Bimetallic nanostructures: combining plasmonic and catalytic metals for photocatalysis

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ABSTRACT
Light has emerged as a promising new reagent in chemical reactions, especially in enhancing the performance of metal nanoparticle catalysts. Certain metal nanoparticles support localized surface plasmon resonances (LSPRs) which convert incident light to strong electromagnetic fields, hot carriers, or heat for directing and improving chemical reactions. By combining plasmonically active metals with traditionally catalytic metals, bimetallic nanostructures promote simultaneous light conversion and strong molecular adsorption, expanding the library of light-controlled reactions. In this review, we cover three bimetallic geometries: antenna–reactor, core-shell, and alloyed nanoparticle systems. Each geometry hosts its own set of intermetallic interactions which can affect the photocatalytic response. While antenna–reactor systems rely exclusively on optical coupling between the plasmonic and catalytic metal to enhance reactivity, core-shell and alloy architectures introduce electronic interactions in addition to optical effects. These electronic interactions usually dampen the plasmonic response but also offer the potential for enhanced reactivity and product specificity. We review both state-of-the-art bimetallic photocatalysts as well as emerging research opportunities, including leveraging quantum effects, new computational methods to understand and predict photocatalysts, and atomic-scale architected materials.

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Metal nanoparticle catalysts drive a variety of industrial chemical reactions. For example, the discovery of iron-based catalysts and the Haber–Bosch process in 1910 allowed ammonia production to reach industrial scales. Ammonia is now the most highly produced inorganic chemical at over 150 million tons each year, generating enough fertilizer to help feed the world and enabling the production of many plastics, fibers, and pharmaceutical intermediates[1]. Countless other critical reactions are catalyzed by metal nanoparticles, including reforming of naphtha for gasoline (using a platinum catalyst)[2]; synthesis of epoxethane for clothing, engine cooling, and cosmetics (using a silver catalyst on alumina) [3]; and most recently, solar fuel generation and carbon dioxide reduction (using gold catalysts) [4]. To overcome the activation barrier for various reaction steps, metal–nanoparticle-catalyzed reactions typically operate at high temperatures but at the expense of high fuel costs and increased byproduct formation. While significant attention has been given to tuning catalysts’ composition, size, and structure to improve overall efficiency, optical excitation has emerged as a new ‘reagent’ to not only control reactions but also as an abundant, renewable source of energy if using solar irradiation.

Upon illumination, many metallic nanoparticles support localized surface plasmon resonances (LSPRs) – collective oscillations of electrons at the surface that depend on the size, geometry, and material of the nanoparticle [5–7]. LSPRs create intense localized electric fields, enhancing a variety of light-matter and light-molecule interactions at the nanoparticle surface. For example, LSPRs can enhance local temperatures, molecular vibrational mode amplitudes, and electron occupation of molecular orbitals [8–10]. Their localized fields and resonant tunability could also improve site-selective molecular turnover frequencies and promote specific reaction pathways for product selectivity. Accordingly, catalysts supporting LSPRs, known as ‘plasmonic catalysts’, offer increased reaction rates and product selectivity at relatively mild thermal and illumination conditions compared to traditional catalysts [10–13].

The vast promise of plasmon photocatalysis has been recognized by both the plasmonic and catalysis communities, as highlighted by a number of recent reviews in the area [14–18]. However, the merging of these two fields requires additional engineering: traditional plasmonic metals (the noble metals: Au, Ag, Cu, etc.) are useful as catalysts for only a limited number of reactions, while common catalytic metals (like Pd, Pt, Rh, etc.) do not support strong plasmonic resonances at visible wavelengths, where solar irradiation is the strongest. Bimetallic nanoparticle catalysts combine these two metals, with an ideal photocatalyst retaining the optical behavior of the plasmonic metal and the reactive behavior of the catalytic metal. Indeed, in recent years, bimetallic catalysts have
demonstrated increased reaction rates [19–23], optical sensitivity [24–27], and product selectivity [28,29] for a greater variety of reactions than their monometallic counterparts due to the larger number of molecular adsorbants that interact with catalytic metals. While ‘bimetallic’ technically encompasses any combination of two metals [30] (i.e. noble-noble or catalytic-catalytic), in this review, we focus on bimetallic systems that combine a plasmonic metal with a catalytic metal (see Figure 1(a)).

Intermetallic effects between these two metals lead to optical and catalytic behavior distinct from the sum of their parts. For example, the extinction spectrum of a bimetallic, core-shell Au@Pd nanoparticle is strikingly different than the summation of the extinction spectra of its two components, with the LSPR blue-shifting in energy, losing intensity, and broadening in spectral shape (Figure 1(b)). Despite this dampened plasmonic response, bimetallic systems are generally more functional than monometallic systems due to their photocatalytic abilities. Under illumination, a similar core-shell nanorod system shows greater catalytic yield at Suzuki coupling than a mixture of its individual components [24] (Figure 1(c)).

