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# Plasmonic Hybrid Nanostructures in Photocatalysis: Structures, Mechanisms and Applications

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## Abstract

(Sun)Light is an abundantly available sustainable source of energy that has been used in catalyzing chemical reactions for several decades now. In particular, studies related to the interaction of light with plasmonic nanostructures have been receiving increased attention. These structures display the unique property of Localized Surface Plasmon Resonance, which converts light of a specific wavelength range into hot charge carriers, strong local electromagnetic fields, and/or heat, which may all boost the reaction efficiency in their own way. These unique properties of plasmonic nanoparticles can be conveniently tuned by varying the metal type, size, shape and dielectric environment, thus prompting a research focus on rationally designed plasmonic hybrid nanostructures. In this review, the term 'hybrid' implies nanomaterials that consist of multiple plasmonic or non-plasmonic materials, forming complex configurations in the geometry and/or at the atomic level. We discuss the synthetic techniques and evolution of such hybrid plasmonic nanostructures giving rise to a wide variety of material and geometrical configurations. Bimetallic alloys, that result in a new set of opto-physical parameters, are compared to core shell configurations. For the latter, the use of metal, semiconductor and polymer shells are reviewed. Also, more complex structures like Janus and antenna reactor composites are discussed. Furthermore, this review summarizes the studies exploiting plasmonic hybrids to elucidate the plasmonic-photocatalytic mechanism. Finally, we revise the implementation of such plasmonic hybrids in different photocatalytic application domains like H<sub>2</sub> generation, CO<sub>2</sub> reduction, water purification, air purification and disinfection.

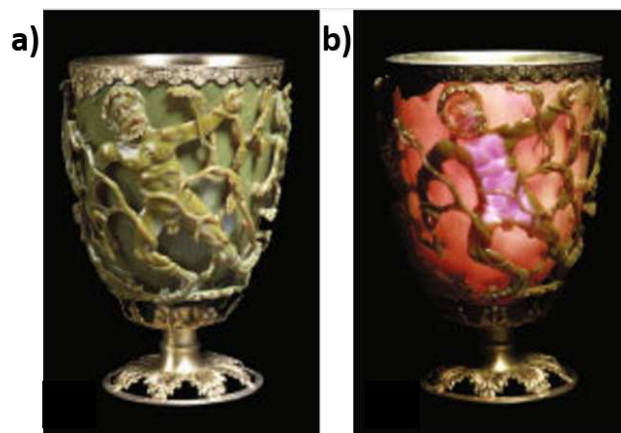
**Keywords:** Surface Plasmon Resonance, hybrid nanostructures, photocatalysis, core-shell, alloy, hydrogen, CO<sub>2</sub> reduction, air purification, water purification, antibacterial

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## 1. Introduction

Already for multiple hundreds of years, people have been coloring glass [1, 2] and other objects (*e.g.* the Lycurgus cup from the 4<sup>th</sup> century AD (Fig. 1) [3]) with specific metal nanoparticles (NPs), yielding beautiful bright colors upon illumination. It took until the 20<sup>th</sup> century, before scientists brought the origin of these colors to light, attributing the effect to the (localized) surface plasmon resonance ((L)SPR) of plasmonic NPs [4]. Incident light with a frequency matching the natural frequency of the oscillating conduction band (CB) electrons of a metal NP, is strongly absorbed by these NPs. The CB electrons oscillate against the restoring force of the positive nuclei [5]. Due to this unique optical characteristic, plasmonic NPs like Au, Ag, and Cu gained enormous interest over the past decades. Due to their strong interaction with ultraviolet (UV), visible (VIS), and even near infrared (NIR) light, plasmonic nanoparticles are envisaged as a promising light-harvesting and light-intensification structures in many important light-driven processes such as photovoltaics [6], biosensing [7], surface-enhanced Raman spectroscopy (SERS) [8] and photocatalysis [5, 9]. In view of the growing concerns over climate change, solar light mediated photocatalysis stands out as a crucial research area for sustainable H<sub>2</sub> generation, CO<sub>2</sub> conversion, air and water pollutant degradation. In 2019 alone, more than 43 billion metric tonnes of CO<sub>2</sub> were emitted [10]. Furthermore, it is believed that deep decarbonization (>80%) is impossible without the wide use of H<sub>2</sub> as fuel [11]. Yet, the large-scale application of photocatalysis even with widely investigated materials, as for instance TiO<sub>2</sub>, is still hindered by the fact that only a small portion of the solar spectrum is sufficiently energetic to drive the photocatalytic reactions using these pristine materials. Thus, the fairly large bandgaps of most semiconductors (SCs) only allow UV light for photoexcitation (<5% of sunlight), while the remaining energy of the solar spectrum remains unused [4]. In this regard, plasmonic NPs provide a viable solution for more efficient utilization of the solar spectrum. The energetic coupling of their oscillating free electrons to the broad spectral incident light, results in strong enhancements in several photocatalytic processes [5].



**Fig. 1** Lycurgus cup from the British Museum a) without and b) under illumination. Adapted with permission from [3]. CC BY-NC 2.0

Over the years, the field of plasmonics has been growing in different directions for improving the light-matter interaction, application-targeted functionality, chemical stability, and so on. One such progressively developing field is that of hybrid plasmonic nanostructures, in which different materials with different functionalities are combined in one hybrid composite. The activity, selectivity, and stability of photo-induced processes may thus be improved by the appropriate design of such nanostructures. In this review, the term ‘hybrid’ implies nanomaterials that consist of multiple plasmonic or non-plasmonic materials, forming complex configurations in the geometry and/or at the atomic level. These can be broadly classified into three main categories, each with its specific structural properties. The first category deals with alloys, where the constituting elements are distributed homogeneously over the nanostructure, leading to a new set of characteristics. The combination of plasmonic with either another plasmonic or a non-plasmonic metal (with other functionalities) will be discussed in this regard. The second category includes the configurations where a plasmonic core is

covered by shell consisting of either another metal, a semiconductor, or a polymer. The third category includes a variety of other structural configurations, such as Janus particles, metal organic frameworks (MOFs), and hybrid two dimensional (2D) arrays. In contrast to other existing reviews based on the synthesis of a certain class of bimetallic NPs [12, 13] or on the use of single or purely metallic plasmonic NPs for a certain application [5, 9, 14–16], this review covers the synthesis and consequent properties of plasmonic hybrids and their impact on several photocatalytic applications.

In the next sections the synthesis and subsequent properties of multimetallic alloys, metal@metal, metal@SC and metal@polymer core-shell configurations, Janus and other hybrid nanostructures will be discussed. This is followed by an analysis of the use of these materials to enhance the photocatalytic activity. Also, special attention is given here to how plasmonic hybrids are exploited to rigorously study the plasmonic-photocatalytic operation mechanism. Finally, various recent innovative structures are compared towards a selection of important photocatalytic applications, including H<sub>2</sub> production, CO<sub>2</sub> conversion, pollutant degradation and disinfection.

## 2. Synthesis and Structural Properties

The above-mentioned three main categories of plasmonic hybrid nanostructures will be treated in the following sections. Along with the synthetic techniques to obtain these different configurations, the distinct electronic and optical properties are discussed.

### 2.1 Alloy

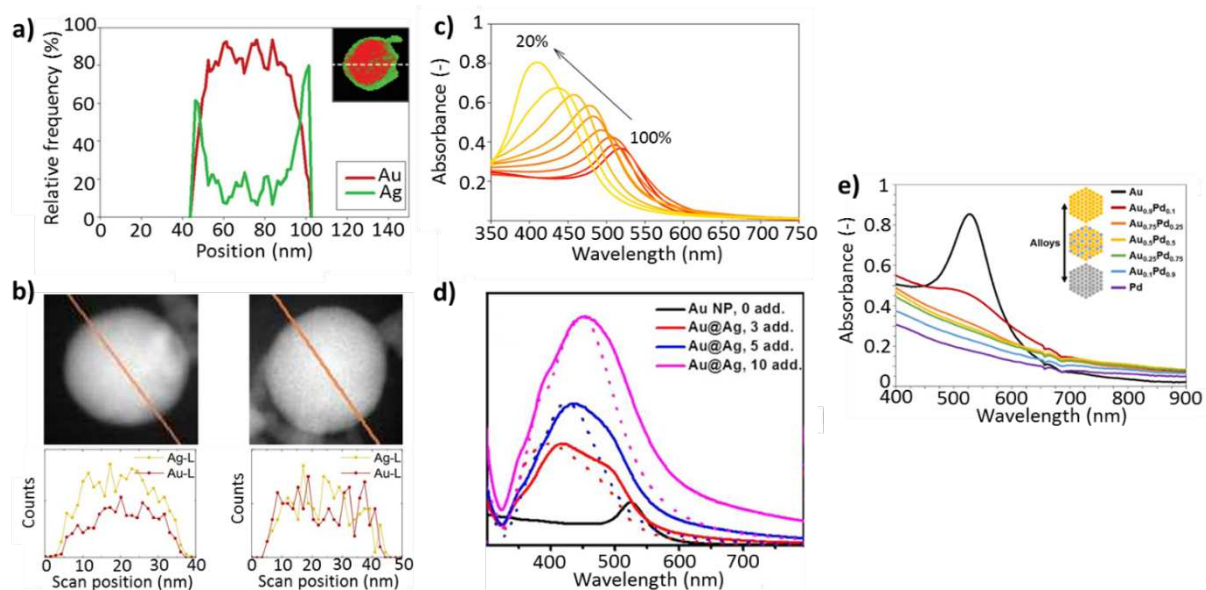
By alloying, new desired intrinsic optical properties or catalytic activity can be obtained, depending on the composition of the alloy. For instance, a second metal can be incorporated into a metal catalyst to control the surface composition, geometry of adsorption sites, selectivity, stability and electronic properties for catalysis, giving rise to a so-called “ensemble effect” [17]. Additionally, the incorporation of a plasmonic metal yields a plasmonic effect, with the eye on improving photocatalytic reactions. Mixing of two or more plasmonic metals can be useful for tuning the plasmonic response itself, as well improving the stability of the particles. Advanced synthesis techniques allow to synthesize not only mixed bimetallic and multi-metallic alloy NPs, but also ordered alloys with different structuring of crystal facets [18–20].

As one of the best-known examples, the strongly plasmonic Ag is often alloyed with the more stable Au to prevent the oxidation of Ag [21, 22]. The simplest way to synthesize such alloy NPs is by colloidal wet chemical methods. This can be achieved by co-reduction of metal ions in solution, seed-mediated growth or galvanic replacement. Co-reduction relies on two metals having similar reduction potentials and/or similar physical characteristics, which is necessary to form a homogenous alloy. An example is the modified Turkevich method to synthesize AuAg alloy NPs [23]. There are several similarities between Au and Ag, e.g. a face-centered cubic (fcc) crystal structure, similar lattice parameters (resp. 4.065 and 4.079 Å [24]), surface energies [25], and so on. Yet, the different reduction potentials still tend to lead to the formation of a rather ‘core-shell type alloyed structure’ with gold-rich cores and silver-rich shells. This was revealed in one of our previous studies, using 3D energy dispersive X-ray (EDX) tomography at several stages throughout the synthesis procedure [23]. To obtain a more homogenous alloy, using appropriate molar ratios, reducing agents and ligands are important for the synchronized reduction of metal ions [26]. Due to its earth abundancy and promising plasmonic and catalytic properties, Al and Cu are deemed to be the future. However, the synthesis of these plasmonic NPs with an even higher tendency to oxidize (Al, Mg and Cu) additionally require a more specialized oxygen- and water-free setup. The use of Schlenk lines and glove boxes is common for such syntheses [27, 28]. Utmost care should be taken in handling the Grignard compounds produced from such protocols. The use of oxygen-free setups deems the process challenging to bring to scale. Yet, in the presence of chemically inert Au, the synthesis of alloy NPs of AuCu by a simple co-reduction method

has been shown to yield stable alloy NPs compared to easily oxidizing Cu NPs [29]. Similarly, alloy NPs of different combinations, including Au, Pt, Pd, Rh, Ni *etc.*, have been synthesized by the co-reduction method [30–33]. Seed-mediated procedures can be used for the growth of different metal ions on separate crystal facets of the seed to have more control over the shape of the NPs [34], although it does not lead to homogeneous alloys and is more suitable for core-shell type structures [35, 36]. Thus, a subsequent thermal alloying step is important in seed mediated processes for uniform distribution of the constituting elements. Furthermore, for galvanic replacement, one metal is oxidized, *i.e.* the sacrificial agent, by ions of another metal with a higher redox potential. Complex bi- and trimetallic alloyed structures can hence be formed [37–39]. However, this technique is more prevalent for the synthesis of core-shell NPs (see 2.2) [40, 41].

