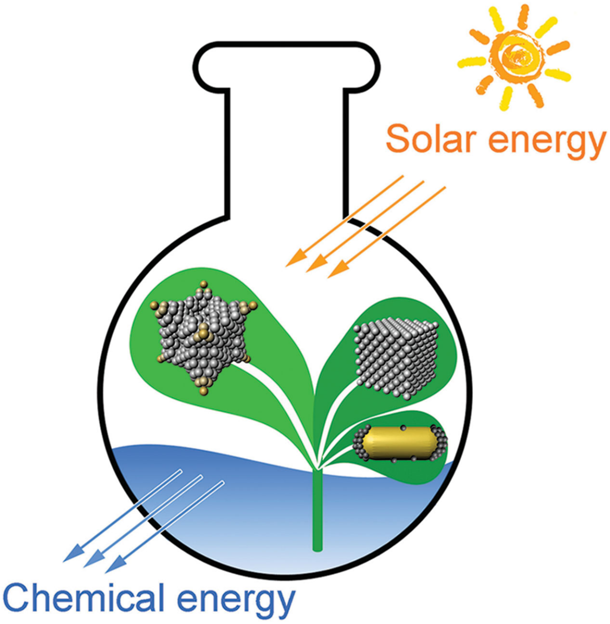
Coupling Solar Energy into Reactions: Materials Design for Surface Plasmon-Mediated Catalysis

*Ran Long, Yu Li, Li Song, and Yujie Xiong**



From the Contents

Enabled by surface plasmons, noble metal nanostructures can interact with and harvest incident light. As such, they may serve as unique media to generate heat, supply energetic electrons, and provide strong local electromagnetic fields for chemical reactions through different mechanisms. This solar-to-chemical pathway provides a new approach to solar energy utilization, alternative to conventional semiconductor-based photocatalysis. To provide readers with a clear picture of this newly recognized process, this review presents coupling solar energy into chemical reactions through plasmonic nanostructures. It starts with a brief introduction of surface plasmons in metallic nanostructures, followed by a demonstration of tuning plasmonic features by tailoring their physical parameters. Owing to their tunable plasmonic properties, metallic materials offer a platform to trigger and drive chemical reactions at the nanoscale, as systematically overviewed in this article. The design rules for plasmonic materials for catalytic applications are further outlined based on existing examples. At the end of this article, the challenges and opportunities for further development of plasmonic-mediated catalysis toward energy and environmental applications are discussed.

1. Introduction

There is no doubt that the Earth and all things on the Earth benefit from solar energy. Light is the electromagnetic radiation carrying energy and commonly involved in various processes relevant to physics, chemistry, and biology. Since fossil fuels have been excessively consumed, there is a natural trend to explore alternative approaches to serve human activities through light harvesting and its conversion into usable forms. The established platforms include photoelectric,[1] photothermal,[2,3] photo-thermal-electric conversions,[4] and many others, among which, photocatalysis provides a scheme that can accomplish chemical transformations utilizing solar energy and thus store chemical energy. Apart from conventional photocatalysis based on semiconductors,[5] surface plasmons (SPs) represent an emerging approach to solar-to-chemical energy conversion at the intersection with catalysis. Surface plasmon conversion mainly works through the mediation of a class of highly optically sensitive materials: metallic nanostructures. Indeed, metallic nanostructures have been extensively studied for their unique optical properties, localized surface plasmons (LSPs) or propagating surface plasmons (PSPs).[6,7] In plasmonics, nanostructures serve as antennas to convert light into localized electric fields or as waveguiding elements to precisely route light to designated locations at the nanoscale. Many metals are active catalysts for various reactions, particularly when their particle sizes enter the nanoscale regime to maximize the number of surface-active sites and to boost catalytic activities. For this reason, metal nanostructures can concentrate light on their surface and provide energy sources for various reactions through several different mechanisms associated with LSP, driving the catalytic reactions that occur on nanostructured surfaces.

In reported systems, chemical reactions take place on metallic nanostructures, directly driven by their plasmonic effects, or on hybrid structures, where the metals are supported on another material (mostly semiconductors) through the interactions of plasmonic effects with semiconductor band structures (including both charge and energy transfer). Specifically, once exposed to light, the metallic nanostructures induce three different effects related to surface plasmons that may impact on chemical reactions: photothermal conversion, local enhancement of the electric field, and generation and injection of hot electrons (see **Figure 1**). Thus far, chemical reactions have been evidenced with the effects from heat generation and hot electron injection, though utilizing local field enhancements to trigger reactions still needs to be further verified and well harnessed. These unique and fascinating properties of metal nanostructures have motivated researchers from different backgrounds to explore a variety of applications including solar energy conversion.[8,9] When metallic nanoparticles are interfaced with other materials to form hybrid structures, numerous physical processes may be involved. For instance, support effects include (but are not limited to) the improved stability of metallic catalysts,[10] charge polarization at the interface between metals and supports,[11] and plasmon-induced heating by metals, all of which may enhance the thermally achievable reactions.[12,13] In addition, surface plasmons of metals can have direct interactions with semiconductors through three different mechanisms (**Figure 2**):[13,14] 1) hot electrons are injected into the conduction bands of semiconductors through so-called "direct electron transfer" (DET); 2) local electromagnetic field enhancement (LEMF) mediated by surface plasmons facilitates the formation of charge carriers in semiconductors, and; 3) the LSP dipoles can transfer energy to electron–hole pairs in semiconductors through resonant energy transfer (RET). Given that the interplay of these effects is mostly present in hybrid structures, it seems impractical to include all the activities in this review article. The scope of this review will be narrowed down to bare metallic nanostructures in the absence of supports toward photodriven chemical reactions. To enable a better understanding of the physical processes behind this, we focus mainly on metallic nanocrystals with well-defined parameters as model systems to analyze cases.

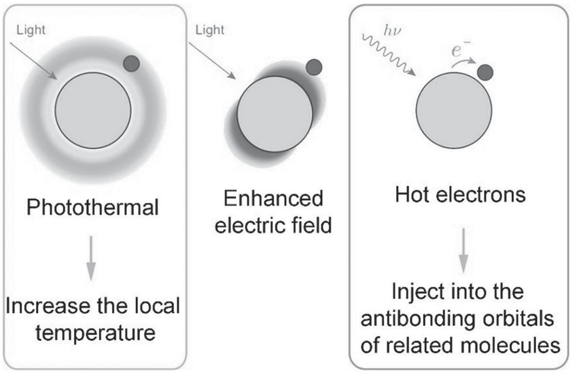


Figure 1. The main physical mechanisms involved in surface plasmon-medicated chemical reactions occurring on metallic nanostructures: photothermal conversion, local enhancement of the electric field, and generation and injection of hot electrons. The role of enhanced electric field in chemical reactions has not been fully verified. Reproduced with permission.[13] Copyright 2014, The Royal Society of Chemistry.

In discussions of plasmon-mediated catalysis, two crucial issues that determine the solar energy conversion efficiency have to be taken into account: light harvesting ability, and catalytic activity, both of which are strongly correlated with the structures of metallic nanocatalysts. To design optimal structures, one has to have a clear picture of the fundamentals behind how they work. In the beginning of this review, a brief introduction of LSPs generated on the surface of metallic nanostructures will be presented, discussing the implications and applications of LSPs in terms of physical mechanisms. We will particularly highlight how to tune the plasmonic

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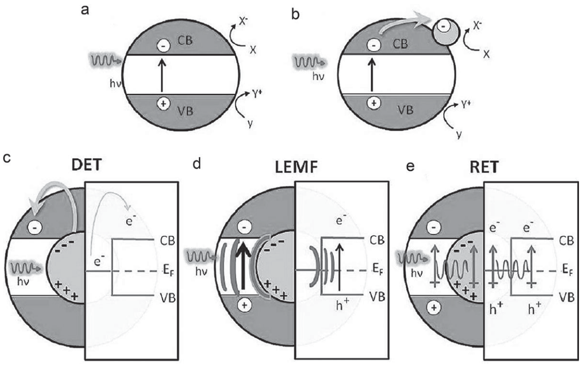
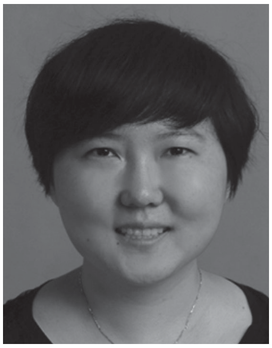


Figure 2. Charge and energy transfer mechanisms between semiconductors and plasmonic metals. a) Generation of electron–hole pairs in photoexcited semiconductors. b) Charge transfer between semiconductors and metals due to their difference in work functions, similar to the working mechanism responsible for charge polarization at an oxide–metal interface.[10] c) Direct electron transfer (DET) of hot electrons by the LSP of metals to semiconductors. d) Local electromagnetic field enhancement (LEMF) of charge separation in semiconductors. e) Resonant energy transfer (RET) from LSP dipoles to electron–hole pairs in semiconductors. Reproduced with permission.[14] Copyright 2012, American Chemical Society.

features of metallic nanostructures by tailoring their parameters. Then we will overview a series of recent advances in plasmon-mediated chemical reactions. Understanding the interactions of metallic nanostructures with light and environmental molecules would enable the design of plasmonic catalysts toward the efficient utilization of solar energy. Further, we will outline the design rules for plasmonic materials for catalytic applications based on recent advances. At the end of this review, we will discuss the challenges and opportunities for the further development of plasmonic-mediated catalysis at the intersection with conventional photocatalysis and characterization techniques.