These intermetallic effects heavily depend on the geometry of the bimetallic structure, and range from plasmon hybridization (optical coupling), to charge transfer (electronic coupling), to a new electronic structure (atomic coupling). In this review, we will focus on how these interactions contribute to a nanoparticle’s plasmonic and catalytic response. We first describe how electronic band structure affects plasmonic and catalytic efficiencies, and how the plasmonic response affects catalytic behavior.
Next, we describe three common bimetallic geometries: antenna-reactor, core-shell, and alloyed nanoparticles, highlighting the intermetallic interactions of each geometry and their implications in photocatalysis. While antenna-reactor systems have a simpler relationship between plasmonic and catalytic effects, core-shell and alloyed nanoparticles promise additional catalytic tunability via finer control over molecular adsorption energies, with recent experiments pushing to understand and enhance their plasmonic behavior. Finally, we discuss future directions for this growing field, including leveraging quantum effects; utilizing advanced theory and computation to understand and improve catalytic architectures; designing multimetallic architectures; and using two-dimensional and layered van der Waals materials for record efficiency.

**Electronic structure of bimetallic systems**

Plasmonic and catalytic metals have innate differences in their electronic band structure that allow for the strong enhancement of one phenomenon typically at the expense of the other. Plasmonic metals have a d-band far from the Fermi level (Figure 2(a)), leading to high quality, intraband plasmons (s to s) at optical frequencies until the onset of interband transitions (d to s). Catalytic metals, on the other hand, have d-band centers close to the Fermi level (Figure 2(b)), which causes their optical response to be dominated by interband transitions. This increased probability of interband transitions dampens the LSPR at all frequencies, making it spectrally broad and lower in intensity. Additionally, catalytic metals are usually optically resonant in the ultraviolet (UV) range due to their high plasma frequency, and thus nanoparticles made of these metals require careful nanostructuring to shift their LSPR to the visible range [31,32]. Accordingly, we compare the simulated optical response of a 20 nm nanoparticle made of either traditionally plasmonic or catalytic metals in Figure 2(c). The noble metals (Ag, Cu, Au) have higher extinction cross sections, with Ag showing the strongest response due to Au and Cu’s shallower d-bands. The catalytic metals (Pt, Rh, Ti), on the other hand, have a much weaker optical response in the visible range, which trends upwards as one moves into the UV.

While a strong plasmonic response requires a d-band far from the Fermi level, a strong catalytic response usually requires a d-band near the Fermi level. Under the d-band model of chemisorption [33,34], when a molecule interacts with a metal surface, it interacts with both the sp- and the d-bands. The broad sp-band renormalizes the frontier molecular orbitals (the HOMO and LUMO levels), broadening and shifting the orbital energy. However, most sp-bands are similar throughout the transition metals, and so differences in catalytic adsorption rates are attributed to
interactions with the d-band. The narrower d-band hybridizes the molecular orbital into metal-adsorbate bonding and anti-bonding modes. For a deep-lying d-band like in plasmonic metals, the anti-bonding mode can be below the Fermi level (Figure 2(a)) such that the molecule is less likely to adsorb to the surface, leading to less effective catalysts [34,35]. However, when a catalytic metal interacts with adsorbates, generally only the bonding states are below the Fermi level (Figure 2(b)), leading to chemisorption, and thus an effective catalyst. This simple model which correlates catalytic reactivity with the location of the d-band (with respect to the Fermi level) can account for many metal-adsorbate interactions, though exceptions have been found [36,37].
Strong chemisorption, however, is not necessarily always beneficial for catalysis. For example, a simple reaction like hydrogen dissociation consists of three steps: first, the molecule adsorbs to the catalyst surface; next, it gains enough energy to undergo a chemical transformation (i.e. dissociate into two H ions); and finally, the products desorb from the catalyst, allowing some other reactant to interact with the surface. Therefore, the adsorption needs to be strong enough such that the reaction happens, but not too strong such that the products do not desorb and they poison the catalyst, preventing further reactions. The delicate balance between these two needs, also known as the Sabatier principle, is often represented in a volcano plot (Figure 2(d)) [38]. The catalytic efficiency peaks at a (reaction-specific) value of the metal-adsorbate binding energy, with weaker-bonded systems being limited by dissociative adsorption and stronger-bonded systems being limited by desorption. These variations in activity are sometimes also plotted across different nanocatalyst geometries, as coordination number and faceting also affect adsorption energies.