In order to gain more control over the NP size distribution in colloidal syntheses, microreactor-based approaches are nowadays being studied [42, 43]. Here, reagents are introduced through microchannels at pre-decided flow conditions. Uniform mixing in the microliter regime results in the production of a highly monodisperse colloidal solution of NPs with an increased control over the size and shape [42]. By simply varying the flow conditions, different structures may be formed in a continuous flow. This offers an important time advantage over time-consuming trial-and-error syntheses using a batch setup. Nonetheless, understanding and controlling the flow and mixing conditions with high precision in a microreactor is challenging [43]. On the other hand, innovative colloidal synthesis techniques such as probe-based lithography also give a more controlled and varied geometry of NPs on a support material [44].

Although colloidal wet chemistry synthesis strategies have evolved significantly over recent years, they do not offer the highest degree of alloy structure control [23, 45]. For the formation of a more homogenous AuAg alloy, sophisticated physical methods such as laser ablation are preferred [45, 46]. As mentioned before, the wet chemical modified Turkevich method leads to the formation of ‘core-shell type alloys’ (Fig. 2a), while laser ablation generates a more homogenous alloy (Fig. 2b). The latter is partially attributed to having no deviations from Vegard’s law which states that a linear relation exists at a constant temperature, between the crystal lattice constant of an alloy and the concentrations of the constituting elements. Compared to laser ablation, colloidal synthesis induces negative deviations to Vegard’s law forming a non-homogenous alloy [45–49]. In laser ablation, the laser energy is absorbed by a macroscopic target material, generating a plasma. This plasma expands and condenses in the liquid environment, forming nano-size materials due to cavitation. Therefore, it can be considered as a combined top-down (target material) and bottom-up (NPs from generation of plasma) approach. Laser ablation is more ecofriendly as laser irradiation produces species with high energy states without producing byproducts and without the need for further high temperature treatment. Furthermore, often ligand-free alloys are produced with no additional chemical agents, apart from the solvent [45]. Very recently, laser ablation has also been used to form alloys by co-reduction of Au and Ag ions. However, it does not form ligand-free alloy NPs [50]. The high initial cost of laser technique is a drawback. Yet, considering operational costs at large scale, a study discussed laser ablation to be cost-effective in the long run. Currently used at an industrial scale, laser ablation can give output of NPs in the range of grams per hour, compared to milligrams per hour for wet chemical synthesis methods [51]. Magnetron sputtering can provide for a homogeneous multi-metal alloy, but is rather limited to be used as a film deposited on a substrate. Consequently, it is difficult to hybridize sputtered metal NPs with another metal, semiconductor, polymer *etc.* and being a surface based phenomenon, it cannot be readily used for formation of nanoparticles inside porous materials [52–54]. Similarly, other chemical and physical methods, such as chemical vapor deposition, lithographic patterning, thermal decomposition, plasma synthesis *etc.*, are either time-consuming, expensive, or do not yield a good control over the structural properties for hybrid systems [55–58].



**Fig. 2** Schematic representations of an EDX line scan of AuAg alloy NPs synthesized by a) wet chemical co-reduction and b) laser ablation. c) Blue-shift of the plasmon absorption band with decreasing Au percentage in AuAg alloy. d) Absorption spectra of Au@Ag core-shell NPs. e) Absorption spectra of a AuPd alloy with a sudden decrease of Au LSPR band with minor addition of Pd. Adapted with permission from a) [23]. Copyright (2019) John Wiley & Sons, b)[45] CC BY-NC 3.0, c)[59]. Copyright 2016 Elsevier, d)[60]. Copyright (2013), American Chemical Society and e)[61] CC BY 4.0

As mentioned above, the combination of metals as alloys allows the tuning of optical properties. For instance, alloying of Au and Ag leads to an optical response which is the intermediary of those of pure Au and Ag [59]. Classically, the optical constants for different alloy compositions can be conveniently modelled with the Lorentz-Drude oscillator framework. Here, the interband transitions introduced by Au are captured by a suitable number of Lorentzian oscillators [62]. Thus, by increasing the Au fraction, the LSPR of NPs can be red-shifted with respect to pure Ag NPs, towards the LSPR of pure Au NPs, as observed from ultraviolet-visible (UV-VIS) absorption spectra in Fig. 2c, leading to structures with a larger VIS light absorption component. However, the incorporation of Au also leads to interband transitions that suppress the overall plasmonic enhancement [63, 64]. The advantage of alloying over incorporation of Au as a shell, core or a Janus particle, is that the compositional homogeneity provides a proportionate displacement of the LSPR with changing composition [62]. In the case of core-shell structures, however, the hybridization of the individual plasmon modes of the core and shell leads to complex spectral features [60, 65]. The proportionate variation of the extinction spectra of AuAg alloy NPs against the very complex extinction spectra of Au@Ag core-shell can be clearly observed from the examples in Fig. 2c and d. The optical features of core-shell NPs will be further discussed in section 2.2.

Also, other alloy combinations including catalytic elements such as Pd, Pt *etc.*, and earth abundant plasmonic metals such as Cu, Al, Mg *etc.*, gained considerable attention due to their promising application potential [30, 66, 67]. For instance, the incorporation of Cu in AuCu alloy NPs of different shapes such as nanospheres, nanorods, nanocubes, nanopentacles *etc.* further push the LSPR band towards the red end of the visible light spectrum as compared to pure Au [29, 68–70]. For AuPd alloy systems, Pd introduces some specific catalytic activity, although it also progressively suppresses the plasmonic excitation, even by an addition as small as 10% (Fig. 2e) [61]. This is due to the large absolute values of the real part and the relatively lower values of the imaginary part of the dielectric constants [71]. On the other hand, the sharp gradient of the imaginary dielectric constant enhances the refractive index sensitivity of the nanostructures [72]. For small NPs, <10 nm, with weaker resonance (either due to size or quantum effects), the addition of a small fraction of a catalytic metal can quench the characteristic plasmonic response [73]. Due to a limited solid-phase solubility, the combination of Au and Pt limits the maximum size to 6 nm for full alloying. Hence, a strong plasmon resonance effect remains difficult for AuPt alloys with these very small sizes [73]. Similarly, such a limit in the solubility of Ag and Pt also leads to the tendency of forming core-shell structures [74].

Still, the addition of such catalytically active metals like Pd and Pt can certainly be beneficial. Several studies have already shown an enhancement in catalytic activity using alloy NPs due to a change in the electronic structure [59, 61, 68, 75, 76]. Alloying causes a shift in *d* band levels with respect to the Fermi energy levels and therefore affecting the overall reactivity. The dielectric constant of an alloy is not just a linear combination of that of the individual metals, partly due to changes in the *d* band structure. In AuPd alloys, Pd loses *s* and *p* band electrons to Au and gains *d* band electrons from Au and *vice versa* [75]. Alloying also introduces different interband and intraband transition states compared to their single metallic counterparts [77]. For example, alloying of Ag with Au can lead to suppression of interband excitations and favor intraband excitations which eventually results in higher hot electron energies [76]. The hot electron energy transfer also depends on the work function and the Fermi energy levels and therefore can be different for various materials including different alloys. Typically, it is ideal for the work function to be closer to the Fermi energy levels. These higher hot electron energies are eventually useful for photocatalytic reactions and will be further discussed in sections 3 and 4 [78]. It is important to note that to understand the properties of the wide spectrum of available materials, intensive computational studies are required. For example, Keast *et al.* studied the plasmonic response of alloying Au with various metal to show that only a set of combinations (AuAl<sub>2</sub>, Au<sub>3</sub>Cd, AuMg, AuCd and AuZn) would have a better plasmonic response [79]. Although most of the computational studies focus only on one aspect such as optical plasmonic response [65], hot electron injection to band structure [80, 81] *etc.*, one alloy combination may behave differently for other catalytic reactions due to various other reasons, such as surface selectivity, surface energy and so on. Therefore, rational design of materials is needed for each specific application (see section 4).

## 2.2 Core-shell

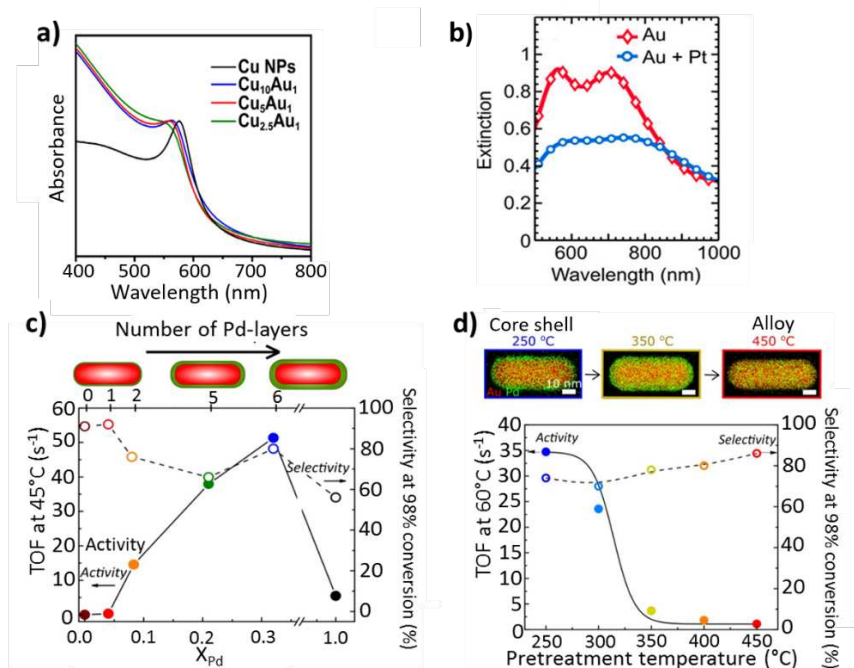
When the constituting materials (metal, semiconductors or polymers) are not homogeneously distributed throughout the nanostructure volume, the intrinsic functionalities of the components remain (largely) intact [82, 83]. It is, however, important to note that the plasmonic component is influenced extrinsically by the presence of the other components, such as an extra shell. For instance, a major effect present in most plasmonic core-dielectric shell configurations is the red shift of the plasmon band as the refractive index of the dielectric environment, *i.e.* the shell, increases [21, 84–87]. In the following section, different core-shell configurations are discussed in sub-classes.

### 2.2.1 Metal@metal

A metal@metal core-shell configuration can broadly be of two kinds. Firstly, both the core and the shell can be plasmonic metals. Secondly, a plasmonic core or shell can also be combined with a shell or core of catalytic metal(s). In the first system, including combinations of Au, Ag, Cu, Al *etc.*, the optical properties are considerably different from their alloy counterparts. In the case of AuAg alloys, the extinction spectra shift linearly from the blue to red spectral region with increasing Au fraction (Au%) (Fig. 2c), whereas in Au@Ag core-shell systems, the spectral characteristics due to the hybridization of the individual plasmon modes of the core and the shell results in band broadening and complicated trends of the LSPR absorption band vs. Au% (Fig. 2d) [60]. The theoretical framework of plasmon hybridization given by Nordlander and co-workers is inspired by the molecular orbital hybridization theory. It explains the optical response of core-shell NPs where the core and the shell are separated by a non-conducting dielectric interlayer [88]. While not much literature is available on the implementation of the hybridization theory on metal@metal core-shell structures with no dielectric interlayer, the rigorous numerical solution of the Maxwell's equations is relatively convenient with established numerical codes to satisfactorily describe the optical properties [65]. Kamimura *et al.* studied core-shell Au@Ag/SrTiO<sub>3</sub> versus alloyed AuAg/SrTiO<sub>3</sub> for converting isopropanol to acetone and CO<sub>2</sub>. It was shown that Ag in the AuAg alloy oxidizes, while being more stable by forming a shell in a core-shell structure. The authors explained the stability by stating that the chemical stability of the Ag shell can be enhanced by coupling to the Au core due to a charge transfer. This should increase electron density within the Ag shell, yielding a negative Ag oxidation state [89]. With the growing importance towards more abundant, but chemically unstable, plasmonic materials such as Cu, Al and



Mg, incorporation of a thin shell of Au is also seen as a viable stabilization strategy [90]. Use of Au as a shell is less detrimental to the plasmonic effect of the nanostructures as shown for Cu@Au NPs, especially compared to the use of catalytic shells having a lower plasmonic response with plasmonic cores (*e.g.* Au@Pt) (Fig. 3a,b) [90, 91].



