

Plasmon-Mediated Chemical Reactions on Nanostructures Unveiled by Surface-Enhanced Raman Spectroscopy

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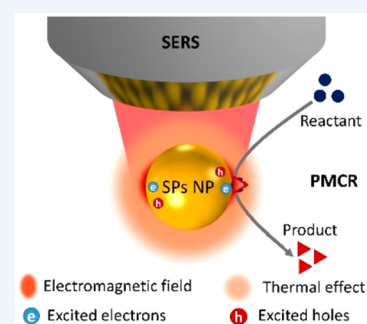
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CONSPECTUS: Surface plasmons (SPs) originating from the collective oscillation of conduction electrons in nanostructured metals (Au, Ag, Cu, etc.) can redistribute not only the electromagnetic fields but also the excited carriers (electrons and holes) and heat energy in time and space. Therefore, SPs can engage in a variety of processes, such as molecular spectroscopy and chemical reaction. Recently, plenty of demonstrations have made plasmon-mediated chemical reactions (PMCRs) a very active research field and make it as a promising approach to facilitate light-driven chemical reactions under mild conditions. Concurrently, making use of the same SPs, surface-enhanced Raman spectroscopy (SERS) with a high surface sensitivity and energy resolution becomes a powerful and commonly used technique for the in situ study of PMCRs.

Typically, various effects induced by SPs, including the enhanced electromagnetic field, local heating, excited electrons, and excited holes, can mediate chemical reactions. Herein, we use the para-aminothiophenol (PATP) transformation as an example to elaborate how SERS can be used to study the mechanism of PMCR system combined with theoretical calculations. First, we distinguish the chemical transformation of PATP to 4,4'-dimercaptoazobenzene (DMAB) from the chemical enhancement mechanism of SERS through a series of theoretical and in situ SERS studies. Then, we focus on disentangling the photothermal, hot electrons, and “hot holes” effects in the SPs-induced PATP-to-DMAB conversion. Through varying the key reaction parameters, such as the wavelength and intensity of the incident light, using various core–shell plasmonic nanostructures with different charge transfer properties, we extract the key factors that influence the efficiency and mechanism of this reaction. We confidently prove that the transformation of PATP can occur on account of the oxygen activation induced by the hot electrons or because of the action of hot holes in the absence of oxygen and confirm the critical effect of the interface between the plasmonic nanostructure and reactants. The products of these two process are different. Furthermore, we compare the correlation between PMCRs and SERS, discuss different scenario of PMCRs in situ studied by SERS, and provide some suggestions for the SERS investigation on the PMCRs. Finally, we comment on the mechanism studies on how to distinguish the multieffects of SPs and their influence on the PMCRs, as well as on how to power the chemical reaction and regulate the product selectivity in higher efficiencies.



INTRODUCTION

Surface plasmons (SPs) originate from the collective oscillation of conduction electrons and play a critical role in the optical properties of nanostructured metals (Au, Ag, Cu, etc.) and heavily doped semiconductors. Growing out of the deep understanding of surface-enhanced Raman spectroscopy (SERS)—the remarkably enhanced Raman scattering process when the observing molecules, ions, radicals, or other materials are adsorbed on or located near some nanostructured metal surfaces^{1–3}—the application of SPs has been expanded to a wider range, such as spectroscopy,^{4–6} sensing,^{7,8} thermal therapy,^{9,10} wave guiding,^{11,12} etc. Nowadays, people found that SPs can mediate some chemical processes through the generation of the enhanced electromagnetic near-field, the excited carriers, or the local-heating effect.^{13–20} Plasmon-mediated chemical reactions include two main types,

enhancing the reaction rate of downhill reactions (the change of Gibbs free energy is negative) and inducing the uphill reactions (the change of Gibbs free energy is positive). For example, the oxygen molecules can be activated in the presence of plasmonic nanostructures under illumination, which helps to overcome energy barriers for the catalytic oxidation of CO, NH₃, etc.²¹ By using the excited electrons and holes generated from the Au nanorod arrays in contact with a TiO₂ film, water splitting, a typical endothermic reaction, can also proceed with an appreciable rate.²² Numerous demonstrations of the plasmon-mediated chemical reactions (PMCRs) have positively proved it as a promising approach to facilitate light-driven chemical conversions under mild conditions.^{13,18,23–27}

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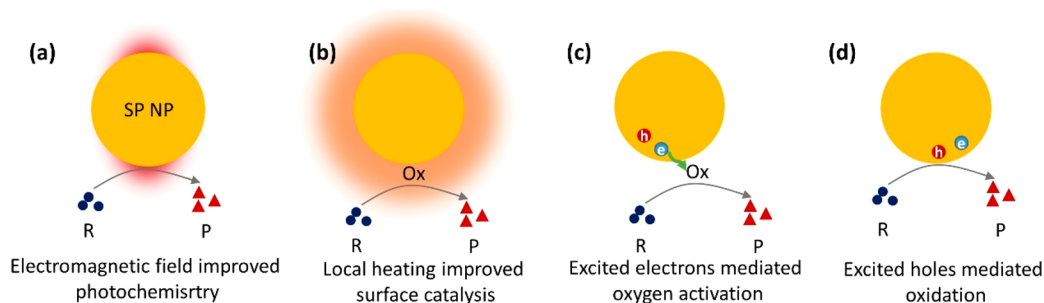


Figure 1. Schematic of the plasmon-mediated chemical reactions (PMCRs), using an oxidation reaction as an example. (a) Electromagnetic near-field improved photochemistry. The enhanced electromagnetic near-field increases the probability of molecular excitation for a molecule near the plasmonic nanostructure. This will increase the rate or the yield of the photochemical reaction but requires overlap of the absorption spectrum of the plasmonic nanostructure with that of the molecule. (b) Local heating improved surface catalysis. (c) SPs excited electrons induced activation of oxygen species. The excited electrons transfer to the oxygen species near the surface and activate it, and then accelerate the oxidation reaction. (d) SPs excited holes mediated oxidation. The excited holes transfer to the reactant to mediate the oxidation reaction.