Plasmonic photocatalysts rely on electromagnetic field enhancement and the plasmon’s various decay mechanisms to reduce the activation energy of these reaction steps. The enhanced electric field can affect the orientation and subsequent adsorption of polarizable molecules [39]. After excitation, the LSPR decays into three main products: photons, hot carriers, and heat. Increased radiation (photons) locally enhances chemical reactions that are photosensitive, such as photodegradation, photoisomerization and light collection in adjacent semiconductors. Meanwhile, hot carriers can promote the metal-adsorbate system to an excited state. This excitation causes the adsorbate to either evolve along the excited potential energy surface and/or relax back to the ground state with additional vibrational energy, both mechanisms causing an effectively lowered activation energy barrier [15]. Hot carriers are of significant interest to the catalysis community as they can potentially target specific reaction pathways due to their narrow and tunable energy distribution [40,41]. Finally, if hot carriers aren’t harvested for a chemical reaction, they can interact with the lattice and cause heating, which increases the overall kinetics of chemical reactions. The fact that heating comes from a nanoscopic source (and thus localized around the nanoparticle) helps minimize the formation of byproducts which is often inevitable with general heating methods. Understanding each plasmon decay mechanism and identifying its relative contribution to the overall reaction efficiency is key to designing better plasmon photocatalysts; for a more extensive discussion, we point the reader to a number of excellent recent reviews and papers [13,42–44].

Bimetallic photocatalysts rely on the combination of these two phenomena: the catalytic metal aids with adsorption of molecules, while the plasmonic metal converts optical excitation to energy. Notably, increases in reactivity are only significant if targeting the rate-limiting step. For
instance, if a reaction depends on the critical coverage of adsorbants, plasmon decay products will not increase reaction rates, and one may instead want to determine if the adsorbant is responsive to electric field, change materials, or use nanoparticle geometries that can modify the electronic structure (via faceting, core-shell, alloys, etc.). Accordingly, since hot electrons and heat add energy (i.e. increases occupation at higher energy orbitals), chemical transformation or desorption-limited reactions will benefit more (i.e. product selectivity) from a plasmon excitation.

**Antenna–reactor systems**

The simplest way to combine the effects from plasmonic and catalytic metals is to place them near each other in a configuration referred to as the antenna–reactor geometry. This system consists of (at least) two separated nanoparticles: a plasmonic antenna which collects light, and a catalytic reactor which facilitates the reaction. Each nanoparticle retains its individual electronic structure as long as there is no electron tunneling (generally true when the separation is >1 nm[45]). However, the resulting photocatalytic response can be different from the sum of the two parts due to optical coupling. This coupling is necessary to transfer optical energy collected by the antenna to the catalytic reactor. Antenna–reactor pairs can be created via top-down methods like lithographic patterning [25,46] (Figure 3(b)), commercially scalable nanoparticle syntheses like colloidal chemistry [28,47] (Figure 3(f)), or a mixture of the two [27] (Figure 3(d)). Top-down fabrication gives easier control over the design of the structure, while colloidally synthesized nanoparticles (bottom-up) are integratable into current catalytic setups and can have better control over the faceting of the nanoparticle. Additionally, out of all three geometries, antenna–reactor systems are the easiest to characterize and model, and currently afford the most control over the optical properties. They are therefore ideal model systems to study the interplay between optical and photocatalytic effects.

From plasmon hybridization and coupled oscillator models, one finds that the plasmonic antenna drives a resonant response in the nearby catalytic reactor [46,48,49]. This coupling increases when the antenna and reactor LSPRs are spectrally close, the reactor placement breaks the antenna’s symmetry, and/or interparticle spacing is reduced [25,50]. The resulting LSPR is spectrally similar to the plasmon resonance of the antenna itself, though usually slightly shifted [25,27,28]. Spatially, the enhanced electromagnetic fields are either highly localized to the interparticle gap or at the reactor surface, creating a plasmonic hot spot. This consistent behavior – spectral peak similar to that of the antenna and enhancement spatially limited to near the reactor – makes these antenna–reactor systems straightforward to design.
Plasmonic enhancement is sensitive to small changes at the nanoscale, with uneven optical and thermal enhancement across a single antenna–reactor system, which can be resolved through single particle measurements. Photocatalytic or plasmonically induced activity is expected to be strongest at the plasmonic hot spots and proportional to the enhancement [51]. Using single particle techniques like ex-situ imaging of nanoparticle markers [52] and super-resolution catalysis imaging [53] as well as single molecule techniques like scanning tunneling microscopy [54], researchers have demonstrated that chemical reactions can be locally enhanced in nanoscale gaps between noble metal nanoparticles. Similar techniques can be used to explore the role of plasmons on the more complex reaction landscape of catalytic metals. For example, we recently studied how plasmons affect the palladium hydride phase transition in individual pairs of Au nanodisks and Pd nanocubes [27] (Figure 3(d)). Out of two different reaction timescales, we found that only one reaction step shows illumination wavelength dependence, indicating a plasmonic effect. Additionally,
by tracking the phase transformation with sub-particle resolution, we
found that the new phase nucleated at corners and edges near the plas-
monic antenna more often than corners that were far away (Figure 3(e)).
Edge nucleation only happened near the hot spot and under resonant
illumination, suggesting that plasmons can unlock new reaction pathways.
Notably, these observations are only possible with high-resolution imaging
that can correlate nanoscopic structure with reaction effects.