**Fig. 3** Schematic representation of a) the blue-shift in UV-VIS absorption spectra of Cu@Au core-shell against b) a dampened UV-VIS response of Au@Pt core-shell NP. Change in activity (represented by the turnover frequency (TOF)) and selectivity in Au@Pd core-shell NPs with c) increasing Pd shell thickness and d) gradually changing from core-shell to alloy. Adapted with permission from a) [90]. Copyright (2021) American Chemical Society, b) [91]. Copyright (2017) American Chemical Society, c-d) [83]. Copyright (2021) Springer Nature

On the other hand, core-shell systems using a catalytic shell may still be preferred, depending on the application (*e.g.* Au@Pd systems for Heck coupling) [92]. In this second class, the plasmonic metal acts as an ‘antenna’ and the non-plasmonic material as the adsorbing and reactive surface [93]. The optical and electronic properties of the plasmonic materials are thus utilized to enhance the reactivity of the non-plasmonic material. While in alloys, a complete new set of intrinsic properties is formed, in the case of core-shell NPs, the non-plasmonic shell has an extrinsic effect on the plasmonic core.[4]. For instance, as mentioned above, a Pt shell around Au nanorods increasingly dampens the plasmonic absorption intensity of the nanorods with increasing shell thickness due to the non-plasmonic response to light by the Pt shell (Fig. 3b) [91]. Similar to Au@Pt, the extinction spectra of Ag@Pd core-shell NPs are different from the extinction spectra of either Au or Pd. The general trend is that the LSPR in extinction spectra loses intensity along with a blue-shift or red-shift of the resonance frequency, while the spectral shape is broadened due to the coupling of both materials. Besides the optical properties, bimetallic core-shells can have starkly different catalytic activities from their alloy counterparts. For example, several Au@Pd core-shell configurations, esp. with sharp branches, may have a slightly higher yield compared to AuPd alloys for both the Suzuki-Miyaura and Heck reactions (conversions of resp. ~80-90 vs. up to 99%) [92]. Core-shell systems can furthermore be more easily tuned towards an antenna reactor system within their structure as compared to alloyed systems. An electronic and optical coupling with the plasmonic core hence enables enhanced activities [94]. Therefore, well-considered reaction-specific structures can be synthesized.

Metal@metal core-shell NPs are more commonly synthesized using colloidal synthesis methods with satisfactory control over NP size, shape and morphology [95]. Co-reduction of metal precursors can yield core-shell structures when the difference between the reduction potentials of the constituting elements is sufficiently large [60]. In such systems, galvanic replacement can also lead to metal@metal

core-shell structures with sub-nanometer shell thickness control [90]. During galvanic replacement, one element in a crystal lattice is replaced by another with higher reduction potential. Hence, certain reagent mixtures, such as Ag nanoparticles with Au<sup>3+</sup> ions, always lead to spontaneous reactions. While the higher electronegativity of Au (1.9) than Ag (1.6) facilitates spontaneous formation of hollow Ag@Au core-shell systems by galvanic replacement, the formation of an Ag shell on Au NPs requires a reducing agent [96, 97].

With the recent advances, the synthesis procedures of core-shell NPs (just as for alloy NPs) have been developing in different directions such as microreactor based synthesis, lithography and laser ablation [98–100]. Some techniques are also specifically convenient for the synthesis of bimetallic core-shell NPs. For instance, Forcherio *et al.* generated a core-shell morphology by the exploiting the plasmonic excitation of the Au NP cores themselves. Sub 5 nm epitaxial growth of Pt ions could be achieved at plasmonic hot spots. The photodeposition of Pt on Au nanorods was activated by the longitudinal surface plasmon excitation of the nanorods [101]. Thus, a thicker shell was formed at the Au nanorod tips, compared to the rest of the nanorod (the mean length extended by 4.7 nm, while the diameter only increased by 0.72 nm). This is due to the fact that the longitudinal plasmon mode is manifold stronger than the transverse mode perpendicular to the axis of the nanorod. Another unique method for obtaining core-shell structures is oxidative etching. Van der Hoeven *et al.* generated core-shell morphologies by the etching of Au@SiO<sub>2</sub> NPs using H<sub>2</sub>O<sub>2</sub> followed by the addition of a shell metal (Ag, Pd or Pt) precursor. Thermal annealing resulted in better control over the shell morphology, while the shell thickness could be regulated from 3 nm to 10 nm via the metal overgrowth reaction time and precursor concentration [102]. The importance of the latter parameter cannot be underestimated. Huang *et al.* used transient absorption spectroscopy to show how the shell thickness affects the hot electron decay pathways in Au@Pd NRs. It was shown that, with the increase in shell thickness from only 0.4 to 2.8 nm, corresponding to 2 to 14 monolayers, Au's hot electrons interacted more with the Pd interface lattice. This led to increased heat generation due to an increase in electron-phonon and phonon-phonon scattering of hot electrons from Au with a decrease in the recombination rate of electrons and holes. For a thicker shell of 5.4 nm or 27 monolayers, hot electrons were generated in the Pd shell itself to increase the Pd lattice temperature and reduce the heat capacity of Pd. Thereby electron-phonon scattering of Au-generated hot electrons are slower when passing through the Pd shell. This also leads to accelerated recombination rates. Consequently, a lower ethylbenzene yield was recorded for the styrene hydrogenation reaction after 1h of 100 mW.cm<sup>-2</sup> illumination (52% for 27 monolayers vs. 76% for 14 monolayers) [82]. In contrast, van der Hoeven *et al.* showed an optimal shell thickness of 6 atomic Pd monolayers around a Au NR core covered with mesoporous SiO<sub>2</sub> (Fig. 3c). They also showed that single-crystalline Au@Pd core-shell structures performed more than 30 times better than the alloyed equivalents, displaying turnover frequencies (TOFs) of resp. 34.7 and 1.1 s<sup>-1</sup> for the butadiene hydrogenation at 60°C (Fig. 3d) [83]. Dedicated examples of hybrid metal@metal nanostructures in particular photocatalytic applications are discussed in more detail in section 3.2.

### 2.2.2 Metal@semiconductor

Mostly, plasmonic NPs are introduced to SCs for enhancing photocatalytic efficiency of the SC, while simultaneously improving the metal stability. In metal@SC systems, the metal and the SC crystals are connected by a Schottky junction that facilitates electron hole separation at the SC. In general, most of the works on metal@SC structures has been with TiO<sub>2</sub> as the shell covering a plasmonic core, resulting in structures like Au@TiO<sub>2</sub>, Ag@TiO<sub>2</sub> and Cu@TiO<sub>2</sub> [85–87]. Photocatalytic SCs mostly include metal oxides but also metal chalcogenides. The most convenient way to synthesize metal@SC core-shell nanostructures is by growing a shell of metal oxide precursor over plasmonic NPs. For the shell growth, metal oxide precursors are added to colloidal plasmonic NPs and the precursor molecules bind to the surface ligands on the particle surface [85]. Using the metal oxide precursor itself as the reducing and capping agent for the formation of plasmonic nanoparticles, further simplifies the process [103]. Generally, titanium isopropoxide, titanium butoxide or titanium fluoride are used as Ti precursors, forming crystalline TiO<sub>2</sub> shells from 5 nm to more than 100 nm in thickness [85, 104]. In order to form

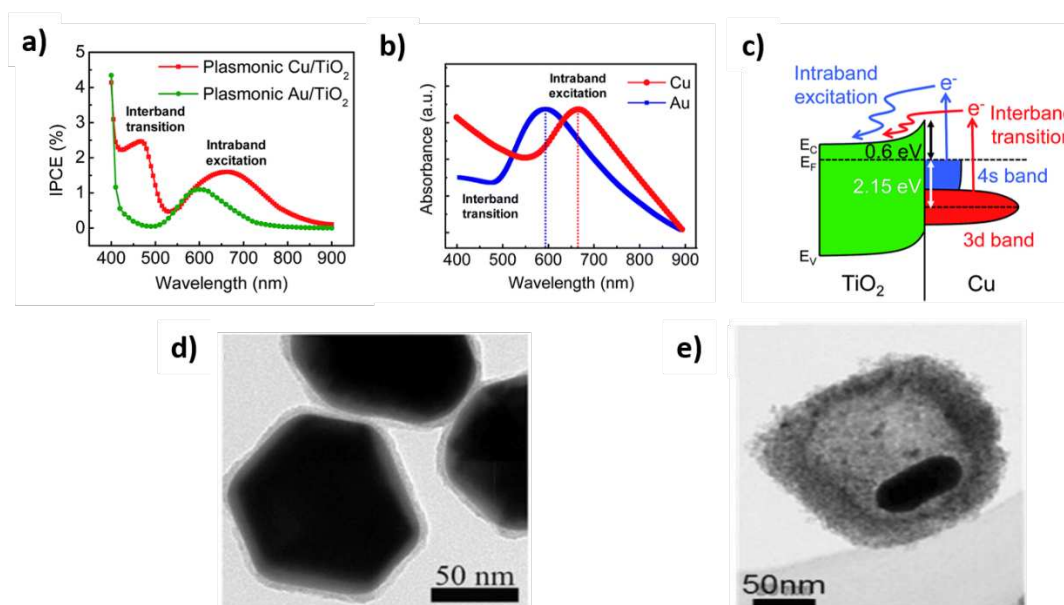
uniform shells, controlled interaction of the precursor with the capping ligands, and controlled hydrolysis and condensation of the precursors, are highly important. Anhydrous solvents or slow hydrolyzing precursors such as titanium(IV) (triethanolaminate) isopropoxide tend to give a more uniform shells of thicknesses down to 2 nm (Fig. 4d) [105]. Since unstable metals like Ag, Cu and Al may oxidize during the subsequent annealing step required for crystallization of the oxide shell, hydrothermal crystallization procedures are often adopted. Alternatively, the photothermal effect of the plasmonic NPs itself can also be used for controlled TiO<sub>2</sub> shell formation by laser irradiation [106]. Different configurations such as Ag@TiO<sub>2</sub> nanowire arrays can also be formed using templated lithography [107]. The feasibility of core-shell structures by atomic layer deposition of ZnO on Ag nanoparticles was demonstrated as well [108]. The effect of the metal oxide shell comes from the interband excitations as well as elastic scattering. For instance, a dielectric SiO<sub>2</sub> shell around plasmonic nanoparticles contributes to the total scattering which increasingly dampens the plasmon band with increasing shell thickness [109]. Importantly, it was also shown for Au@Cu<sub>2</sub>O core-shell systems that the plasmonic response of the core depends on the crystal facets of the shell, which enable further optical tuning of these hybrid structures [110]. Note furthermore that sometimes M@SC core-shell materials form spontaneously. For instance, Al oxidizes very easily, generating a thin 2-3 nm self-limiting oxidized layer [111]. Better stabilization strategies are required for such chemically unstable metals in order to use them in realistic photocatalytic applications at industrial scale.

In the past decades, more VIS light active SCs such as Cu<sub>2</sub>O, g-C<sub>3</sub>N<sub>4</sub>, CuS, CdS *etc.*, gained considerable attention for constructing plasmonic hybrids [112–115]. Lee *et al.* developed Ag@Cu<sub>2</sub>O nanoparticles with varying shell thickness and observed a higher photocatalytic activity with increasing shell thickness. Photocatalytic degradation of methyl orange (MO) under VIS light with 11 nm Ag core@11 nm Cu<sub>2</sub>O shell NPs was completed in 1h compared to only ~5% degradation by Cu<sub>2</sub>O NPs. The higher activity was ascribed to the increase in surface area from 14 m<sup>2</sup>.g<sup>-1</sup> to 25 m<sup>2</sup>.g<sup>-1</sup> as well as the stabilization by the increasing shell thickness. Density Functional Theory (DFT) studies showed that as Cu<sub>2</sub>O is in a metastable state, a thin shell of about 5 nm Cu<sub>2</sub>O transforms into CuO and detaches from Ag. On the contrary, with thicker shells of about 15 nm, Cu<sub>2</sub>O holds Ag and CuO together. This is explained by the large adhesion force between Cu<sub>2</sub>O and CuO or Ag as compared to the adhesion forces between CuO and Ag. The long-term stability of Cu<sub>2</sub>O is still an issue [114]. Interesting non-oxide semiconductors studies include the work of Ma *et al.* Four gap-(Au/AgAu)@CdS nanostructures were synthesized using several Ag and Au shell growth and galvanic replacement cycles. The nanoscale Kirkendall effect yielded nanogaps that resulted in efficient plasmonic coupling. Hence, broad absorption from UV to NIR was created, increasing the H<sub>2</sub> production activity under VIS light ( $\lambda > 420$  nm) 47 times compared to Au@CdS without nanogaps (4.71 vs. 0.10 mmol.g<sup>-1</sup>.h<sup>-1</sup>) [113]. This configuration maintains its activity over 24 h. Nonetheless, CdS is susceptible to photocorrosion, the long-term stability remains an issue. Thus, further modifications may be necessary for true long-term photostability [116].

When selecting a semiconductor shell, an important aspect is the band structure of the material. The characteristics of the metal@SC interface depend on the Fermi level of the metal and the relative position of the band edge potentials of the SC. Also, the induced electronic states at the interface may play a role [117]. For a higher visible light activity, a small band gap (1.6 to 3 eV) is preferred. Yet, the CB level should be high enough and valence band (VB) level should be low enough for the desired redox reactions to be enabled. The plasmonic metal should also be carefully chosen, as selection of plasmonic cores with a strong plasmonic excitement does not necessarily guarantee effective energy transfer and thus activity enhancement of the SC shell. Interband and intraband energy levels also play a very important role in energy transfer from metal to SC. Studies have revealed Cu@TiO<sub>2</sub> lead to higher hot electron injection compared to Au@TiO<sub>2</sub>. Cu@TiO<sub>2</sub> contributes to both interband and intraband energies with a lower Schottky barrier height, whereas Au@TiO<sub>2</sub> has a greater interband energy, but also a greater Schottky barrier height, leading to inefficient hot electron extraction (Fig. 4a-c) [78].