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2. Introduction to Localized Surface Plasmons

It is well known that the electrons from metal surfaces can be described as nearly free.[15] There is a strong interaction between the free electron atmosphere of metals and incident light, which leads to collective oscillations commonly known as a surface plasmon polariton (SPP).[6,7] Depending on the plasmonic modes, SPPs (often referred to as surface plasmons, SPs) can be categorized as a localized effect (LSPs) or a propagating effect (PSPs).[6] Surface plasmons provide a powerful tool to confine light into metal/dielectric interfaces (often simplified as 'metal surfaces'). The dielectric materials mentioned here include the air or solvents such as water that interface with the metal nanostructures. In other words, the electromagnetic field of a metal/dielectric interface is significantly enhanced when surface plasmons start working. There are abundant applications which benefit from this interesting phenomenon, such as surface-enhanced Raman scattering (SERS)[16–18] and light waveguiding.[19,20] In recent years, the plasmon-mediated catalysis has been investigated using metallic nanostructures as model materials, as their LSP effect makes them usable as antennas to concentrate light and harvest solar energy. To gain better catalysts, it is imperative to investigate the fundamentals light response of metallic nanostructures.

2.1. Tunable Plasmonic Nanostructures

As briefly mentioned above, LSPs originate from the fact that, under the irradiation of light, the conduction electrons of metals are driven by the electric field to collectively oscillate at a resonant frequency. For this reason, LSP often refers to localized surface plasmon resonance (LSPR). At the resonant frequency, incident light is absorbed by the metallic nanostructures. Some of the absorbed photons will be released with the same frequency in all directions, and this process is referred to as scattering. Other absorbed photons will be converted into phonons or heat, and this photothermal conversion is known as absorption.

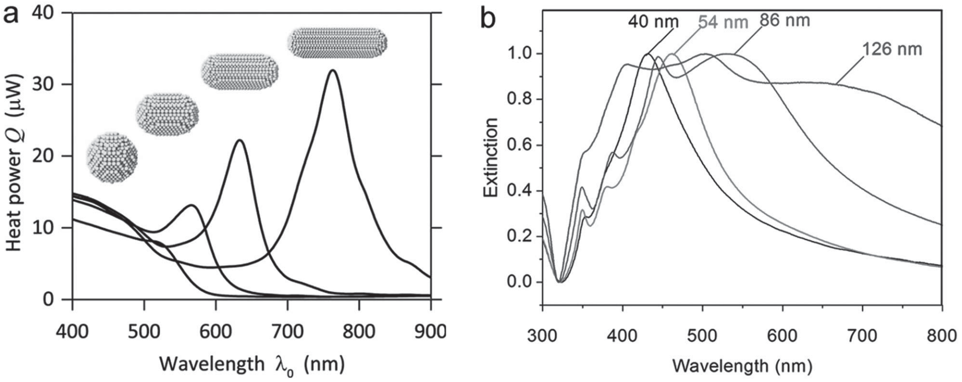

Figure 3. a) Calculated spectra of four Au nanocrystals with the same volume but different length-to-diameter ratios. Reproduced with permission.[36] Copyright 2009, American Institute of Physics. b) UV–vis spectra of aqueous suspensions of Ag nanocubes of different sizes. Reproduced with permission.[22] Copyright 2012, Wiley-VCH Verlag GmbH & Co.

In the use of LSP properties in various applications, people often pay attention to two key parameters: band location, and the intensities of absorption and scattering. These parameters essentially determine the optical responses and the resulting physical outcomes. The band locations represent the spectral range for light absorption, thus reflecting the capability for light harvesting. The intensities of absorption and scattering can be quantitatively expressed as cross sections, whose sum shows as extinction in nanoparticle suspensions (which results in different suspension colors and can be measured by UV–vis spectroscopy). Both the band locations and intensities are strongly correlated with the shape and size of a metallic nanostructure.[6] For example, the LSP transverse and longitude modes of Au nanorods can be maneuvered by tailoring the aspect ratio (see **Figure 3**a):[21] dipole resonance gradually red-shifts and quadrupole resonance emerges in LSP bands when the sizes of Ag nanocubes are increased (see Figure 3b);[22] Pd nanoplates show an extinction at 500–600 nm, behaving very differently from Pd nanocubes (typically around 300 nm).[17] In general, reducing shape symmetry may broaden the spectral range of LSP modes.[22,23] In addition to these extrinsic parameters, the LSP properties of metallic nanostructures are determined by some intrinsic factors such as dielectric functions.[5] The dielectric functions have particularly significant impact on the cross sections of absorption and scattering. These fundamentals have been extensively discussed in previous review articles,[6,7,24] therefore, we do not intend to elaborate on the detailed mechanisms in this article. Certainly the plasmonic bands of metallic nanostructures are also highly dependent on their dielectric coatings;[25] however, we would anticipate bare metal surfaces to sustain catalytic activities for chemical reactions, so this tuning knob should not be the focus of discussions here.

Now let us get back to the focus of this review: surface plasmon-mediated catalysis. In principle, metallic nanostructures should have sufficient plasmonic cross-sections for light harvesting in a relatively broad spectral range, in order to more efficiently harvest solar energy for chemical reactions. According to the shape- and size-dependent LSP relationships, efficient light absorption can be readily attained by the controllable synthesis of metallic nanostructures. It should be noted that large plasmonic cross sections do not necessarily mean that the solar energy can truly be coupled into chemical reactions. To make plasmon-mediated reactions feasible, one has to look into the interactions of surface plasmons with the reaction systems, from which critical parameters for plasmonic catalyst design can be sorted out. In the next section, we would like to overview the behavior of metallic nanoparticles under incident light, whose physical mechanisms may have implications in catalysis once the nanoparticles are implemented in chemical reaction systems. Upon acquiring the information, we can further analyze the surface plasmon–chemical reaction interactions based on the success that has been achieved in plasmon-driven catalysis (see on in Section 3 for several typical cases).

2.2. Behavior of Metallic Nanoparticles under Incident Light

Three basic processes involved in nanoplasmonics may have an impact on catalytic reactions: optical near-field enhancement, photothermal conversion, and the generation of hot electrons (see Figure 1).[13] In this section, we will discuss the fundamentals and implications of these three processes occurring on metallic nanostructures.

2.2.1. Photothermal Conversion

The environmental temperature is always a critical parameter for chemical reactions. Under the irradiation of light, chemical reactions can benefit from the increasing temperature around nanocatalysts due to photothermal conversion. When the metallic nanostructures are employed as catalysts in reactions, plasmonic photothermal conversion (mostly known as absorption) can generate heat on the catalysts and induce a local temperature increase, usually followed by heat transfer to the environment such as reaction molecules and solution. Prior to a discussion of photothermal behavior, basic rules for quantifying efficiency should be clarified. First, the relationship between extinction (σ_{ext}), absorption (σ_{abs}), and scattering (σ_{scat}) cross sections of a metallic nanostructure

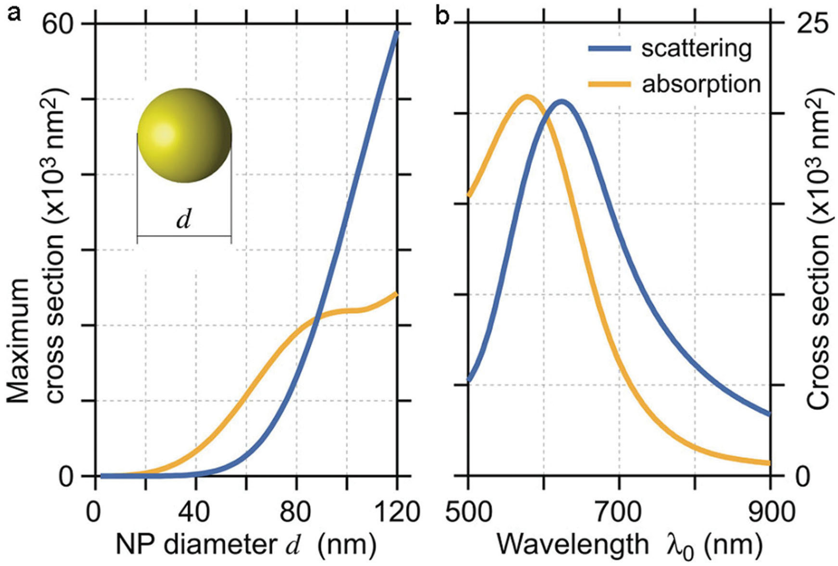

Figure 4. Demonstrations of size-dependent absorption and scattering, taking Au nanospheres as an example. a) Trend of the maximum absorption and scattering cross sections with increasing diameters (*d*), indicating that smaller nanospheres give a higher photothermal efficiency (μ). b) Absorption and scattering cross-section spectra for 88 nm Au nanospheres in water. The absorption and scattering have equal cross-section maxima; however, the spectral shift might lower the photothermal efficiency at certain wavelengths. Reproduced with permission.[27] Copyright 2012, Wiley-VCH Verlag GmbH & Co.

