Review article

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Toward a mechanistic understanding of plasmon-mediated photocatalysis

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Abstract: One of the most exciting new developments in the plasmonic nanomaterials field is the discovery of their ability to mediate a number of photocatalytic reactions. Since the initial prediction of driving chemical reactions with plasmons in the 1980s, the field has rapidly expanded in recent years, demonstrating the ability of plasmons to drive chemical reactions, such as water splitting, ammonia generation, and CO₂ reduction, among many other examples. Unfortunately, the efficiencies of these processes are currently suboptimal for practical widespread applications. The limitations in recorded outputs can be linked to the current lack of a knowledge pertaining to mechanisms of the partitioning of plasmonic energy after photoexcitation. Providing a descriptive and quantitative mechanism of the processes involved in driving plasmon-induced photochemical reactions, starting at the initial plasmon excitation, followed by hot carrier generation, energy transfer, and thermal effects, is critical for the advancement of the field as a whole. Here, we provide a mechanistic perspective on plasmonic photocatalysis by reviewing select experimental approaches. We focus on spectroscopic and electrochemical techniques that provide molecular-scale information on the processes that occur in the coupled molecular-plasmonic system after photoexcitation. To conclude, we evaluate several promising techniques for future applications in elucidating the mechanism of plasmon-mediated photocatalysis.

Keywords: nanomaterials; photocatalysis; plasmons; spectroscopy.

1 Introduction

The growing necessity for clean and renewable forms of energy production has had a significant effect on developing new technologies capable of achieving environmentally conscious and energetically efficient methodologies for driving industrial catalytic reactions. Photocatalysis, which relies on harvesting an abundance of photons from an external source, has been repeatedly demonstrated as a plausible option for driving energetically demanding chemical reactions. The concept of directly converting solar energy to chemical energy has proven promising, as it negates the need of devoting a high amount of electrical or other forms of energy to carry out the process [1]. Initially, the groundbreaking research performed by Fujishima and Honda in 1972 ushered in a wave of studies focused on implementing semiconducting materials for solar-driven photocatalysts [2]. However, semiconducting materials generally absorb in the ultraviolet, a relatively inefficient region in the solar spectrum; despite extensive research, photoconversion efficiencies have remained below the limit needed for widespread application. Present-day catalyst design has been focused on implementing materials capable of harvesting the most abundant region of the solar spectrum, the visible region [3]. Still, the current options for photocatalysts leave much to be desired regarding their efficiencies and energetic demands that are required to power them.

In the development of industrially relevant photocatalytic processes, challenges impeding their progress must be considered. Many of the desirable catalytic processes have large energetic barriers, require the transfer of multiple electrons, and frequently require bimolecular collisions on the catalyst surface. Therefore, these reactions typically require high temperature, high pressure, and lots of time to produce desired products. For example, steam methane reforming, a key method in hydrogen production and the Fischer-Tropsch process, is highly endothermic and requires reaction conditions exceeding 1000 K at high pressure (15–30 atm) [4]. Other key industrial catalytic

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reactions require high specificity to produce products with high purity, as in the hydrogenation of acetylene to ethylene, a key feedstock for many industrial products. In addition to meeting strict reaction conditions, the scale of such processes must continually rise to meet increasing global demands. Table 1 provides a glance at the relative scale of several important industrial catalytic processes, which reflects the vast amount of capital invested in the development of the necessary infrastructure for their implementation. In view of these challenges, for photocatalytic processes to be competitive with standard industrial practices, highly efficient and robust catalysts that can maintain their catalytic activity under harsh reaction conditions are required. The application of photocatalytic processes will likely require integration into existing infrastructure and must prove to be financially viable at large scales to be competitive and comply with ever-expanding global consumer demands. Additionally, significant research effort has been directed toward implementing photocatalysts into energy-demanding situations that do not require mass-scale production. For example, photocatalysts have the potential to be used in the production of electricity on an individual household scale. Regardless, the development of plasmonic photocatalysts could eventually leave a dramatic impact on both large- and small-scale catalytic processes.

Significant progress has been made in recent years toward the application of plasmonic materials as catalysts for driving chemical reactions, as highlighted by examples in Table 1 [5, 13–19]. These materials are considered promising candidates for driving highly selective chemical processes due in part to their ability to host surface plasmons. The extinction spectrum of a plasmonic material can be finely tuned to match the output of the solar spectrum by changing the size or shape of the nanomaterial. Plasmonic materials harvest energy from resonant photons and partition it into multiple different pathways. Once generated, the surface plasmon produces highly enhanced localized electromagnetic fields, creates elevated thermal environments, ejects highly energetic hot

carriers, and/or modifies the potential energy landscape of a nearby molecular species [20–22]. Each of these possible pathways of energy partitioning may contribute to mediating a catalytic process, with the preferential pathway heavily dependent on the targeted chemical reaction and the plasmonic substrate's design. Due to the complexity of these potential pathways, designing a plasmonic system capable of achieving optimal turnover numbers and yields is a nontrivial task. Ultimately, to make a significant leap in device fabrication, in the absence of an unpredicted technological development, it is imperative to study the individual mechanistic contributions and dynamics during the energy transformation after plasmon excitation. With this highly pertinent information in hand, plasmonic substrates may be designed to preferentially dictate the flow of energy as the surface plasmon decays and efficiently channel it into mediating a chemical reaction. Herein, we have thoroughly discussed and reviewed the leading spectroscopic and electrochemical techniques used to explore the mechanism behind plasmon-mediated photocatalysis.

One of the most promising aspects of plasmon-mediated photocatalysis is the ability to achieve a high level of chemical selectivity. Chemical selectivity is used to quantify how successful a given catalytic system is at producing the desired product over undesired byproducts. In many commercial catalytic systems, the chemical selectivity of the catalyst can be quite poor due to the existence of a number of competing chemical processes, requiring expensive separation processes. However, plasmonic materials are suitable materials for achieving high selectivity compared to most thermally activated catalytic processes, as they may be specifically designed to selectively generate charge carriers containing the required energies [5]. It is crucial to employ a system capable of producing highly selective products to reach a level of optimization for achieving practical applications of plasmonic photocatalysts. Once fully optimized, one can envision the prospect of a tunable solar-driven photocatalytic device capable of selectively driving a wide range of chemical reactions.

Table 1: List of plasmon-mediated industrially-relevant catalytic processes.

Process	Endo/exo	Standard catalyst	Approx. production scale (megaton per year)	Plasmon-mediated (prominent catalyst)
Acetylene hydrogenation	Exothermic	Pd/Al ₂ O ₃	N/A	Yes, AINC-Pd NP [5]
Haber-Bosch process (ammonia generation)	Exothermic	Fe/K ₂ O	200 [6]	Yes, Au NP coupled systems [7, 8]
Reverse water-gas shift reaction	Endothermic	Cu	N/A	Yes, Au NP/TiO ₂ [9]
Steam methane reforming	Endothermic	Ni/Al ₂ O ₃	215 (H ₂) [10, 11]	Yes, Au-Pt NP [12]
Water electrolysis	Endothermic	Ni & Pt	20 (H ₂) [11]	Yes, Au NR/TiO ₂ [13]

Throughout this review, we have provided a discussion and critique of the current literature that is focused on studying plasmon-mediated photocatalysis from a molecular viewpoint. Probing the interactions between strongly coupled molecule-plasmon systems may help provide a beneficial insight into better understanding the nontrivial mechanism driving fundamental plasmonic processes. Whereas a singular technique may not entirely provide a definitive description of plasmon-molecule interactions on its own, the collective knowledge garnered from various experimental approaches may produce a cohesive picture of how surface plasmons and molecules behave as the plasmon decays, leading to the rational design of highly optimized and selective plasmonic photocatalysts.

The goal of this review is to provide a narrative centralized on highlighting the capabilities and future promise of a number of advanced experimental methods employed to study the transient energetic dynamics of plasmonic materials and their effect on mediating catalytic processes. Ultimately, we aim to recognize the current challenges found in the field of plasmon-mediated photocatalysis, to discuss the notable scientific efforts to better understand the interactions between plasmons and molecules, and to provide an evaluation on the future landscape for applied plasmonic photocatalysts. We begin with a review of the relevant plasmon dynamics and possible energetic decay pathways, highlight a number of exceptional experimental studies that were successful in further explaining the intricate details found in plasmonic systems, and conclude with an outlook on the future of plasmon-mediated photocatalysis.

2 Fundamentals of plasmon generation and decay

2.1 Surface plasmons

Plasmons are the collective oscillation of the free charge density within a material with negative real and small positive imaginary dielectric components, which include materials such as gold (Au), silver (Ag), aluminum (Al), titanium nitride [23], metal oxides [24], and copper (Cu) chalcogenides [25], among a growing list of many others. Surface plasmons are confined to the surface of nanostructured materials [26]. After photoexcitation, the free electron charge density begins to oscillate at the surface of the plasmonic material, leading to the focusing of the

far-field radiation to highly localized and dramatically enhanced nanoscale electromagnetic fields. Materials that support surface plasmons have the ability to amplify an electromagnetic wave from free space within an effective volume well below the diffraction limit [27], allowing for a wide range of applications, including fueling photocatalytic reactions [5, 13–18, 28–30], increasing the efficiency of photovoltaics [31–37], and serving as vehicles for photothermal therapy [38–44].