Hence, using an alloy NP with an appropriate energy band structure as a core would be promising [76]. More detailed mechanistic insights are provided in section 3.

Finally, yolk-shell structures can be considered as an extension of core-shell configurations. These consist of a plasmonic core material covered by a hollow shell of, for instance, a SC material (Fig. 4e). Such structures lead to different optical properties as only a fraction of the plasmonic core material is in physical contact with the shell. The cavity volume leads to total internal reflections which enable the incoming light to be further used for photocatalytic reactions [118]. Au@TiO<sub>2</sub> yolk-shell structures were shown to have a reflectance of less than 15% compared to 63% for commercial P25 TiO<sub>2</sub>. This is thus attributed to the internal reflections within the cavity of the yolk-shell structure [119]. For obtaining such structures, one can use a sacrificial material (e.g., organic compounds) to form a temporary shell. The latter will be removed after the real SC shell formation [120]. Apart from sacrificial templating, other mechanisms such as Ostwald ripening and the Kirkendall effect may also lead to a yolk-shell structure [121, 122]. Along with a change in the optical properties, such structures make way for higher specific surface areas. Li *et al.* reported a surface area of 310 m<sup>2</sup>.g<sup>-1</sup> for yolk-shell Au@TiO<sub>2</sub> NRs compared to 56.9 m<sup>2</sup>.g<sup>-1</sup> for Au@TiO<sub>2</sub> core-shell nanoparticles [123]. For more details, one can refer to the outstanding review of Li *et al.* on the complex formation mechanism of yolk-shell nanostructures along with the photocatalytic mechanisms involved [118].



**Fig. 4** Schematic representation of the interband transition and intraband excitation in a) Au@TiO<sub>2</sub> vs. Cu@TiO<sub>2</sub> material system, showing the incident photon to current efficiency (IPCE) as a function of the wavelength, and b) single Cu and Au NPs. c) Contribution of both intraband excitation and interband transition in Cu@TiO<sub>2</sub> contact material system. TEM image of d) Au@TiO<sub>2</sub> core shell nanoparticle and e) Au@TiO<sub>2</sub> nanorod yolk shell structure Adapted with permission from a-c) [78]. CC BY-NC 3.0, d) [105]. CC BY-NC-ND 4.0, e) [123]. Copyright (2015) John Wiley and Sons

### 2.2.3 Metal@polymer NPs

Introducing an organic layer around metal NPs can be done for several reasons such as improving stability, ensuring compatibility with organic solvents, influencing the activity and improving the optical properties. Firstly, a distinction should be made between surface ligands and polymer shells. Surface ligands such as thiols, amines, oleate, xanthate *etc.*, are often used for the colloidal stabilization of plasmonic NPs [124, 125]. Conventionally, plasmonic NPs are synthesized by wet chemistry techniques consisting of metal precursor reduction with reductants like NaBH<sub>4</sub> (fast nucleation) or ascorbic acid (slower growth). The ligand may be added along with or after the reductant. When both are added simultaneously, the ligand may act as shape-directing agent by preferentially binding to a specific crystal facet [126]. Importantly, in some instances, the same reagent

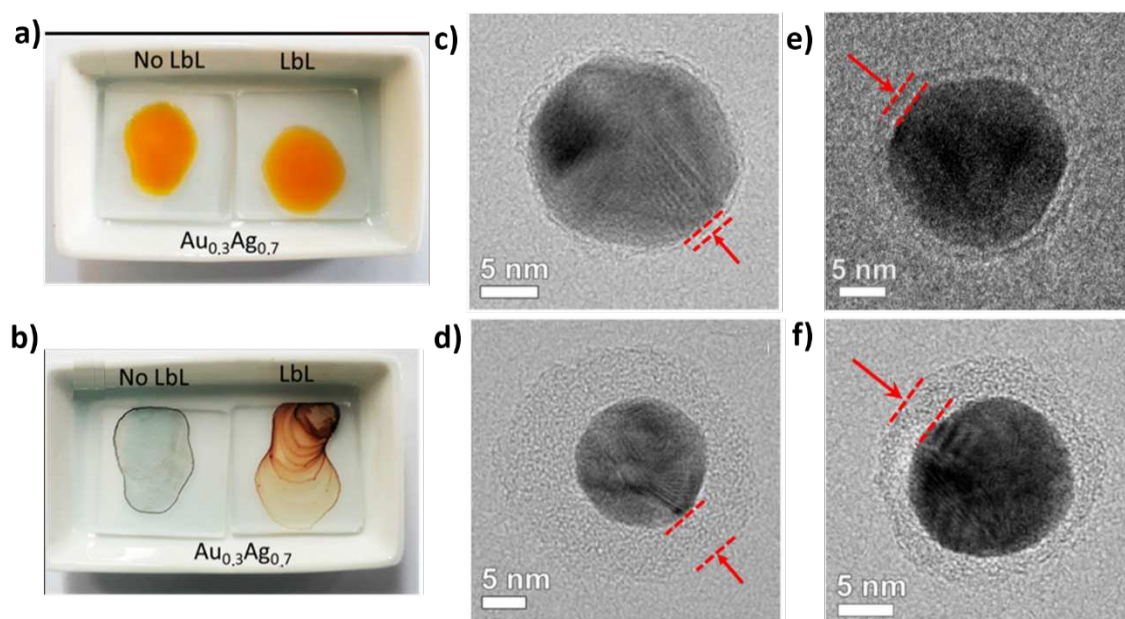
can function as both reducing agent and the stabilizer. *E.g.*, citrate in the modified Turkevich method for the synthesis of Au<sub>x</sub>Ag<sub>1-x</sub> NPs [23, 59, 127, 128]. The longer the alkyl chain, the easier the transfer to organic media, although nonpolar solvents may remain difficult for the suspension of plasmonic NPs [125, 129]. From the perspective of stability, xanthate capped NPs show relatively high oxidative corrosion resistance compared to thiol or oleate capping. In contrast, it is more temperature-sensitive, due to the thermal decomposition of xanthate [125].

Polymer shells, on the other hand, can be created around the NPs by a separate polymerization step [129], or in a simultaneous process of NP and shell formation [130]. Other synthesis methods such as electrospinning provide geometric confinement from nanofibers and therefore bring control over the optical and electrical properties. Chen et al. (2014) prepared Ag@poly(vinyl pyrrolidone) (PVP) nanofibers by coaxial core-shell electrospinning with Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> [131]. The PVP enabled appropriate viscoelastic properties for the nanofiber patterns and protection of Ag, which proved to be more effective than for smaller molecules like citrate [132]. Kvítek et al. also demonstrated the superiority of a PVP coating for Ag NPs in terms of the aggregation resistance, compared to another neutral polymer, poly(ethylene glycol) (PEG), due to the strong bond between Ag and the N atom in the pyrrolidone group [133].

However, the drawback with most organic linkers and single polymers is the lack of shell thickness control [21]. This is of paramount importance as the near-field enhancement (NFE) generated by the excited plasmonic NPs decreases with distance and the coupling of plasmons is strongly distance dependent as well [5]. Electromagnetic near-field hot spots may be generated by placing plasmonic NPs in close proximity of each other (up to  $\times 10^6$  field enhancement for an interparticle distance of  $\sim 1$ -3 nm depending on the dielectric constant of the surrounding medium [5, 84]). Since the reaction rate of photocatalytic reactions is proportional to the square of the near-field, stronger electromagnetic fields are highly beneficial for photocatalytic reactions (cfr. section 3.1.1) [5]. In order to meet these requirements of accurate control over thin shell thicknesses, the Layer-by-Layer (LbL) technique has been applied where alternately different polymer layers are deposited around a metal core. Lisunova *et al.* for example applied water soluble PVP and poly(methylacrylic acid) (PMAA) layers on Ag nanocubes based on hydrogen bonding. A buffered pH 3.5 environment ensured PMAA acted as an H bond donor and PVP as an H bond acceptor. Excess polymers were removed by careful centrifugation. This enabled nanometer level control over the shell thickness [134]. Schneider and Decher introduced the use of polyelectrolytes to 13.5 nm Au NPs, namely the positively charged poly(allylamine) hydrochloride (PAH) and negatively charged polysodium-4-styrenesulfonate (PSS). Up to at least 20 layers could be applied based on electrostatic attraction with minimal particle aggregation (>95% NP recovery), yielding 7.5 nm shells [135]. Furthermore, to prepare eventual scale-up, they determined the range of practical concentrations to avoid bridging flocculation [136]. Asapu *et al.* further improved the LbL protocol by replacing PSS by the cheaper polyacrylic acid (PAA), also lowering the deposition time from 12h to 0.5h. They were able to deposit layers on 20 nm Ag [21, 137] and Au [138] nanospheres with sub-nanometer precision. These LbL stabilized Ag nanoparticles were shown to be ultra-stable in harsh reactive environments (hot air, and NaCl solutions) [22]. A similar LbL approach is also extended to bimetallic AuAg nanoparticles wherein the nanoparticles were proved to be stable after aging the sample for 10 months. Stability of LbL stabilized against bare bimetallic AuAg nanoparticles in hot air can be observed in Fig. 5a-b [139]. Note that due to the centrifugation steps to discard the excess polymers, LbL techniques are mainly suited for bigger NPs. It is considered that NPs smaller than 7 nm would lead to disproportionate centrifugation losses.

The aforementioned polymers are however all non-conductive which excludes the potential transfer of hot electrons (see also section 3.1.1). Therefore, the use of conductive polymers such as poly(3,4-ethylene dioxythiophene), poly(pyrole) and poly(aniline) (PANI) have also been studied [130, 140]. Yang et al. assembled Au-TiO<sub>2</sub> using PANI. They proposed that PANI can also act as an electron donor because of the electron excitation from  $\pi$  to  $\pi^*$  orbitals, induced by visible light [141]. Xing et al. designed a kinetically controlled in-situ polymerization protocol for aniline with sodium dodecyl

sulphate (SDS) on the Au surface. This one-step synthesis enables control over the shell thickness by adjusting the polymerization time. Shells on 22 nm Au nanospheres grew up to 14 nm after 4 h. A further increase (14-92 nm) was achieved after multiple growth cycles by this ‘mix-and-wait’ technique. Furthermore, the formation of nanochains of 2-20 NPs could be controlled by the timing of SDS addition [130]. Asapu et al. compared varying thickness of PANI shells against polymer shells of PAH and poly(styrene sulfonate) sodium (PSS) synthesized using LbL strategy (Fig. 5c-f). Conductivity of PANI shells was effectively proven using conductive tip atomic force microscopy [84]. Later, this synthesis protocol has also been applied for other particles such as Au nanocubes [142] and Ag nanospheres [143].



**Fig. 5** LbL stabilized and bare bimetallic AuAg NPs a) before and b) after treatment at 100 °C. TEM image of varying polymer shell thickness of Au@PANI core shell NP as a function of time from c) 30min to d) 180 min. TEM image of LbL stabilized Au@polymer core shell nanoparticle with increasing shell thickness by varying number of layers from e) 4 layers to f) 12 layers. Adapted with permission from a-b) [139]. CC BY 4.0, c-f) [84]. Copyright (2019) American Chemical Society

The addition of a polymer shell also affects the optical properties due to the change in the dielectric environment [144]. As mentioned before, an increasing refractive index yields spectral red-shifts, while the opposite leads to spectral blue-shifts. Thus, small red-shifts (1-3 nm) in the UV-VIS spectra can be observed with the formation of each PAH and PAA polymer layer over AuAg alloy nanospheres in the LbL process [139]. On the other hand, Lisunova *et al.* demonstrated blue-shifts after the addition of PVP or PMAA. When the fluorescent poly(*p*-phenylene ethynylene) was coated as final layer on this LbL assembly, the actual shell thickness did not seem to change the fluorescence peak positions [134]. Recently, more research has been done on ‘plasmonic switching’ where shifts are quickly induced for metal@polymer NPs. Hence, Lu *et al.* (2016) showed that when applying small potentials (-0.1 - +0.5 V vs.  $V_{AgCl|Ag}$ ), large plasmon shifts up to 150 nm can be attained for both colloidal Au nanospheres, NRs and nanobipyramids covered by PANI. The small potential changes enable swift switching in less than 10 ms between the half-oxidized and fully reduced states, without degradation of the PANI shell. This is 20,000 times faster than for proton doping and de-doping by adding acids or bases [145]. Finally, for certain volume phase transitions (VPT) polymers, the optical properties of metal@polymer NPs can be adjusted easily by varying an external parameter [146]. *E.g.*, poly(*N*-isopropylacrylamide) (PNIPAM) is a thermo-responsive polymer that undergoes a VPT in aqueous media. The condition for this is a temperature larger than its lower critical solution temperature (~32 °C). Hence, the wavelength dependent dielectric constant peak increases and shifts from 555 nm at 23 °C to 587 nm at 44 °C [146]. These features may be advantageous for *e.g.* sensing applications. For more information about

sensing, optical data storage, imaging and photothermal gels applications using plasmonic metal-polymer nanohybrids, the interested reader is referred to the outstanding review of Pastoriza-Santos *et al.* [147]. Metal@polymer NPs in photocatalytic applications will be further discussed in section 3.2.