follows $\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}}$. Second, the photothermal efficiency (μ) can be simply described as $\mu = \sigma_{\text{abs}}/\sigma_{\text{ext}}$.[26–28] As both the absorption and scattering cross sections have strong correlations with the morphology of metallic nanostructures, it would be feasible to design nanostructures with a high μ through shape and size selection. Taking Au nanospheres as an example, smaller nanocrystals typically show higher μ (see **Figure 4**a). Baffou and co-workers reported that particle size would have more effect on the photothermal conversion. The temperature increase is limited by the heat release from nanoparticles, depending on the nanoparticle size.[29] Another issue that needs special attention is the spectral shift that may exist between absorption and scattering maxima, lowering the photothermal efficiency at certain wavelengths (see Figure 4b). In light of these issues, it is imperative to perform a systematic selection of metallic nanostructures when employing plasmonic photothermal conversion to drive catalytic reactions through a temperature effect. The parameters of metallic nanostructures affecting the absorption/extinction ratios hold the key to plasmonic catalysis in further reactions.[30] It is worth noting that the photothermal effects not only can be used for catalysis, but also have found their use in cancer therapy and energy-conversion devices.[4,31] In this section, the photothermal effects will be discussed from three angles: 1) theoretical calculations for the behavior of nanoparticles; 2) behavior of nanoparticles when fixed on a certain substrate as individuals or dimers; 3) behavior of nanoparticles when suspended in solution.

Theoretical Simulations for the Behavior of Nanoparticles: Computational simulations are powerful tools to reveal the plasmonic behavior of metallic nanostructures under incident light. A number of theories and methods have been developed in recent years. In the case of spherical shape, Mie theory has been found convenient and efficient in analyzing cross sections.[6,32] When the shapes of nanostructures become more complicated with lower symmetries, the discrete dipole approximation (DDA) and finite-difference time-domain (FDTD) calculations have been commonly employed to simulate the cross sections and field distributions.[6,33,34]

Here we take some basic geometrical shapes (cube, octahedron, and rod) as examples to demonstrate the field distributions in plasmonic nanostructures. Relative field amplitudes across the front and middle planes of a Pd nanocube and a Pd octahedron are shown in **Figure 5**a and b, respectively.[35] Like most nanostructures, the optical near-field enhancement responsible for local heat generation is more concentrated at their corners and edges. Based on the absorption cross section and incident light intensity, the distribution of the heating-power density can be simulated.[4,36] As such, spatial temperature variations can be estimated by the Poisson equation.[73] For instance, Figure 5c shows the heating-power density distributions of Au nanorods with different aspect ratios,[36] from which one can see strong spatial variations in heating power density along the axial direction. Nevertheless, a dimensional analysis on the Poisson equation indicates that temperature variation is as limited as 0.1 °C along the nanoparticles, simply because thermal diffusion is so fast at the nanoscale. In other words, heat generation is often concentrated at specific locations such as sharp corners and edges; however, in order to efficiently deliver this heat to chemical reactions, the reaction molecules adsorbed to catalytic active sites have to be present nearby. Otherwise, the fast thermal diffusion along the metallic nanostructures would transfer this heat to the solution, which limits the efficacy of sustaining reactions given that the reactions mostly occur at a catalyst surface. For this reason, it is necessary to make the spots with strong heat generation the catalytic active sites. If achievable, it would be a powerful combination between plasmonic photothermal conversion and catalytic reactions, leading to developments of high-efficiency catalysts for photodriven reactions. Section 3.1 will discuss the related design in detail.

Particle Behavior on Substrates: When metallic nanostructures are placed on substrates, it becomes more feasible to directly measure the actual temperature increase on the particles under incident light. Lounis and Orrit have demonstrated that 5 nm Au particles on a glass substrate can increase in temperature by about 15 K when the light intensity is set at 20 mW cm^{-2}; however, such a temperature increase is confined in a nanoscale region.[3] At a 13 nm distance from particle center, the temperature change drops down to only 3 K, clearly showing the localized effect of temperature variations by surface plasmons.[3] Moreover,

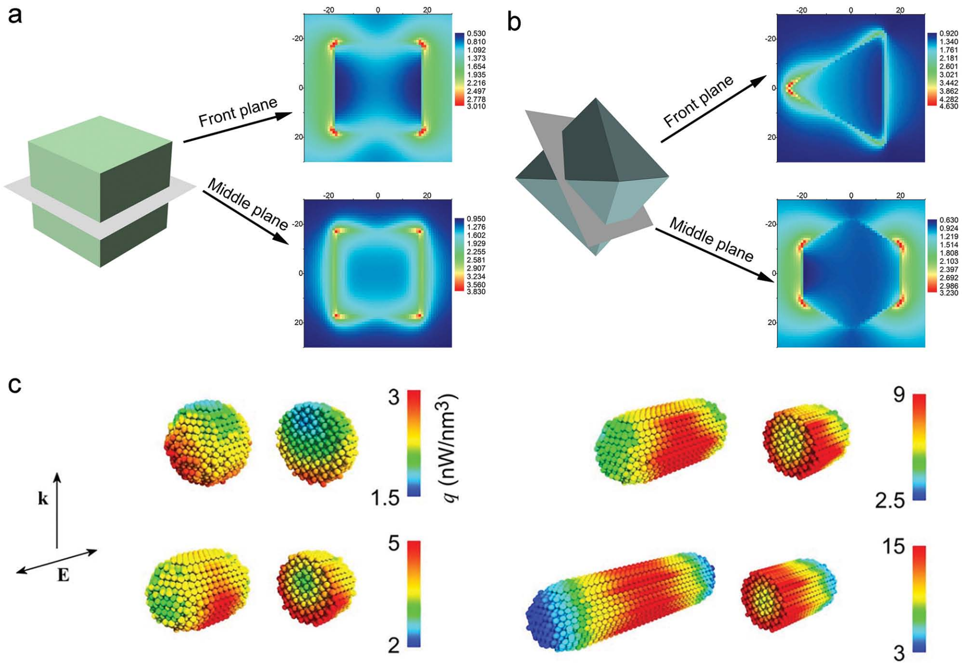

Figure 5. a) DDA-calculated relative field amplitude across the front and middle planes of a) a Pd nanocube and b) a Pd octahedron. Reproduced with permission.[35] Copyright 2014, Wiley-VCH Verlag GmbH & Co. c) 3D mapping of the heat power density on Au nanorods with different aspect ratios. Reproduced with permission.[36] Copyright 2009, American Institute of Physics.

the photothermally induced temperature change dramatically varies when the sizes of nanoparticles are tuned, as heat released from the nanoparticles is affected by particle size.[30] Orrit et al. have employed photothermal microscopy to image Au nanoparticles on a glass substrate (see **Figure 6**a). As a result, 20 nm Au nanoparticles show much higher temperature increases than their 5 nm counterparts (28 K versus 0.5 K).[37]

The attachment of metallic nanoparticles to substrates provides opportunities for investigating the effect of plasmonic coupling on photothermal conversion as well. When two nanoparticles (i.e., a dimer) are placed close to each other, the plasmonic coupling can concentrate the electric field in their gap, resulting in a highly localized and giant field enhancement. This commonly known "hot-spot" phenomenon also induces enhanced photothermal effects in the dimer gap. Baffou and co-workers have investigated the temperature increase and heat distribution of Au nanowires and nanorods on glass substrates under light illumination (see Figure 6b–e).[38] The temperature increase by a single Au nanowire turns out to be about 16 K with a light intensity of 40 mW μm^{-2}, which can be significantly enhanced by placing two Au nanorods "head to head" with a narrow 60 nm gap.[38,39]

Particle Behavior in Solution: The solution temperature can be increased over 50 K by shining light on Au nanorods,[26] dramatically higher than the temperature increase by a single nanoparticle measured on the substrate. Thus there should be suspension-related factors responsible

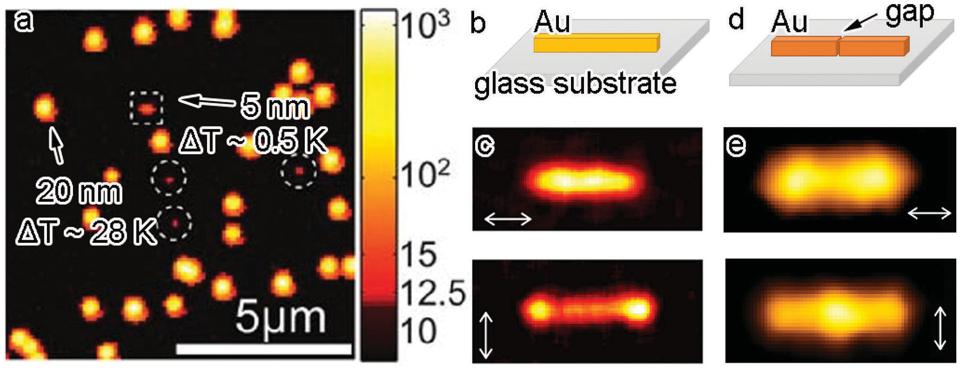

Figure 6. a) Photothermal microscopy image of 20 nm- and 5 nm-diameter Au nanoparticles on a glass slide in glycerol. Reproduced with permission.[37] Copyright 2010, American Institute of Physics. b) Schematic for the configuration and c) heat source density of a single Au nanowire on a glass substrate under incident light (parallel or perpendicular to the nanowire axis, marked with arrows). d) Schematic and e) heat source density of two adjacent nanorods on a glass substrate. Reproduced with permission.[38] Copyright 2010, American Institute of Physics.

