4]. SPPs is extensively applied in sensors, thermal cancer therapy, photovoltaics, surface enhanced Raman scattering (SERS), photo detection, single molecule detection, photocatalysis, [5–12] etc.

In photocatalysis field, SPPs could generate 'hot electrons' to realize a quite huge enhanced electromagnetic (EM) field, which drives the catalysis reaction further. This plasmon-driven surface catalytic reaction provides a new way to synthesize new molecules induced by local surface plasmons (SPs), and can be revealed by SERS spectroscopy [13]. SERS is widely studied for its utmost high surface sensitivity and powerful applications on fingerprint vibrational spectroscopy in qualitative and quantitative, even at single-molecule level.

Recently, a series of experimental and theoretical studies have been performed on SERS of P-aminothiophenol (PATP) or 4-nitrobenzenethiol (4NBT) molecule adsorbed in the junction of metal-molecule-metal system [14,15]. The PDSC reaction of PATP or 4NBT in this metal-molecule-metal sandwich structure was identified by three strong enhanced SERS peaks at 1143, 1390 and 1432 cm^{-1}, and these peaks were explained by chemical enhancement of SERS since 1994 [16]. However, the prediction that *p,p′*-dimercaptoazobenzene (DMAB) could be produced from PATP molecule on Ag nanoparticles by a catalytic reaction was firstly proposed by Wu and co-workers, and then subsequently demonstrated experimentally and theoretically [17–23]. Afterwards, numerous studies have been done to provide further evidence. Sun et al. also testified that DMAB can be produced from 4-nitrobenzenethiol (4NBT). Due to the variation of surface plasmons in different metal nanostructures, a series of metal surfaces were applied to attest the PDSC reaction, such as colloids [14,15], nanoparticles dimer [24], nanowires [25], single nanoparticle [26], film [15,27], etc. Among them, nanoparticle-film system has been widely studied due to its simple configuration and highly confined EM field in the nanogaps between particle and film [28,29]. Unlike metal colloids SERS system, nanogaps in nanoparticle-film could achieve selective enhancement of EM filed in a subwavelength area on film because of its better uniformity [30]. More studies have shown that this enhancement in nanogaps mainly depends on the size, composition, shape, the number of nanoparticle, and the thickness of film [24–30].

In this letter, we investigate the PDSC reaction of DMAB produced from 4NBT or PATP molecule confined in the gap between Au triangular nanoplate and film combined with SERS and FDTD

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http://dx.doi.org/10.1016/j.cplett.2015.09.004
0009-2614/

methods. A 633 nm laser was incident onto different regions of this Au triangular nanoplate-molecule-film sandwich structure, and the corresponding SERS spectra of PATP or 4NBT were measured separately. Our results indicate that surface catalysis reactions have more possibility to occur on some particular regions of our sandwich system, identified by the strongly enhanced SERS peaks. We also find these particular catalyzed regions change along with the polarization direction of the incident laser. To further clarify this selective catalysis phenomenon, the distribution and the enhancement of electric field in the Au triangular nanoplate-film gap were analyzed with FDTD method.

2. Experimental methods

P-aminothiophenol (PATP) and 4-nitrobenzenethiol (4NBT) were purchased from Aladdin Industrial Corporation. Au film on a silicon wafer was prepared by using the electron beam evaporation system (model Peva-600E) under high vacuum condition. The evaporation conditions were controlled to achieve a uniform layer of Au film with an average thickness of 100 nm. The surface roughness of Au film and thickness of Au triangular nanoplate were evaluated to be about 2.249 nm and 50 nm, respectively, with atomic force microscopy (AFM).

The Au triangular nanoplates were prepared with a surfactant-promoted reductive route. Specifically, we adopted hydrothermal treatment of chloroauric acid in the presence of surfactant CTAB without using reducing agent [31]. In a typical synthesis, 25.5 mg of hexadecyltrimethyl ammonium bromide (CTAB) was dissolved in 20 mL of distilled water (the concentration of CTAB is 3.5 mM) under continuous magnetic stirring, after that, 1 mL of $HAuCl_4$ solution (12.5 mM) was added. Thirty minutes later, the mixtures were transferred into a 50 mL autoclave, sealed and kept at 160 °C for 8 h in a furnace, and then cooled to room temperature. The precipitates were collected and washed with distilled water. The size and shape of nanoplates were measured by the scanning electron microscopy (TESCAN MIRA 3 FE-SEM). The side length of nanoplates has a typical size of a few microns. One such triangular nanoplate is illustrated by SEM image in Figure 1c.