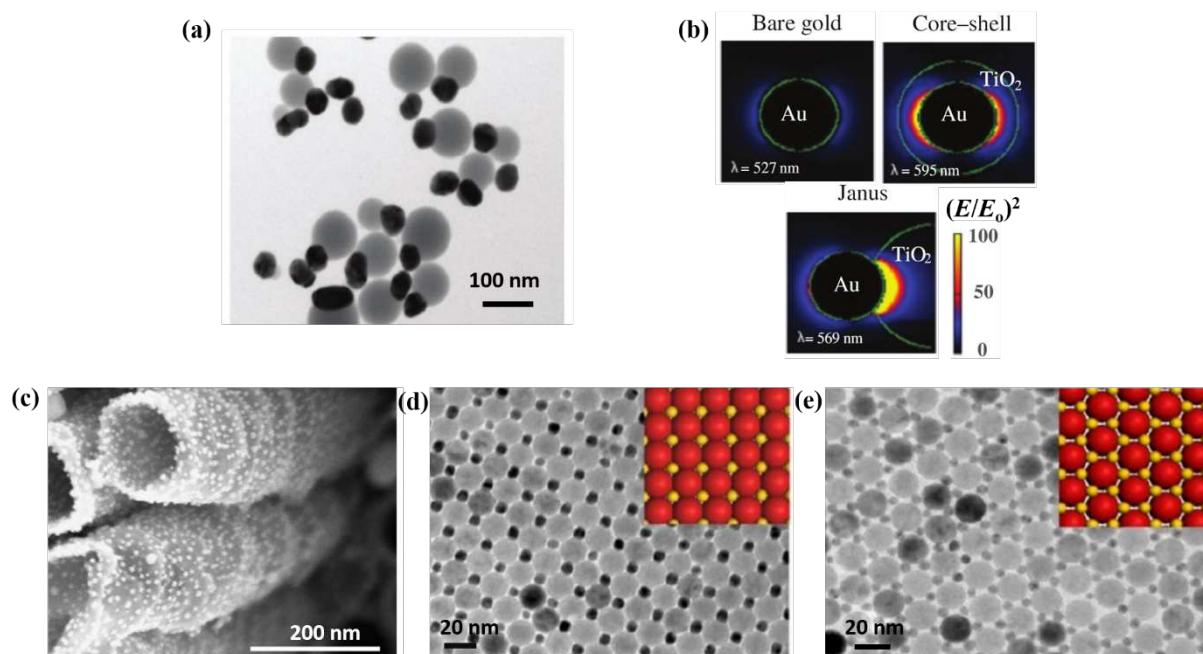
## 2.3 Other structures

Combination of plasmonic materials with another functional material may also lead to other structures than conventional alloys or core-shell NPs. For instance, Janus nanoparticles are formed when the plasmonic part has a partial interface with another material, either metal or semiconductor of a comparable size [148]. Partially covering shells are engineered to expose the plasmonic metals to the chemical environment. The interface can be the most reactive part of the plasmonic photocatalyst as the energy transfer from plasmons to the catalyst would be theoretically considered to be the highest directly at the interface. Further, it decreases as the shell thickness increases [149]. Au-TiO<sub>2</sub> usually dominates the field of metal-metal oxide-based Janus materials in photocatalysis (Fig. 6a). Such Janus structures can also be synthesized for various shapes of plasmonic NPs such as NCs and NRs [150]. Fig. 6b shows how Janus NPs can create a higher near-field enhancement at the Au-TiO<sub>2</sub> interface as compared to core-shell NPs. Synthesis of such nanoparticles, going from Janus to core-shell, can be controlled by varying the volume of TiO<sub>2</sub> precursor solution [148]. Templated methods have also been used to synthesize Janus nanostructures [151].

Since a conformal shell can cause significant plasmon damping, some studies developed a method to selectively deposit catalytic material at the hot spots of a plasmonic antenna, *e.g.* the edges of cubes, the tips of a rod *etc.* [152, 153]. Partial shell formation on the antenna retains the strong plasmonic response, thus leading to higher enhancements in reactions compared to fully shielded particles. Electron energy loss spectroscopy (EELS) maps of Au octopods with AuPd tips show spatially localized resonances around the tips and edges relating to different plasmon modes [154]. Protocols for similar Au-semiconductors heterostructures have been designed as well, *e.g.* CdSe NRs with Au tips. Introducing the Au tips resulted in more than 27% increase in the photocatalytic quantum efficiency for hydrogen generation [155]. Lee *et al.* showed furthermore that the deposition of Cu<sub>2</sub>O on hexaoctahedral Au vertices resulted in twice as high TOFs for CO oxidation under VIS light illumination compared to their core-shell counterpart [156]. High charge transfer efficiency is also observed for flower-shaped Au-ZnO hybrid Janus type NPs [157]. The fact that only Au has been used as a plasmonic metal in Janus structures is due to the limitations offered by this structure. Other plasmonic metals such as Ag, Cu and Al would oxidize too easily in a Janus structure due to the partial exposure of the metal to the (oxidative) environment. More insights on the effect of several configurations on the actual photocatalytic activity are described in section 3.2.

In similar structures, the plasmonic or the non-plasmonic part is much smaller than the other. In those cases, the smaller part can be present in a large number over the surface of the bigger core [158–161]. The advantage of such structures is quite similar to that of Janus structures. For instance, when a metal oxide is decorated with Au NPs, such as in Fig. 6c, the plasmonic NPs in large numbers give rise to the plasmonic coupling effect with further enhancement in the plasmonic excitation [162]. Apart from the usual plasmonic enhancement in photocatalysis by such structures [163, 164], the broader spectral bandwidth facilitates solar energy harvesting applications such as solar seawater desalination [165, 166]. When plasmonic NPs are combined with a magnetic core in a similar fashion, an additional magnetic functionality can be exploited in their applications [159, 167]. Similar plasmonic incorporated structures can be made with different materials such as ZnO, WO<sub>3</sub>, WS<sub>2</sub>, MoS<sub>2</sub> *etc.* [168–173]. Simple photo-impregnation and electrodeposition of plasmonic nanoparticles are widely known techniques for the synthesis of such hybrid NPs [128, 174]. Conversely, a plasmonic core can also be decorated with non-plasmonic smaller clusters for different targeted applications. For instance, Au NPs decorated

with clusters of Pt [175, 176], Pd [177] *etc.*, are interesting for plasmon-enhanced catalytic applications.



**Fig. 6** a) Transmission electron microscopy (TEM) images of Janus Au-TiO<sub>2</sub> NPs b) Near-field enhancement map showing maximum enhancement for Janus NPs compared to bare Au and Au@TiO<sub>2</sub> core-shell NPs, c) Scanning electron microscopy (SEM) image of Au NP decorated TiO<sub>2</sub> nanotubes ((T)NTs), d) TEM image of binary superlattice of Au and Fe<sub>2</sub>O<sub>3</sub> NPs in 1:1 and e) 1:3 Au:Fe<sub>2</sub>O<sub>3</sub> ratio for catalytic applications. Adapted with permission from a-b) [148]. Copyright (2012) John Wiley and Sons, c) Royal Society of Chemistry [162]; permission conveyed through Copyright Clearance Center, Inc. , d-e) [178]. Copyright 2013 American Chemical Society

Although they are difficult to hybridize due to their tendency to aggregate, single atoms and atomic clusters (<2 nm) form another peculiar class of plasmonic materials. Plasmonic atomic clusters have unique properties due to quantum confinement effects that occur at such small sizes [179–184]. Zheng *et al.* stated that sub-nanometer sized clusters have discrete energy levels. They are too small to contain a continuous density of states which is the basis of plasmonic characteristic of free electron metal NPs [182]. The jellium model was used to predict plasmon width and nanocluster transition energy ( $E_{\text{gap}}$ ) and it was identified that both these properties scale inversely with the cluster radius. As the number of atoms in the cluster increases, the energy gap decreases, quantitatively fit by the following expression for small nanoclusters (<25 atoms) (eq. 1):

$$E_{\text{gap}} = E_{\text{Fermi}}/N^{1/3} \quad (1)$$

With  $E_{\text{gap}}$  the nanocluster transition energy,  $E_{\text{F}}$  the Fermi energy of the metal and N the number of atoms.

Due to such quantum effects, plasmonic metal clusters show a different photocatalytic behavior. The high ratio of surface atoms in such metallic clusters allows for a better interaction with the reactants. However, the high availability of active surface sites does not always lead to a suitable catalyst for a specific product. The number of atoms within the atomic cluster plays an important role because of the changing physical properties at the discrete energy levels, in turn having an effect on the kinetics of the reaction under consideration [185–187]. Metal clusters have a strong tendency to migrate and aggregate into NPs of larger size. Thus the synthesis of such atomic clusters and more hybridized derivatives is also far from easy as it is difficult to stabilize a precise number of atoms without coalescence [188]. Cluster beam deposition (CBD) is one such solvent-free technique used to synthesize alloyed and core-shell atomic or nanoclusters. Here, aggregates formed in gas phase are processed in a molecular beam source. Hence, a collimated beam of particles is generated which can then be intercepted by a substrate to form thin films [189]. To characterize such atomic clusters in



detail, one would need state of the art synchrotron facilities [188, 190]. Liao *et al.* have applied the CBD method for depositing 2-8 monolayer equivalents of Au nanoclusters on a TiO<sub>2</sub> surface for self-cleaning applications under pure visible light [180].

Plasmonic nanoclusters can also be incorporated in zeolites, covalent organic frameworks (COFs) and metal organic frameworks (MOFs) due to the high porosity and surface areas of the latter (up to 10<sup>3</sup>-10<sup>4</sup> m<sup>2</sup>.g<sup>-1</sup>) [191–193]. By combining zeolites, COFs and MOFs with plasmonic materials, another class of plasmonic hybrids is created. In a recent study by El Roz and co-workers, ZX-Bi zeolites played the role of support material to grow Ag clusters. The <1 nm clusters being in close proximity inside the zeolite cages tends to exhibit unique optical properties. Here the zeolites do not show any methanol photooxidation but the photocatalysis tends to occur directly on surface of the Ag clusters with a methanol photooxidation rate of 49.60 mmol.g<sup>-1</sup>.cm<sup>-2</sup> [192]. However, next to their role as support materials, zeolites, COFs and MOFs may also act as photocatalysts, similar to metal@SC systems [192, 194, 195]. In addition, these highly porous structures can have selective functional groups. For example, in the case of aluminum crystals enclosed with MIL-53 as a core-shell structure, MIL-53 enhances CO<sub>2</sub> adsorption by five times due to the hydroxyl groups present in the MOF structure. It also enhances CO<sub>2</sub> reduction by a factor of 2 [196].

Apart from these inherently hybrid nanostructures, plasmonic enhancement can also be achieved extrinsically by ordered hybrid systems. For instance, binary superlattices of a plasmonic and another functional NP are hybrid plasmonic systems extending over large areas [178, 197, 198]. Fig. 6d-e show two conformations of a binary Au and Fe<sub>2</sub>O<sub>3</sub> superlattice. Ordered 2D layers of such hybrid structures possess tremendous potential for different applications such as catalysis, sensing *etc.* Chemical reactions can be locally enhanced in a nanogap between plasmonic and catalytic antenna reactor systems. These systems consist of (at least) two separated NPs: a plasmonic antenna which collects light, and a catalytic reactor which facilitates the reaction [199]. Each NP retains its individual electronic structure as long as there is no electron tunneling (true only for a separation of greater than 1 nm) [200].

### 3. Hybrid plasmonic nanostructures in Photocatalysis

Later in this review article, the potential of the aforementioned classes of plasmonic hybrids will be discussed for several major photocatalytic applications such H<sub>2</sub> generation, pollution abatement and CO<sub>2</sub> conversion. But first, a closer look is briefly taken into the underlying mechanisms of hybrid plasmonic enhanced photocatalysis. Since this review aims at plasmonic hybrids and their role in photocatalysis, the interested reader is referred to the excellent review of Ma *et al.* for a more detailed discussion of the underlying plasmonic physics [201]. Here, also special attention is given to how these hybrids are helpful in the elucidation of the right mechanism.