2.2 Plasmonic energy partitioning

A coherent surface plasmon can be generated by introducing an incident photon source that is on-resonant with the nanoparticle's extinction spectrum. The wavelength of light used to interact with the particles is much larger than the size of the material itself and produces a coherent oscillation of the electron density locally confined to the nanosized particle. After the surface plasmon has been photoexcited, its energy may rapidly decay through either radiative or nonradiative pathways. The surface plasmon only maintains its coherence for 1–10 fs and begins to convert its energy into multiple pathways as it decays [45]. However, depending on the substrate's composition, shape, and size, multiple distinct chemical and physical processes may be triggered as the plasmon relaxes. The following sections will detail the various decay pathways the plasmon may undergo as it loses coherence and relaxes. Once the plasmonic energy is dispersed through the preferential pathways, the energy can be used to power a plethora of applications (Figure 1).

2.2.1 Enhanced electromagnetic fields

Surface plasmons give rise to dramatically enhanced electromagnetic fields near the surface of the nanostructure [27]. The plasmonic nanoparticles can be specifically engineered to host various nanoscale physical structures that allow for extreme light concentration to subwavelength dimensions, resulting in highly localized electric fields. Resonant interactions between the oscillating free electron density near the surface of the nanostructure and the incident electric field produce these exponentially decaying fields. The regions of amplified electromagnetic fields typically form between the crevice of two or more physical feature or at a sharp, distinct edge on the surface. Examples of a plasmonic field enhancement can be seen in constructs such as the nanoparticle oligomer and bow-tie antenna substrates shown in Figure 2 [46, 47]. When

Figure 1: Present-day applications for plasmonic materials.

(Top left) Plasmonic nanoparticles have been employed to target cancerous cells within live organisms. Once photoexcited, the plasmonic energy is intentionally converted into a thermal energy to annihilate the targeted cells. (Top right) Sensing platforms constructed with plasmonic materials are used to detect specific analytes at an ultralow concentration. (Bottom left) Nanolevel architectural design can be achieved by inducing chemical reactions that link two or more individual nanoparticles to assemble a new plasmonic structure. (Bottom right) Plasmonic nanostructures are capable of mediating highly selective catalytic processes.

positioned within a region of dramatically enhanced electromagnetic fields, a molecule may experience dramatically enhanced scattering due to the subwavelength confinement of electromagnetic light. This phenomenon led to the development of multiple surface-dependent processes and applications, such as surface-enhanced Raman [48, 49], infrared (IR) [50, 51], and fluorescence [52, 53] spectroscopies and the invention of light-harvesting plasmonic photovoltaics [31–37]. Once photoexcited, the coherent electromagnetic field decays rapidly and effectively acts like an AC field being driven by the photoexcitation source, making it unlikely to have a direct impact on the photocatalytic reaction pathway.

2.2.2 Hot carrier generation

After the surface plasmon loses coherence, the nonradiative decay pathway produces a distribution of hot carriers that may be used in initiating photocatalytic reactions. This multistep decay process occurs primarily via Landau damping [54], where energy is transferred from a coherent

plasmon to individual electron-hole pair excitations. Initially, the hot carrier distribution is nonthermal and contains charged species far from the Fermi level of the material [55, 56]. Then, hot electrons and holes rapidly thermalize, reaching a Fermi-Dirac distribution that corresponds to a high effective electron temperature. This initial thermalization is carried out through a redistribution of the energy via electron-electron scattering interactions during the next several hundred femtoseconds (1–100 fs) [57, 58]. During this time, the hot electrons and holes may contain energies ranging from the Fermi level to the work function. These charge carriers are sufficient in quantity and lifetime to initiate external chemical processes (Figure 3) [55]. The hot carriers further dephase through an additional relaxation mechanism consisting of electron-phonon interactions over a timescale of 1–10 ps [59, 60]. It is during these two time intervals that the charge carriers may contain sufficient energy to transfer to a nearby chemical species to initiate a single or multistep chemical reaction.

The ultrafast timescales described above can present challenges in using plasmonic substrates to

Figure 2: Calculated electric field enhancements for Au: (A) nanoparticle oligomers [46] and (B) bow-tie antennas [47]. The maximized field enhancement for both systems is produced at the interfaces between the nanoparticles and the regions containing sharp structural features. (A) Reprinted with permission from Ref. [46]. Copyright 2013 American Chemical Society. (B) Adapted with the permission from Ref. [47]. OSA Publishing.

drive photocatalytic processes. A large majority of industrial significant catalytic processes rely on bimolecular reactions that are induced through collisions in the gas phase. However, due to the extremely short lifespans of plasmonic hot carriers, current reaction activities and turnover frequencies are limited by the low probability of interactions between molecules in free space and the hot carriers generated near the surface. Plasmon-mediated catalysis would be more efficient if the reactants can be preloaded onto the surface, as is common in most heterogeneous catalytic processes, dramatically increasing the likelihood of inducing the interactions between the hot carriers and targeted reactants. Unfortunately, achieving

Figure 3: Theoretical modeling of the hot carrier distribution as a function of their energy in AgNPs with diameters of (A) 15 nm and (B) 25 nm.

An abundance of hot electrons (red) and holes (blue) are generated via plasmon decay in the 15 nm particle, whereas the hot carrier generation is significantly diminished in the 25 nm particle. Reprinted with permission from Ref. [55]. Copyright 2015 American Chemical Society.

controlled preloading is quite difficult for the most prevalent plasmonic materials (Au and Ag) [61]. Coupling these plasmonic materials with more reactive metals may be the most promising route for achieving high-efficiency catalysis [5].

2.2.3 Localized heating

After the electrons have undergone the fast electron-electron and electron-phonon scattering events (10 fs–10 ps) and have reached a thermalized distribution, the remaining energy is transferred to the localized environment (both

solvent and adsorbed molecules) in the form of heat [20, 21]. Plasmonic photothermal heating has received a considerable amount of attention in the past due to its potential of using plasmonic nanoparticles as an excellent agent for delivering thermal energy in a highly localized manner [14, 62, 63]. In fact, an exciting field using photoinduced plasmonic heating is plasmonic photothermal therapy [38–44]. This form of cancer therapy employs nanoparticles with plasmons specifically tailored to the near-IR to minimize absorption by any tissue above the nanoparticles. The particles are targeted at cancerous cells and irradiated with an external near-IR light source to initiate a phase of cell death via localized thermal heating and induce tumor remission. In addition to photothermal therapy, localized plasmonic heating has also been applied in other applications such as drug delivery and release [64], steam generation [65], photothermal therapeutics [66], and growth manipulation of nanoscale structures [67, 68].

Localized plasmonic heating has also been demonstrated as a fundamental mechanism for carrying out or assisting certain catalytic reactions [14, 19, 69]. A surplus of localized heat is typically a vital condition for a variety of endothermic reactions. During the plasmon decay process, the formation of highly localized thermal environments, both on the nanoparticle's surface and on the surrounding medium, can be an excellent source of thermal heat transferred to a nearby molecular species. In fact, localized heating is one of the few benefits of the lossy nature of plasmons [70]. While working in tandem with the plasmonic hot carriers, the released thermal energy could play an integral role in reducing energetic barriers preventing a reaction from taking place. A consideration of the interplay between local heating and hot carrier generation is necessary for successfully mediating a photocatalytic process.

2.2.4 Modified molecular potential energy surfaces

Another aspect of plasmonic photocatalysis is the formation of new energy levels as a molecule adsorbs to the surface of a plasmonic material. In this scenario, the strong coupling between the plasmon and molecule may lead to an alteration to the molecular resonances. An analogous effect was discussed by Boerigter et al. in 2016 [71]. Boerigter et al.'s work described new hybridized metal-adsorbate states that form as a result of molecular chemisorption to a metal surface, producing a new charge transfer pathway from the nanoparticle to the molecule. These chemical interactions on the surface resulted in a highly modified coupled system that allowed for resonant

energy transfer between the plasmon and the adsorbate. A more detailed discussion of this study is provided in the surface-enhanced Raman spectroscopy (SERS) section (3.1.1) further on in this review. This proposed pathway was successful in providing empirical evidence of the effects of molecule-surface interactions on plasmonic photocatalysis. In 2018, Kazuma et al. were successful in identifying a plasmon-induced single-molecule dissociation of dimethyl disulfide $[(\text{CH}_3\text{S})_2]$ on Ag and Cu surfaces with scanning tunneling microscopy (STM) [72]. Here, the authors found that the dissociation was mediated by an energy transfer from the localized surface plasmon to the adsorbed molecular species. The direct adsorption of the $(\text{CH}_3\text{S})_2$ onto the metal substrates resulted in the LUMOs of $(\text{CH}_3\text{S})_2$ to be weakly hybridized with the metal. The weak hybridization significantly reduced the likelihood of excited-state relaxation to the ground state, which gave rise to an accessible dissociative potential energy surface. There is a substantial literature within the surface science community that has detailed the interactions between molecular adsorbates and surfaces, which may be quite helpful for further understanding the interplay between surface and plasmonic effects on the electronic states of adsorbed molecules [73–77]. The results from these studies ultimately laid a groundwork for understanding surface and molecular plasmonic effects. However, a discussion into these interactions is beyond the scope of this review. Due to this complexity of the coupled molecular-plasmonic system, a variety of technical approaches are needed to examine the transient mechanisms relevant to plasmonic photochemistry.