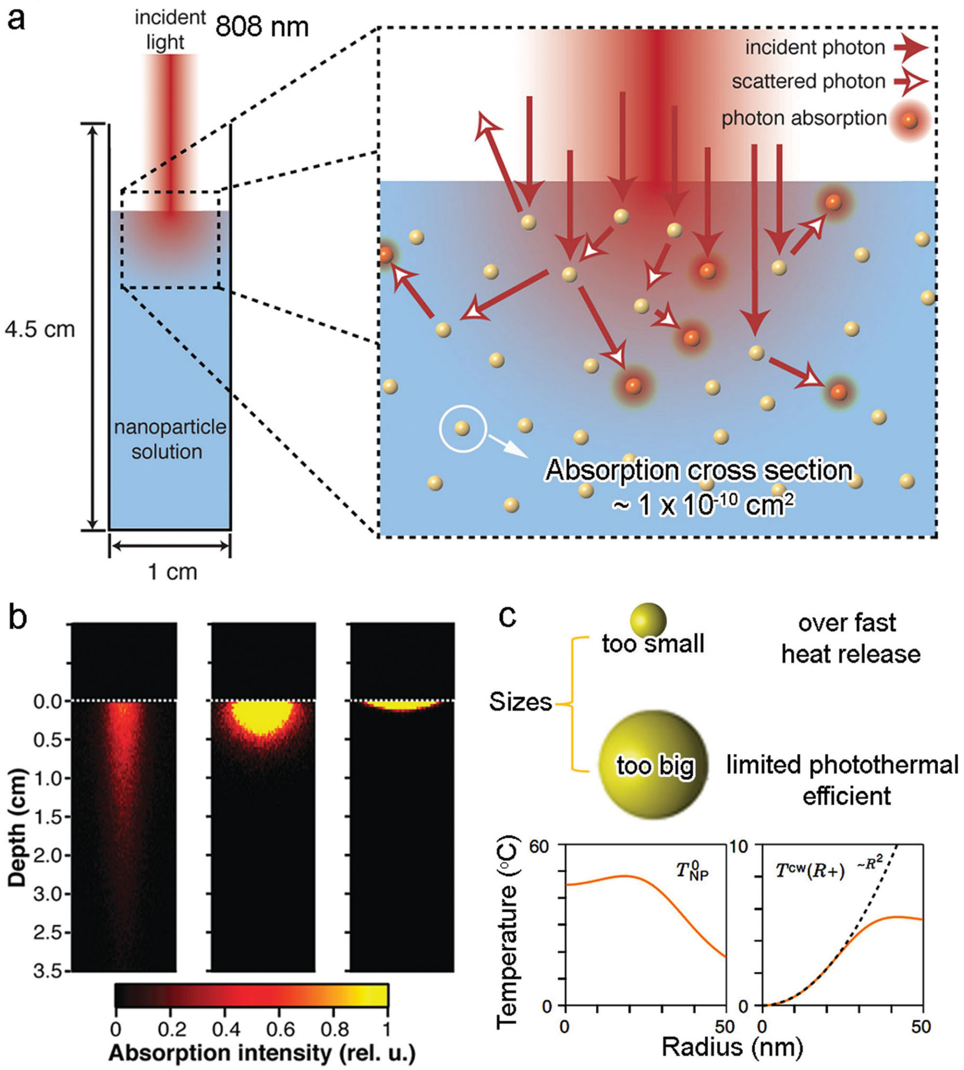

Figure 7. a) Schematic illustrating the multiparticle optical interactions of nanoparticles in solution where photons are scattered and/or absorbed. b) Side view of Monte Carlo (MC) simulated absorption intensities at different concentrations of nanoparticles. Reproduced with permission.[29] Copyright 2014, American Chemical Society. c) Ideal temperature increase (left) and surface temperature under continuous illumination (right) as a function of nanoparticle radius. Reproduced with permission.[30] Copyright 2011, American Institute of Physics.

for this additional temperature increase. Halas and co-workers proposed that multiple light scattering between the nanoparticles may improve photon absorption, inducing the higher temperature (see **Figure 7**a).[29] To verify this mechanism, they have performed systematic measurements using aqueous solutions containing metallic nanoparticles with different particle numbers under irradiation. The concentrations of nanoparticles turn out to affect the process of multiple light scattering and, in turn, influence the photon absorption intensity (see Figure 7b). This case highlights the importance of rationally designing reaction systems such as particle concentration, illumination area, and reaction container depth, to achieving high reaction-solution temperatures.

Besides multiple light scattering, particle size is another factor to affect the photothermally induced temperature tuning. As demonstrated by Baffou and co-workers, a temperature rise would be damped by the extremely fast heat release when the sizes of nanoparticles are too small (see Figure 7c).[30] However, if the particle sizes are above a certain level, the temperature increase would be limited by small photothermal efficiency (μ). As such, one has to compromise photothermal efficiency with heat release toward high reaction temperatures. As a result, nanoparticles with sizes of about 30–40 nm are ideal candidates to achieve optimal surface temperature increases.

2.2.2. Hot Electrons

Another effect caused by the photon absorption of surface plasmons is the generation of hot electrons, that can be transferred to an adjacent material or reactant. With the absorption of a photon ($h\nu$), a nearly free electron of the metallic nanostructure can be elevated from the Fermi level (E_f) to a higher energy level ($E_f + h\nu$).[13] This high-energy electron (hot electron) will lose energy through electron–electron scatting in about 10–100 fs. During this excitation and energy redistribution process, a portion of hot electrons may undergo transfer to a nearby acceptor (which can be reaction molecules or semiconductors). When the acceptor is a molecule, the light-excited electrons can be injected into the lowest unoccupied molecular orbitals (LUMOs) directly or indirectly (**Figure 8**a).[13,40] In the case of strong metal–molecule interactions, the orbital of the strongly adsorbed reactant and the *d* band of the metal surface would be hybridized, resulting in bonding and antibonding orbitals (see Figure 8b).[41] The energized *d* electrons are then injected into the antibonding hybridized orbitals, initiating chemical reactions. The effect of hot electrons on chemical reactions will be overviewed in Section 3.2 with specific experimental demonstrations. It is worth mentioning that the working mechanisms for plasmonic hot electrons should be intrinsically differentiated from those for semiconductors in conventional photocatalysis. As a result, these two reaction systems induced by light absorption exhibit very different charge behavior, such as carrier lifetimes and fundamental limitations for further applications.[40,42] For instance, plasmonic damping and cooling rather than electron–hole recombination are the critical issues to the metallic system.

2.2.3. Enhanced Electric Field

An enhanced electric field has been found useful for molecule detection[16,17,43,44] and photochemistry.[45] It is well known that SERS has greatly benefited from the plasmonic properties of metallic nanostructures.[46] There are mainly two mechanisms involved in SERS: chemical enhancement and electromagnetic enhancement.[6,47] As the name implies, the chemical enhancement (at a scale of 10–10^3) arises from the chemisorption of relevant molecules involving electron transfer from metal substrates to molecules. Electromagnetic enhancement, resulting from the strong local electric field (E) near the metallic nanostructures (as shown in Figure 1b), can increase the Raman scattering of molecules in their vicinity by a factor of E^4 (at the scale of 10^5–10^8). Similar to photothermal effect, there is a field distribution on a given nanostructure (see **Figure 9**) depending on many factors, in which the shape of nanostructure plays a particularly important role. In general, the electric field enhancement is locally concentrated on the sharp corners and edges of metallic nanostructures. Again, the "hot-spot" effect that a highly localized and giant field enhancement can create in the nanoscale gap of two metallic nanoparticles would enable higher sensitivity of SERS detection.[48] The ultrahigh sensitivity of the SERS technique makes it possible to detect organic molecules at single-molecule resolution. Thus it is anticipated that SERS would offer an in-situ, time-resolved, spectroscopic characterization technique for decoding reaction mechanisms in plasmonic catalysis, as plasmonic metallic nanostructures can serve as both light-harvesting elements for reactions and substrates for SERS detection.

This brings to our attention that certain chemical reactions (for example, the transformation from p-aminobenzenethiol to 4,4′-dimercaptoazobenzene) can be triggered by a "SERS condition".[49] Although laser-generated OH^- rather than photothermal or other plasmonic effects are mainly responsible for the case of p-aminobenzenethiol, it prompts us to consider the possibility that the enhanced electric field may activate some specific bonds of molecules adsorbed on metallic nanostructures and thus promote reaction rates. As a matter of fact, position shifts or variations in relative intensity ratios have been often observed for specific SERS vibrational peaks of molecules in reference to their normal Raman spectra when the molecules are placed on different metallic nanostructures.[50,51] The frequency and intensity of molecule bond vibrations are mostly related to bonding strength and interactions of molecules with metals, so we assume that local giant field enhancements may selectively cleave specific chemical bonds of adsorbed molecules. In Section 3.3, we will discuss the possibility of utilizing local electromagnetic field to enhance chemical reactions by analyzing some cases of photosensitive reactions. However, we have to point out that all three mechanisms (photothermal conversion, hot electrons, and enhanced electromagnetic fields) are simultaneously involved in most plasmonic reaction systems and inevitably have complex and interlinked effects on the reactions, formulating an obstacle to depicting the function of each mechanism.

