纳米光子学丛书

Plasmon and Plasmon Exciton Hybrids for Surface Catalytic Reactions

表面等离激元及其与激子杂化在表面催化反应中的应用



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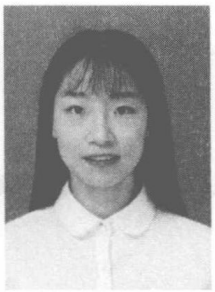
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CHAPTER 1

Introduction

When light shone a precious metal surface, the SP was a collective oscillation about free electrons present at the interface between the metal and the dielectric. There are two types of SP: the local SP and the propagating SP. According to local SP resonance, the tip-enhanced Raman scattering (TERS) and the surface-enhanced Raman scattering (SERS) spectra had been extensively used in the field of nanoscale ultra-sensitive Raman analysis. Surface catalysis accelerated the rate of the chemical reactions as a result of the less active energy required to add the catalyst. Therefore, we need to find more efficient and stable catalysts to accelerate the chemical reactions rate, which is a huge challenge we are facing now. In order to enhance the efficiency and probability about plasmon exciton co-driven chemical reactions, we could consider the application of electrooptical synergy.

In our previously studies, the plasmonic waveguide had been used in the field of the remotely excited SERS spectroscopy successfully. Remotely excited SERS had many special advantages over the traditional SERS. In normal SERS, when the excited light was concentrated on the detected spot, called local SERS, and in the remote SERS, the excitation point was far from the observed target, and the SP polaritons(SPPs) with the remote mode excited the target. Because the gold and silver waveguides transmit optical signals through the SPPs, they provided a method to go below size limit. The SPPs could propagate down the metal waveguide and transmit free photons at the end of

the waveguides or at the imperfections, some of which were lost owing to the ohmic damping.

In this book, to begin with, plasmon catalysis for the activation energy offered by plasmonics-induced hot electrons had been exposed in a large number of chemical reactions, such as in atmospheric, liquid and HV conditions and so on. In addition, we used the femtosecond pump-probe transient absorption spectroscopy to learn the physical principles of the plasmon exciton coupling interaction about the surface catalytic reactions. Then, we reported the electrically enhanced about the surface oxidation or reduction catalytic reactions at the plasmon exciton hybrid interface. Next, we presented the latest research progress report about the surface catalytic reactions driven by propagating SPPs (plasmon waveguides). Furthermore, we could know that *p*, *p*′-dimercaptoazobenzene (DMAB) could be produced from the *p*-aminothiophenol (PATP) by propagating SPPs (PSPPs), which was a plasmon driven oxidation reactions, while DMAB was generated from the 4-nitrobenzenethiol (4NBT) by transporting SPPs, which was a reduction reactions driven by a plasmon waveguide. Last but not least, we researched the molecular resonance dissociation about the surface-adsorbed molecule by plasmon nanoscissors.

All the color figures please scan the QR code.

CHAPTER 2

SP-Driven Oxidation Catalytic Reactions

2.1 SP-Driven Oxidation Catalytic Reactions by SERS in Atmosphere Environment

2.1.1 Genuine SERS Spectrum of PATP

In previously studies, the authors researched the genuine SERS spectra of PATP by selecting the appropriate SERS substrate and by a lower concentration of PATP solution, however, the authors did not observe the vibrational mode of the DMAB at 1140 cm^{-1}, 1390 cm^{-1}, and 1432 cm^{-1}, and the SERS spectrum was equal to the Raman spectrum of the PATP powder. This experiment used a He-Ne laser as the excitation source with 632.8 nm. In the Raman experiment, the laser power was limited to 0.01 mW and a 100× objective used on the SERS sample. The data acquisition time was 10 seconds. Here the authors detected the NRSS about the PATP as a control experiment.

Figure 1(a) displayed the normal Raman scattering (NRS) spectroscopy of PATP powder, and Fig. 1(b) showed the SERS spectrum[1]. The authors could find that the former and the latter had the same spectrum. However, the authors did not observe DMAB vibration mode at 1140 cm^{-1}, 1390 cm^{-1}, and 1432 cm^{-1}, respectively. This demonstrated that the SERS spectrum was derived from a PATP monomer rather than a DMAB dimer consisting of two PATP molecules. The Fig. 1(c) displayed the simulated Raman spectrum about

