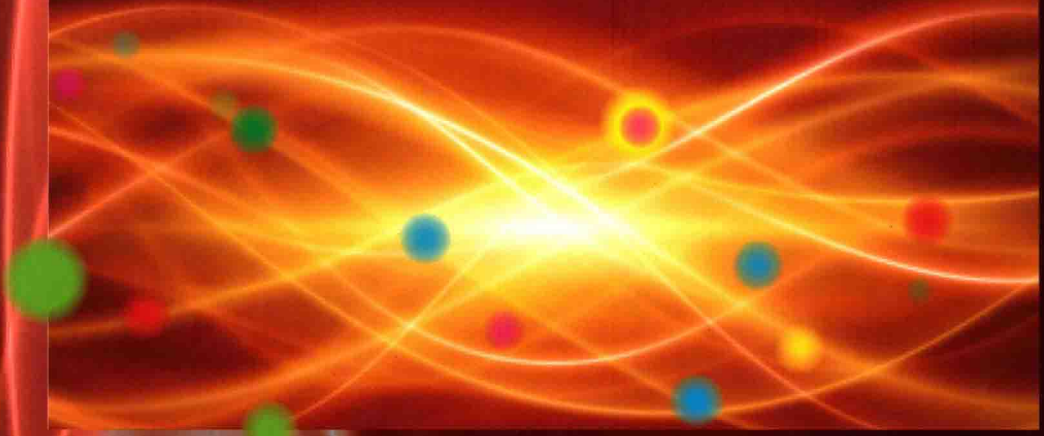
纳米光子学丛书

Plasmon-Exciton Interaction:

Principles and Applications

等离激元-激子相互作用：

原理和应用



孙萌涛 林炜铧 梁文杰 著

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内 容 简 介

本书从原理和应用两个方向展开，详细介绍了多种环境中的等离激元驱动催化反应和等离激元-激子耦合驱动催化反应。主要可分为以下部分：基于表面增强拉曼散射(SERS)的等离激元驱动催化反应在大气和液相中的机理和应用、基于针尖增强拉曼散射(TERS)的等离激元驱动催化反应在高真空中的机理和应用、等离激元-激子耦合相互作用的物理模型和特性研究、等离激元-激子耦合驱动催化反应在电化学液相中的应用，以及光电协同调控下的耦合驱动催化反应。通过介绍大量经典研究案例，结合相应理论计算与模型简介，深入浅出地介绍了等离激元-激子相互作用的意义与发展前景。

本书适用于有一定理论基础的物理学本科生和有光学相关研究经历的研究生和科研工作者。

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编 委 员

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CONTENTS

CHAPTER 1

Introduction

In this book, from principles to applications, we introduce plasmon-driven and plasmon-exciton co-driven surface catalytic reactions in atmosphere, liquid and high vacuum environments. Since the discovery of plasmon-driven chemical reaction in 2010[1,2], plasmonic chemistry has been one of important branches of plasmonics[3,4]. While, the lifetime of plasmonic hot electrons generated from plasmon decay is about 150 femtoseconds, which is too short to surface catalytic reaction, and then the probability and efficiency of plasmon-driven chemical reactions are low. To increase them, the lifttime and amounts of plasmonic hot electrons should be significantly increased.

The plasmon-exciton coupling interaction for surface catalytic reactions has been reported in 2015, in which the probability and efficiency of plasmon-exciton co-driven chemical reactions have been significantly increased, where the lifetime of hot electrons has been enlarged to several hundred picoseconds[5-8]. The ultrafast femtosecond pump-probe absorption spectroscopy reveals the nature of plasmon-excition coupling interactions, and demonstrates the ultrafast electron transfer between the plasmon metal and the exciton semiconductor.

To further improve the probability and efficiency of plasmon-exciton co-driven chemical reactions, the gate voltage and the bias voltage and current have also been employed by us. The electro-optical synergy has been applied in plasmon-excitonco-driven surface reduction reactions in 2017[9]. The voltage manipulates plasmon-exciton co-driven chemical reactions can reach up to

higher probability and efficiency in surface catalytic reactions.

In this book, we introduce plasmonic chemistry in the field of surface catalytic reactions in detail, including the principles and applications of interactions among plasmon, exciton and molecule on the plasmonic nanostructure covered by monolayer semiconductors. The book is suitable for the research scientists, Ph. D. candidates and bachelor students, who would like to learn or study plasmon-exciton co-driven chemical reactions.

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CHAPTER 2

Plasmon-Driven Chemical Reactions Based on SERS in Atmosphere

2.1 Brief introduction

It is widely known that Raman scattering can be measured as the fingerprint of specific molecules. And the major obstacle is that the intensity and resolution are relatively weak. Hence, as a developed technology, surface-enhanced Raman scattering (SERS) was found in 1974 by Fleischmann[1,2], which has more general applications on fingerprint vibrational spectroscopy with single-molecule sensitivity[3].