3 Select methods to elucidate the mechanism of plasmon-mediated photocatalysis

3.1 Spectroscopy

3.1.1 Surface-enhanced Raman spectroscopy (SERS)

3.1.1.1 Ensemble SERS

One of the more effective and frequently used techniques to explore plasmon-molecule interactions is SERS. SERS is a vibrationally sensitive technique that exploits the fundamental nature of plasmonic systems by enhancing the Raman-scattered signal generated by molecules positioned within the substrate's regions of most dramatic field enhancement, which are known as hot spots in the

SERS community [78, 79]. SERS is an excellent method for probing and monitoring plasmon-mediated photoreactions *in situ* and in real time due to its remarkably high signal enhancement, which can enable microsecond acquisition times [80]. These experiments are typically highly sensitive to the signal arising from the most enhanced hot spots on the plasmonic substrates [81]. Traditionally, the nanostructures are noble metals (e.g. Au and Ag) that have been specifically fabricated or synthesized to host sharp, nanoscale features that couple together to form hot spots.

The magnitude of a collected signal can be quantified by calculating an SERS enhancement factor (EF) for the plasmonic substrate used in the experiment. The SERS EF can be calculated by the following equation [82]:

$$EF = \frac{I_{\text{SERS}}/N_{\text{surf}}}{I_{\text{NRS}}/N_{\text{vol}}}$$

where I_{SERS} and I_{NRS} are the Raman intensities on the SERS substrate and under normal conditions, respectively. N_{surf} is the number of molecules probed on the substrate and N_{vol} is the number of molecules probed during the normal Raman collection. This equation is evaluated at a set excitation wavelength for a specific Raman-active vibrational mode. Multiple assumptions, such as the molecular probe's surface coverage and estimated Raman cross-sections, can be made during these calculations and may lead to discrepancies in the values reported throughout literature. Understanding SERS EFs is essential for appropriately evaluating the work performed within this field, as it can be a useful metric of the localized electric fields experienced by the molecular probes [83]. However, it is important to note that the EF in nearly all SERS experiments are ensemble averaged. This ensemble averaging can include contributions from hot spots with EFs ranging across approximately six orders of magnitude, although the strongest enhancing sites produce a vast majority of the collected Raman signal. Fang et al. published an exceptional study that examined the distribution of individual hot spots and how they contribute to the overall SERS intensity [81]. They found that fewer than 0.01% of probed hot spots in a single SERS exposure account for nearly 25% of the collected SERS signal. Therefore, the reported SERS EFs in most publications are typically a lower bound to overall signal magnitude due to the assumption that every adsorbed molecule contributes to the SERS signal. There is currently a huge focus in the literature on developing new SERS substrates [84–90], but until atomically defined nanostructures are available in geometries large enough to support a surface plasmon, they will fundamentally be limited by this ensemble averaging, making absolute quantitative analysis difficult.

In fact, SERS has a myriad of advantages for examining the mechanism behind plasmon-mediated photocatalysis. Being a vibrationally sensitive spectroscopic technique, SERS offers much more detail and information about the molecular probe's structure than electronic spectroscopic techniques. SERS is capable of discerning any minor alterations to the molecule's orientation on the surface through discrete changes in the spectra. Also, the rapid decay of the electromagnetic fields near the plasmonic nanostructure's surface ensures that the signals are generated from molecules on or near (r^{-10} distance dependence for spherical nanoparticles) the surface [78, 91, 92], making it a highly selective technique. The selectivity of SERS ensures that the probed molecules are the most susceptible to interactions with any plasmon-induced effects.

However, the inherent limitations of SERS must also be addressed. The selectivity of this technique comes with a cost: the molecular probe typically contains specific functional groups that have a strong affinity to the surface. Certain chemical moieties (thiols, amines, N-heterocyclic carbenes) undergo chemisorption onto the surface of traditional plasmonic metals and may be confined within the intense electromagnetic fields produced during excitation. Another constraint is the limited options currently available for surface plasmon-hosting substrates. The most commonly used substrates are Au, Ag, Cu, and, more recently, Al due to their enhancement capabilities that cover most of the visible and near-IR spectra. Nevertheless, the dramatic signal enhancement found in a wide range of Au and Ag substrates has resulted in these metals being the leading materials for exploring plasmon-mediated reactions with SERS.

One of the most interesting aspects of using SERS to study surface plasmons and their subsequent dynamic processes is how the technique is capable of simultaneously initiating a photocatalytic reaction while also probing the vibrational features of reacting adsorbates. The most meticulously studied chemical reaction using SERS is the dimerization of both 4-nitrobenzenethiol (4-NBT) and 4-aminothiophenol to 4,4'-dimercaptoazobenzene (DMAB) [83, 93–99], which will be a common reaction discussed throughout this review. Most variants of SERS techniques collect signals that effectively describe how the molecules are behaving in the steady-state regime, which can contain data rich with information about reaction yields, efficiencies, and rates. However, this experimental constraint may be viewed as a limitation as it does not allow for an analysis pertaining to the transient dynamics that occur during a chemical reaction [55]. To address this concern, multiple research groups are aggressively attempting to develop ultrafast SERS techniques that can

monitor the step-by-step mechanism of various plasmonic dynamics (Section 3.1.3).

An elegant study published by Boerigter et al. used SERS to examine the mechanism of charge transfer from a plasmonic system to adsorbates [71]. Their findings suggest that, by considering the effects of molecular adsorption on the flow of charge within the plasmonic nanostructure, the yield of extracted hot electrons potentially could be substantially higher than the theoretical yields derived from traditional metal-centric models. The conventional models describe the process of charge excitation in plasmonic nanoparticles and the subsequent transfer to an adsorbed species, which disregards any potential influence the adsorbate may have on the transient dynamics. Here, the authors proposed an alternative mechanism for charge transfer that introduces a new pathway capable of a direct and on-resonant charge transfer into the high-energy adsorbate states (Figure 4A and B). This alternative mechanism circumvents the “losses” that occur during the electron-electron and electron-phonon thermalization pathways that are present in the present-day mechanism [70]. The experimental work to support

this proposal examined the anti-Stokes and Stokes scattered photons to simultaneously measure the vibrational temperatures within the chemical adsorbates and metal nanoparticle (Figure 4C and D). During these studies, they found that methylene blue experienced an elevated vibrational temperature when excited by 785 nm photons and not 532 nm photons. These results hint at the possibility of an observed charge transfer between the metal and the adsorbate during 785 nm excitation, which is resonant with the proposed hybrid metal-adsorbate states that are formed upon chemisorption.

The conclusions proposed in this work suggest that the community may need to direct more attention toward the effects of molecular adsorption and hybridized states on plasmonic charge transfer leading to photocatalysis. The hybridized metal-adsorbate states formed during chemisorption may give rise to the possibility of a direct, ultrafast pathway from the metal to the adsorbate at the interface between the two materials.

Initiating and monitoring chemical reactions across a wide range of localized field enhancements may provide helpful insights toward optimizing plasmon-mediated

Figure 4: Formation of an alternative pathway of resonant energy transfer for plasmonic charge carriers into the high-energy states of the molecular adsorbates.

(A) This pathway is generated when an adsorbate or semiconductor interacts with the metal’s surface and can circumvent the thermalization of hot electrons before transfer occurs. (B) Density of state visualization of the proposed mechanism of direct, resonant transfer. (C and D) Data representing the anti-Stokes (blue) and Stokes (red) spectra collected with (C) 785 nm and (D) 532 nm lasers. There is a noticeable increase in the 785 nm anti-Stokes signal due to a resonant charge transfer into the adsorbates. Reprinted with permission from Ref. [71]. Copyright 2016 American Chemical Society.

photochemistry. Recently, Brooks and Frontiera published a study that looked into the effect of field enhancement on the plasmon-mediated dimerization reaction of 4-NBT to DMAB [83]. The ensemble-averaged field enhancement was effectively tuned at multiple different spatial locations across a heterogeneous Au film-over-nanosphere substrate. Changes in the localized surface plasmon resonance (LSPR) for each probed region were present due to the random variation of nanoparticle packing defects, producing a range of EFs from 5×10^6 to 3×10^7 . Interestingly, no identifiable correlations were found between the reaction rate and the yield with an increased plasmonic field enhancement, suggesting that plasmon-driven processes are not rate limiting for this reaction (Figure 5). The photoreaction rate is likely limited by the local concentration of protons used in the initial reduction of 4-NBT. Additionally, this work found that the presence of alternative plasmon-induced processes, such as a molecular degradation and/or atomic-level substrate alteration, may dramatically impede the reaction's rate or potentially hinder the overall molecular conversion.