While single particle studies give insight into the mechanism behind reac-
tions, they do not necessarily reflect how efficient a catalyst is when put in more
traditional, large-scale chemistry environments. For example, Li et al. demon-
strated how these ensemble environments affect the overall catalytic efficiency
\[47\]. From simulations, larger Ag nanoparticles should be better antennas since
they lead to the greatest enhancements in the nearby Pt nanoparticles. However,
in experiment, particles consisting of medium-sized Ag antennas were more
efficient at CO oxidation than particles with larger Ag antennas (Figure 3(g)).
Using Monte Carlo simulations, they showed that this difference in efficiency is
most likely from increased scattering in the catalyst bed. Therefore, interparticle
interactions that can have a considerable effect on the overall catalytic efficiency
should be incorporated in optical computations, via either multiscale modeling
or periodic boundary conditions.

As researchers design more antenna–reactor structures, it is imperative
to understand the extent to which these reactions can be enhanced via this
interparticle gap. From classical electrodynamics, plasmonic enhancement
is inversely proportional to interparticle distance, and so the gap between
two particles should be as small as possible to increase photocatalytic
reactions. However, as the two metals are brought closer together, quan-
tum effects, like localization of surface charges (gap <2-5 nm) and tunnel-
ning (gap <1 nm), can decrease the plasmonic enhancement \[45,55,56\].
Molecules can further increase the tunneling probability for larger gaps
by decreasing the tunneling barrier \[57\]. When these gaps are shrunk to
atomic scales (‘picocavities’), the high field localization leads to strong
coupling between the molecule and the plasmonic cavity modes, poten-
tially modifying the energetics for bond dissociation \[58\] or changing
reaction pathways via Rabi splitting, similar to what has been seen in
macroscopic optical cavities \[59,60\]. Quantum plasmonics is still
a growing field, both in terms of understanding the behavior of plasmons
at the quantum regime, as well as their subsequent interaction with
molecules \[56,61,62\]. All of the above studies have focused on noble
metal systems and to extend to catalytic metals, one would need to account
for the different band structure of transition metals, as the electrons
involved in a plasmonic excitation (i.e. sp or d-band) affect the spatial
distribution of screening charges \[63\]. With these insights, one could
better understand and exploit the limits of antenna–reactor systems.
Core-shell structures

A more complicated bimetallic architecture has an interface between the plasmonic and catalytic metals, leading to both optical coupling and modification to the electronic structure. In practice, this has been mainly realized in core@shell nanoparticles, in which the plasmonic core is surrounded by a thin (continuous or discrete) catalytic shell which is exposed to the chemical environment. In this geometry, the core acts as the antenna and the shell as the reactor, but they cannot always be thought of as two separate nanoparticles with plasmonic and catalytic effects happening in different locations. These particles are almost exclusively made via colloidal synthesis and advances in the field of colloidal chemistry have lead to the controlled growth of core-shell structures with specific shapes, faceting, and sizes [64–66].

Core-shell nanoparticles have long been used in catalysis as they have different electronic properties than their monometallic counterparts [30]. By introducing another element as a core material, one can modify the position of the d-band center relative to the Fermi level in the shell material, which affects how molecules adsorb to the catalyst surface. This d-band modification arises from mechanical strain and/or a direct charge transfer between the core and the shell, termed the ligand effect. Tensile strain in the shell (from a core with a larger lattice parameter) causes d-band widths to narrow and shift closer to the Fermi level; conversely, compressive strain (core with a smaller lattice parameter) would then cause the opposite effects [67]. The ligand effect is a result of interfacing two materials with different Fermi levels. The contact potential across the interface causes charge transfer, shifting the Fermi level (and thus, its distance from the d-band center) either up or down. While these effects are typically computed for planar slab structures, they also qualitatively hold true for core-shell systems [68]. Notably, the strain effect is only valid for epitaxially grown shells, and both effects vanish for thick shells (i.e. 7-9 nm of Pd shell on a Au core [69]). Similar effects take place within the plasmonic core and can affect its catalytic efficiency (if active), specifically in cases where the interface is exposed to reactants [20,70], like via a discontinuous shell.