As a spectroscopic technique making use of the SPs excitation, SERS has been successfully applied for the in situ investigation of PMCRs with an ultrahigh surface sensitivity and a high energy resolution.^{28,29} In the initial stage of SERS study, changes in Raman spectra have been discovered by some groups including us, but they are often considered as negative examples of the thermal decomposition or photo-decomposition caused by focused lasers. As early examples, the SPs accelerated photochemical decomposition processes were tracked using the time-evolved SERS spectra.³⁰ About ten years ago, the transformation of para-aminothiophenol (PATP) to *p,p'*-dimercaptoazobenzene (DMAB) induced by SPs, one of the most typical PMCR example, was discovered during the SERS measurement.^{31–33} Thereafter, its reaction mechanism has been continuously explored, for example, the pH effect and the effect of surface ligands, which greatly promotes the development of PMCRs.^{23,34–37} Numerous PMCR systems have been reported and in situ investigated by SERS.^{38–41} In such circumstances, the nanostructure-based plasmonic enhancement was exploited in two ways: to mediate the chemical reaction and to measure over time the concentrations of the reactants, intermediates, or products, which are often in meagre quantities. However, compared with SERS, whose mechanism has been thoroughly studied, our physicochemical understanding of PMCRs is still far from complete. Almost all effects induced by SPs, including the enhanced electromagnetic field, local heating, excited electrons, and excited holes, could mediate or promote the chemical reaction (Figure 1), but they are usually intertwined and hard to decouple from each other (Figure 1). Using the PATP transformation as an example, except the enhanced electromagnetic near-field effect (Figure 1a), which is probably absent because of the light-absorption mismatch between the plasmonic nanostructure and the PATP molecule, three processes can promote its occurrence. The first is the local heating effect combined with a surface catalytic process (Figure 1b). The second is the oxygen-activation mechanism induced by the SPs-excited electrons, which has been widely accepted to promote the oxidation reaction (also known as hot electrons, Figure 1c). The third is the direct utilization of the SPs-excited holes (also known as hot holes, Figure 1d). As one of the most important approaches for the mechanism investigation, recent studies have begun to address the challenge of distinguishing photothermal from photoelectronic (excited electrons and holes) effects.^{27,35,42,43}

In our previous Review, we discussed to what extent the lessons that can be learned on the SERS development over the past four decades may enlighten our understanding and development of PMCRs.¹³ In this Account, based on years of studies, we will demonstrate how to use SERS combined with theoretical calculations to study PMCRs and reveal the mechanism step by step, using the transformation of PATP as an example. First, a discussion will be made on how to attribute the changes in SERS spectra to surface reactions rather than the chemical enhancement. Then, we will move to correlate the PATP transformation with the SPs effect, and distinguish the effects of heat, hot electrons, and hot holes on its conversion. Our results show that PATP can selectively transform to different products either on account of the oxygen activation induced by hot electrons or entirely due to the action of hot holes in the absence of oxygen. In both case, the interface between plasmonic nanostructures and reactants plays a critical role. Finally, we will propose some considerations for the in situ SERS investigation of PMCRs.

■ PLASMON-MEDIATED CHEMICAL REACTION OR CHEMICAL ENHANCEMENT OF SERS

SERS is a powerful tool for obtaining the spectral information on surface or interface species at a molecular level with an ultrahigh sensitivity. It is widely accepted that the enhancement of the Raman signal have two origins.^{4–6} One is the electromagnetic enhancement (EM),^{2,3} which originates from the enhanced electromagnetic near-field in the vicinity of the plasmonic nanostructure as a consequence of SPs excitation and dominates the total enhancement in SERS. The other is the chemical enhancement (CE), also known as charge-transfer enhancement (CT),^{44,45} which arises from the complex interaction among the adsorbed molecule, the plasmonic substrate and the incident light.

The charge transfer between the plasmonic nanostructure and the interacting molecules, either directly (also known as chemical interface damping) or indirectly, plays a key role in both PMCRs and CT enhancement of SERS. For the direct approach, SPs decay occurs through an interfacial electronic transition from the plasmonic nanostructure to the adsorbed molecule or vice versa (Figure 2, dashed arrows). For the indirect process, SPs experience a nonradiative decay that produces excited carriers in the plasmonic nanostructure prior to the subsequent CT to the molecule or vice versa (Figure 2, solid arrows). As a consequence, the CT process in both

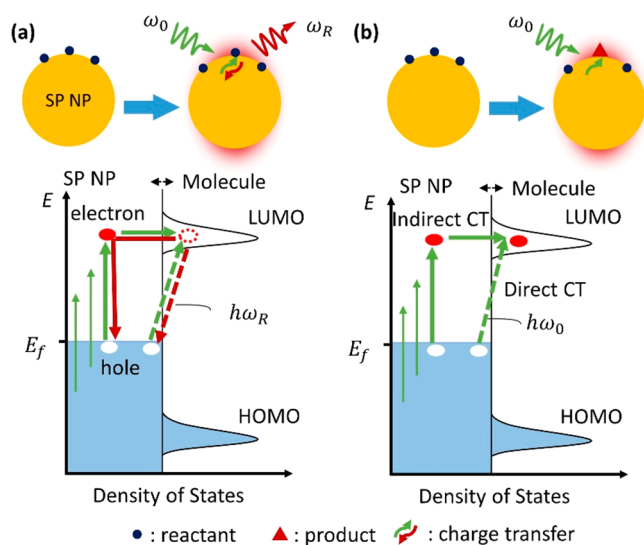


Figure 2. Charge transfer enhancement in SERS and PMCRs. (a) CT enhancement in SERS. A resonant-like Raman scattering process through photon-induced CT is illustrated at the metal–molecule interface, where the Fermi level of plasmonic substrates can be easily tuned by the applied potential to bring about resonance with the incident photon energy $\hbar\omega_0$. (b) CT-induced PMCRs. Similar to the CT process happened in SERS, but the excited charge carriers transfer to the molecule and induced the chemical reaction or molecular activation.

PMCRs and CT enhancement of SERS can lead to the change of SERS spectra, especially on the relative intensity of different vibrational modes, which actually caused confusion during the study of PMCRs. The main difference between them, on the mechanistic aspect, is the final destination of the excited carriers. In SERS, the transferred excited carriers quickly decay back to the metal or the surface complex, leading to a resonance-like enhancement of the Raman signal (Figure 2a). On the other hand, in PMCRs, the excited carriers transferred from the SP nanostructure to the molecule participate in chemical reactions (Figure 2b). The probability of excited carriers used for chemical reactions can be increased by extending the time that they occupy the orbitals of reactants.^{13,18,19}

Here, we will introduce a typical example to demonstrate how to distinguish the PMCRs and CT enhancement of SERS. PATP was once considered as an ideal probe molecule in SERS studies because of its strong affinity with most SERS substrates, which can produce strong SERS signal that is sensitive to the substrate electronic properties.⁴⁶ In the early time, investigations of PATP mainly focused on the CT mechanism of SERS. By performing an elegant potential and wavelength-dependent SERS study of PATP on a roughened silver electrode, some researchers found that the intensities of some vibrational modes of PATP that were assigned to the b_2 symmetry, including the bands at ~ 1142 , 1391 , and 1440 cm^{-1} , are remarkably high and very sensitive to the change of the electrode potential.⁴⁷ The potential, where the SERS intensities of these b_2 modes are maximized, moved to more positive potentials when lasers with increasing energy (shorter wavelength) were used. The above phenomena fit well with the theoretical prediction of CT enhancement of SERS by taking the Herzberg–Teller vibronic coupling term into consideration.⁴⁸ The dynamic change in intensity and position of these bands has been used to demonstrate some interesting effects,

such as the single-molecule nature of PATP in a molecular junction.⁴⁹ By comparing the intensity of these bands, the estimated enhancement factor for CT is on the order of 10^7 , comparable to that of the EM enhancement, when the PATP was placed in an Au bowtie junction.⁵⁰