With the developed properties, SERS has been widely used in many fields, such as sensors, biology and material science[1,4-10]. Two enhancement mechanisms of plasmon-enhanced Raman scattering are widely accepted, which are electromagnetic enhancement (EME) and chemical enhancement (CE)[7,11-14]. The EME attributes to the localized surface plasmon resonance (LSPR) mainly on the rough metal surfaces radiated by a laser[12]. And the EME is considered as a nonselective amplification mechanism for enhancing the Raman signals of all vibration modes of adsorbed molecules of 10^{10}–10^{11}. However, the CE, which is up to 10^3, can result in some specific Raman peaks being selectively enhanced enormously instead. And the CE, which mainly attributed to the charge transfer mechanism, can be considered as a resonance Raman process between

the ground electronic state of the molecule-metal hybrid system and the metal-molecule charge transfer electronic state[15-18].

Since its discovery, SERS had been long regarded as a noninvasive technique. The Raman peaks of para-aminothiophenol (PATP) at 1 140 cm^{-1}, 1 391 cm^{-1} and 1 440 cm^{-1} on Ag nanoparticles (NPs) were once considered as the enhanced "b_2 modes" induced by CE[19-28], because the selective and tremendous enhancements only of the four "b_2 modes" could not be explained by the EME[24]. However, Fujishima and co-workers doubted that the "b_2 modes" may come from other surface azobenzene species[29]. In 2010, Wu and co-workers predicted that "b_2 modes" were assigned to the N=N bond of p,p′-dimercaptoazobenzene (DMAB) theoretically, which was generated from PATP on Ag NPs through a surface catalytic reaction, and their chemical structures are shown in Fig. 2-1. For further reinterpretation, Sun and co-workers[30] investigated the existence of DMAB, and Huang studied the relation between the chemical transfer and the power density of laser in conventional SERS. In the meantime, surface mass spectroscopy (SMS) and SERS measurements on the synthesized DMAB convincingly support the proposal[22,28,31-47].

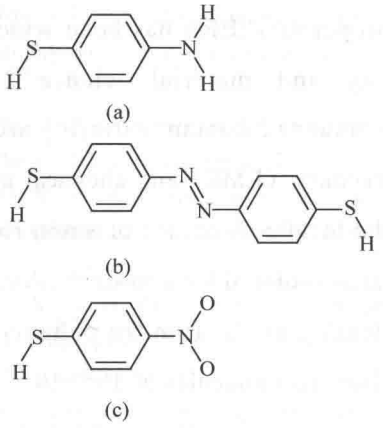

Fig. 2-1 The molecular structures of (a) PATP, (b) DMAB and (c) 4NBT, respectively

Many PATP-Ag junction models are used for theoretical studies whether the "b_2 modes" of PATP can be reproduced. After considering several cases, it can be concluded that the "b_2 modes" of PATP agree well with a_g modes of DMAB[48]. As an additional evidence, Huang also found that when the laser intensity decreased, the intensities of the "b_2 modes" of PATP would diminish. The characteristic that the intensities of "b_2 modes" depend on the laser intensity[33] conflicts with the photon-driven charge transfer (PDCT) model due to the quasi-resonance-enhanced Raman. In PDCT model, the intensities of the "b_2 modes" should be tuned by the wavelength and the potential instead of the laser power. The details will be introduced later[24].

After confirming that the surface plasmons (SPs) can not only enhance the Raman signals of molecules but also induce the surface catalytic reactions, the systematic works on the novel application of SPs on both plasmon-driven oxidation and reduction reactions have been reviewed[49].

In this chapter, we mainly focus on the novel phenomenon of plasmon-driven surface catalytic reactions in the atmosphere. As mentioned above, PATP is widely used in investigating the deeper mechanism of plasmon-driven surface oxidation reactions, which can be oxidized to DMAB with the help of SPs. On the other hand, 4-nitrobenzenethiol (4NBT) is a proper candidate for plasmon-driven reduction reactions. Then, for further investigation, we thoroughly study several cases which have different conditions such as adjusting the substrates and the wavelengths of laser. Finally, to comprehensively study the problem, we also take the priority between the plasmon-driven oxidation and reduction reactions in the atmosphere.

2.2 Plasmon-driven oxidation reactions

The plasmon-driven surface catalytic reactions are related to many aspects. To thoroughly address this problem, we will divide it into several parts. First, we will introduce the genuine SERS spectrum of PATP, which indicates that SPs

are able to only enhance the Raman signals of PATP without inducing the catalytic reactions. Then, plasmon-driven oxidation reactions on different substrates will be presented, such as Au/Ag/Au film and hybrid systems. Normally, three-dimensional finite-difference time domain (3D-FDTD) method is used for deeper investigating the differences between the effects of substrates on the CMEs. Besides, the CE can be stimulated using dependent density functional theory. Moreover, the effect of the wavelengths of laser, as well as the mechanism of the plasmon-driven oxidation reactions will also be investigated.