These findings argue that plasmon-mediated chemical processes are not always most effectively powered in

the strongest regions of field enhancement. Having a firm grasp on the energy partitioning after plasmon excitation for a specific plasmonic system is a necessity for optimizing the targeted output. Redirecting the flow of energy away from the undesired pathways (local environmental heating, molecular cleavage/dissociation, alternative chemical reactions, etc.) and toward the preferred chemical reaction or catalytic process is the ideal, yet nontrivial, solution for producing plasmonic systems suitable for integration into energetically demanding industrial processes. SERS can also quantify the spectral relationship between the far-field LSPR and near-field Raman scattering events that occur during the typical SERS experiment. Work performed by Kleinman et al. provided a unique viewpoint on how to consider the interplay between far-field and near-field scattering in hot spot-dominated SERS collections [46]. They found that the presence of hot spots in single-particle SERS studies can clearly modify the optimal excitation wavelength for maximized SERS enhancement. To study these far-field and near-field interactions, they developed a correlated LSPR-transmission electron microscopy surface-enhanced Raman excitation spectroscopy technique. Their results clearly identify that

Figure 5: Field effects on plasmon-mediated dimerization of 4-NBT to DMAB tracked with SERS.

(A) Time-dependent SERS spectra of the dimerization process monitored in real-time. (B) Plot of the final reaction yield's dependence on the ensemble SERS field enhancement. The final reaction yield is a ratio of the final amplitudes of the product and reactant peaks. (C) Comparison of the rate constants for the reactant loss (red) and product formation (green) against the ensemble SERS field enhancement. Reprinted with permission from Ref. [83]. Copyright 2016 American Chemical Society.

the spectral dependence in individual nanoantennas, which are aggregated nanoparticles encapsulated within a silica coating, and their SERS intensity is dramatically dominated by near-field Raman scattering produced within the hot spots between the two or three aggregated Au nanospheres. In fact, they found that the maximum enhancement was completely independent of the far-field LSPR spectra of both individual Au nanoantennas and an ensemble-averaged collection in their experiments. The maximum ensemble-averaged EF of 5.0×10^7 peaked at an excitation wavelength of 830 nm, although the far-field LSPR scattering intensity was most intense at ~600 nm.

This report is an excellent example of carefully evaluating hot spot-dominated systems and identifying how they can be optimally used for future experiments. As the authors appropriately described, the commonly accepted assumption that far-field spectral scattering determines the ideal excitation wavelength for SERS enhancement may not always hold true. This work clearly demonstrates the importance of using complimentary computational modeling methods and experimental techniques [55, 100] to develop a full description of the plasmonic modes, both bright and dark, for any given system.

3.1.1.2 Single-molecule SERS (SMSERS)

The preceding section evaluated several SERS experiments that were all performed with a monolayer or near monolayer of molecules residing on the plasmonic substrate's surface. Results collected with this level of molecular concentration have clearly been used to construct fully developed and highly impactful conclusions pertaining to a wide range of photochemical and catalytic reactions. However, as the name implies, an ensemble-averaged measurement can only describe the physical nature of the adsorbed molecules as a whole, which can hinder the identification of clear structure-function relationships. For instance, ensemble-averaged studies are limited to gathering information that is generated from a remarkably wide range of localized field enhancements rather than exploring the sensitive behavior of individual molecules as they interact with their highly specific and unique local environment. SMSERS was first reported in two pioneering articles in 1997 [86, 101] and the field has vastly grown since its discovery [102–107].

Several studies have been key in the development of SMSERS over the last 20 years. A bianalyte method was developed by the Etchegoin lab in 2006 by statistically comparing the unique spectral information collected from two distinct molecules [104]. A year later, the Van Duyne group developed a similar method that

used two isotopologues of a single chemical species [105]. When working in ultralow concentrations of both molecular species, on average, only one variant of the isotopologues is adsorbed to the metal within the effective probing area. Each isotopologue produces a vibrational spectrum containing Raman bands that make it easily distinguishable from the other. Since then, similar techniques have been used to study single-molecule dynamics on plasmonic substrates. Recently, SMSERS has been used in the detection of plasmon-driven electron transfer. In 2017, Sprague-Klein et al. presented a study where 4,4'-bipyridine (BPY- h_8) and its deuterated isotope (BPY- d_8) were adsorbed between Au nanosphere oligomers and subjected to a single-particle pump-probe experimental probing technique [108]. The single particles were exposed to a 532 nm pump CW laser to excite the monomer plasmon while simultaneously being probed by a 785 nm CW laser for the signal collection. They observed a delayed (>2 min) plasmon-mediated charge transfer of surface electrons from the Au oligomers to produce long-lived BPY radical anion products (Figure 6A and B). The authors suggested that an accumulation of surface electrons was required before a neutral BPY molecule could successfully accept a nearby hot electron. In fact, a low 3% yield of electron transfer to an adjacent BPY molecule was reported. A similar study was published in 2017 and was also successful in identifying hot electron-driven redox chemistry at a single-molecule level using methyl viologen [110].

Typical SMSERS signals are inherently intricate and difficult to analyze due to dramatic temporal and spectral fluctuations. These fluctuations are caused by several sources, including variations of molecular orientation in an isolated hot spot, atomic-scale surface modifications throughout prolonged photoexposure, and possible Brownian diffusion of the molecule [105, 111, 112]. Recently, an innovative SERS-based method to suppress these issues was published by Choi et al. [109]. Here, they explored a single-molecule catalytic reaction of 4-NBT to DMAB in real time by monitoring discrete step-like transitions of the reaction's products. These experiments implemented a self-assembled Ag nanoparticle (AgNP)-4-NBT-Au thin-film substrate to induce and monitor the dimerization of 4-NBT to DMAB in the junctions between the nanoparticles and Au film, which were capable of reaching SERS EFs of 1.7×10^8 . Rather than attempting to isolate distinct SERS signals from their collected spectra, the authors developed an innovative method to identify discrete transitions tracking the formation and annihilation of individual DMAB molecules within a single, intense hot spot. Figure 6C depicts a time-resolved SERS trajectory

Figure 6: Time-dependent single-molecule SERS.

(A and B) Anion formation event for BPY on a Au nanoantenna substrate with the associated isotopologue analysis to confirm single-molecule limit and (C) single-molecule step transitions after the formation of DMAB in real time. (A and B) Reprinted with permission from Ref. [108]. Copyright 2017 American Chemical Society. (C) Reprinted with permission from Ref. [109]. Copyright 2016 American Chemical Society.

of the DMAB species as they react within the nanoparticle-thin-film junctions. In conjunction with computational modeling, the transitions present in time-dependent data are clear spectral evidence of a single-molecule plasmon-mediated photocatalytic reaction.

Developing new methods to monitor individual molecules as they undergo a chemical transformation is nontrivial. Choi et al.'s unique approach of data analysis was capable of extracting data rich with information describing the behavior of individual molecules in a highly complex environment [109]. They addressed the

common difficulties found in SMSERS experiments (spectral and temporal fluctuations) and designed a plasmonic system that systematically removed a majority of the randomness by ensuring that the adsorbed molecules were situated in the center of well-characterized hot spots. If anything, these studies identify the need for a new class of intricately designed plasmonic substrates that employ well-defined, easily accessible, and dramatically enhancing hot spots. Recent studies have done an excellent job of using cucurbit[*n*]uril structures to generate well-defined hot spots for ensemble [113] and single-molecule

[114] SERS detection. Constructing a system that directs the flow of hot electrons to these regions of enhancement should provide a significant improvement to the present-day yields and efficiencies reported. This level of nanoscale design will allow the community to probe the globally relevant photochemical and catalytic reactions, which are currently limited by their low Raman cross-sections in the single-molecule regime.

The advancement of SERS and its ability to probe single molecules has left a clear impact on the field of plasmonics and, more specifically, plasmon-mediated photochemical processes. Having a technique that is inherently linked to surface plasmon generation has ignited a boom in publications heavily invested in better understanding the complex molecule-plasmon interactions. For example, SERS studies were crucial in the identification of the role that metal-adsorbate hybridized states may play in modifying the preferred pathway of charge transfer from a plasmonic surface to the molecular probe. Implementing an equal level of well-defined experimental design may help in identifying new phenomena and SERS can continue to be used as an excellent technique for further elucidating the complex mechanism of plasmon-mediated photocatalysis.

3.1.2 Tip-enhanced Raman spectroscopy (TERS)

Another valuable vibrationally sensitive method used to explore plasmon-mediated photocatalysis is TERS. TERS is a spectroscopic technique capable of imaging physisorbed or chemisorbed molecules with nanoscale or even submolecular spatial resolution while simultaneously providing the ability to manipulate the highly localized environment surrounding the molecules. The concept of coupling scanning probe microscopy with SERS was first introduced in the 1980s [115]. This technique was successfully demonstrated in decades to be followed by multiple independent research groups, each reporting Raman signatures belonging to surface-bound molecules positioned within plasmonic tip-enhanced localized fields [115–118].