We were intrigued by such an incredible SERS enhancement of charge transfer between PATP and Ag and Au substrates, considering that the CT enhancement factor is usually less than 3 orders of magnitude.^{44,45} However, our DFT study cannot reproduce the b_2 modes of PATP linking to the Ag cluster model, no matter the size of the cluster, the binding manner of the molecule and the functions used in calculation.³¹ Instead, it demonstrated that the abnormally enhanced SERS peaks originates from the a_g modes of 4,4'-dimercaptoazobenzene (DMAB), an oxidative coupling product of PATP that may be generated during the SERS measurement. The Raman cross section of DMAB is more than 3 orders of magnitude higher than that of PATP with the synergic effect of the resonance Raman and binding effect to silver.³¹ In accordance with the theoretical results, we found that the appearance of the so-called b_2 modes is highly dependent on the laser power and illumination time. Through a combination of directly lowering the laser power and the defocusing method,⁵¹ we confirmed the b_2 modes are completely absent in the SERS spectra at a low power density ($\sim 8 \times 10^2$ mW cm^{-2}), irrespective of the applied potential and the plasmonic substrate. Nevertheless, under a normal SERS measurement condition, where power density is usually much higher ($\sim 1 \times 10^8$ mW cm^{-2}), those bands appeared with their relative intensity to the total-symmetric a_1 mode (~ 1004 , 1078 , 1176 , 1488 , and 1595 cm^{-1}) being sensitive to the metal substrate, the electrode potential, and the laser wavelength.^{32,46} Making use of a mass spectrometry analysis for the surface adsorbates (Figure 3a) and the standard SERS spectrum of DMAB synthesized by a special protocol of our own (Figure 3b), we conclude with no doubt that the aromatic azo compound can be catalytically produced on the Ag and Au nanoscale rough surfaces and nanoparticles under the SPs excitation (Figure 3c).³² The aforementioned CT enhancement mechanism of PATP (or DMAB) was confused with surface reaction because the surface accumulation and electrochemical reduction of DMAB were synergistically impact on the potential-dependent SERS intensities.

The above example corroborates the occurrence of PMCRs through SERS measurements, even though it took a long time to distinguish the PMCRs and CT enhancement of SERS. There are some suggestions can be used to avoid the misinterpretation of the SERS results. First, the SERS spectra should change with the laser power and illumination time in the case of PMCRs because new species are generated and accumulated during the measurement; otherwise, the SERS spectra should keep consistent irrespective of the laser power and illumination time in the case of CT process in SERS. Second, the CT process in SERS is reversible during the potential and wavelength-dependent SERS study. But for PMCRs, when the reaction happens, the Raman spectra is changed. Third, it is recommended that other analytical techniques, not limited to SERS, should be combined to characterize the PMCR products. Theoretical calculations are also preferred to instruct the understanding of the measured SERS spectra.

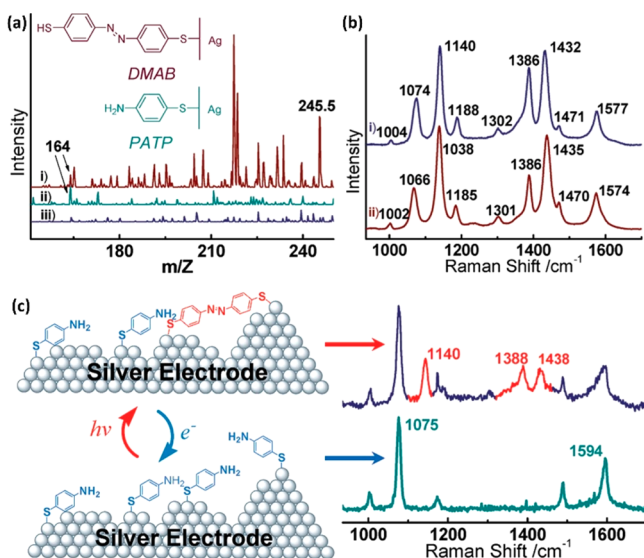


Figure 3. Chemical transformation of PATP to DMAB. (a) Desorption electrospray ionization mass spectrometry (DESI-MS) spectra of PATP adsorbed on roughened Ag electrodes illuminated with laser (i) and without any irradiation (ii) and a roughened Ag free of PATP (iii). (b) Raman spectra of PATP (i) and DMAB (ii) on the roughened Ag electrode excited by a laser at a power density of $\sim 1 \times 10^8$ mW/cm². (c) Transformation of DMAB from PATP adsorbed on roughened Ag electrode in the electrochemical surface-enhanced Raman spectroscopy (EC-SERS) measurement. Reproduced with permission from ref 32. Copyright 2010 American Chemical Society.

CHEMICAL REACTION MEDIATED BY HOT ELECTRON-ACTIVATED OXYGEN

Once the reaction on silver or gold nanostructures under the excitation of SPs is verified, the next question raised to the forefront is how does the reaction proceed. Because oxygen molecules often participate in the oxidative chemical reactions carried out in the air and the SPs-excited electrons can greatly improve the catalytic oxidative reactions by forming the oxygen transient negative-ions,²¹ a possible mechanism of the PATP transformation by the hot electron-activated oxygen was proposed on the basis of theoretical calculations.^{52,53} Later through the in situ SERS study, we confirmed the participation of oxygen molecules in this reaction and provide a strong evidence of the activation mechanism by the hot electrons.

The role of O₂ for the DMAB production was investigated by the SERS measurement of PATP in the presence or absence of O₂.²³ The gap-mode SERS of the metal film/PATP/metallic nanoparticles junctions were used because the PATP conversion is highly efficient and its adsorption is well understood in such place.⁵⁴ The transformation of PATP to DMAB, evidenced by the increasing a_g modes of DMAB at ~ 1140 , 1388, and 1434 cm⁻¹ over time in the Au film/PATP/Au NPs, is clearly observed in the SERS spectra when the air is present (Figure 4a). In contrast, if O₂ was excluded, only the a₁ modes of PATP at ~ 1004 , 1078, 1176, 1488, and 1595 cm⁻¹ were detected (Figure 4b), suggesting that the PATP transformation was suppressed without the participation of O₂. Furthermore, no signal of DMAB was detected in Au(111)/PATP/Au@SiO₂ NPs (Figure 4c). Here, the Au@SiO₂ NPs were used to avoid the contact between the Au NPs and the air by coating their surfaces with a thin and compact silica layer.⁵⁵ Together, it is clear that the oxidative coupling of PATP molecules to the DMAB is a consequence of the oxygen