#### 3.1 Plasmon-enhanced photocatalytic mechanism

##### 3.1.1 General aspects on photocatalysis and the role of plasmonics

Over the past four to five decades, a large variety of semiconductor photocatalysts have been studied that generate electron–hole pairs upon the absorption of light with an energy content large enough to overcome the SC band gap (Fig. 7a). These photogenerated charge carriers (*i.e.* holes in the valence band and electrons in the conduction band) migrate to the surface of the photocatalyst, where they initiate (a cascade of) redox reactions forming reactive oxygen species (ROS). Among all SCs studied, TiO<sub>2</sub> has been investigated more extensively than any other material, due to its high chemical and thermal stability, appropriate conduction band and valence band positions, low cost and non-toxicity [202]. However, as mentioned before, the photoactivity of TiO<sub>2</sub> is hampered by a large band gap value (*ca.* 3.2 eV) which restricts its use to applications involving UV light only [201]. In that context, plasmonic nanostructures have emerged as a promising solution for a more optimal utilization of the solar spectrum due to the presence of the LSPR phenomenon. Unlike conventional light absorption

processes by molecular sensitizers or interband excitation of metals, LSPR involves a *multi*-electron excitation that concentrates the absorbed light energy at the NP surface in the form of intense electric fields [203]. Thus, plasmonic nanostructures can work as nano-antennas in light-driven processes to capture electromagnetic energy. Direct potential applications of this phenomenon (other than photocatalysis), are several orders of magnitude enhancement of IR and Raman signals, enabling highly sensitive surface-enhanced infrared absorption (SEIRA) [204] and SERS [205].

Once a plasmon is excited, it can decay in two competitive ways: through re-emission of photons, or by non-radiative relaxation through electron–electron, electron–phonon, electron–surface, or electron–adsorbate scattering [206–208]. The re-emission phenomenon is captured by the classical electromagnetic framework as the elastic scattering of an electromagnetic wave. Hot electrons that are not in thermodynamic equilibrium with the atoms in the material, are generated during the non-radiative relaxation process, primarily through electron–electron scattering [201]. The intense LSPR energy generated near the surface of the plasmonic NPs can then be transferred to a SC photocatalyst in contact with the plasmonic NPs. In this way, the photocatalytic activity of the SC is improved by the plasmonic NPs ‘indirectly’, as will be further discussed. On the other hand, the LSPR energy can also be transferred ‘directly’ to molecules adsorbed at the surface of the plasmonic NPs [209]. In that case, the plasmonic NPs thus simultaneously act as the light absorber and as the catalytic active site. An increased photoactivity, as well as selectivity, have been demonstrated for reactions based on this direct plasmonic reaction concept [210]. Three different main mechanisms have been proposed to explain this direct activation of adsorbed molecules by plasmonic excitation under visible light, as illustrated in Fig. 7b for the specific case of CO<sub>2</sub> activation:

*(i) NP charging/discharging* ((i) in Fig. 7b): Plasmonic NPs are charged by steady-state excitation in the presence of a hole scavenger, and subsequently discharged by transferring photoexcited electrons to the lowest unoccupied molecular orbital (LUMO) of the metal (M)–CO<sub>2</sub> complex, thus forming CO<sub>2</sub><sup>\*-</sup> or a related species.

*(ii) Chemical interface damping* ((ii) in Fig. 7b): A fraction of the hot electrons can coherently scatter into the unoccupied states of the adsorbed CO<sub>2</sub> molecule [211], leading to vibrational activation of CO<sub>2</sub> for further reaction [212].

*(iii) Direct photoexcitation of the M–CO<sub>2</sub> complex* ((iii) in Fig. 7b): CO<sub>2</sub> molecules adsorbed onto a plasmonic metal surface are activated through direct excitation of the hybridized electronic states of the M–CO<sub>2</sub> complex [213].

As mentioned earlier, the activity of a semiconductor photocatalyst can also be improved ‘indirectly’ by coupling it to a plasmonic NP. This is the most common and widely encountered type of plasmonic photocatalysis, and has been demonstrated for various metal/SC composites such as metal/TiO<sub>2</sub>, metal/ZnO, metal/Fe<sub>2</sub>O<sub>3</sub>, metal/CdS *etc.*, with photocatalytic applications in organic pollutant degradation, hydrogen production and CO<sub>2</sub> conversion, amongst others [214–217]. The main mechanisms that have been proposed to determine this plasmon-enhanced SC photocatalytic activity include:

*(i) Promoting charge separation in the SC* ((i) in Fig. 7c). When a junction between an *n*-type SC such as TiO<sub>2</sub> and a metal NP is formed, a Schottky barrier is created at the equilibrated interface, which limits the reverse metal to SC transfer [218]. This is also known as the electron sink effect. Although this is not a plasmonic effect as such, it may still contribute significantly to the overall efficiency enhancement.

*(ii) Hot electron injection from plasmonic metal NPs to the SC conduction band* ((ii) in Fig. 7c). LSPR-mediated hot electrons and holes produced and separated at the interface between the

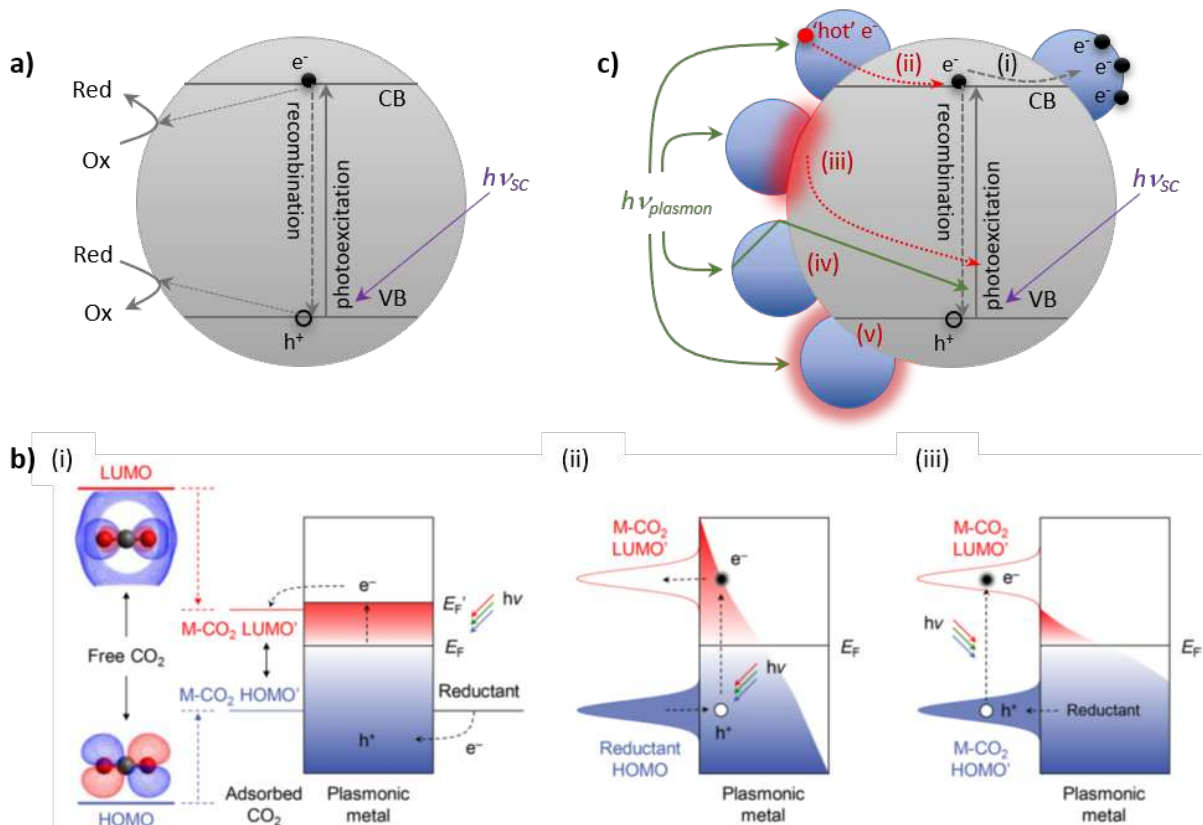
plasmonic metal NP and the SC, diffuse to the SC surface to participate in the further photocatalytic reaction. It is important to understand that this mechanism absolutely requires that the SC is in electrochemical contact with the plasmonic metal [219–221].

(iii) *Near-field enhancement in the SC* ((iii) in Fig. 7c). The strong plasmon-induced electric field near the plasmonic metal surface can significantly enhance the rate of photoexcitation in the nearby SC. In this case it is crucial that the SC absorption spectrum and the LSPR spectrum overlap [222].

(iv) *Increase of the optical path through resonant scattering* ((iv) in Fig. 7c). Especially for large metal NPs (sizes comparable to the light wavelength [4]), the contribution of scattering to the total extinction becomes important. The more efficient scattering of incident light creates the effect of a mirror that prolongs the optical path length of incident photons throughout the SC. Hence, the probability of successful photo-excitations increases [5].

(v) *local heating* ((v) in Fig. 7c). The non-radiative damping of the excited plasmons eventually leads to energy dissipation to the surrounding environment as heat. Depending upon the intensity of radiation and the thermal properties of the surrounding, this can result in temperature rise in the vicinity of the NPs. This effect is mainly important for ordered NP assemblies that can exhibit enhanced absorption by plasmonic coupling and high particle density per unit area with the additional condition that the incident irradiance is sufficiently strong. Thus, the heating effect is less dominant for single NPs and under ambient conditions [223].

In what follows we will mainly focus on plasmon-enhanced SC photocatalysis as this also offers high impact real-life applications under ambient conditions. Indeed, while several excellent reports are available on direct plasmon-catalyzed reactions, these systems typically rely on more stringent reaction conditions, such as high irradiance levels (*e.g.* up to 20 sun equivalents or lasers), dedicated optical hardware (parabolic reflectors, lenses, *etc.*) or involve the interplay with heat [209].



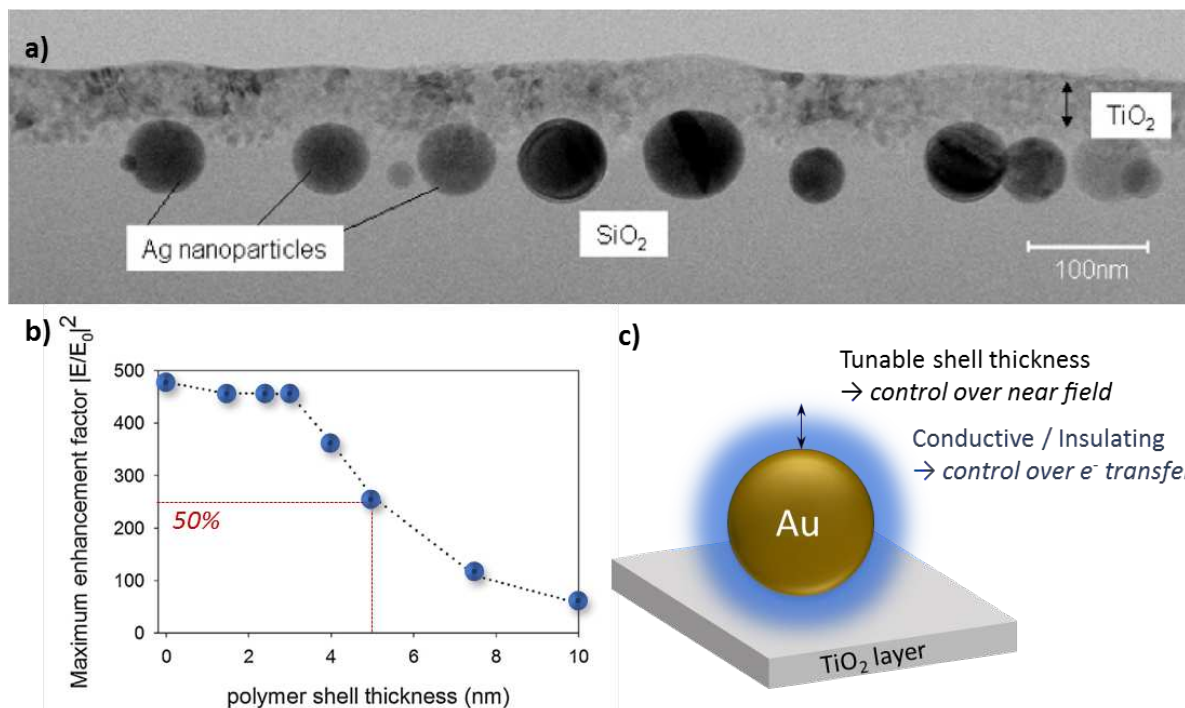
**Fig. 7** Schematic representations of a) the activation of a SC photocatalyst, b) the potential mechanisms driving direct plasmonic catalysis illustrated for CO<sub>2</sub> activation: (i) charging/discharging of the plasmonic NP, (ii) chemical interface damping, (iii) direct photoexcitation of the metal-CO<sub>2</sub> complex, c) the potential mechanisms driving plasmon-mediated SC photocatalysis: (i) the electron sink effect, (ii) hot electron transfer, (iii) near-field enhancement, (iv) resonant scattering, (v) local heating. Adapted with permission from b) [224]. Copyright 2017 American Chemical Society

### 3.1.2 Mechanistic studies using hybrid plasmonic nanostructures

Unraveling the precise plasmonic-SC interaction mechanism driving the photocatalytic reactions is quite challenging. The relative importance of the various potential pathways (cfr. Fig. 7c) is still a matter of ongoing debate. The radiative damping of the plasmons results in scattering, *i.e.* energy loss to the surrounding, while non-radiative damping leads to generation of energetic hot electrons which can enhance photocatalytic reactions. In most cases, however, the loss by scattering can be safely neglected, as the scattering component contributing to the total extinction of a plasmonic metal NP only becomes important for particle sizes well over 50 nm [225], while in the majority of studies much smaller nanostructures are involved. In addition, for the local heating effect to occur effectively, high incident irradiance levels are required, as provided by lasers, powerful solar simulators or light concentrators [226, 227]. Using a standard solar simulator with a maximal output of 1-2 Sun(s), or generic 300-500 W Xe-sources with optical filters, the temperature rise around plasmonic NPs in aqueous or gaseous media is usually insignificant [228]. Hence, in the majority of cases, this leaves either hot electron transfer, near-field enhancement, or an interplay of both as most likely mechanisms.