For plasmon photocatalysis, bimetallic particles with different types of shells have all shown promise, from single-crystalline or dendritic, continuous or sporadic, and with a conformal or differently shaped shell. In these structures, the resulting plasmon is damped, i.e. spectrally shifted, spectrally broadened, and lower in intensity compared to the core’s original plasmonic response. Using Mie theory, Zhang et al. found that spherical core-shell structures support two types of plasmon resonances: one whose energy is concentrated at the outer surface of the shell (ordinary mode) and one whose energy is concentrated at the interface between the
core and shell (extraordinary mode) [71], similar to bonding and antibonding modes in plasmon hybridization, though not all systems will show both modes in the visible range. The LSPR peak of bimetallic systems will be red-shifted or blue-shifted depending on the type of mode or the effective permittivity of a shell [72,73]. These shifts can also arise from charge transfer and vary for asymmetric particles [74,75]. The spectrally broadened LSPR peak can be beneficial when trying to match the broad solar spectrum. For example, Wang et al. demonstrated that a mixture of various Au@Pd nanostructures with different aspect ratios could enhance Suzuki coupling reactions under solar radiation [24]. The broad optical response from both the core-shell nanoparticles and the combination of different particle shapes matched the solar spectrum better than Pd nanoparticles alone. The bimetallic nanoparticle mixture then demonstrated higher yield under solar radiation at much milder reaction temperatures (38°C) compared to just thermal catalysis at similar temperatures.

To better design core-shell structures, researchers have been interested in the branching ratio between photons (scattering) and hot electrons/heat (absorption) upon LSPR decay. Using finite element simulations, Chavez et al. studied the relative scattering and absorption cross-sections in core-shell Ag@Pt and Au@Pt cubes and nanorods [76]. They found that the Pt shelling caused the relative ratio of overall absorption to scattering to increase, mainly from increased absorption in the Pt shell (Figure 4(a,b)). Additionally, using Au@Pt nanorods, they showed that higher energy plasmons that excite interband transitions (transverse mode) lead to lower relative absorption in the shell compared to lower energy plasmons that excite intraband transitions (longitudinal mode) (Figure 4(c,d)). Their simulations suggested that more energy is dissipated in the catalytic shell when the probability of interband transitions (reflected in the imaginary part of the permittivity, ε₂) is higher in the shell compared to the plasmonic core.

Experimentally, this fractional increase in absorption relative to scattering has been seen in both ensembles of Ag@Pt nanocubes [21] and single Au@Pt nanorods [77]. Joplin et al. measured the scattering, absorption, and photoluminescence of individual Au@Pt dendritic nanorods (Figure 4(e,f)) and found that scattering decreased upon shelling, as predicted by simulations. However, the measured absorption was relatively similar or dampened upon shelling, contrary to simulations which predicted an increase in absorption. The lower absorption also varied across particles as some particles retained a damped plasmon resonance (Figure 4(f), blue) while others were almost featureless (Figure 4(f), orange). The variation between particles and between experiment and theory is likely due to the inhomogeneous distribution of the Pt dendritic islands’ sizes and shapes, implying that accurate modeling of nanoscopic structure (e.g. via electron tomography) is
needed [78], but could also imply that additional information beyond the classical model is needed in computations (see Future Directions). Finally, the photoluminescence spectra of individual nanorods were quenched and dampened, indicating that less hot carriers were available for radiative recombination. Similar photoluminescence behavior has been seen in other core-shell architectures [20, 79, 80] and could be due to either increased production of hot carriers in the catalytic shell or charge transfer of hot carriers from the plasmonic core to the catalytic shell.

To understand hot carrier dynamics, one can use ultrafast spectroscopy to track hot carrier generation and their lifetimes [81]. For example, using transient absorption spectroscopy, Huang et al. demonstrated that the thickness of a conformal shell affects the hot carrier decay pathways in Au@Pd nanorods [26]. They showed that as the shell thickness increased from 2 to 14 monolayers (corresponding to 0.4–2.8 nm), the excited hot electrons interacted more with the Pd lattice, generating more heat, while their recombination lifetime decreased. For a thicker shell of 27 monolayers (5.4 nm), a competing
process came into play as hot electrons were generated in the Pd shell itself. This process slowed the electron-phonon scattering relaxation of Au-generated hot electrons and extended their lifetime, both of which negatively contributed to their hydrogenation reaction.

Since a conformal shell causes significant plasmon damping, colloidal chemists have developed a variety of methods to selectively deposit catalytic material at the hot spots of a plasmonic antenna [20,79,80,82,83]. Partial shelling of the antenna maintains its strong plasmonic response, thus leading to higher enhancements in reactions compared to fully shelled particles [20], as well as larger surface area for a given amount of catalytic material. However, balancing plasmon enhancement and catalyst amount is critical when considering overall reaction efficiency. For instance, in a plasmon-enhanced hydrogen generation reaction, Pt-tipped Au nanoprisms showed similar catalytic performance as fully coated Au@Pt nanoprisms (Figure 5(b)) despite the tipped particles’ higher extinction spectrum (Figure 5(c)) and catalytic efficiency when normalized by Pt weight (Figure 5(d)). Pt-edged Au nanoprisms, on the other hand, demonstrated the highest overall catalytic efficiency despite their moderate plasmonic response [80]. In another example, Guo et al. used transient absorption spectroscopy to demonstrate that ordered Pd nanoarrays on a Au nanorod lead to enhanced hot electron generation compared to fully shelled or randomly dendritic shelled nanoparticles [22]