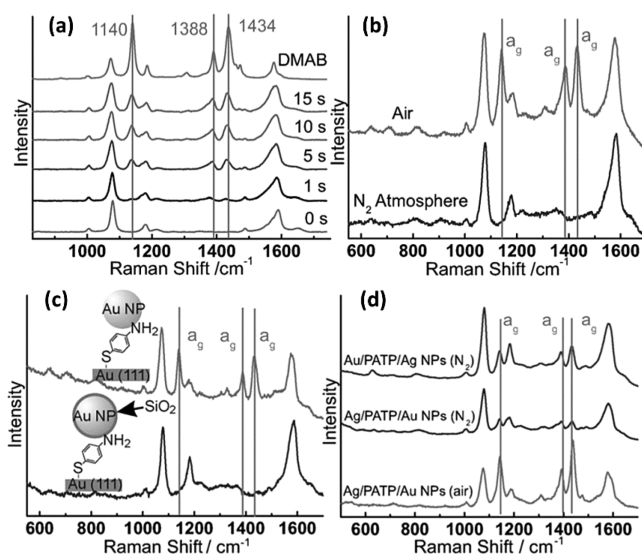


Figure 4. PATP transformation mediated by hot electron-activated oxygen. (a) Illumination-time-dependent Raman spectra of Au/PATP/Au nanoparticle in air and (b) comparative Raman spectra of Au/PATP/Au NPs recorded in air and N₂ atmosphere. (c) Raman spectra of Au(111)/PATP/Au NP (top) and Au(111)/PATP/Au@SiO₂ NP (bottom) junctions. (d) Raman spectra of Ag film/PATP/Au NP and Au film/PATP/Ag NP junctions recorded in N₂ atmosphere and in air. Reproduced with permission from ref 23. Copyright 2014 John Wiley and Sons.

activation induced by the hot electrons. However, DMAB can also be detected in the SERS measurements of Au film/PATP/Ag NPs and Ag film/PATP/Au NPs carrier out in the N₂ atmosphere, where the former gives a relatively stronger signal of the DMAB a_g modes even though their intensities are obviously lower than those recorded in the air (Figure 4d). The X-ray photoelectron spectroscopy (XPS) demonstrated that there are some native oxide species on the surface of Ag NPs and films, which also can induce the oxidative coupling of PATP under illumination when the O₂ molecules are absent. Once the surface oxide layer of the Ag surface was eliminated, the oxidation reaction can be suppressed.²³ So far, a reaction pathway of the SPs-induced PATP transformation can be concluded based on the SERS study. First, the excited SPs of the Au and Ag nanoparticles under illumination generate the excited electrons, which transfer from plasmonic nanoparticles to O₂ molecules and activate them to form the activated oxygen species. Then, the activated oxygen induces the transformation of PATP to DMAB. A similar mechanism based on the oxygen activation induced by SPs is discovered in other plasmon-enhanced oxidation reactions in the present of oxygen.¹⁶

CHEMICAL REACTION MEDIATED BY HOT HOLES

On the basis of the SERS study, we had proved that the transformation of PATP to DMAB on the Au and Ag nanostructures is a result of the oxygen activation induced by the hot electrons. On the other hand, we also predicted the oxidation of PATP entirely by the action of hot holes in the absence of oxygen through the theoretical investigation.^{56,57} As shown in Figure 5, the density functional theory (DFT) calculation was performed to explore the surface catalytic coupling reactions of PATP on a PATP-Ag cluster model. In the presence of O₂, the transformation of PATP to DMAB was

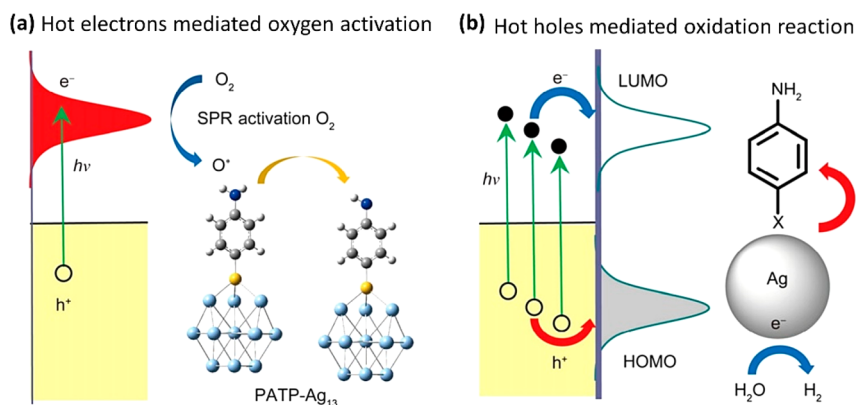


Figure 5. Oxidation mechanisms of PATP on noble metal surfaces. (a) Surface oxidation coupling reaction of PATP oxidized by surface oxygen species activated by hot electrons under oxygen atmosphere in the gas/solid phase based on the PATP-Ag₁₃ cluster. (b) The hot-hole oxidation mechanism in the solid/liquid interfaces. Water molecules were reduced by hot electrons to yield the hydrogen gas. Reproduced with permission from ref 56. Copyright 2015 Springer Nature.

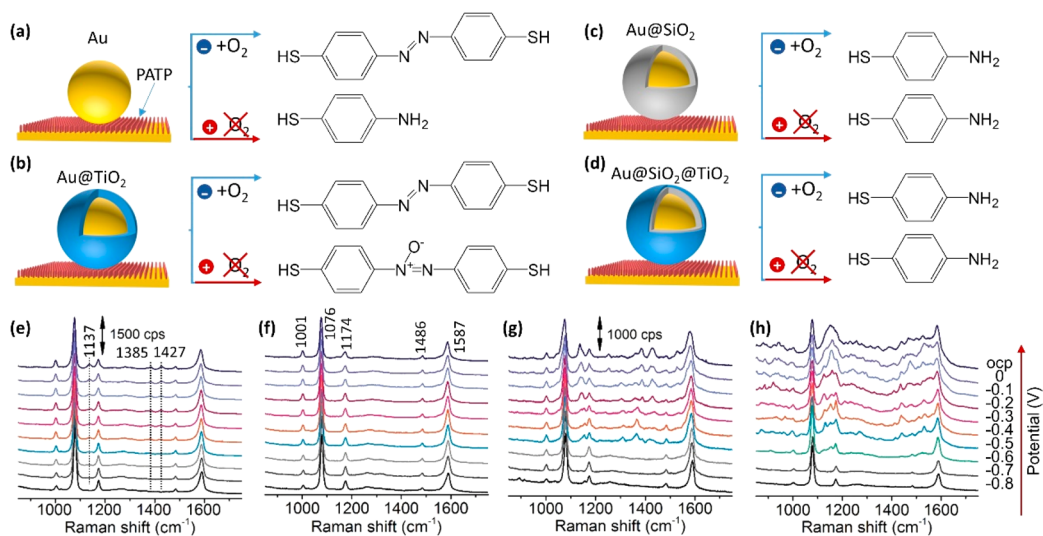


Figure 6. Schematic of the SPs-induced PATP oxidation, which is regulated by the interface between the SPs source and reactant. Four type of plasmonic nanoparticles including (a) Au NPs, (b) Au@TiO₂ (7 nm), (c) Au@SiO₂ (5 nm), and (d) Au@SiO₂@TiO₂ (5 nm SiO₂ shell, 2 nm TiO₂ shell) are used to construct the gap-mode system to carry out electrochemical surface enhanced Raman spectroscopy. (e) EC-SERS spectra of Au/PATP/Au NPs with oxygen. (f) EC-SERS spectra of Au/PATP/Au NPs without oxygen. (g) EC-SERS spectra of Au/PATP/Au@TiO₂ NPs with oxygen. (h) EC-SERS spectra of Au/PATP/Au@TiO₂ NPs without oxygen. Reproduced with permission from ref 35. Copyright 2019 American Chemical Society.