The existence of the hot electron transfer mechanisms has been demonstrated by the Beller group [229], as well as our team [230], by means of Electron Paramagnetic Resonance (EPR) studies on traditional noble metal-TiO<sub>2</sub> composite materials. Excitation of the plasmonic composite by a visible light laser resulted in the detection of unpaired electrons associated with the TiO<sub>2</sub> phase, which was not the case when exciting the pristine SC alone. This evidences that the electrons originate from the plasmonic noble metal NP and are transferred to the TiO<sub>2</sub> conduction band.

The existence and influence of the near-field enhancement effect, on the other hand, has been convincingly demonstrated by the pioneering work of Awazu et al., who also introduced the term 'plasmonic photocatalysis' for the first time. They used a hybrid plasmonic composite in which Ag@SiO<sub>2</sub> core-shell NPs are deposited on a SiO<sub>2</sub> substrate and subsequently covered by a photocatalytic TiO<sub>2</sub> layer (Fig. 8a) [231]. In this structure, the SiO<sub>2</sub> shell acts as a spacer layer between the plasmonic metal and the SC, which was varied in thickness between 5 and 100 nm. While the insulating nature of the SiO<sub>2</sub> shell inhibits the transfer of (hot) electrons, it was shown that for thin shells a strong near-field enhancement was achieved, which resulted in the greatest enhancement of the photocatalytic activity, while for SiO<sub>2</sub> shells as thick as 100 nm, the near-field was completely repressed, and the resulting activity was similar as for the pristine TiO<sub>2</sub> photocatalyst. The presence of a thin shell may even intensify the near-field compared to bare plasmonic NPs, due to the polarizability of the shell electrons. This polarizability increases with the dielectric constant, favoring most shell materials over air or liquid environments for strong metal-dielectric coupling [232]. The ability of a nanoshell to gradually repress the near-field enhancement brought about by plasmonic NPs has also been demonstrated experimentally as well as theoretically for the case of Ag@polymer core-shell NPs of varying shell thickness [21, 233]. It is shown that for a polymer shell of 3 nm, the near-field enhancement protruding beyond the shell is well retained when compared to a bare Ag 18 nm nanosphere, while it is reduced already by 50% for a shell as thin as 5 nm (Fig. 8b).



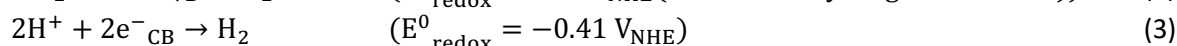
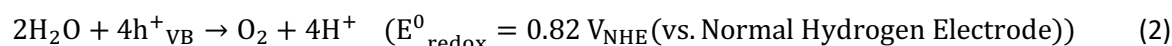
**Fig. 8** a) the plasmonic hybrid TiO<sub>2</sub>/Ag@SiO<sub>2</sub>/SiO<sub>2</sub> structure used by Awazu et al. b) Simulated near-field enhancement of Ag@polymer NPs as a function of shell thickness. Adapted with permission c) schematic representation of the experimental strategy used by Asapu et al. for disentangling hot electron transfer and near-field enhancement effects. Adapted with permission from a) [231]. Copyright 2008 American Chemical Society, b) [21]. Copyright 2017 Elsevier.

Inspired by the properties of the core-shell concept described above, Asapu et al. proposed a versatile experimental strategy to disentangle the relative contributions of hot electron transfer and near-field enhancement based on metal@polymer core-shell NPs of which the shell thickness as well as the shell's conductive nature can be tuned (Fig. 8c) [84]. Au@polymer NPs with electrically insulating shells of varying thicknesses were prepared using a controlled Layer-by-Layer approach, while Au@polymer NPs with electrically conductive shells of varying thickness were prepared using time-dependent in-situ polymerization of PANI. Hence, by altering the conductive nature of the shells, the existence of hot electron transfer could be regulated, while the tunability of the shell thickness enabled to control the extent of near-field enhancement. This way, both phenomena could be selectively repressed or evoked. By corroborating SERS measurements, theoretical field simulations, and photocatalytic activity measurements, it was concluded that for the tested photocatalytic reaction (stearic acid degradation), the near-field enhancement mechanism clearly played a dominant role [84]. However, the strategy has not yet been applied to other photochemical reactions, which may yield a different outcome.

## 3.2 Applications

### 3.2.1 H<sub>2</sub> evolution

An important photocatalytic application of plasmonic NPs is the evolution of green H<sub>2</sub> from water through the hydrogen evolution reaction (HER) (eq. 2-3) [234].

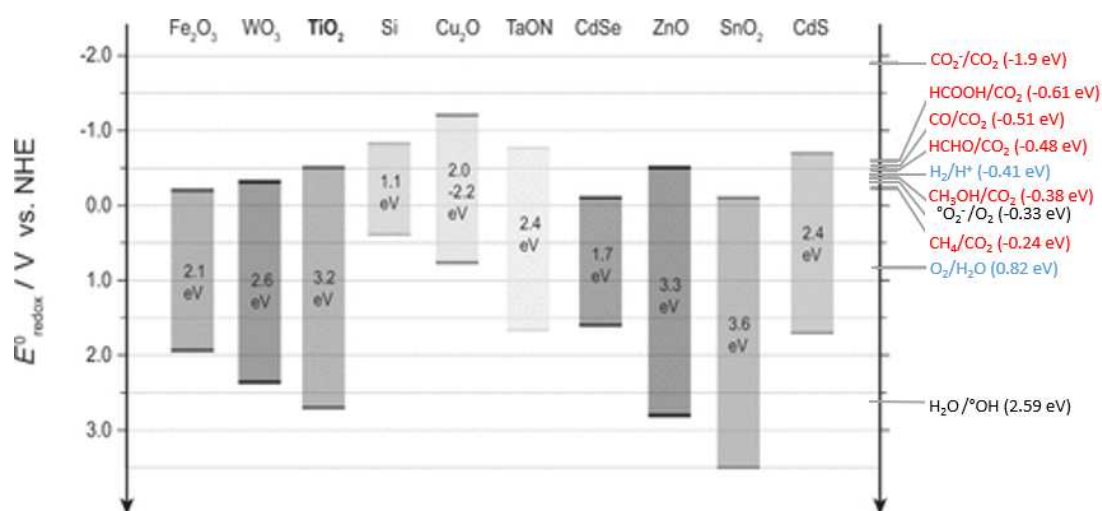


With  $E^0$  the standard redox potential

For this, core-shell structures containing SCs are the most studied class of hybrid plasmonic materials [148]. A comprehensive overview of selected pioneering and recent studies of hybrid HER photocatalysts is given in Table 1, reporting on the reaction conditions, activity and stability.

Unfortunately, an accurate comparison among different studies is hampered, since the experimental conditions (*e.g.* the light intensity) are often not mentioned in sufficient detail, nor standardized.

Earlier, mostly Au@CdS chalcogenides were investigated due to the small band gap and favorable band edge positions of CdS (Fig. 9). The CB level allows H<sup>+</sup> reduction (-0.7 < -0.41 V<sub>NHE</sub>). While the small band gap (2.4 eV) results in broad overlap with LSPR of Au, leading to efficient use of the near field mechanism, next to hot electron transfer [235]. The H<sub>2</sub> production activity is often further boosted using co-catalysts (*e.g.* large Ag@SiO<sub>2</sub> antennas [236]), and morphological optimization (*e.g.* introduction of nanogaps in (AuAg/Ag)@CdS [113], see 2.2.2)



**Fig. 9** Band gaps and VB/CB energy levels of common photocatalysts, shown with the relevant redox potentials for water splitting (blue) and CO<sub>2</sub> conversion (red) and ROS generation half reactions (black). Adapted with permission from [235]. Copyright 2013 John Wiley and Sons, Royal Society of Chemistry [237]; Permission conveyed through Copyright Clearance Center, Inc. and [238]

However, Cd species are notorious for being toxic and susceptible to photocorrosion [116]. Even though it is shown that the Au core may partially prevent the latter by hole scavenging [112], more sustainable alternatives are highly requested. Ha *et al.* introduced the less toxic Au@Cu<sub>2</sub>FeSnS<sub>4</sub>, even though these Cu<sub>2</sub>FeSnS<sub>4</sub> species still remain relatively unknown [239]. On the contrary, a vast amount of literature exists on more sustainable, stable SCs such as g-C<sub>3</sub>N<sub>4</sub> [115, 240] and especially TiO<sub>2</sub> [148, 241, 242]. These are often combined with plasmonic NPs to overcome their low light absorption capabilities due to relatively large band gaps (*resp.* 2.7 and 3.2 eV). Pioneers for the synthesis of metal@C<sub>3</sub>N<sub>4</sub> were Zhu and co-workers [115]. Via their facile reflux treatment of C<sub>3</sub>N<sub>4</sub> nanosheets, they produced 10 wt% Ag@C<sub>3</sub>N<sub>4</sub> photocatalysts which yielded 30 times higher H<sub>2</sub> evolution rates (~25 μmol.g<sup>-1</sup>.h<sup>-1</sup>) than pure C<sub>3</sub>N<sub>4</sub> under VIS light (λ > 420 nm). Metal@TiO<sub>2</sub> core-shell nanostructures for H<sub>2</sub> evolution are studied even more extensively. They also proved to be superior to catalysts consisting of metal particles simply deposited on the TiO<sub>2</sub> surface [243, 244]. Further morphological optimization within the core-shell structure may enhance the H<sub>2</sub> production rate even more. *E.g.*, Au@mesoporous TiO<sub>2</sub> hollow nanospheres core-shell (yolk-shell) structures outperform Au deposited on TiO<sub>2</sub> spheres (69.77 vs. 37.80 mmol.g<sup>-1</sup>.h<sup>-1</sup>). The mesoporous hollow nanospheres facilitate internal multiple light scattering, greatly enhancing the light absorption by Au [244].

Other studies indicate that Janus metal-SC structures may be more optimal for H<sub>2</sub> production than the core-shell equivalent, due to strongly localized near-fields [148]. Note again that for efficient use of these near-fields, the absorption spectra of both metal and SC should overlap (see 3.1.1) [4]. Seh *et al.* synthesized non-centrosymmetric Janus Au-amorphous TiO<sub>2</sub> structures, with a HER activity of 56 mmol.g<sup>-1</sup>.h<sup>-1</sup> under VIS light illumination (irradiance not mentioned). This value was about twice the rate of the core-shell equivalent [148]. Lou *et al.* also found a 5 times higher H<sub>2</sub> production rate for Pt

edged Au triangular nanoprisms compared to Au triangular nanoprisms completely covered by Pt (0.167  $\mu\text{mol}\cdot\text{h}^{-1}$  vs. 0.031  $\mu\text{mol}\cdot\text{h}^{-1}$  under VIS-NIR illumination) [245]. On the other hand, a completely full shell surrounding a metal core is more beneficial for stability purposes, especially when working with harsher water sources such as wastewater or saline seawater [234, 246]. An interesting solution might be the Janus composite of (stable) metal@polymer core-shell particles and a chemostable SC like  $\text{TiO}_2$ . Since the strength of the localized fields will be affected by the polymeric shell, accurate shell thickness control is of paramount importance. Hence, the LbL strategy of Asapu et al. (see 2.2.3) seems promising [21]. Besides, LbL stabilized Ag and AuAg NPs already proved to be stable in saline media [21, 139].