Figure 5. Increased plasmon catalysis upon partial shelling. (a) TEM images of Au triangular nanoprisms (TNP) with edge lengths of 141 nm shelled with Pt at either the edges (red), tips (blue), or all over (pink). (b) The overall H₂ generation over the three core-shell particles under visible-NIR light irradiation (>420 nm). (c) The measured extinction spectra of the three geometries. (d) The H₂ generation rate (from (b)) normalized by the amount of Pt on each geometry. (e) TEM image of a Au@Pd superstructure. (f) The measured hot electron generation and computed maximum electric field enhancement across pure Au nanorods and three different shell geometries (superstructure, nanodendrites, and continuous core-shell). (g) The turnover frequency of a Suzuki-coupling reaction for various nanoparticle geometries and mixtures under dark and illumination conditions. (a-d) Adapted with permission from [80]. Copyright 2016 American Chemical Society; (e-g) Adapted with permission from [22]. Copyright 2017 American Chemical Society.
These hot electrons also had a slower decay rate, attributed to the minimal contact between the Au core and Pd nanoparticles which reduces electron–phonon interactions. They further investigated these nanostructures in a Suzuki-coupling reaction whose bond dissociation time was on the same timescale as hot electron relaxation. The superstructures showed the highest reaction efficiency relative to other bimetallic structures and nanoparticle mixtures (Figure 5(g)) with the catalytic enhancement under illumination scaling similarly to the hot electron decay time.

The current library of available syntheses is mainly limited to Au@Pd, Au@Pt, and Ag@Pt nanoparticles due to their combination of traditional plasmonic and catalytic metals, as well as their applications in other fields such as plasmonic sensing [30,84]. Exploring the vast design space of possible materials and architectures would require significant experimental effort; it is thus more promising to use computational resources to narrow down which materials are worth pursuing. For example, Kumar et al. recently used an ab initio approach to identify shell materials that, upon hot carrier excitation, would efficiently couple to CO vibrational modes [85]. They found that coupling between hot electrons and different vibrational modes depended on the spatial extent of d-orbitals and the metal-adsorbate bond length. Since these two quantities are independent of the d-band center, one could potentially control molecular adsorption and electron-vibrational mode coupling (i.e. the first two steps of a reaction) independently. However, since ab initio approaches can only reasonably simulate small (≤1000 atoms, or generally <2 nm) nanoparticles, researchers also use more continuum and qualitative models for high throughput studies. In Ranno et al., they computed hot carrier generation in a core-shell structure with 100 different combinations of 10 metals (Ag, Al, Au, Cu, K, Li, Na, Sn, and Zn) and calculated their likelihood for efficient water splitting, or hydrogen and oxygen evolution reactions [86]. They found that a combination of transition metals with alkali/alkaline-earth metals would lead to efficient hot carrier generation for water splitting, with the alkali/alkaline-earth metal in the core and transition metal in the shell so there is easier extraction. Further work could be in data-mining techniques to further search material combinations for photocatalytic reactions that are also experimentally feasible to synthesize.

**Alloys**

Alloyed nanostructures atomically mix the plasmonic and catalytic metals to create a new electronic structure. Here, we will focus on alloys with random distributions of the two atoms, also known as a solid solution. Alloyed nanoparticles include all the intermetallic effects of core-shell particles, like strain and ligand effects, along with additional effects due to the atomic distribution of the catalytic metal. Notably, any change to the composition...
modifies both the plasmonic and catalytic properties, and it is more difficult to deconvolve the two. While alloys have been the least studied in plasmonic photocatalysis, they are an extremely promising and vast set of materials to explore.

Similar to core-shell catalysts, alloyed nanoparticles are being explored to modify catalyst behavior. Without any illumination, alloyed nanoparticles have demonstrated improved catalytic behavior due to modifications in the electronic structure of the catalytic metal via different atomic bond lengths, the ligand effect and/or atomic distributions [87,88]. The strain and ligand effect work similarly to that of core-shell particles, though in alloyed nanoparticles, the electronegativity of the atom dictates charge transfer. Even so, the charge transfer is not as straightforward. For example, in AuPd alloys, Pd gains d-band electrons from Au but loses s- and p-band electrons (and vice versa) [88]. Alloying also creates isolated catalytic sites and these highly active islands (or single atomic sites in some mixtures) can prevent side reactions and reduce poisoning of the catalyst due to weaker interactions between the catalytic metal and adsorbate [89,90].