Overall, both experimental and simulation results have revealed that light trapping by metallic nanostructures through multiple scattering and/or photon absorption processes can concentrate solar energy at the nanoscale, endowing the nanostructures with the functionality of energy media for solar-to-chemical energy conversion. Three different effects—photothermal effects providing local heat to drive catalytic reactions at low exotic temperatures, direct injection of energized hot electrons into reaction molecules, and local electromagnetic field enhancements to reduce bonding strength—all may play roles in plasmonic catalysis. The examples of metallic nanostructures in surface plasmon-driven reactions and the related chemical behaviors will be introduced in the next section, corresponding to the fundamental properties in this section, respectively. Understanding the physical nature of metallic nanostructures under irradiation will provide guidance for the design of efficient plasmon-mediated catalysts.

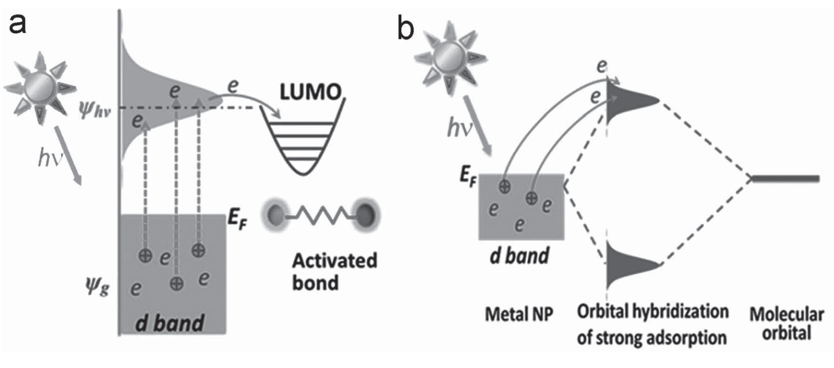

Figure 8. Proposed mechanisms for the hot electrons injected into a) the LUMOs of adjacent reactants, and b) the antibonding of hybridized orbitals. Reproduced with permission.[41] Copyright 2014, Wiley-VCH Verlag GmbH & Co.

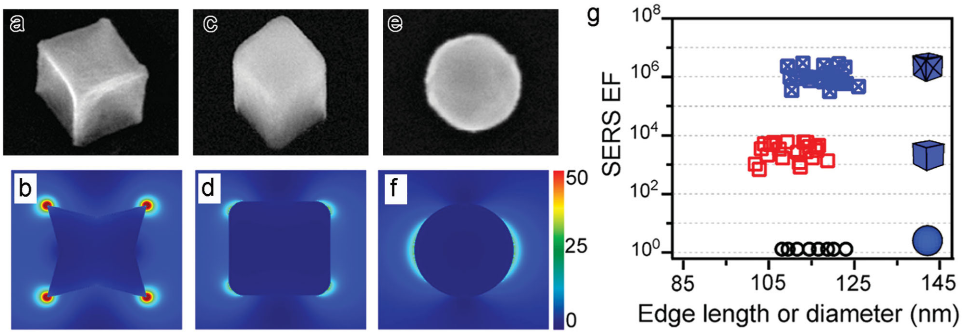

Figure 9. Scanning electron microscope (SEM) images and simulated near-field enhancements of a,b) a Au concave nanostructure, c,d) a Au nanocube, and e,f) a Au nanosphere. g) SERS enhancement factors from single particles with three different shapes and at different sizes. Reproduced with permission.[95] Copyright 2012, Wiley-VCH Verlag GmbH & Co.

3. Plasmonic Effects on Catalytic Reactions

In this section, we introduce the most recent developments in harvesting solar energy through plasmonic metallic nanostructures, mainly based on two physical mechanisms: photothermal conversion and the injection of hot electrons. The photothermal effect makes metallic nanostructures become nanoscale sources that locally generate heat for chemical reactions; hot electrons generated on plasmonic metals show complex effects on chemical reactions, leading to promoted bond cleavage or side effects in different types of reactions. The potential implications of local electromagnetic field enhancements will also be outlined in this section. A deeper understanding of these effects would facilitate the design of efficient catalysts converting solar light into chemical energy.

3.1. Photothermal Conversion Creating Local Heaters for Chemical Reactions

Since metallic nanostructures have demonstrated their ability to generate heat through the photothermal effect, they are a class of promising materials to provide heat for chemical reactions in response to incident light. As nanoscale heaters, metallic nanostructures possess unique advantages that otherwise can be hardly attained: they can behave as efficient sources of heat for transfer to solution under the irradiation of light, making solvent superheating possible; surface reactions of molecules can be dramatically facilitated, given that the generated heat is localized on the specific locations on nanostructure surface.[13,29]

3.1.1. Designed Plasmonic Catalysts: Modified Au Nanostructures

Photothermal conversion by Au nanostructures has been widely studied and employed for various biomedical applications.[21,52,53] As we summarized in Section 2.1, the plasmonic properties of Au nanostructures are tunable based on their size and shape control. However, it has been found that Au nanocrystals exhibit an efficient light response as compared with Au clusters, but their larger sizes limit activities in catalytic reactions.[54–60] In this case, there seems to be a potential contradiction between plasmonic properties and reactive activities. Nevertheless, Au nanocrystals under the irradiation of light can serve as efficient heat sources to increase the temperature of reaction systems.[61] Thus, it becomes a promising approach to overcome the limitations of Au nanocrystals in catalysis by modifying them with other catalytic metals such as Pd and Pt. In Au–M (M = Pd or Pt) nanostructures, the Au substrates serve as a light absorber to provide local heat, and the additive metals would play the role of the active sites for catalytic reactions.

Yan and co-workers designed hybrid nanostructures with the tips of Au nanorods modified with Pd that can harvest light energy for organic catalytic reactions (see **Figure 10**a,b).[62] Under the illumination of an 809 nm laser (corresponding to the longitude plasmonic band of Au nanorods) at different powers, the system temperature increases quasi-linearly with the light intensity (see Figure 10c), indicating efficient photothermal conversion by the Au nanocrystals. The measurements also show a nearly linear relationship between reaction yield and laser power (see Figure 10d), clearly demonstrating the feasibility of generating heat to drive chemical reactions through photothermal conversion. Certainly hot electrons, whose specific effects will be discussed in Section 3.2, should be inevitably generated in the system. Following this tactic, Huang and co-workers synthesized AuPd nanowheels for benzyl alcohol oxidation and Suzuki coupling reactions.[63] Similar approaches were employed to obtain Pt-modified Au nanorods that show high activities in the production of nicotinamide adenine dinucleotide under light illumination as well, efficiently coupling solar energy into reactions.[64]

3.1.2. Designed Plasmonic Catalysts: Pd Nanostructures

Pd-based catalysts are capable of handling multiple types of reactions such as coupling reactions, oxygen activation, hydrogen storage, hydrogenation, and formic acid decomposition.[65–71] However, Pd nanocrystals from solution-phase synthesis typically possess small sizes, confining their plasmonic bands to the UV region with small cross sections.[72] In principle, their plasmonic bands can be tuned toward the visible spectral region, or be broadened by increasing particle size[73,74] or lowering shape symmetry.[6]

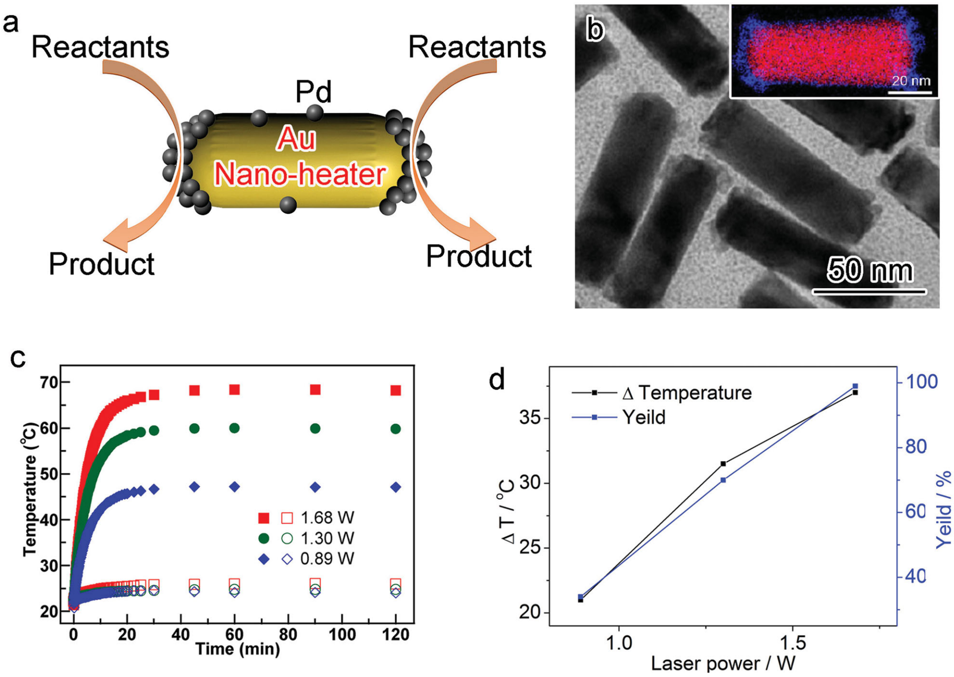

Figure 10. a) Schematic of Pd-tipped Au nanorods harvesting light energy for catalytic reactions. b) Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Pd-tipped Au nanorods. c) Temperature monitoring of a reaction solution as a function of light intensity. The solid symbols reflect the system containing Pd-modified Au nanorods, while the hollow symbols show the blank. Reproduced with permission.[62] Copyright 2013, American Chemical Society. d) Temperature increase and reaction yield of the system depending on laser power. The data for (d) were collected from the literature.[62]