The power of TERS lies in its inherent ability to provide spatially resolved and spectroscopic information pertaining to one [119, 120] or many molecules positioned on a surface. TERS combines the advantages found in SERS and scanning probe microscopy to produce dramatic electromagnetic field enhancements capable of amplifying the chemically sensitive Raman scattered photons while reaching subdiffraction spatial resolution. This is achieved by replacing the nanoparticle substrates used in traditional SERS experiments with a sharp tip made of or

coated with a plasmonic metal. These tips typically have an extremely sharp radius of curvature (<50 nm) and can generate highly localized electromagnetic field enhancements in the effective volume between the tip apex and the substrate used to host the molecular probes [121]. The sharp, needle-like tip apex serves as a physical point-source for the surface plasmon generation and can generate a localized field that rapidly decays as it extends away from the tip [122]. When the tip is brought within close proximity to a flat metal substrate, the highly confined electromagnetic field is further amplified due to coupling between the tip and the surface. This phenomenon, which is known as the gap-mode effect, is achievable when the tip is positioned approximately 1–2 nm away from the metal surface. The enhancement produced in this confined gap-mode effect experiences a d^{-10} distance dependence, where d is the distance between the tip apex and the flat metal surface [123, 124].

One of the more helpful aspects of TERS is its ability to selectively probe individual or multiple molecules at well-defined regions on a planar substrate composed of both metallic and nonmetallic materials [125]. In fact, if the proper molecular analytes are selected, TERS is capable of initiating and tracking plasmon-mediated catalytic reactions in real time in a similar manner as SERS [126–129]. However, if the goal of the experiment is to study the effects of the tip alone, the technique can be modified to replace the metallic substrate with a material that does not have the proper dielectric constants to host a surface plasmon. This removes the inherent requirement to have the molecules locally adhered to the plasmonic substrate and gives more flexibility in the experimental approaches the user may explore.

One key difference between SERS and TERS is that the SERS signal is typically produced from the regions of highest field enhancement and is generally ensemble averaged and has much higher throughput. In TERS, the dramatically high spatial resolution provides a more detailed analysis of the studied environment. In a similar manner, the hot electrons (or holes) can transfer to the excited state of the adsorbed molecules and drive a chemical reaction. In this configuration, the tip may be selectively positioned over specific molecules or clusters for the controlled transport of hot carriers to the desired molecules. When using STM-TERS, the tip can also be used as an additional source of electrons with a tunable energy range, allowing for a more detailed analysis of the studied material or chemical reaction.

Unfortunately, a handful of complications may be present when attempting to mediate and characterize plasmon-driven chemical reactions with TERS. One of the

more difficult challenges in performing TERS experiments is reproducibly fabricating the nanoscale plasmonic tips [130]. Presently, the most common method for tip fabrication is electrochemically etching Ag and Au wires [131]. A solution-based etching method such as this will produce tips that are highly heterogeneous in shape, especially near the tip apex. This lack of reproducibility introduces a wide range of local environments for enhancing the collected Raman signal or mediating a chemical reaction, making it extremely difficult to produce consistent results across multiple tips. The tip stability can even be quite poor during the course of a typical TERS measurement, resulting in data that are potentially flawed or inconsistent in nature. Another challenge when approaching plasmon-mediated photocatalysis with TERS is quantifying any contributions that may arise from electrons tunneling from the metal tip to the adsorbed molecule. To work around this issue, users have also coated the plasmonic TERS tips with an ultrathin oxide film. The oxide layer protects and isolates the plasmonic tip away from the probed surface and minimizes undesirable interactions [129].

Plasmon-mediated photocatalytic reactions were first tracked with TERS in 2012. van Schrojenstein Lantman et al. published a report that monitored the well-studied dimerization reaction of 4-NBT to DMAB [127]. Here, the authors implemented a dual-wavelength approach to monitor the photocatalytic process. They employed a 633 nm excitation source to monitor the vibrational spectra corresponding to both 4-NBT and DMAB, whereas short, discrete periods of 532 nm laser light were directed toward a Ag-coated tip to initiate the dimerization. Using the 532 nm laser source alone to probe the surface-bound molecules resulted in an instantaneous conversion to DMAB and no relevant information could be extracted. However, by exciting the plasmon with short bursts of low-power 532 nm laser light, they could significantly slow down the rate of the ensemble-averaged reaction and monitor the molecular conversion during a slower timescale. By starting with a stable spectrum of 4-NBT, the authors were able to produce time-dependent TERS measurements that tracked the growth and subsequent decay of the DMAB and 4-NBT, respectively (Figure 7A). Ultimately, this study demonstrated the feasibility of using TERS to study the molecular dynamics that are occurring at the nanoscale level, clearly highlighting the potential to employ TERS to extract information that may help describing the interactions between plasmons and molecules.

Kumar et al. also reported an impressive study that experimentally mapped out the catalytic activity in the photoinduced reaction with nanoscale spatial resolution using atomic force microscopy-TERS [129]. The authors

studied a similar dimerization reaction, where they reacted two *p*-mercaptoaniline (pMA) moieties together to form DMAB. To prevent the molecules from physically interacting with the tip, they protected an Ag-coated tip with an ultrathin layer of alumina film. The alumina film prevented any interactions between the Ag tip and the thiol-containing molecules, which include chemisorption and unintentional spontaneous catalysis, and allowed for the acquisition of chemical reactivity maps with nanoscale resolution on nanostructured Ag substrates. With the alumina-coated Ag tip, they were able to probe a nanostructured Ag substrate and identify the regions of greatest photocatalytic activity by monitoring the production of DMAB (Figure 7B). The experimental design allowed for probing conditions capable of achieving a spatial resolution of 20 nm, allowing the authors to map the chemical reactivity on individual plasmonic nanoparticles. This was the first reported publication that successfully mapped the substrate-dependent catalytic activity of a reaction in a TERS configuration. In addition, the TERS configuration allowed the users to identify the catalytically active and inactive regions on a plasmonic substrate with a 20 nm spatial resolution, which was unprecedented in the field of plasmonics.

Both of these studies are excellent examples of using TERS to induce a chemical process and monitor as the molecules undergo a physical transformation. The plasmonics community stands to gain valuable insights once TERS is able to study industrially relevant catalytic processes. However, it is clear that using TERS to reproducibly study alternative chemical reactions or heterogeneous catalytic processes will be challenging, and improvements in tip fabrication methods would be extremely useful for quantitative measurements.

3.1.3 Ultrafast SERS

Ultrafast SERS is a burgeoning field that combines the plasmonic enhancements discussed in the previous sections with ultrafast time-resolved Raman spectroscopies to investigate the dynamics of plasmon-molecule coupled systems on picosecond and femtosecond timescales (Figure 8A). Here, in the first portion of this section, we used the term ultrafast SERS to refer to all pump-probe plasmon-enhanced Raman scattering spectroscopies with time resolution in the picosecond to femtosecond range.

In recent years, these techniques have been applied toward understanding plasmon-molecule interactions [132–135] and single-molecule dynamics [136, 137]. The field of ultrafast SERS has been discussed at length in

Figure 7: Plasmon-mediated photocatalytic reactions monitored with TERS.

(A, left) Time-dependent TERS measurements before and after irradiation with 532 nm laser light. Raman signatures begin to appear in the TERS spectra after the tip is illuminated with a 532 nm excitation source. (A, right) Raman spectra corresponding to 4-NBT (black) and DMAB (red). (B) Topography image of the Ag substrate (left) and TERS chemical reactivity map of DMAB after inducing dimerization of pMA (right). (A) Reprinted with permission from Ref. [127]. Copyright 2012. (B) Reproduced from Ref. [129] with permission of The Royal Society of Chemistry.

recent reviews [138, 139]. Here, to fit the scope of this review, we will be highlighting and discussing the recent applications, developments, and challenges in ultrafast SERS as applied to plasmonic photocatalysis.

With a time resolution on the order of molecular vibrational periods, and thus the timescale of the nuclear motions involved in chemical reactions, ultrafast SERS has the capability to monitor key photophysical processes and reaction dynamics of such phenomena in real time, elucidating underlying mechanisms and providing a pathway toward their optimization. Of interest are the complex interactions between adsorbed molecules and plasmon generated phenomena: hot electrons and localized hot spots, which can be observed via transient changes in intensity and line shape in ultrafast SERS [132, 133, 136, 140]. In conjunction with complimentary spectroscopic techniques and theoretical modeling, ultrafast SERS has great potential as a tool for observing these interactions

across a complete reaction coordinate, monitoring how energy partitions with variations in environment and plasmonic substrate morphology. Ultimately, the transient data extracted from ultrafast SERS studies may help to elucidate fundamental principles in plasmon coupled systems, leading to improved photocatalytic technologies and plasmonic substrates as well as providing empirical data toward the development of a unified electromagnetic and chemical SERS theory [141].

A recent study by Keller and Frontiera has shown promise toward the time-resolved quantification of hot electron generation at plasmonic surfaces [133]. In this study, Keller et al. obtained ultrafast SERS of 4-NBT reporter molecules on 70 ± 10 nm Au nanoparticles (AuNPs). Peak depletions from 4-NBT ring breathing (1079 cm^{-1}) and NO_2 symmetric stretch (1343 cm^{-1}) vibrational modes were observed, maximized as the pump and probe pulses overlap, and decayed over a period of

Figure 8: Ultrafast SERS probing of the photophysical responses of plasmon-molecule coupled systems.