One can gain some insight into the optical properties of faceted alloyed nanoparticles by studying the permittivity and electronic structure of alloyed thin films as well as lithographically patterned alloyed nanoparticles. The permittivity of an alloy is not just a linear combination of the two metals due to changes in the d-band structure. From studies of alloyed AgPd and AuPd films, for low amounts of Pd, there were broad virtual resonant states at low frequencies (centered at 2.6eV for AgPd and 2.0eV for AuPd), denoting new interband transitions [91]. The increased $\varepsilon_2$ at those frequencies would then dampen a plasmon spectral peak. Accordingly, Nugroho et al. studied the plasmonic properties of AuPd nanodisks of various Au:Pd concentrations and found that most alloy concentrations had wider plasmon peaks than their monometallic counterparts (Au or Pd disks), suggesting these additional interband transitions [92]. They also found that the plasmon peak position (which in a simple model, follows $\varepsilon_1$, or Re($\varepsilon$)) and plasmon linewidth (follows $\varepsilon_2$) followed different trends in concentration (Figure 6(b)), and postulated that Au and Pd’s contribution to the real and imaginary parts of permittivity may be different at different concentrations. More recently, Kadkhodazadeh et al. studied the same alloyed AuPd nanodisks using electron energy loss spectroscopy to calculate their complex permittivity function and found that the permittivity of AuPd alloys are more similar to Pd than Au [93]. Additionally, using a Drude-like analysis, they found that most alloy concentrations show similar electronic orbital behavior as Pd, suggesting strong hybridization of the Au and Pd d-bands.

Plasmon photocatalysts can combine plasmonic enhancements with these innate alloy compositional effects. For instance, in the aforementioned AuPd
nanodisks (and extended to CuPd), the catalytic properties of Pd, namely its ability to interact with hydrogen, are only slightly affected under illumination as the hydrogen storage properties only depend on Pd concentration [94]. The presence of Au (or Cu) decreases the hydrogen binding energy to Pd and/or the attractive hydrogen–hydrogen interaction upon hydrogen absorption [95]. In another example, with small (3-7 nm) AuPd nanoparticles, Sarina et al. found that plasmonic and compositional effects can be used in conjunction with each other [19]. By studying three different chemical reactions that use Pd as a catalyst, they found that illumination effects were stronger than compositional effects, and reactions reach peak efficiency when optimizing for both (Figure 6(c)).

The plasmonic response can lead to changes in the electronic structure of the catalyst which then affect the overall reactivity. Lin et al. demonstrated how illuminating AgPt nanocages suppressed the formation of hydrogen peroxide (Figure 6(e)), an unwanted byproduct in oxygen reduction reactions,
with byproduct suppression following trends in the Pt d-orbital population [29]. Using x-ray absorption near edge structure spectroscopy, they found less vacancies in the Pt$_{5d}$ state when the alloyed particles were under illumination versus in the dark (Figure 6(f)). When comparing across different alloy concentrations, the decrease in peroxide yield corresponded with the increase in Pt$_{5d}$ population, suggesting that plasmonically excited hot electrons play a major role in suppressing hydrogen peroxide formation.

One of the major challenges of understanding the plasmonic and subsequent photocatalytic response of alloyed structures is the lack of syntheses for fully alloyed nanocrystals with defined shapes [64]. Many catalytic and photocatalytic insights have been from planar structures or small, supported nanoclusters with ill-defined facets. Extending these insights to nanoparticles would give a better idea on how structure, composition, and illumination each affect the photocatalytic response, without having to deconvolve size and faceting effects. The LSPR is also weaker for small nanoparticles (either due to size or quantum effects), so even low additions of a catalytic metal can quench the optical signal [96]. However, common nanocrystal synthesis techniques like co-reduction rely on the two metals having similar reduction potentials and/or physical characteristics. Since many metal combinations do not, some plasmonic-catalytic bimetallic geometries result in a gradient-alloy structure, which can also be beneficial for enhancing the plasmonic fields. For example, electron energy loss spectroscopy maps of Au octopods with AuPd tips show spatially localized resonances around the tips [97]. Alternatively, one can sacrifice distinct faceting by conventional alloying techniques like thermal annealing [92,98], or new colloidal synthesis techniques like probe-based lithography [99].

**Future directions**

Bimetallic nanoparticle systems have shown great promise for adding optical functionality for a more expansive library of reactions only accessible by a catalytic metal. The geometry and structure of a bimetallic catalyst play a major role in determining the intermetallic effects, which then affect the photoresponse and overall catalytic behavior. As the landscape of what constitutes a plasmonic metal or a catalytic metal expands (i.e. doped semiconductors [100], UV-plasmonics [101,102]), a mechanistic understanding of intermetallic effects can help design new photocatalysts. However, to move forward, improved efficiency complemented by both theoretical and experimental advances is essential to establish more quantitative understanding of these structures.