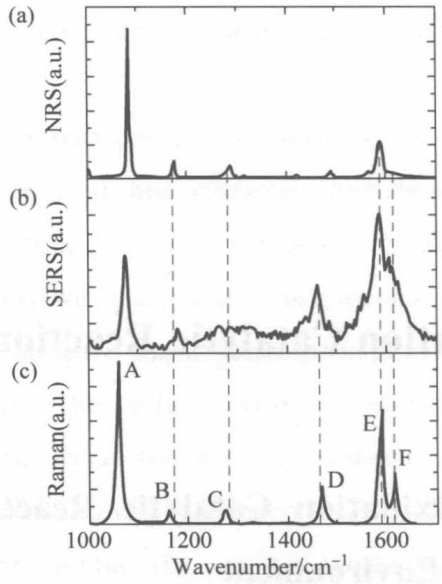


Fig. 1 (a) NRS spectrum of PATP powder; (b) SERS spectrum of PATP; (c) The simulated Raman spectrum of PATP adsorbed on Ag_5 cluster[1]

the PATP adsorbed on the Ag_5 cluster, and the experimental results in Fig. 1(b) were proved. Six vibration modes were shown in Fig. 2. Figures 3(a) and (b) revealed the SERS spectrum of the PATP at the beginning and after 60

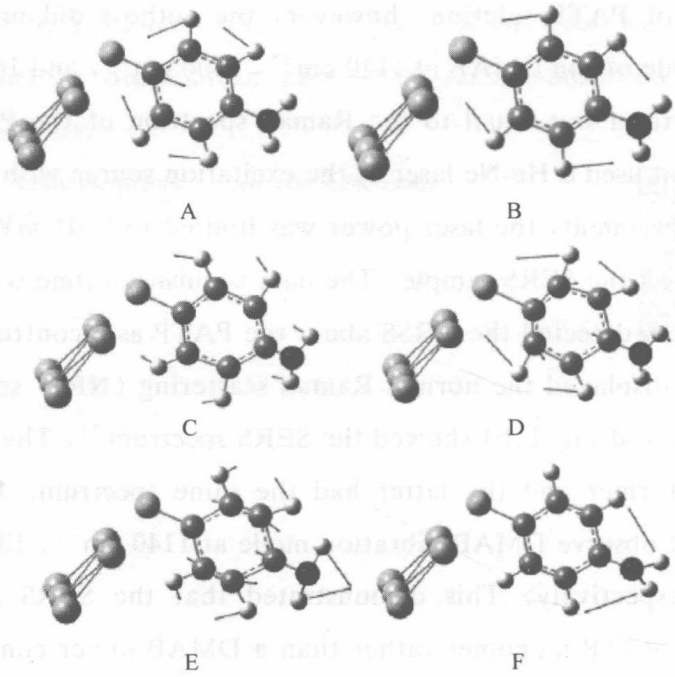


Fig. 2 Vibrational modes of PATP adsorbed on Ag_5 cluster in Fig. 1(c)[1]

(For colored figure please scan the QR code on page 2)

seconds, respectively, when the laser was continuously illuminated on the sample. Using the spectrum in Fig. 3(a) as a control, three strong Raman signals about DMAB at 1140 cm^{-1}, 1390 cm^{-1}, and 1432 cm^{-1} could be observed clearly in the Fig. 3(b). In addition, the vibration of the Raman signal of the PATP at 1610 cm^{-1} could be observed in Fig. 3(a) but not observed in Fig. 3(b). This demonstrated that PATP underwent a dimerization reaction to convert to DMAB by increasing the irradiation time. As was demonstrated in the Fig. 3(c), a characteristic SERS spectrum about the PATP in a silver aggregation system, where the experimental conditions were the same as described above. The authors could see that Fig. 3(c) displayed three stronger Raman signals about the DMAB at 1140 cm^{-1}, 1390 cm^{-1}, and 1432 cm^{-1}, with a radiation time of only 10 seconds[2,3]. Since, in such a system, it was impossible to find the genuine SERS spectrum about the PATP practically. Therefore, the authors made the chemical reactions rate of dimerization faster by increasing plasmon enhancement. And the mode assignments about the DMAB was displayed in Fig. 3(c)[2].

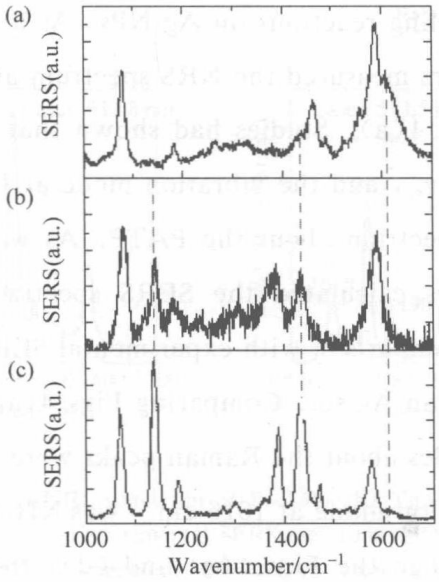


Fig. 3 (a),(b) SERS spectra of PATP measured at the very beginning and after 60 s of laser radiating in Ag nanowires (NWs) on Ag film system, respectively; (c) The SERS spectrum of DMAB in Ag aggregation system[1]