(A) Representation of the transient dynamics that ultrafast SERS is capable of measuring and tracking on aggregated AgNPs. (B) Ultrafast SERS describing the behavior of 4-NBT molecules as the AuNP's plasmon experiences a photoinduced energy shift. (C) Fano-like signatures indicate that the energy transfer between the plasmon and the adsorbates is an indirect mechanism. (A and C) Reprinted with permission from Ref. [132]. Copyright 2016 American Chemical Society. (B) Modified with permission from Ref. [133]. Copyright 2017 American Chemical Society.

50 ps (Figure 8B). In accordance with transient absorption (TA), electrochemical, and theoretical models, it was determined that the transient peak depletions were caused by a red shift in the structure's LSPR, resulting from the delocalization of the hot electrons. The calculations suggested that the charge density shift resulted in the displacement of approximately 10^9 free electrons in the metal. Although they did not directly observe the product of the hot electron-induced LSPR shift, they proposed that the charge delocalization may be due to a charge transfer between the hot electrons and the adsorbed molecules, uneven distribution of the hot electrons across the probed regions, or potential electron-phonon interactions that result in the heating of the metal lattice. This study corresponds well with a similar

study by Brandt et al., which used the same ultrafast SERS methodology to probe the plasmon-driven photochemical dimerization of 4-NBT to DMAB on AgNPs [132]. This study proposed a hot electron charge transfer mechanism for the dimerization, evidenced by transient Fano line shapes and transient changes in 4-NBT/DMAB signal amplitudes. Here, as seen in Figure 8C, the Fano features are attributed to the coupling of the broad AgNP emission and the more narrow SERS photons. The relevant amplitudes of product and reactant in the transient spectra compared to the ground state spectra proved that the nanoscale regions generating the broadband emission were most efficient at driving the photoreaction. Thus this work indirectly proved the role of localized hot electrons in driving the plasmon-induced process.

Together, these studies use the time resolution of ultrafast SERS to provide a description of charge delocalization and charge transfer from a plasmonic substrate to an adsorbed molecule. Interestingly, the Fano line shapes observed by Brandt et al. were not apparent in the study by Keller et al. suggesting a different mechanism of broadband light emission in AuNPs and AgNPs. These results not only display the capability of ultrafast SERS to observe and interpret changes to the coupled plasmon-molecule system in real time but also highlight the dependence of ultrafast SERS measurements on the substrate composition. This is critical to the development of application-specific ultrafast SERS substrates, where differentiation in the identity and morphology of the plasmonic substrate may allow the tuning of interactions between scattered photons and other light-induced processes. Unfortunately, due to the fact that collected SERS signal is spontaneous, the aforementioned ultrafast SERS techniques are limited to probing transient dynamics that occur on the picosecond timescale, as with spontaneous Raman the spectral resolution and temporal

resolution are inversely related. This resolution is sufficient to resolve many of the nuclear structural changes but unable to track the early plasmonic dynamics that occur after photoexcitation.

Other recent work has been devoted to the optimization of ultrafast SERS techniques that implement stimulated Raman spectroscopies to achieve femtosecond time resolution for probing the effects of photoexcited plasmons on proximal adsorbates. This is enabled through the use of surface-enhanced coherent anti-Stokes Raman scattering (SE-CARS) and surface-enhanced femtosecond stimulated Raman scattering (SE-FSRS) experiments [134, 136]. Both techniques are similar in experimental design but involve different Raman scattering pathways to provide vibrational information describing the molecular analyte, optimally with time resolution in the 10–100 fs regime. Both spectroscopic techniques employ two to three laser pulses that interact at the sample of interest to produce the stimulated Raman signal. A CARS experiment is designed to generate a stimulated beam of blue-shifted signal (Figure 9A), whereas the four-wave mixing that is dominant in FSRS

Figure 9: Surface-enhanced coherent Raman spectroscopies.

Energy diagram depicting the photon interactions leading to the generation of surface-enhanced (A) CARS and (B) FSRS signal. (B)

Comparison of ps-SE-CARS spectra (red and black traces) and cw-SERS spectra (gray, shaded peaks). (D) Raman spectra of BPE using

cw-SERS (red) and SE-FSRS (black). (C) Reprinted with permission from Ref. [136]. Copyright 2016 American Chemical Society. (D) Reprinted with permission from Ref. [142]. Copyright 2017 American Chemical Society.

stimulates Stokes-shifted photons (Figure 9B). Although both techniques are excellent in producing stimulated signals useful for both molecular imaging and time-resolved measurements, they are both generally limited to a high concentration of molecules or materials with large Raman cross-sections. To bypass this issue, multiple attempts have been made to locally enhance the Raman signal by the means of plasmonic surface enhancement.

Crampton et al. demonstrated the novelty of SE-CARS to study plasmonic materials and their enhancement capabilities [136]. In this study, the authors probed core-shell Au-silica dumbbells ($\text{Au@SiO}_2\text{-NTs}$) with *trans*-1,2-bis(4-pyridyl)ethylene (BPE) adsorbed at the nanojunction of the participating Au nanospheres (Figure 9C). The results highlight several conclusions regarding the development of surface-enhanced nonlinear spectroscopies. The enhanced local electric field results in a limited accessible power range between observation of signal and damage to the sample. Also, the stimulation of the Raman field in the SE-CARS process is easily saturated using relatively low pulse energies (100 fJ in a 100 fs pulse). The authors also found that, when working in a few-molecule regime with SE-CARS, the time-domain and frequency-domain measurements are not direct Fourier transforms, with the time-domain measurements revealing more in-depth information on the molecular dynamics.

An alternative stimulated Raman technique is SE-FSRS, which was first introduced in 2011 by Frontiera et al. [142]. The SE-FSRS signals have Fano line shapes, which result from coupling between the broadband plasmonic response from colloidal nanoparticles and the narrowband vibrational coherences in the molecular adsorbates (Figure 9D) [140, 143, 144]. Interestingly, the vibrational coherence's dephasing time was independent of the coupling between the plasmon and the molecule [140]. This initial study laid the groundwork for the future attempts toward applying and further understanding the mechanism behind SE-FSRS. Follow-up work by Gruenke et al. described the optimal concentration of particles and identified the path length dependence in SE-FSRS measurements [134, 139]. They emphasized that extinction and enhancement in SE-FSRS, and other surface-enhanced resonance Raman techniques, must be appropriately balanced to achieve optimal signal intensity and signal-to-noise ratios, particularly in the transmission geometry used here. These studies serve to elucidate fundamental factors in designing efficient ultrafast SERS experiments. Understanding the factors that play a role in signal intensity, sensitivity, degradation, and interpretation are key to the development of a technique that can be readily adopted and applied by the scientific community at large.

However, currently both SE-CARS and SE-FSRS studies have been primarily limited to Au@SiO_2 nanoantennas, which has limited applications. The continuation of such diagnostic work is key toward the characterization and development of reliable ultrafast SERS experimentation.

Despite recent advances, some hurdles must still be overcome in the development of femtosecond SERS techniques. Present studies have been limited to a narrow range of model systems, which still require optimization for expansion into studying more complex plasmon-molecule interactions. Furthermore, numerous processes that occur within plasmonic-molecular systems, particularly in the interrogation in the few molecule limit, can greatly complicate data interpretation [145, 146]. Although the above techniques have come a long way to understanding these interactions, there is still much fundamental work that needs to be done to make them more efficient and effective as analytical tools for understanding plasmon-molecule dynamics. To date, there is no study that has been successful in obtaining structural snapshots of evolving chemical reactants on plasmonic surfaces, although, once the technical hurdles are surmounted, these techniques should be tremendously useful approaches for identifying the vibrational character of a molecular species as it undergoes a plasmon-mediated chemical reaction. Having the tools to spectroscopically track the intermediate states as a molecular transformation takes place would dramatically increase our understanding of these nontrivial mechanisms involved in plasmonic photocatalysis. However, complicated in experimental design, the advancement of ultrafast SERS has far-reaching implications in fully realizing applications of plasmon-related processes and deserves continued attention in coming years.

3.1.4 Transient absorption (TA)

The previous sections have contained numerous experimental examples where all the significant data were collected by probing a set of molecules or an individual species as they interact with a photoexcited surface plasmon. However, to effectively probe and understand the interactions between surface plasmons and the electronic states of a given material, a different flavor of ultrafast spectroscopy is required. Here, we discuss the efficacy of TA spectroscopy as a tool to elucidate the key parameters of plasmon-induced processes. The configuration of TA spectroscopy used to study plasmonic materials employs two femtosecond laser pulses: a pump pulse for photoexcitation and a probe pulse to track the subsequent plasmon-induced dynamics. For a more detailed

description, Berera et al. [147] and Ruckebusch et al. [148] have provided excellent reviews on the subject. By evaluating the entire collection of transient spectra, one can deduce the effect of plasmonic excitation on adsorbed species. Specific parameters such as energy transfer rates and efficiencies can be extracted by monitoring the differential spectra. To date, most TA experiments on plasmonic systems have looked at the effect of plasmon excitation on proximal semiconductor materials. Studies on transient plasmon-molecule dynamics are challenging as the optical cross-sections of plasmonic materials far exceed the absorption cross-sections of molecules, meaning that the plasmonic response obscures the transient molecular signal. Therefore, directing a concerted effort toward the development of new plasmonic-semiconductor nanostructures for TA studies may help with the pursuit of better understanding the fundamental mechanism behind plasmon-mediated photocatalysis [149, 150].