attributed to the hot electrons-induced oxygen activation (the SPs-assisted surface catalysis mechanism, Figure 5a), consistent with experimental results.²³ In the absence of O₂, the major reaction channel was altered to the excited hole-driven photo-oxidation of PATP (the SPs-driven photocatalysis mechanism, Figure 5b), which, however, is contradicted with the SERS spectrum of PATP recorded on gold nanoparticles in the absence of O₂ (Figure 4b).

A possible reason for the above contradiction between the theoretical prediction and the experimental observation could rely on the inefficient CT process, which often limit the utilization of PMCRs. To verify this possibility and to distinguish the role of the local-heating, surface catalysis and SPs-excited electrons or holes, we compared the SERS results at different potentials on four types of gap modes comprising of Au film/PATP/plasmonic NPs, where for the plasmonic NPs, the pristine Au, Au@TiO₂, Au@SiO₂, and Au@SiO₂@TiO₂ NPs were selected.³⁵ The selection of the above nanoparticles covers a wide gamut of materials and electronic

properties: a conductor, a conducting core surrounded by a semiconducting shell, a conductor surrounded by an insulating shell, and a conductor surrounded by an insulating shell and a second, semiconducting shell.

As shown in Figure 6, when the EC-SERS experiments were carried out with or without O₂, each of these systems displayed different behaviors. For the Au film/PATP/Au NPs system supporting SPs and gold-reactant interface, PATP molecules transformed to the DMAB in the presence of O₂, whereas no reaction took place in the absence of O₂ (Figure 6a, e, and f). In contrast, for Au@TiO₂ NPs with TiO₂ as a shell, the reaction of PATP occurred in the presence or absence of O₂, and the reactions were more efficient than that in Au film/PATP/Au NPs system (Figure 6b). With oxygen, the transformation of PATP to DMAB is due to the action of excited electrons assisting oxygen activation (Figure 6g) but is accelerated by the TiO₂.³⁸ In the absence of O₂, the chemical transformation of PATP was also observed but the resulting products were different (Figure 6h). Two mechanisms may

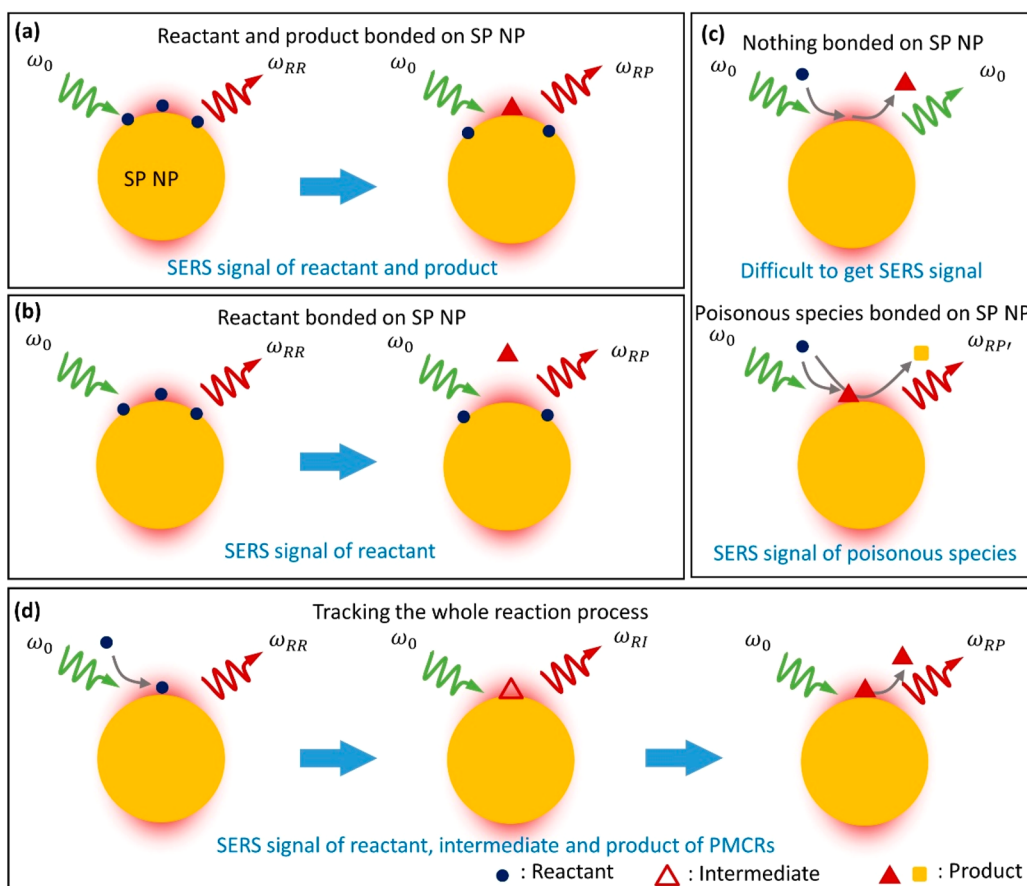


Figure 7. Comprehensive consideration of PMCR systems using SERS for in situ study. (a) The reactant and product both can adsorb on the surface of plasmonic nanostructure. (b) Only the reactant can place on/near the plasmonic nanostructure; the intermediate and product quickly react or desorb from the surface. (c) Neither the reactant nor the product can stay on the surface for a sufficient time (top). Two different reaction pathways exist, one is efficiency, but the intermediate and product quickly react or desorb from the surface, the other is the poisoning path that the product or intermediate strongly adsorb on the surface and block the active sites. (d) The SERS technique can track the whole reaction process of PMCRs, including the reactants, intermediates, and products over time.

account for this reaction: one is surface catalysis by the TiO_2 coating layer, the other is hot hole-induced PATP transformation facilitated by the TiO_2 charge transfer mediator. To distinguish these different mechanisms, the SERS study of the Au film/PATP/Au@ SiO_2 NPs and Au film/PATP/Au@ SiO_2 @ TiO_2 NPs systems were compared (Figure 6c and d). As no transformation of PATP was observed in these gap modes, where CT processes were completely blocked by the insulating SiO_2 shell, no matter O_2 was present or not, it is corroborated that both the heating effect of Au core SPs and the surface catalytic effects of the TiO_2 shell can be excluded.