Xiong and co-workers designed a class of concave Pd nanostructures with a particle size of 40 nm (see **Figure 11**a).[35] As anticipated, the concave nanocrystals show broad plasmonic bands covering the visible region (see Figure 11b). As shown in Figure 11c,d, local heat generation can be more concentrated at their corners and edges. From the angle of catalysis, the concave nanostructures possess a large number of active sites for the hydrogenation reaction at the corners and edges,[75] which happen to be the locations for heat generation. Given this situation, a high efficiency for styrene hydrogenation has been achieved with Pd concave nanostructures under light irradiation. Again, the hot-electron effects involved in this system will be separately discussed in Section 3.2.

3.2. Sources of Hot Electrons to Enhance or Suppress Chemical Reactions

As we briefly mentioned in Section 2.2.2, the effect of plasmonic hot electrons on catalytic reactions undergoes a different mechanism from the conventional semiconductor-based photocatalysis, that relies on the efficient separation of photoexcited electron–hole pairs. For instance, Wu and Zhu discovered from AuPd alloy nanoparticles that the C–I bond of iodobenzene can be elongated from 2.14 Å to 3.0 Å with an additional electron from plasmonic metals.[76] As C–I bond cleavage is the rate-determining step for Suzuki–Miyaura cross coupling reactions, the injection of hot electrons would help activate the reaction. In parallel, Christopher and Linic demonstrated for the first time that low-intensity visible light comparable to solar light can be coupled by Ag nanostructures into commercially important reactions.[9] In their system, it has been proven that energetic electrons from surface plasmons are transferred to adsorbed molecular O_2, promoting O_2 dissociation: the rate-limiting step for epoxidation reactions.

The examples listed above envision a bright future for plasmonic hot electrons in catalysis; however, we should be aware that the mechanistic studies for hot-electron effects on chemical reactions are still at the early stage. Several mechanisms have been brought out to draw an holistic picture for catalytic reactions utilizing hot electrons. For example, Christopher divided the photocatalytic rate into four categories as a function of light intensity (I) (Rate $\propto I^n$): sublinear ($n < 1$); linear ($n = 1$); superlinear ($n > 1$); and exponential ($n = f(I)$).[40] The case of sublinear relationships have only been observed in semiconductor catalysts, which falls out of the scope of this review. Linear and superlinear relationships have been commonly observed in various cases.[35,62,77] Linear relationships evidence the first-order process in terms of photons, suggesting that each reaction is triggered by a single photon (see **Figure 12**a). The transition from linear to superlinear relationships has been observed in O_2 desorption on Pt[78] and Ag.[25] To explain this nonlinear relationship, the process of desorption induced by multiple electronic transitions (DIMET) has been proposed.[78] In the DIMET mode, each reaction interacts with the electrons driven by more than one photon (see Figure 12b).[40] However, the possibility that a photothermal process contributes to the exponential relationship cannot be completely excluded, complicating mechanistic studies for hot electrons.

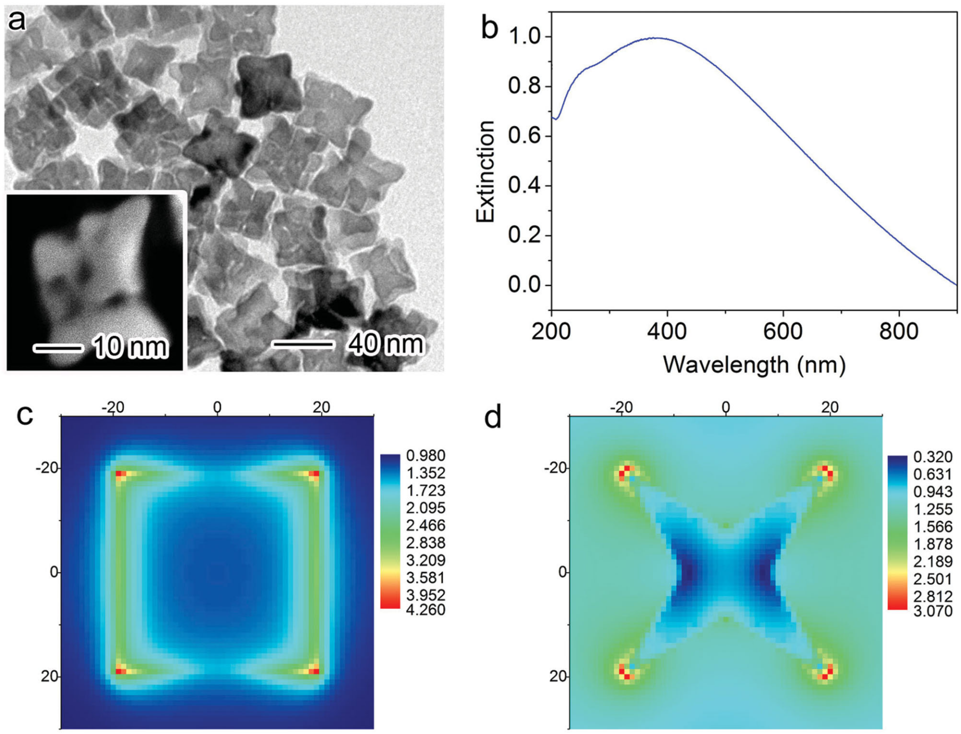

Figure 11. a) TEM and STEM images of concave Pd nanostructures. b) Normalized UV–vis extinction spectra of concave Pd nanostructures. Plots of the relative field amplitude across the c) front and d) middle planes of a concave Pd nanostructure by discrete dipole approximation (DDA) calculations. Reproduced with permission.[68] Copyright 2014, Wiley-VCH Verlag GmbH & Co.

The cases outlined above all demonstrate that the injection of hot electrons into molecules is favorable for chemical reactions; however, this is not always the case. Sykes and coworkers found that strong binding of adsorbed H atoms (H_{ad}) to metal sites was detrimental to hydrogenation reactions.[79] In the hydrogenation reaction catalyzed by plasmonic Pd nanostructures, it was demonstrated both experimentally and theoretically that the binding of H_{ad} can be enhanced by additional electrons, disfavoring the hydrogenation reaction.[35] This story informs us that we should fully consider the nature of reaction types when designing catalysts for plasmon-mediated reactions.

It is also worth clarifying that plasmonic hot electrons are essentially different from photoexcited electrons through interband transitions, although both are generated in metals upon light absorption. Here, we would like to name a case from which one can differentiate surface plasmon from interband transitions. Tachikawa and Majima demonstrated that hydrogen gas could be generated by shining visible–IR light onto Pt-modified Au nanorods in the absence of semiconductors.[80] **Figure 13** illustrates the working mechanisms for this unique H_2 production pathway. Under irradiation above a certain intensity, the interband transition of electrons in Au produces electron–hole pairs. Meanwhile, Au

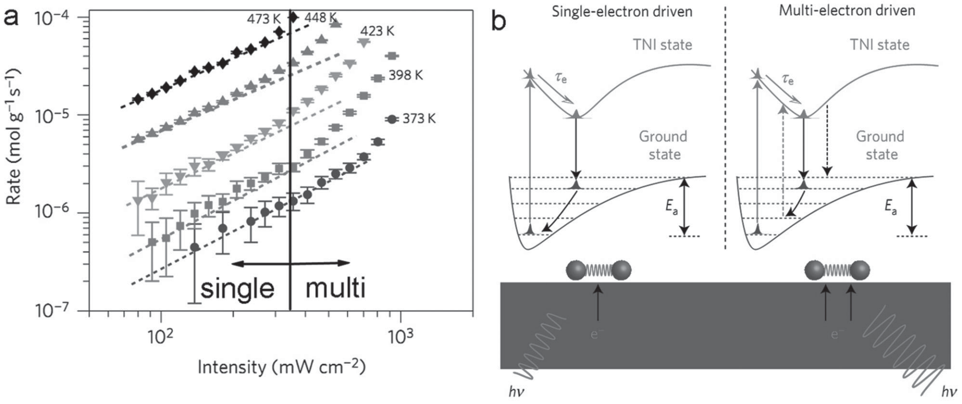

Figure 12. a) Reaction rate as a function of light intensity in linear and superlinear relationships. b) Proposed molecular mechanisms for linear (left, single-electron driven) and superlinear (right, multi-electron driven) relationships. Reproduced with permission.[25] Copyright 2012, Nature Publishing Group.