TA spectroscopy of plasmon-semiconductor systems has been used to directly probe interfacial charge transfer reactions, as seen by Wu et al. in 2015 [151]. This alternative route for plasmon-induced hot-electron transfer (PHET) is plasmon-induced metal-to-semiconductor interfacial charge transfer transitions (PICTT), which combines the strong light-absorbing power of a plasmonic transition with the charge separation properties of a semiconductor-metal system (Figure 10A). Due to the strong coupling between the plasmonic material and the semiconductor's electronic states, a new decay pathway is formed between the two materials. The first demonstration for the PICTT pathway was provided by TA studies involving colloidal quantum-confined CdSe-Au nanorod (NR) heterostructures, where the PHET occurs within 20 fs (Figure 10B) [151]. The plasmon decays directly by the transfer of an electron to CdSe; therefore, the quantum yield of the charge separation process is independent of the excess energy above the CB edge, as long as the excitation energy is above the absorption threshold. The recorded high yield (>24%) of the electron transfer provides a potential bridge to evade the various competitive channels into which the plasmonic energy may partition, providing an alternative design protocol for fabricating efficient plasmon-mediated devices.

TA spectroscopy has also been used to monitor energy transfer between a metal and a semiconductor through a plasmon-induced resonance energy transfer (PIRET) process [29, 152–154]. Here, rather than transferring electrons, the surface plasmon decays by donating its energy to a nearby species, analogous to Förster resonance energy transfer (FRET). PIRET was first directly observed by Cushing et al. in 2012, where they monitored Au@SiO₂@Cu₂O heterojunctions using TA [29]. The spectral overlap

Figure 10: Transient absorption studies of plasmon-induced interfacial charge transfer.

(A) Energy schematic of PICTT in CdSe-Au NR systems, where the Au tip is strongly damped. Green dashed arrow corresponds to the interband absorption that occurs in the visible region and red arrow indicates the intraband transition in the IR region. (B) Kinetic trace highlighting the intraband absorption in the IR region (probed at ~3000 nm, red circles) and the 1 Σ -exciton-bleach (probed at ~580 nm, green line) after 800 nm excitation. From Ref. [151]. Reprinted with permission from AAAS.

between Au and Cu₂O allows for PIRET through dipole-dipole interactions even with the SiO₂ barrier. By monitoring PIRET with TA spectroscopy, they observed PIRET with SiO₂ barrier thicknesses over which direct electron transfer would not be possible. The high-energy transfer efficiency at and below the band edge has the potential to increase the Cu₂O photoconversion range, which is independent of the charge transfer process. The ability to transfer plasmonic energy to a blue-shifted region opens up a wide possibility for improving light-harvesting yields. Even for the smallest ~1.5 nm SiO₂ barrier, PIRET excited at 650 nm created ~1.4 times the number of charge carriers in Cu₂O as the above-bandgap excitation of the same incident flux, with the enhancement spanning the entire plasmon distribution. With proper modifications of the device aimed at minimizing the back transfer of energy by FRET, as well

as maintaining a sufficient spectral overlap between the plasmon and the thin-film semiconductor, this method can be used in effective solar light-harvesting devices over a wide spectral range with high yield.

These examples highlight the importance of employing TA to study plasmon-mediated processes to help elucidate the underlying mechanism for charge separation in plasmonic systems. The use of semiconductors to separate plasmon-generated charges may lead to more efficient harvesting of these charges for plasmonic photocatalysis. However, with the scope of the review article in mind, it is likely that present-day TA techniques will not readily surpass ultrafast Raman approaches in determining chemical mechanisms of catalytic steps in plasmonic photocatalysis. Yet, the results compiled with both of these highly useful spectroscopic approaches could be further supplemented by employing or integrating nonspectroscopic methods, such as electrochemistry.

3.2 Electrochemistry

A number of electrochemical techniques have recently been employed to examine plasmon-induced processes, particularly with regard to understanding charge transfer and heating processes in the coupled plasmon-molecule system. By monitoring overpotentials, it is possible to determine the energy levels of reactive intermediates [13]. In addition, scanning electrochemical microscopy (SECM), which monitors the current at an ultramicroelectrode as it is scanned across an active surface, has played a crucial role in determining the contributions of heating during plasmon-mediated processes [155, 156]. Ultimately, electrochemical techniques can be employed to provide a wealth of information about the mechanism of plasmonic photocatalysis and to what extent electrons play a role in driving reactions [157].

A common approach is to pair electrochemical potential control with dark-field microscopy, which monitors the scattering from the plasmonic sample [158–160]. This has the advantage of providing precise control over the charge carrier density by altering the applied potential as well as allowing for the active monitoring of the LSPR and its response to charge density changes [159–161]. Most of these techniques measure the charging of plasmonic nanostructures by adsorbing them to a conductive substrate, which is typically indium tin oxide (ITO) [159, 160]. Upon manipulation of the charge density of a plasmonic nanostructure, various changes to the plasmonic nanoparticle and the local environment can occur, including ionic rearrangement of the electrolyte solution, modifications

to the particle morphology, and the ability to mediate specific chemical reactions at the particle surface [162–164]. As an example of the sensitivity of this approach, Collins et al. correlated a 0.02 nm blue shift in the LSPR to the addition of 110 electrons to a single Au NR in an ion gel device [163]. Dark-field microscopy used in tandem with an applied electrochemical potential is clearly a powerful tool for monitoring electron transfer events by closely tracking the LSPR, which may allow for a deeper analysis of the rate-limiting steps and catalyst-specific reaction mechanisms.

Additional modifications to this technique, such as including dynamic potential control and achieving single nanoparticle analysis, has allowed for an increased understanding of the electrochemical tuning of nanoparticles and the role of particle heterogeneity in the various responses [159, 162]. Byers et al. used hyperspectral dark-field imaging to show that, upon electrochemical tuning, a population of nanoparticles can undergo several different processes ranging from nanoparticle charging, as described previously, to electrochemical reactions, such as chloride ion oxidation and hydrogen evolution reaction (HER) (Figure 11) [162]. These responses vary based on a combination of nanoparticle or nanoparticle/substrate properties that either favor nanoparticle charging or charge transfer. Depending on the local environment and nanoparticle properties, nanoparticles also undergo irreversible or reversible electrochemical reactions that may include HER under negative potentials or metal-halide formation under positive potentials [162, 164]. Although there is still room for further understanding of the fundamental principles driving these phenomena, it is clear that these techniques can be used to illustrate a picture of the chemistry occurring around plasmonic nanostructures.

In addition to monitoring how adding or removing charge can manipulate plasmonic behavior, electrochemical techniques can also be used to monitor plasmonic photochemical reactions. When the plasmons are intentionally photoexcited with an external source, the electrons in the systems undergo a perturbation and the photocurrent of an integrated plasmonic device or overpotential changes for the half-reaction can successfully be recorded. For solar water splitting, the plasmonic electrochemical cell can be modified such that either the HER is plasmon driven or the device can be modified to form a plasmonic photoanode where the oxidation reaction occurs [13, 17]. For example, Lee et al. built a plasmonic photoanode capable of splitting water by modifying Au NRs. In this device, they successfully separated the hot carriers and used the hot holes to generate O_2 from water. When they compared the measured photocurrent of their

Figure 11: Heterogeneity observed during electrochemical tuning of individual AuNPs on ITO.

(A) Hyperspectral dark-field image of AuNPs at open circuit potential. (B) Organization of AuNPs into three categories based on the behavior during potential scan with corresponding spectral response of a nanoparticle for (C) reaction 1 (irreversible electrochemical reaction), (D) reaction 2 (reversible electrochemical reaction), and (E) charge density where electrons are added to the AuNP. (F) LSPR shift reported as energy (meV) as a function of potential scanned for seven individual nanoparticles averaged together. Reprinted with permission from Ref. [162]. Available at: <https://pubs.acs.org/doi/abs/10.1021/jp504454y>. Copyright 2014 American Chemical Society.

device with the production of H_2 , they related the various kinetics they observed to cell efficiency [13]. Since then, multiple groups have performed similar measurements where the enhanced photocurrent upon illumination due to integrated plasmonic nanostructures is used as a metric for device efficiency toward solar water splitting [17, 165–167]. These efforts are excellent demonstrations of the novelty and the potential impact of using the power of plasmonic photocatalysts to mediate chemical processes that are relevant to society today.