Thus, we proved that the SPs-excited hot holes can be utilized to oxidize the PATP molecules as long as an appropriate CT mediator is combined. The different products of the reaction with and without O_2 suggest that the reaction pathways are different under different conditions. For the reaction carried out in the absence of O_2 , water should take part in the reaction as proposed in the theoretical work (Figure 5b). From a different view, PATP molecules can act as the hole sacrificial agent that can support the SPs-mediated water splitting reaction. This work suggests that the interface between the SPs nanostructures and the reactant molecules not only determines the utilization of hot carriers but also controls the reaction pathway of PMCRs. Appropriate CT

mediators are critical to improve the efficiency of the hot carrier utilization and eventually the PMCRs.

■ COMPREHENSIVE CONSIDERATION OF PMCR SYSTEMS STUDIED BY SERS

Using PATP transformation as a model system, we have demonstrated that SERS is a powerful technique for the in situ investigation of the PMCRs system with a high surface sensitivity and energy resolution. However, we should emphasize that SERS and PMCRs also differ in crucial ways, and the development of the PMCR systems should follow different rules. For example, usually, a higher detection sensitivity is achieved in SERS measurements when the probed molecules are strongly bound to the plasmonic metal surfaces. But the strong adsorption of the reactant, intermediate, or product species to the plasmonic surfaces may block the active sites for PMCRs.

Figure 7 shows several different types of PMCR systems in situ studied by SERS. If the reactant and product both strongly adsorb on the surface of plasmonic nanostructure, a higher SERS sensitivity can be achieved (Figure 7a). At present, almost all systems of PMCRs studied by SERS fall into this category. But when the reaction intermediate is consumed fast and the desorption of product proceeds quickly, it becomes more challenging to gain good quality SERS signals (Figure

7b). A more difficult situation is that neither the reactant nor the product can stay on the surface for a sufficient time to obtain effective SERS signals (the upper panel in Figure 7c) or there are two different reaction pathways: one is more efficient but the intermediate and product quickly react or desorb from the surface thus the SERS signal is weak, and the other is the poisoning path, where the intermediate or the product can strongly adsorb on (block) the surface but mainly contribute to the SERS signal (the lower panel in Figure 7c). Considering these circumstances (Figure 7b and c), it is highly desirable to further improve the sensitivity and time resolution of SERS to better track the reactants, intermediates, and products of PMCRs over time (Figure 7d), which has been demonstrated in some electrocatalysis/catalysis system in situ studied by SERS.⁵⁹ Some details should also be taken into consideration: One is reasonable design of plasmonic structures to meet the strong SERS enhancement and high PMCR efficiency, which usually needs complex nanostructures, for example, antenna-reactor, satellite, or core-shell nanostructures, and the other is the control of surface and reaction condition to eliminate the interference. For example, when investigating the effects of hot holes, we should exclude the influence of surface oxygen species and dissolved oxygen. More techniques, which may include but are not limited to the chromatography and mass spectrometry, should be adapted to comprehensively investigate the PMCRs. Moreover, as shown in this Account, one can find that theoretical calculation is necessary for these experiments. It can at least play two important roles: one is to interpret the SERS spectrum to determine the product or intermediate, especially for the intermediate, which usually has no standard samples, and the other is to predict the reaction mechanism from the microscopic view.

CONCLUSIONS AND PERSPECTIVES

PMCRs and SERS both are three body interactions, including photons, molecules, and nanostructures. Combined with the electrochemistry and various plasmonic nanostructures, SERS can powerfully drive the in situ investigation of PMCRs and provide fingerprint information concerning important mechanism insights. Nevertheless, because of the molecular transformation, there are more challenges in PMCRs than in SERS. The growth and future of PMCRs critically depend on the fundamental understanding of SPs properties and how they enable chemical reactions. Two main challenges have risen to the forefront: one is how to distinguish the multieffects of SPs, such as the photothermal, hot electrons, and hot holes, and their influence on the chemical reaction; the other is how to power the chemical reaction more effectively and regulate the product selectivity. To distinguish the multieffects, one can design various plasmonic nanostructures or by making use of techniques with high time resolution, such as transient absorption spectroscopy. Theoretical calculation is also an indispensable means.

For the improvement in the efficiency of PMCRs, we believe that mediators, including the surface catalytic mediator (e.g., Pt) and the charge-transfer mediator (e.g., the semiconductor), are critical according to our research. To regulate the selectivity, we believe at least three processes in PMCRs should be paid more attention. (1) The excited carriers transferred to molecules can form the charged state of the reactant, which can change the reaction pathway comparing with the reaction under the ground state. (2) Combining with the mass transfer process, the confinement of the electro-

magnetic field and thermal field may influence the happening of consecutive reactions. Moreover, the ultrahigh spatial confined fields, which can be used to access the structure and conformation of a single molecule with both chemical accuracy and subnanometer resolution, provide the possibility of mediating the reaction of specific parts of a single molecule under plasmonic excitation. (3) SPs in specific energy region, such as mid-infrared region, may provide a new opportunity to selectively excite the vibrational modes of molecules for bond-selective chemistry. Moreover, these processes can synergistically regulate the selectivity of chemical reaction and, even, specifically obtain target products that cannot be achieved under conventional conditions.

By deeply understanding the reaction mechanism and rationally designing plasmonic nanostructures, such as the heretical structures, PMCRs which exhibit some obvious differences from and potential advantages over existing photo and thermal-reaction systems can create new possibilities for the chemistry.