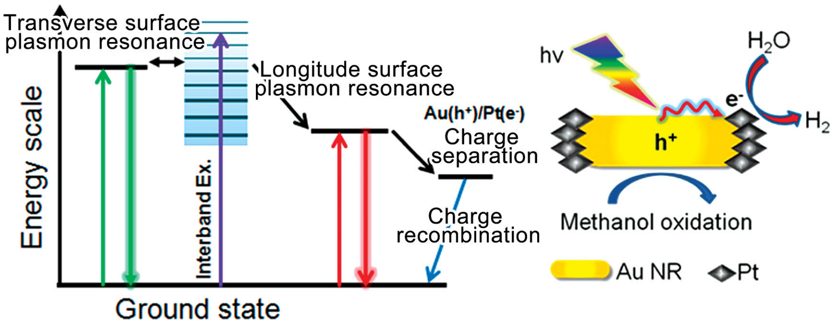

Figure 13. Schematic illustrating the mechanism for H_2 production based on the energy and electron transfer between different surface plasmon modes and interband transitions. Reproduced with permission.[80] Copyright 2014, American Chemical Society.

nanorods exhibit two plasmonic modes, transverse and longitudinal surface plasmon resonance. The interband-transition electron–hole pairs interconvert with transverse surface plasmon resonance, which promotes energy transfer from transverse to longitudinal surface plasmon resonances. The directly excited electrons from interband transitions may lose energy by nonradiative decay and convert into longitudinal surface plasmon resonance. The hot electrons generated by transverse/longitudinal surface plasmon resonance or interband excitations are all capable of transferring from the Au to the tip-coated Pt, where H^+ can be reduced to H_2. In addition to giving important insight into electrons and energy transfer, this work provides an alternative pathway for light-driven H_2 production from water, as opposed to conventional ones with semiconductors[81] or complexes.[82–84]

3.3. Enhanced Electromagnetic Fields with Implications in Chemical Reactions

3.3.1. Photosensitive Reactions

There is a class of reaction extremely sensitive to light. For instance, photoexcited free radicals with high energy often show superb reaction activities. In fact, a typical approach to efficiently preparing carbene works through photoexcited free-radical reactions.[85] As the reactions involving photosensitive species can be readily triggered by light, they may benefit from the enhanced electromagnetic field near metallic nanocatalysts. Tsuboi and co-workers also demonstrated that the ring-opening reaction of a diarylethene derivative can be induced by light irradiation in the presence of Au nanoparticles.[45] It is well known that organic molecules can be excited from a low-energy state to a high-energy state by incident light. The reactant molecules in excited states have elongated bond lengths, lowering reaction barriers.[86] The generation of local electromagnetic fields may thus offer opportunities for producing unique excited states and enhancing chemical reactions.

3.3.2. Possible Mechanisms: Chemical Bond Activation

The enhanced electric fields of metallic nanostructures have been extensively investigated for other applications such as SERS; however, it still remains elusive as to whether or not the field enhancement can facilitate chemical reactions between metal-adsorbed species and even selectively cleave chemical bonds. In the case of Pd concave nanostructures (see Sections 3.1.2 and 3.2), photothermal effects on solution temperature increases seem not strong enough to sustain styrene hydrogenation by light irradiation, and the injection of hot electrons disfavors the hydrogenation reaction. Logically thinking, the only other mechanism—enhanced electromagnetic fields—may contribute to the catalytic performance enhancement under illumination in this case. As briefly proposed at the start of this section, the frequency and intensity variations of Raman vibrations indicate that giant local fields may weaken some specific chemical bonds. In the future research, more SERS investigations on well-designed nanostructures should be performed to verify this possibility. The major obstacle for this research comes from the interplay of three different mechanisms. To decode the mechanisms, utilizing well-designed nanostructures as model materials may make important contributions. For instance, in order to examine the effect of hot electrons on hydrogenation, Xiong and co-workers employed TiO_2-supported Pd nanostructures as a reference sample to benchmark bare Pd nanostructures in catalytic hydrogenation under light irradiation.[31] The TiO_2 supports can provide conduction bands to accept plasmonic hot electrons from Pd, thus controlling the population of hot electrons. From the catalytic performance comparison, one can then reveal whether the injection of hot electrons into molecules promotes the reactions.

In this section, surface plasmon has clearly demonstrated its function in driving chemical reactions under light illumination (see **Table 1**). Elucidating the exact physical mechanisms behind this will undoubtedly enable the design of metallic nanostructures toward improved solar energy conversion efficiency. In the next section, the structural design of photocatalysis will be summarized.

4. Materials Design for Surface Plasmon-Mediated Catalysis

It is necessary to summarize the critical parameters of plasmonic nanostructures for surface plasmon-mediated catalysis. The rules for materials design should be based on an understanding of the correlation of plasmonic effects with catalytic performance. In this section, we highlight a few principles for designing plasmonic materials for catalytic reactions (see **Figure 14**), derived from the existing examples mentioned in Section 3. Among various parameters, two keywords should be the focus of parameter tuning: plasmonic bands, and catalytic sites.

Firstly, the designed materials should have high capabilities to harvest solar energy. Nanostructures with broad plasmonic bands, which can be tailored by precisely controlling

Table 1. Physical mechanisms for the interactions of plasmonic metallic nanostructures with chemical reactions under irradiation.

Mechanisms	Processes	Outcomes	References
Photothermal conversion	Enhancement of photothermal effect by multiple photon scattering in solution	Positive in thermally driven reactions	[35,41,62]
Hot electrons	Injection of additional electrons into adsorbed molecules	Positive in hydrogen production	[80]
		Positive in hydrogen dissociation on Au	[77]
		Positive in ethylene epoxidation (O_2 dissociation)	[9]
		Negative in hydrogenation reaction	[35]
Enhanced electric field	Not verified	Positive in photochemistry	[45]

the synthesis, will undoubtedly increase the solar energy conversion efficiency. Given the spectral properties and energy distribution of solar light, nanostructures with a plasmonic band covering the visible and NIR regions would be an ideal structure for utilizing solar energy in catalytic reactions. The cross section is a parameter for assessing the performance of plasmonic materials with regard to absorbing light, which can be calculated using DDA or FDTD methods. The locations and intensities of plasmonic bands are strongly correlated with the size and shape symmetries of the nanostructures, providing options for band tuning. In addition to the sizes and shapes, there is another class of promising nanostructure for light harvesting: nanocages and nanoframes with hollow structures. When the structure of a metallic nanoparticle becomes hollow, the plasmonic band would be gradually tuned from the visible to the NIR region.[87,88]

Secondly, the active sites for chemical reactions are another prerequisite for catalysis, over which the rationally designed synthesis can provide precise control. It is worth noting that many metals such as Au that have large plasmonic cross sections are catalytically inactive in organic reactions. For this reason, forming hybrid structures between plasmonic metals and catalytic metals is a strategy for designing materials for plasmon-mediated catalysis. **Figure 15** illustrates some hybrid nanostructures based on basic geometrical shapes that have shown or are expected to show high efficiencies in surface plasmon-driven catalytic reactions. Thus far, controlled synthesis has demonstrated that these nanostructures can be easily prepared with well-defined parameters,[73,87–92] among which only a few have been implemented in plasmon-mediated chemical reactions.

In the case that entire surface facets of plasmonic metals are covered by catalytic metals, the active sites for some specific types of reactions can be maximized, particularly when facet atoms, instead of corner and edge atoms, are the sites with high reaction activities. However, the plasmonic properties of the core metal will be decayed by shell coatings. To maintain the optical properties of core metals, shells should be kept as thin as possible. Single or two-layer covered nanostructures might be ideal for further applications. Tip-modified nanostructures represent the opposite situation, where the optical properties can be well inherited from a plasmonic metal but the amount of catalytic metal is too limited to provide sufficient active sites. Meanwhile, we can predict that some other configurations should also have high plasmonic catalytic activities, and ideally anticipate that a single material can be identified as highly active for both surface plasmon and catalysis. As such, it would become unnecessary to compromise catalytic sites with plasmonic cross sections and vice versa. Given the infeasibility of finding a single metal to meet the criteria, alloy nanostructures (e.g., AuPd or CuPd alloys) with well-defined corners and edges might be a promising class of candidates.[93,94] Under this consideration, alloy hollow nanostructures providing extra active sites would be excellent candidates for catalytic reactions.