Foremost, bimetallic plasmonic photocatalysts currently suffer from low quantum efficiencies. While light absorption can be high, the subsequent conversion of photon to reaction product has been quantified at no more
than 2% for a variety of reactions at room temperature [44]. Improving efficiency crucially depends on identifying the main mechanisms behind a plasmon photocatalytic reaction, whether it is direct hot electron transfer, resonant energy transfer to the adsorbed molecular orbitals, increased vibrational energy, or heating. Among these mechanisms, certain energy transfer steps are known to be inefficient; for example, the extraction and direct transfer of hot carriers is inefficient due to both the small fraction of high-energy hot carriers and their shorter lifetimes compared to chemical reactions (tens of femtoseconds vs milliseconds) [103]. Semiconductor supports have been used to lengthen hot carrier lifetimes in monometallic nanoparticles by separating electrons and holes at the metal–semiconductor interface [17]. Alternatively, researchers have shown that adding a hole scavenger, like ethanol or other aliphatic alcohols, to the reaction can also lengthen hot carrier lifetimes such that multi-electron processes can take place [104].

Theory is crucial to understanding efficiency limits, but first requires a better understanding of bimetallic systems, starting with incorporating modifications of the electronic band structure to the plasmonic response of core-shell and alloyed structures. To model the plasmonic enhancement in core-shell systems, researchers generally use electromagnetic solvers which solely depend on the choice of geometry and material permittivity values (usually taken from bulk or thin films). Therefore, any modifications to the d-band from charge transfer or strain are not taken into account, which can affect the optical response [105]. This band-structure modification also makes it difficult to predetermine the plasmonic properties of alloyed nanoparticles. There has been much progress in calculations of hot carrier generation in monometallic, traditionally plasmonic nanoparticles, but current methods cannot capture both nanoparticle size and d-band electron behavior [106,107]. A fuller theory could better inform hot carrier behavior in purely catalytic nanoparticles as well as bimetallic systems. Such techniques would especially be useful for core-shell systems that utilize a thin (3–5 monolayers) shell, which exhibit quantum effects that cannot be included in a classical electromagnetic model [108].

From the experimental side, ultrafast experiments (like transient absorption spectroscopy, ultrafast electron diffraction, and ultrafast Raman spectroscopy) show great promise in differentiating and quantizing the effects of hot carriers versus photothermal heating [109]. As highlighted in our core-shell section, ultrafast optical experiments provide better insight to not only the mechanism behind the photoresponse of these bimetallic structures but also identify how reactions can benefit from them. In combination with ultrafast x-ray or electron diffraction, these studies can more definitively identify how these systems behave under illumination. Additionally, single and subparticle imaging and characterization techniques like transmission electron microscopy, electron energy loss spectroscopy [110], cathodoluminescence spectroscopy
and super-resolution imaging can give nanoscopic insight as to how structure (i.e. shape, crystallinity, size) dictates intermetallic effects. Low efficiencies can also be addressed by engineering innovations. For simplicity, we have limited our review to combinations of two metals, but more complex configurations such as a plasmonic core with an alloyed shell, or combinations of three or more metals can increase plasmon hybridization [92,112] and further tune catalytic efficiency. Moreover, the support (i.e. the substrate) is an integral part of the catalytic system because they not only have an impact on the stability of catalysts [113] but also can transform dark plasmonic modes into bright modes exhibiting Fano-like lineshapes or high-quality factors [114]. Another promising direction is to expand the variety of materials used, including plasmonically active metals like Al and Cu which are naturally more abundant and affordable than noble metals like Au and Ag [102,115]. Nanoparticles consisting of these earth-abundant metals are still experimentally difficult to synthesize and limited by their natural oxide layer, but the oxide layer can be used to the system’s advantage in antenna–reactor systems [28] or prevented via alloying. Alternatively, 2D materials and layered van der Waals materials have emerged as potential catalysts due to their tunable electronic structure and can sustain plasmon resonances on their own (albeit at the mid-infrared regime) or couple easily with plasmonic nanoparticles for enhanced photoreactivity [116–118]. Incorporation of these atomically thin materials can not only reduce the amount of material needed to promote chemical reactions, but also improve control over the electronic and photonic density of states via layering. Though the champion materials and geometries of bimetallic photocatalysts are still to be determined, one thing is clear: there is untapped potential for light as a new reagent in chemistry, with plasmonically active metals promising increased product selectivity, high product yield, and tunability for next-generation photocatalysts.

Note

1. This is also known as the ensemble effect in literature. Here, we have refrained on using the terminology as to not confuse readers with the (nanoparticle) ensemble effects mentioned in the antenna–reactor section.

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Disclosure statement

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