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REFERENCES

- (1) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. Raman spectra of pyridine adsorbed at a silver electrode. *Chem. Phys. Lett.* **1974**, *26*, 163–166.
- (2) Jeanmaire, D. L.; Van Duyne, R. P. Surface raman spectroelectrochemistry: Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *84*, 1–20.
- (3) Moskovits, M. Surface roughness and the enhanced intensity of Raman scattering by molecules adsorbed on metals. *J. Chem. Phys.* **1978**, *69*, 4159–4161.
- (4) Moskovits, M. Surface-enhanced spectroscopy. *Rev. Mod. Phys.* **1985**, *57*, 783–826.
- (5) Stiles, P. L.; Dieringer, J. A.; Shah, N. C.; Van Duyne, R. P. Surface-Enhanced Raman Spectroscopy. *Annu. Rev. Anal. Chem.* **2008**, *1*, 601–626.
- (6) Ding, S.-Y.; Yi, J.; Li, J.-F.; Ren, B.; Wu, D.-Y.; Panneerselvam, R.; Tian, Z.-Q. Nanostructure-based plasmon-enhanced Raman spectroscopy for surface analysis of materials. *Nat. Rev. Mater.* **2016**, *1*, 16021.
- (7) Mayer, K. M.; Hafner, J. H. Localized Surface Plasmon Resonance Sensors. *Chem. Rev.* **2011**, *111*, 3828–3857.
- (8) Willets, K. A.; Van Duyne, R. P. Localized surface plasmon resonance spectroscopy and sensing. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267–297.
- (9) Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A. Noble metals on the nanoscale: optical and photo-thermal properties and some applications in imaging, sensing, biology and medicine. *Acc. Chem. Res.* **2008**, *41*, 1578–1586.
- (10) Lal, S.; Clare, S. E.; Halas, N. J. Nanoshell-Enabled Photothermal Cancer Therapy: Impending Clinical Impact. *Acc. Chem. Res.* **2008**, *41*, 1842–1851.
- (11) Lal, S.; Link, S.; Halas, N. J. Nano-optics from sensing to waveguiding. *Nat. Photonics* **2007**, *1*, 641.
- (12) Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G. Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides. *Nat. Mater.* **2003**, *2*, 229–232.
- (13) Zhan, C.; Chen, X.-J.; Yi, J.; Li, J.-F.; Wu, D.-Y.; Tian, Z.-Q. From plasmon-enhanced molecular spectroscopy to plasmon-mediated chemical reactions. *Nat. Rev. Chem.* **2018**, *2*, 216–230.
- (14) Baffou, G.; Quidant, R. Nanoplasmonics for chemistry. *Chem. Soc. Rev.* **2014**, *43*, 3898–3907.
- (15) Zhang, Y.; He, S.; Guo, W.; Hu, Y.; Huang, J.; Mulcahy, J. R.; Wei, W. D. Surface-Plasmon-Driven Hot Electron Photochemistry. *Chem. Rev.* **2018**, *118*, 2927–2954.
- (16) Aslam, U.; Rao, V. G.; Chavez, S.; Linic, S. Catalytic conversion of solar to chemical energy on plasmonic metal nanostructures. *Nat. Catal.* **2018**, *1*, 656–665.
- (17) Kim, S.; Kim, J.-M.; Park, J.-E.; Nam, J.-M. Nonnoble-Metal-Based Plasmonic Nanomaterials: Recent Advances and Future Perspectives. *Adv. Mater.* **2018**, *30*, 1704528.
- (18) Brongersma, M. L.; Halas, N. J.; Nordlander, P. Plasmon-induced hot carrier science and technology. *Nat. Nanotechnol.* **2015**, *10*, 25–34.
- (19) Christopher, P.; Moskovits, M. Hot Charge Carrier Transmission from Plasmonic Nanostructures. *Annu. Rev. Phys. Chem.* **2017**, *68*, 379–398.
- (20) Hou, W.; Cronin, S. B. A Review of Surface Plasmon Resonance-Enhanced Photocatalysis. *Adv. Funct. Mater.* **2013**, *23*, 1612–1619.
- (21) Christopher, P.; Xin, H.; Linic, S. Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat. Chem.* **2011**, *3*, 467–472.
- (22) Mubeen, S.; Lee, J.; Singh, N.; Kramer, S.; Stucky, G. D.; Moskovits, M. An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat. Nanotechnol.* **2013**, *8*, 247–251.
- (23) Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chem., Int. Ed.* **2014**, *53*, 2353–2357.
- (24) Mukherjee, S.; Zhou, L.; Goodman, A. M.; Large, N.; Ayala-Orozco, C.; Zhang, Y.; Nordlander, P.; Halas, N. J. Hot-Electron-Induced Dissociation of H₂ on Gold Nanoparticles Supported on SiO₂. *J. Am. Chem. Soc.* **2014**, *136*, 64–67.
- (25) Li, H.; Qin, F.; Yang, Z.; Cui, X.; Wang, J.; Zhang, L. New Reaction Pathway Induced by Plasmon for Selective Benzyl Alcohol Oxidation on BiOCl Possessing Oxygen Vacancies. *J. Am. Chem. Soc.* **2017**, *139*, 3513–3521.
- (26) Kim, Y.; Smith, J. G.; Jain, P. K. Harvesting multiple electron-hole pairs generated through plasmonic excitation of Au nanoparticles. *Nat. Chem.* **2018**, *10*, 763–769.
- (27) Zhou, L.; Swearer, D. F.; Zhang, C.; Robotjazi, H.; Zhao, H.; Henderson, L.; Dong, L.; Christopher, P.; Carter, E. A.; Nordlander, P.; Halas, N. J. Quantifying hot carrier and thermal contributions in plasmonic photocatalysis. *Science* **2018**, *362*, 69–72.
- (28) Brus, L. Noble Metal Nanocrystals: Plasmon Electron Transfer Photochemistry and Single-Molecule Raman Spectroscopy. *Acc. Chem. Res.* **2008**, *41*, 1742–1749.
- (29) Tian, Z. Q.; Ren, B. Adsorption and reaction at electrochemical interfaces as probed by surface-enhanced Raman spectroscopy. *Annu. Rev. Phys. Chem.* **2004**, *55*, 197–229.
- (30) Suh, J. S.; Jang, N. H.; Jeong, D. H.; Moskovits, M. Adsorbate photochemistry on a colloid surface: Phthalazine on silver. *J. Phys. Chem.* **1996**, *100*, 805–813.
- (31) Wu, D.-Y.; Liu, X.-M.; Huang, Y.-F.; Ren, B.; Xu, X.; Tian, Z.-Q. Surface catalytic coupling reaction of p-mercaptoaniline linking to silver nanostructures responsible for abnormal SERS enhancement: a DFT study. *J. Phys. Chem. C* **2009**, *113*, 18212–18222.
- (32) Huang, Y.-F.; Zhu, H.-P.; Liu, G.-K.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. When the Signal Is Not from the Original Molecule To Be Detected: Chemical Transformation of para-Aminothiophenol on Ag during the SERS Measurement. *J. Am. Chem. Soc.* **2010**, *132*, 9244–9246.
- (33) Fang, Y.; Li, Y.; Xu, H.; Sun, M. Ascertaining p, p'-dimercaptoazobenzene produced from p-aminothiophenol by selective catalytic coupling reaction on silver nanoparticles. *Langmuir* **2010**, *26*, 7737–7746.
- (34) da Silva, A. G. M.; Rodrigues, T. S.; Correia, V. G.; Alves, T. V.; Alves, R. S.; Ando, R. A.; Ornellas, F. R.; Wang, J.; Andrade, L. H.; Camargo, P. H. C. Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen. *Angew. Chem., Int. Ed.* **2016**, *55*, 7111–7115.