2.2.1 Genuine SERS spectrum of PATP

Before proving the existence of surface-catalyzed reaction that DMAB can be produced from PATP on several substrates, the genuine SERS spectrum of PATP itself needs to be confirmed. However, the phenomenon is hard to observe because the monomer of PATP is easy to convert to dimer in the atmosphere.

With the help of the designed substrate, the SERS spectrum of PATP can be obtained without the "b_2 modes". The SERS spectrum fits well with the NRS spectrum and the theoretical Raman spectrum of PATP, indicating that PATP on the special substrate does not be oxidized to DMAB, as shown in Fig. 2-2. The substrate is prepared as Ag nanowire-Ag film junction structure, where the thickness of the Ag film is about 120 nm and the diameter of Ag nanowire is about 300 nm. The advantages of this substrate can be concluded in two parts. First, the metallic nanowire can disperse the plasmon, so the effect of plasmon coupling can be reduced noticeably compared with in the hot spots between NPs[50]. The other reason is that the number of molecules between the Ag nanowire and Ag film can be well controlled by adjusting the concentration of PATP solutions. When the number of PATP molecule is controlled in small quantities, DMAB cannot be produced easily. As a result of the two aspects, the plasmon-driven oxidation reactions can be well controlled and even avoided.

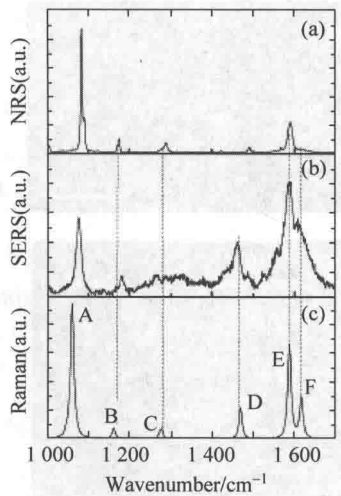

Fig. 2-2 (a) Normal Raman scattering NRS spectrum of PATP powder; (b) genuine SERS spectrum; (c) the stimulated Raman spectrum of PATP[51]

To further investigate the mechanism, the related calculations are presented which indicate that the plasmon enhancement based on the Ag nanowire-Ag film system is too weak to induce the plasmon-driven oxidation reactions. As a control group, Fig. 2-3 is presented where the radius of NPs is 40 nm and the distance is 1 nm. The incident laser is chosen as a plane wave with a wavelength of 633 nm. And according to the calculation, it is obvious that the EM enhancement in the gap between the Ag nanowire and Ag film is much weaker than that between Ag NP, which explains why genuine SERS of PATP can be observed in the hybrid system. In a word, the EME plays a key role in affecting surface catalytic reactions.

2.2.2 Experimental and theoretical investigations of plasmon-driven oxidation reactions

After realizing that the EME plays a crucial role in the surface catalytic reactions, there are other several factors we need to reveal whether they are vital in SERS. First of all, the incident laser is indispensable to produce the SPs and further induces the surface catalytic reactions, where the time-dependent

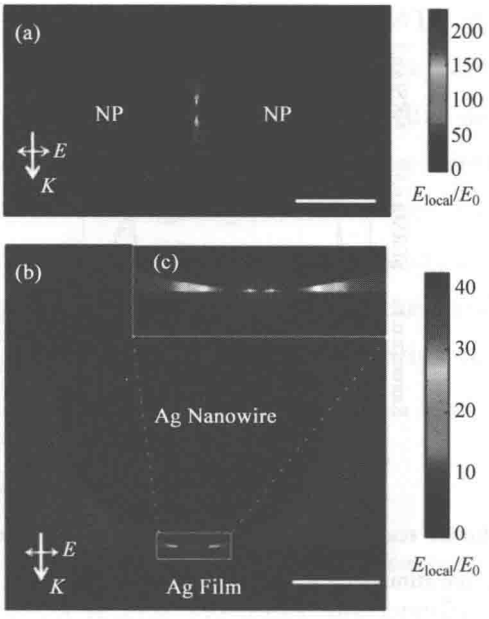

Fig. 2-3 The calculation of EMEs in (a) Ag NP dimer; (b) Ag nanowire-Ag film hybrid system[51]

(Colored picture attached at the end of the book)

SERS spectra can be used to reveal the relationship. The wavelength of laser also affects the probability and efficiency of plasmon-driven surface catalytic reactions in many aspects significantly. Besides, the substrate should be available instead of dispersing plasmons.

1. Laser-dependent plasmon-driven oxidation reactions

In this part, we will introduce the effects of incident laser on plasmon-driven oxidation reactions, which are divided into two important parts as the time-dependent and wavelength-dependent SERS catalytic reactions. Before investigating the effect of these conditions, there is no doubt that the laser exists or not plays a decisive role in plasmon-driven surface catalytic reactions. According to the surface mass spectroscopic (SMS) measurement, PATP adsorbed on Ag electrodes ($r = 40$ nm) can transform to DMAB with the help of high-power laser. The spectra of PATP adsorbed on Ag electrodes under