Certainly the combination of large plasmonic cross sections with a large quantity of active sites does not guarantee high performance in plasmon-mediated catalysis. Surface plasmons are a complex phenomenon involving multiple physical

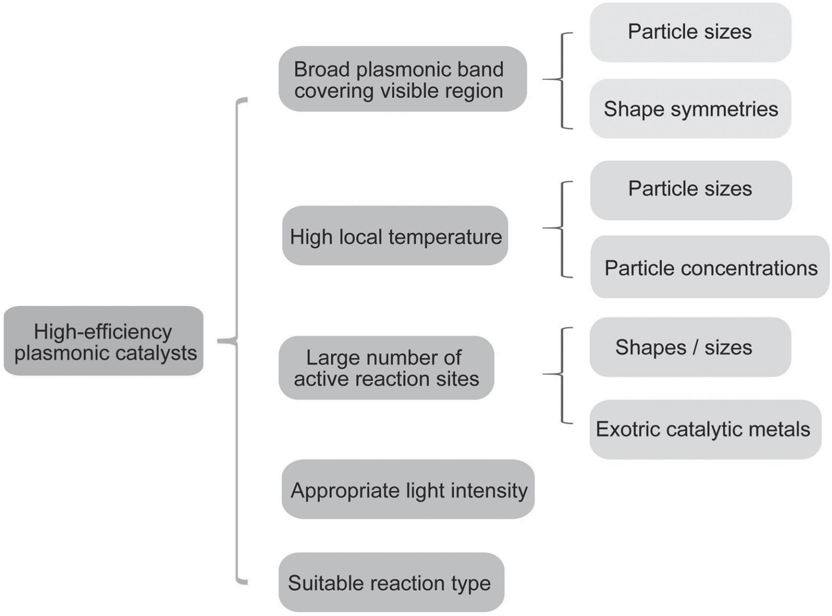

Figure 14. Summary of critical parameters for the design of efficient plasmonic catalysts for solar-to-chemical energy conversion.

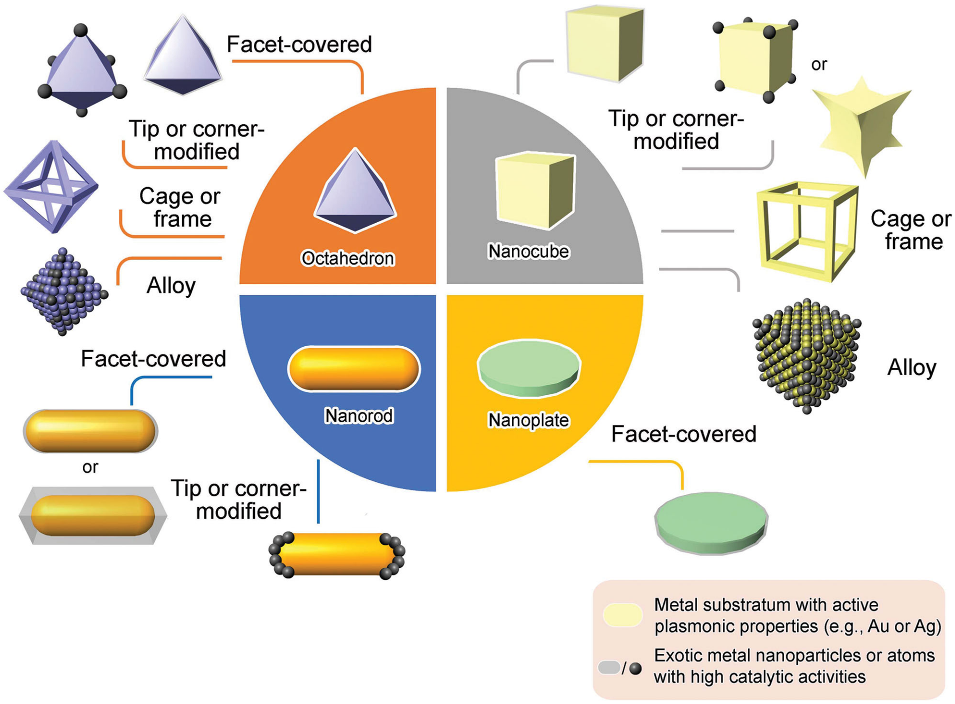

Figure 15. Schematics illustrating the strategies for designing high-efficiency plasmon-mediated catalysts.

mechanisms in addition to photothermal conversion. As such, we have to fully understand the impact of these effects on chemical reactions prior to materials design.

There is no doubt that high temperatures usually favor chemical reactions, so understanding the photothermal effect is relatively straightforward. To this effect, metallic nanostructures dispersed in solution can induce high local temperatures near their surfaces under light irradiation and, in turn, increase solution temperature via heat transfer. Based on theoretical simulations, the best nanoparticle sizes for photothermal conversion in solution are about 30–40 nm. The solution temperature effect is rather limited as compared to the local heat that can be gained from a nanoscale heater to sustain catalytic reactions. Intense local heat makes it possible to utilize solar energy instead of conventional heat as the energy source. As long as the locations for heat generation and molecular activation are consolidated or designated close to each other, the efficiency of catalytic reactions can be highly promoted.[35] In light of this consideration, hybrid metallic nanostructures can be designed toward efficient plasmon-mediated catalysis. Local heat generation is mainly determined by the field distribution of the LSP that should generally be concentrated at sharp corners and edges. For this reason, low-symmetry shapes with catalytic materials on their corners and edges represent the directions for materials design toward the consolidation of heat generation and catalytic reactions. Given the size and shape effects on photothermal conversion, nanostructures with low symmetries at the size of 30–40 nm with their plasmonic bands tuned toward long wavelengths would be ideal candidates for surface plasmon-driven catalysis.

In contrast to the photothermal effect, the implications of other plasmonic mechanisms are rather complicated. Yet the effect of enhanced electromagnetic fields on chemical reactions has not been fully verified, and it is predicted that this effect only exists in specific types of organic reactions that the chemical bonds of molecules can be weakened by the field. It is anticipated that future research will identify the reaction type to which this working mechanism can be applied. The influence of hot electron injection has become relatively clear through research in the past years. This influence depends on the effect of electron density on the interactions of reaction species with catalytic materials. In the case that hot electron injection favors catalytic reactions, the materials design rules should be consistent with those for the photothermal effect. If the electron injection plays the role as a side effect, we have to rationally adjust the intensity of illumination or alter support materials (e.g., semiconductor supports) to minimize this side effect. Overall, the prerequisites of materials design for plasmon-mediated catalytic reactions are to have strong solar absorbance over broad regions and high catalytic activity in organic reactions, with potential side effects suppressed. In addition to the basic geometrical shapes outlined in Figure 15, the other structures that can meet these criteria should also have high performance in plasmon-catalytic reactions.

5. Conclusion

Plasmonic catalysis is a newly emerging alternative to conventional semiconductor-based photocatalysis. Given the typically high catalytic activities of metals, plasmonic catalysis represents a promising solution to organic reactions by utilizing solar energy instead of heat. The success of this approach relies on the efficient coupling of solar energy into chemical reactions by tailoring metallic nanostructures. As the research unfolds toward higher efficiency, it becomes imperative to decode the mechanisms behind it; otherwise, we will have no clue how to design nanostructures with both high catalytic activities and strong plasmonic responses. Thus far, the nature of local heat generated through photothermal conversion is relatively clear. Although hot electrons have demonstrated a significant impact on chemical reactions, the mechanisms still needs further clarification toward the improvement of control over behavior. Promoting plasmonic catalysis via an enhanced electromagnetic field is a promising concept, not to mention being an almost unexploited field.

In this review, we have overviewed the fundamental mechanisms that may be responsible for performance tuning in plasmonic catalysis, along with guidelines for designing plasmonic nanostructures. Here, we would like to elaborate on a few key facts:

1. There is a size window around 30–40 nm for plasmon-mediated nanocatalysts. This results from the compromise of heat release with photothermal efficiency. The size range of 30–40 nm might be not ideal for high surface-to-volume ratios in terms of catalysis, but a solution would be to tailor the particle shapes toward a large number of corner and edge atoms or high-index facets: well-known sites for typically high reaction activities.
2. In addition to enabling large plasmonic cross sections, nanostructures should provide sufficient active sites for catalytic reactions. Thus, it would be necessary to integrate desired plasmonic and catalytic properties on the same nanoparticle. In ideal configurations, we anticipate that the field enhancement maxima are consolidated with the catalytic active sites on the same or neighboring locations. Hybrid metallic nanostructures or alloys represent designs toward this goal, but better control should be achieved during their synthesis.
3. "Hot spots" are the gaps between two plasmonic nanoparticles that exhibit dramatically enhanced electric fields. It would bring about additional benefits to plasmon-mediated catalytic reactions if active reaction sites can be designated inside "hot spots". Controlling nanoparticle agglomeration or developing self-assembly techniques would enhance the functionality of "hot spots" in catalysis.
4. More effort must be made to analyze the situation of chemical reactions in terms of utilizing hot electrons, as they do not always favor reactions. For certain types of reactions to which the hot electrons are detrimental, the light intensity has to be controlled within a certain window. Another limitation for hot electrons is their limited lifetime, as surface plasmons are a transient effect. Hot electrons lose energy during damping and cooling, so transferring them into conduction bands of semiconductors would prolong their lifetime. In this sense, the integration of surface plasmons with conventional photocatalysis is another promising ongoing direction. However, opportunities always come with challenges: the interplay of multiple plasmonic effects and semiconductor physics results in very complicated mechanisms.

Overall, the integration of plasmonic features with catalytic active sites should still be the focus of plasmonic catalysis in terms of materials design. To acquire design rules, we have to reveal the involved mechanisms at high spatial and temporal resolutions and at molecular levels. SERS may be a convenient tool to in-situ monitor chemical reactions, as there is no need to introduce additional materials for detection substrates.[34] However, spatial resolution might be an issue: sharp corners and edges are usually the centers of local field enhancements and catalytic active sites, but it seems difficult to differentiate their activities from those of other sites from SERS measurements given the large spot sizes of incident light. There is no doubt that the development of new characterization techniques will facilitate this research.

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