- (35) Zhan, C.; Wang, Z.-Y.; Zhang, X.-G.; Chen, X.-J.; Huang, Y.-F.; Hu, S.; Li, J.-F.; Wu, D.-Y.; Moskovits, M.; Tian, Z. Interfacial construction of plasmonic nanostructures for the utilization of the plasmon-excited electrons and holes. *J. Am. Chem. Soc.* **2019**, *141*, 8053–8057.
- (36) Sun, M.; Huang, Y.; Xia, L.; Chen, X.; Xu, H. The pH-controlled plasmon-assisted surface photocatalysis reaction of 4-aminothiophenol to p, p'-dimercaptoazobenzene on Au, Ag, and Cu colloids. *J. Phys. Chem. C* **2011**, *115*, 9629–9636.
- (37) Kafle, B.; Poveda, M.; Habteyes, T. G. Surface ligand-mediated plasmon-driven photochemical reactions. *J. Phys. Chem. Lett.* **2017**, *8*, 890–894.
- (38) Sun, M.; Xu, H. A Novel Application of Plasmonics: Plasmon-Driven Surface-Catalyzed Reactions. *Small* **2012**, *8*, 2777–2786.
- (39) van Schroyen; Lantman, E. M.; Deckert-Gaudig, T.; Mank, A. J. G.; Deckert, V.; Weckhuysen, B. M. Catalytic processes monitored at the nanoscale with tip-enhanced Raman spectroscopy. *Nat. Nanotechnol.* **2012**, *7*, 583.
- (40) Xie, W.; Schlücker, S. Hot electron-induced reduction of small molecules on photorecycling metal surfaces. *Nat. Commun.* **2015**, *6*, 7570.
- (41) Chen, X.-J.; Cabello, G.; Wu, D.-Y.; Tian, Z.-Q. Surface-enhanced Raman spectroscopy toward application in plasmonic photocatalysis on metal nanostructures. *J. Photochem. Photobiol., C* **2014**, *21*, 54–80.
- (42) Zhang, X.; Li, X.; Reish, M. E.; Zhang, D.; Su, N. Q.; Gutiérrez, Y.; Moreno, F.; Yang, W.; Everitt, H. O.; Liu, J. Plasmon-Enhanced Catalysis: Distinguishing Thermal and Nonthermal Effects. *Nano Lett.* **2018**, *18*, 1714–1723.
- (43) Yu, Y.; Sundaresan, V.; Willets, K. A. Hot Carriers versus Thermal Effects: Resolving the Enhancement Mechanisms for Plasmon-Mediated Photoelectrochemical Reactions. *J. Phys. Chem. C* **2018**, *122*, 5040–5048.
- (44) Otto, A. In *Light Scattering in Solids IV*; Springer, 1984; pp 289–418.
- (45) Birke, R.; Lombardi, J. In *Spectroelectrochemistry-Theory and Practice*; Plenum: New York, 1988; p 263.
- (46) Huang, Y.-F.; Wu, D.-Y.; Zhu, H.-P.; Zhao, L.-B.; Liu, G.-K.; Ren, B.; Tian, Z.-Q. Surface-enhanced Raman spectroscopic study of p-aminothiophenol. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8485–8497.
- (47) Osawa, M.; Matsuda, N.; Yoshii, K.; Uchida, I. Charge transfer resonance Raman process in surface-enhanced Raman scattering from p-aminothiophenol adsorbed on silver: Herzberg-Teller contribution. *J. Phys. Chem.* **1994**, *98*, 12702–12707.
- (48) Lombardi, J. R.; Birke, R. L.; Lu, T.; Xu, J. Charge-transfer theory of surface enhanced Raman spectroscopy: Herzberg–Teller contributions. *J. Chem. Phys.* **1986**, *84*, 4174–4180.
- (49) Zhou, Q.; Li, X.; Fan, Q.; Zhang, X.; Zheng, J. Charge Transfer between Metal Nanoparticles Interconnected with a Functionalized Molecule Probed by Surface-Enhanced Raman Spectroscopy. *Angew. Chem., Int. Ed.* **2006**, *45*, 3970–3973.
- (50) Fromm, D. P.; Sundaramurthy, A.; Kinkhabwala, A.; Schuck, P. J.; Kino, G. S.; Moerner, W. E. Exploring the chemical enhancement for surface-enhanced Raman scattering with Au bowtie nanoantennas. *J. Chem. Phys.* **2006**, *124*, 061101.
- (51) Lin, X.-M.; Cui, Y.; Xu, Y.-H.; Ren, B.; Tian, Z.-Q. Surface-enhanced Raman spectroscopy: substrate-related issues. *Anal. Bioanal. Chem.* **2009**, *394*, 1729–1745.
- (52) Zhao, L.-B.; Huang, R.; Huang, Y.-F.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Photon-driven charge transfer and Herzberg-Teller vibronic coupling mechanism in surface-enhanced Raman scattering of p-aminothiophenol adsorbed on coinage metal surfaces: A density functional theory study. *J. Chem. Phys.* **2011**, *135*, 134707.
- (53) Wu, D.-Y.; Zhao, L.-B.; Liu, X.-M.; Huang, R.; Huang, Y.-F.; Ren, B.; Tian, Z.-Q. Photon-driven charge transfer and photocatalysis of p-aminothiophenol in metal nanogaps: a DFT study of SERS. *Chem. Commun.* **2011**, *47*, 2520–2522.
- (54) Hu, J.; Tanabe, M.; Sato, J.; Uosaki, K.; Ikeda, K. Effects of Atomic Geometry and Electronic Structure of Platinum Surfaces on Molecular Adsorbates Studied by Gap-Mode SERS. *J. Am. Chem. Soc.* **2014**, *136*, 10299–10307.
- (55) Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; Ren, B.; Wang, Z. L.; Tian, Z. Q. Shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nature* **2010**, *464*, 392–395.
- (56) Wu, D.-Y.; Zhang, M.; Zhao, L.-B.; Huang, Y.-F.; Ren, B.; Tian, Z.-Q. Surface plasmon-enhanced photochemical reactions on noble metal nanostructures. *Sci. China: Chem.* **2015**, *58*, 574–585.
- (57) Zhao, L.-B.; Zhang, M.; Huang, Y.-F.; Williams, C. T.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Theoretical Study of Plasmon-Enhanced Surface Catalytic Coupling Reactions of Aromatic Amines and Nitro Compounds. *J. Phys. Chem. Lett.* **2014**, *5*, 1259–1266.
- (58) Clavero, C. Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nat. Photonics* **2014**, *8*, 95–103.
- (59) Dong, J.-C.; Zhang, X.-G.; Briega-Martos, V.; Jin, X.; Yang, J.; Chen, S.; Yang, Z.-L.; Wu, D.-Y.; Feliu, J. M.; Williams, C. T.; Tian, Z.-Q.; Li, J.-F. In situ Raman spectroscopic evidence for oxygen reduction reaction intermediates at platinum single-crystal surfaces. *Nat. Energy* **2019**, *4*, 60–67.