Many of these studies also use cyclic voltammetry (CV) to measure how illumination may affect the oxidation or reduction reactions of a redox couple. CV is an electrochemical measurement in which the current is monitored as the working electrode is ramped linearly and cycled through a potential range [157]. In plasmon-enhanced photochemical reactions, illumination of the cell leads to several deviations from traditional CV characteristic traces, such as discrete shifts in the onset potential

for the half-reactions and an increase in the photocurrent, which provide useful information pertaining to the energetic barriers for the reaction [168]. Additionally, the redox energies for a studied molecule can be significantly altered by adsorption to the plasmonic material, which is observable in the distinct formation of new features in the CV [169]. Quantifying the changes observed in CV upon illumination of a plasmonic electrochemical cell may help identify how plasmons enhance and modify the observed reactions. However, these techniques focus on ensemble measurements of the system. Due to the potential heterogeneity of plasmonic samples, techniques that measure a smaller subset of the system are necessary to unravel the contributions of different mechanisms.

SECM uses an ultramicroelectrode or a nanoelectrode to sample a more localized environment at interfaces compared to other electrochemical techniques. SECM probes surface reactions and can provide information regarding electron transfer kinetics. For example, Yu et al. separated the individual contributions of hot carriers and thermal effects for the plasmon-driven oxidation of ferrocyanide to ferricyanide [155]. They controlled the reaction by holding the electrodes at a fixed potential at various regimes where the hot carriers and thermal effects worked synergistically or competitively (Figure 12). Using this technique, they were even able to quantify the degree of heating that occurred during the plasmon-driven oxidation of ferrocyanide [156]. For many plasmon-enhanced chemical reactions, the ability to probe surface reactions and measure the surface-dependent current changes allow for a better understanding of the underlying mechanisms that influence plasmon-mediated photochemistry.

Although SECM probes a smaller population of a plasmonic system, it is still an ensemble measurement due to the heterogeneous nature of the plasmonic substrate. With the heterogeneity of plasmonic nanostructures and the utility of site-specific catalytic activity, techniques with higher spatial resolution may be necessary. One approach may be to couple electrochemical techniques, such as sample biasing, with techniques such as SERS or TERS, which may aid the tracking of electron transfer events at the molecular level [170]. However, it is necessary to characterize the changes in TERS and SERS signals under these conditions as shown by Kourouski et al. [171] and Di Martino et al. [172], where, depending on changes of the LSPR due to electrochemical tuning or changes between the redox couple, the Raman signal magnitudes can diminish or disappear. Ultimately, the development of an electrochemically integrated TERS technique may be an optimal route for explaining these phenomena.

Figure 12: Proposed mechanisms for photoinduced oxidation based on the contributions of hot holes and thermal effects. (A) Isolating hot hole contribution for photoinduced oxidation by comparing how the reaction potential changes at various laser intensities. Substrate 1 (black) contains contributions from hot holes and heating. Substrate 2 (blue) only has thermal contributions. Hot hole contribution for substrate 1 (red) is isolated by subtracting out the thermal contributions. (B) Pictorial depiction of proposed mechanisms: (i) hot hole generation and (ii) thermal contribution leading to altered equilibrium potential of redox couple. Reprinted with permission from Ref. [155]. Copyright 2018 American Chemical Society.

Electrochemical techniques hold promise for elucidating plasmon-mediated reactions especially with their ability to manipulate and monitor the flow of electrons and the resulting chemical effects, as shown in the above examples. These techniques face some difficulties due to the ensemble nature of these measurements and the fact that majority of these studies are performed with well-understood electrochemical reactions. Although broader applications of these techniques to other plasmon-mediated reactions may be challenging, the information that

may be gathered from such studies would greatly benefit the understanding of plasmon-mediated processes and their underlying mechanisms.

4 Outlook

The maturation of the above experimental techniques, both spectroscopic and electrochemical, has been instrumental for the advancement of new applications and fundamental insight in the plasmonics field. Enormous strides have been made in the past decade, as evidenced by the exceptional growth in the number of plasmonically powered processes. However, there is still crucial quantitative information that needs to be extracted to help propel plasmon-mediated catalysis toward becoming a competitive and rational option for industrial applications. To help confront these elusive critical parameters in our collective knowledge, we would like to briefly highlight a few technical approaches that clearly hold abundant promise or may be fruitful to explore.

The experimental approaches covered in this review have focused on spectroscopic and electrochemical characterizations of interactions between plasmonic nanostructures and molecular species. These techniques have a number of advantages that make them well suited for understanding plasmonic photocatalysis, particularly due to their ability to probe the molecular response of the evolving coupled system. However, there are a number of other experimental approaches that have great promise for understanding the mechanism of plasmonic photocatalysis. Magnetic resonance approaches have recently found great success as a characterization technique for the growth and evolution of plasmonic particles [173], and the molecular specificity could find great use in quantifying and tracking the progress of some plasmon-driven reactions. Other experimental approaches such as electron paramagnetic resonance, time-resolved terahertz spectroscopy, or pump-probe IR spectroscopy could also provide new insight into the mechanism of plasmonic photocatalysis.

Although this review has focused on experimental approaches to monitor plasmonic photocatalysis, theory and computational work has guided much of the current understanding of the decay processes and branching ratios in molecular-plasmonic systems, and many of the experimental interpretations presented here would not be possible without theoretical support. A major challenge in furthering theoretical approaches to the study of plasmon-driven photocatalysis lies in the large scale

of the system coupled with the importance of quantum mechanical effects and difficulties in determining the landscape of highly reactive molecular potential energy surfaces. A 20 nm diameter Au sphere contains ~60,000 Au atoms, some of which may be strongly coupled and have significant wavefunction overlap with adsorbed molecular species. High-level quantum mechanical calculations on a system of this magnitude are generally intractable with current processing power. However, a number of reasonable approaches have led to significantly improved understanding of these large and complex systems. For example, work by the Nordlander group has provided quantitative values for the hot carrier energy distribution [55] and the relaxation pathways and dynamics of these photoexcited carriers [174]. On the other end of the spectrum, work by the Carter group has applied embedded correlative wavefunction approaches to calculate energy levels of adsorbed molecular species, which has been highly effective at understanding the mechanism of some plasmon-induced processes [18, 175], and in guiding the design of more efficient plasmonic photocatalysts. This approach has recently been applied to complex multistep multielectron reactions such as N_2 dissociation [176, 177]. Recent theoretical work aimed at understanding the complete and strongly coupled molecular-plasmonic system includes atomistic electrodynamics and quantum mechanical models [178, 179], many-body Green's function formalism approaches to probe quantum emitters coupled to plasmonic systems [180], and combination of Drude model plasmonic systems with time-dependent density functional theory molecular calculations [181], among many others. There are many exciting possibilities for future directions for theoretical models of plasmonic photocatalysis, particularly with the incorporation of methods to track reactive molecular potential energy surfaces, such as the *ab initio* multiple spawning approach [182], which has been highly successful in looking at reaction dynamics of molecular species in vacuum.

Although the recent focus has been directed toward engineering useful plasmonic nanostructures to serve as catalysts, there is an immense amount of promise in integrating traditional catalysts to enhance the practical usage of plasmon-mediated catalysis. With this mindset, efforts are currently being made to develop plasmon-metal catalyst coupled systems to effectively improve the metal catalyst's general efficacy. For instance, Swearer et al. synthesized a heterometallic antenna-reactor complex composed of an Al nanocrystal (AlNC) antenna and Pd catalytic nanoparticle to initiate highly selective photocatalysis [5]. This reactor complex is driven by the direct

coupling of the plasmonic AlNC with the Pd nanoparticle, which dramatically enhanced the absorption character in the catalytic metal. A depiction of this nanostructured architecture can be seen in Figure 13A. The enhanced production of HD during H_2 dissociation was more strongly correlated to the optical wavelengths that were on resonant to the AlNC's absorption cross-section, clearly demonstrating the plasmon's ability to substantially enhance the Pd nanoparticle's ability to facilitate a photocatalytic reaction. Improved selectivity was also achieved when acetylene was added during H_2 exposure. The authors noted a remarkable 40:1 increase in the relative selectivity of ethylene/ethane production (Figure 13B). Ultimately, their work launched a new wave of studies tailored toward engineering similar reactor complexes that are fueled by a near-field coupling between a traditional metal catalyst and plasmonic material. An original and inventive design such as this is essential for identifying new pathways for

Figure 13: Plasmon-mediated photocatalytic reactions using a heterometallic antenna-reactor complex. (A) Cartoon depiction of the coupled AlNC-Pd nanoparticle system. (B) This fabricated substrate is capable of achieving a high level of chemical selectivity, reaching a maximum 40:1 relative selectivity in ethylene/ethane production. Modified with permission from Ref. [5]. Copyright 2016 National Academy of Sciences.

refining the present-day attempts of selective plasmon-mediated photocatalysis.

A practical and rational integration of plasmon-mediated photocatalysis into widespread applications may be on the horizon, as the recent findings and scientific advancements have been heavily influential for highly efficient plasmonic catalytic platforms. To achieve this goal, it is imperative to direct a united front toward understanding the mechanism of plasmon decay and the subsequent preferential partitioning of the desired energy. Throughout this review, we hope the readers have grown aware of the nontrivial balance between this partitioning, as the plasmonically generated hot carriers, thermal elevations, and enhanced local electric fields can all play a role in mediating a given chemical reaction. Once the necessary understanding of this dynamic mechanism is obtained, we believe the field will find great success in designing highly tunable and selective plasmonic catalytic systems to carry out significant light-driven chemical reactions.

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