The Au film was immersed in a 5×10^{-5} M ethanol solution of PATP (or 4NBT) for more than 2 h. Then it was washed with distilled water or ethanol for several times to eliminate thick clusters of molecules on the Au film and achieve a uniform one-nanometer-thick molecule layer. After that, the Au nanoplates were spin coated on Au film. The measurements of SERS were conducted by a commercial Micro Raman spectrometer (Horibba) with a 633 nm laser. Figure 1a is a cartoon illustrating the Au triangular nanoplate-molecule-film sandwich structure. Yellow color indicates Au, aqua color illustrates the PATP or 4NBT molecule layer, red color indicates the incident laser. The side length and thickness of the Au triangular nanoplate were 6 μm and 50 nm, respectively, and the gap thickness between the Au triangular nanoplate and Au film was 1 nm as shown in Figure 1a. For the numerical simulation part, the distribution and enhancement of electric field in the Au triangular nanoplate-film gap were analyzed by using FDTD method. The side length and thickness of the Au triangular nanoplate were set as 6 μm and 50 nm respectively to be consistent with experiment parameters. The gap thickness between the Au triangular nanoplate and Au film was set as 1 nm. The excitation source was a plane light with a wavelength of 633 nm. The light was vertically incident upon the center of the Au triangular nanoplate. These two approaches (SERS and FDTD) were combined to reveal a complete picture.

As comparison, the normal Raman spectrum of 4NBT or PATP in ethanol solution was measured firstly by dropping them onto the SiO_2 substrate. Four strong Raman peaks at 1084, 1175, 1336 and

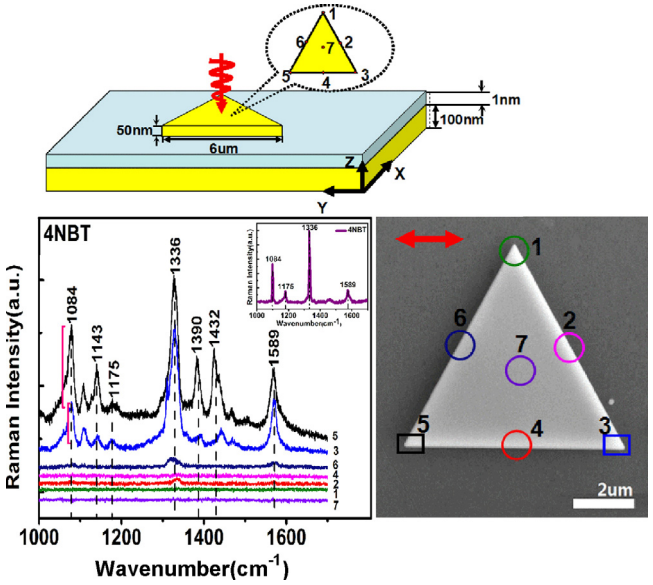

Figure 1. (a) A cartoon illustrating the Au triangular nanoplate-molecule-film sandwich structure. Yellow color indicates Au, aqua color illustrates the PATP or 4NBT molecule layer, red color indicates the incident laser. (b) The experimental SERS spectra of DMAB produced from 4NBT excited by a 633 nm laser, the number at the right end of each spectrum corresponds to the region in gap zone, respectively. The inset shows the normal Raman spectrum of 4NBT. (c) The corresponding SEM image of Au triangular nanoplate on Au film used in the experiment. The polarization of the laser is parallel to the base of Au triangular nanoplate illustrated by the red double-headed arrow. Colorized circle indicates the part hard to be catalyzed or even not to be catalyzed, while the colorized rectangle stands for the part that has more possibility to be catalyzed. The color and number of circle or rectangle are in consistence with the SERS spectrum in (b). The side length of the Au triangular nanoplate is about 6 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

1589 cm^{-1} turn up for 4NBT molecule, while the Raman spectrum of PATP exhibits three strong peaks at 1084, 1175 and 1589 cm^{-1}.

3. Results and discussion

3.1. SERS spectra of 4NBT exited by 633 nm laser (DMAB produced from 4NBT)

The SERS spectra of 4NBT in seven special regions of the Au triangular nanoplate-4NBT molecule-Au film sandwich system were measured individually as shown in Figure 1b. The polarization direction of incident laser with a wavelength of 633 nm was parallel to the base of Au triangular nanoplate as illustrated by the red double-headed arrow in Figure 1c. Three additional Raman peaks at 1143, 1390 and 1432 cm^{-1} turned up for our sandwich system compared with the normal spectrum of 4NBT molecule in ethanol solution (see the inset in Figure 1b). These newly formed peaks were related to N=N of DMAB molecular vibrational modes [13,27,32], and only appeared at two particular regions around the base angles of the triangular nanoplate (labeled with number 3 and 5 in Figure 1b). The obvious Raman feature of DMAB in Figure 1b illustrate that 4NBT was converted to DMAB around the two base angles when the polarization direction of laser was parallel to the base of the triangular nanoplate. Moreover, SERS intensities were greatly enhanced around these two catalyzed regions indicating that a greater electric field was generated. However, the PDSC reaction of 4NBT did not show up at the other five regions for our sandwich system. In other words, only two special regions with strong electric field are catalyzed obviously, which are also marked with blue and black rectangles in Figure 1c, while other five regions