Finally, as mentioned earlier, water splitting is also feasible with purely metallic photocatalysts. Often Pt is involved in these metal hybrids for its excellent electron sink and  $\text{H}_2$  evolution capacities [247]. It benefits from its low Fermi level, large work function and special catalytic sites for  $\text{H}_2$  formation. Compared to Pt; Au, Ag and Cu have a lot weaker metal-H bonding capacity due to the rather high occupancy of antibonding 1s hydrogen and d metal states [248]. On the other hand, Pt yields a weaker LSPR signal [249, 250]. Hence Pt is regularly combined with plasmonic metals like Au, both as alloys or core-shell structures [245]. Nonetheless, these metal hybrids are often combined with SCs to boost the  $\text{H}_2$  generation. Hung *et al.* claimed the combination of SCs with core-shell Au@Pt to be superior to an alloy approach due to a better charge separation and migration. They contributed this to an extra electric field caused by the descending Fermi level in the well-defined Au@Pt nanostructure. This could facilitate the electron transport towards the reagent [247]. Bian et al. also noticed that their homogeneous AuPt alloys do not show a plasmon band in the VIS range [241]. A study involving MOFs, comparing Pt@MIL-125/Au and Pt/MIL-125/Au, also found that spatial separation between Au and Pt may be beneficial for  $e^-/h^+$  separation. Upon illumination with VIS light, the former yielded  $\text{H}_2$  production rates of 1.743  $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , while the latter with Pt and Au touching at the surface could only achieve 0.161  $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  [251]. For more information about  $\text{H}_2$  evolution composites consisting of bimetallic cocatalysts and SCs, the reader is referred to the recent review of Liu et al. [252]. Nowadays, there is also a push to substitute Pt for more abundant metals. Ding et al. proposed therefore the  $\text{H}_2$  production potential of AuCu-CaIn $_2$ S $_4$  [253]. Remarkably, they observed that the photocatalysts containing AuCu alloys outperformed the Au@Cu core-shell equivalents. They contributed the lower activity of the latter to more shielding of the Au and less efficient charge transport [253]. More recently, promising bimetallic CuCo photocatalysts were suggested by Zhang et al., since Co may simultaneously offer a modest  $\text{H}_2$  storage property (0.42 wt%) [254].

Table 1 Recent  $\text{H}_2$  evolution studies using plasmonic hybrid nanostructures, given with their reaction conditions, activity and reaction time of which at least 90% of its mentioned activity is retained ( $t_{>90\%}$ )

Photocatalyst	Light (intensity) <sup>a</sup>	Reaction medium (temperature, pressure) <sup>a</sup>	Activity [ $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ]	$t_{>90\%}$ [h]	Ref.
<b>Nanogap engineered (Au/AgAu)@CdS</b>	VIS (>420 nm, NA) <sup>b</sup>	0.25 M $\text{Na}_2\text{SO}_3$ and 0.35 M $\text{Na}_2\text{S}$ in $\text{H}_2\text{O}$ (RT) <sup>b</sup>	4.71	24	[113]
<b>Au@CdS</b>	VIS (>420 nm, NA)	0.1 M $\text{Na}_2\text{SO}_3$ and 0.1 M $\text{Na}_2\text{S}$ in $\text{H}_2\text{O}$	0.3836	16	[112]
<b>Half-cut Au@CdS</b>	Red light (640 nm, 3.4 $\text{mW}\cdot\text{cm}^{-2}$ )	$\text{H}_2\text{O}$ (25 °C)	~0.08	>200	[255]
<b>Au<math>_{0.4}</math>Cu<math>_{0.1}</math>/CaIn<math>_2</math>S<math>_4</math></b>	450-750 nm (NA)	0.25 M $\text{Na}_2\text{SO}_3$ and 0.25 M $\text{Na}_2\text{S}$ in $\text{H}_2\text{O}$ ; $\text{N}_2$	45.28	8	[253]

<b>Cu<sub>0.1</sub>@Au<sub>0.4</sub> /CaIn<sub>2</sub>S<sub>4</sub></b>	450-750 nm (NA)	0.25 M Na <sub>2</sub> SO <sub>3</sub> and 0.25 M Na <sub>2</sub> S in H <sub>2</sub> O; N <sub>2</sub>	20.57	8	[253]
<b>Au@Cu<sub>2</sub>FeSnS<sub>4</sub></b>	Solar (100 mW.cm <sup>-2</sup> )	0.25 M Na <sub>2</sub> SO <sub>3</sub> and 0.35 M Na <sub>2</sub> S in H <sub>2</sub> O	0.090	19	[239]
<b>Au@mesoporous TiO<sub>2</sub> hollow nanospheres</b>	>420 nm (200 mW.cm <sup>-2</sup> )	0.1 M ascorbic acid in methanol:H <sub>2</sub> O (1:1 v/v); N <sub>2</sub>	69.77	12	[244]
<b>Au NRs @TiO<sub>2</sub> nanodumbbells</b>	Solar (NA)	10 mM NaHCO <sub>3</sub> in methanol:H <sub>2</sub> O (1:4 v/v); Ar (28-35 °C)	0.0116	NA	[256]
<b>SiO<sub>2</sub>@1wt% Au@TiO<sub>2</sub></b>	UV-VIS (NA)	Methanol:H <sub>2</sub> O (1:3 v/v)	12	5	[243]
<b>Janus Au-TiO<sub>2</sub></b>	>400 nm (NA)	Isopropanol:H <sub>2</sub> O (1:2 v/v); Ar (1 atm)	56	3	[148]
<b>10 wt% Ag@C<sub>3</sub>N<sub>4</sub></b>	>420 nm (NA)	20 vol.% triethanolamine in H <sub>2</sub> O; 2.7 kPa Ar (RT)	~0.025	10	[115]
<b>SiO<sub>2</sub>/Ag@TiO<sub>2</sub></b>	Solar (100 mW.cm <sup>-2</sup> )	20 vol.% glycerol in artificial seawater	0.857	2	[246]
<b>Pt edged Au triangular nanoprisms</b>	VIS-NIR (>420 nm, NA)	Methanol:H <sub>2</sub> O (1:2 v/v); Ar	~1	NA	[245]
<b>Pt tipped Au NRs</b>	VIS-NIR (460-820 nm, NA)	Methanol:H <sub>2</sub> O (1:4 v/v)	~1.96	6	[257]
<b>TiO<sub>2</sub> NTs-Au@Pt</b>	Solar (100 mW.cm <sup>-2</sup> )	0.5 M NaSO <sub>4</sub> in methanol:H <sub>2</sub> O (1:4 v/v); Ar	2.971	15	[247]
<b>TiO<sub>2</sub> NTs-AuPt</b>	Solar (100 mW.cm <sup>-2</sup> )	0.5 M NaSO <sub>4</sub> in methanol:H <sub>2</sub> O (1:4 v/v); Ar	2.18	15	[247]
<b>Homogenously alloyed AuPt-TiO<sub>2</sub> NTs</b>	Solar (100 mW.cm <sup>-2</sup> )	Ethanol:H <sub>2</sub> O (1:4 v/v); N <sub>2</sub>	12.04 μL.h <sup>-1c</sup>	5	[241]
<b>PtAu/g-C<sub>3</sub>N<sub>4</sub></b>	UV-VIS (NA)	0.25 M NaSO <sub>3</sub> and 0.25 M Na <sub>2</sub> S in H <sub>2</sub> O; N <sub>2</sub> (43-45°C)	1.009	20	[240]
<b>AuPt/Ti<sup>3+</sup> inverse opal TiO<sub>2</sub></b>	Solar (150 mW.cm <sup>-2</sup> )	10% ethanol in H <sub>2</sub> O (35 °C)	181.77	6	[242]
<b>0.5 wt% AuPd/g-C<sub>3</sub>N<sub>4</sub></b>	>400 nm (35 mW.cm <sup>-2</sup> )	10 vol.% triethanolamine in H <sub>2</sub> O	0.326	6	[258]
<b>Cu<sub>7</sub>Co<sub>3</sub> bimetal</b>	Solar (NA)	H <sub>2</sub> O, no sacrificial agent	0.0771	24	[254]

<sup>a</sup> if known

<sup>b</sup> NA and RT are resp. the abbreviations for not available and room temperature.

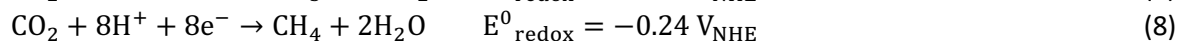
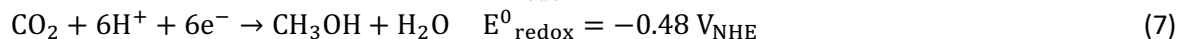
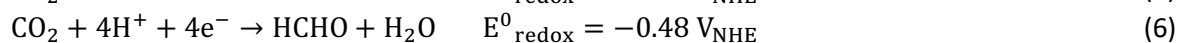
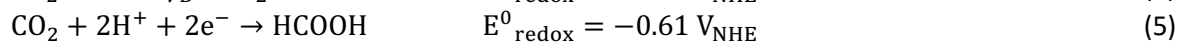
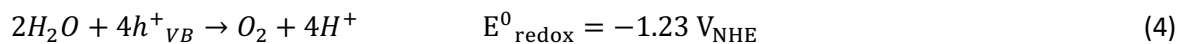
<sup>c</sup> No catalyst mass mentioned.

### 3.2.2 CO<sub>2</sub> conversion

Next to photocatalytic H<sub>2</sub> evolution, CO<sub>2</sub> conversion to CO, CH<sub>4</sub> and other valuable carbon compounds are also regarded as a promising route towards solar fuel production. However, due to the inertness of the linear CO<sub>2</sub> molecule, the one electron reduction to the CO<sub>2</sub><sup>-•</sup> radical anion comes with a significant energy cost. The reduction potential of 1.9 V vs. V<sub>NHE</sub> exceeds practically all SC CB levels [259]. Therefore, the use of a single SC is in theory excluded for this pathway. Nonetheless, already in the 70's, it was discovered that TiO<sub>2</sub> could catalyze the reduction of CO<sub>2</sub> to C<sub>1</sub> compounds like formic



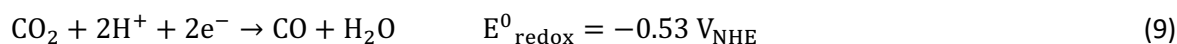
acid, formaldehyde, methanol, and methane under UV illumination in the presence of water molecules (eq. 4-8) [260].



With  $E^0_{\text{redox}}$  the standard redox potential.

It should be noted that although these overall proton-assisted conversions are thermodynamically feasible for common photocatalysts such as  $\text{TiO}_2$  and  $\text{CdS}$  (see Fig. 10), the real mechanisms are not fully elucidated. Nevertheless, it is shown that metallic plasmonic photocatalysts are able to facilitate the  $\text{CO}_2$  radicalization rate determining step via the mechanisms described in 3.1.1. Note that the photothermal effect may also drive these reactions. Since this is not exclusively ‘photocatalysis’, the interested reader is referred to the recent review of Verma et al. [259]. Jain and co-workers showed the presence of hot electron transfer to radicalize  $\text{CO}_2$  for PVP-coated Au NPs, though the activity was still moderate ( $<1 \text{ NP}^{-1} \cdot \text{h}^{-1}$ ) [132]. These activities can be further improved by modifying the reaction medium (*e.g.* the use of ionic liquids to stabilize the transition state) [261]. Another interesting option is the further hybridization of the plasmonic photocatalyst. Hybrid composites of plasmonic Au [262, 263], Ag [86, 264] and Cu [94] (for VIS light absorption) and more active catalytic metals like Pt [265], Pd [262] and Ni [266] are occurring in literature, mostly as metal cores with SC shells.

Hong et al. demonstrated the superiority of the  $\text{Ag@TiO}_2$  core-shell configuration over conventional Ag deposited on  $\text{TiO}_2$  (4.9 vs. 1.5  $\mu\text{mol CH}_4 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  under AM (Air Mass) 1.5 simulated sunlight) [86]. Similar observations were made for  $\text{Au@TiO}_2$  core-shells vs. Au deposited on  $\text{TiO}_2$  [85]. Pougin et al. furthermore optimized the  $\text{TiO}_2$  shell thickness for  $\text{Au@TiO}_2$ -Au. They revealed 20 nm shells as the most optimal for 20 nm Au core nanospheres, due to a better developed  $\text{TiO}_2$  crystal structure (1.4  $\mu\text{mol CH}_4 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  vs. 0.7 (11 nm) and 0.4 (8 nm)  $\mu\text{mol CH}_4 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  under UV-VIS illumination) [85]. On the other hand, the increased activity with increasing shell thickness is not a universal trend for all SCs and Au core sizes. Wei et al. for example showed that for 3.5 nm Au nanosphere cores, the thinner CdS shells (maximal molar CdS to Au ratio of 1) were superior for  $\text{CH}_4$  production in terms of activity (41  $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  under UV-VIS illumination) and selectivity (98.6%) [263]. Bera et al. further studied the optimal size of a spherical Au core in a  $\text{Au@SiO}_2/\text{Pt}/\text{TiO}_2$  catalyst [265]. In a 4-26 nm diameter range, 18 nm appeared to yield the highest  $\text{CH}_4$  production activity (2.98  $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  under 530 nm and 365 nm co-irradiation, for a  $\text{SiO}_2$  shell of 8-10 nm) [265]. Next to  $\text{CH}_4$ , CO may be targeted as well (eq. 9).



With  $E^0_{\text{redox}}$  the standard redox potential.

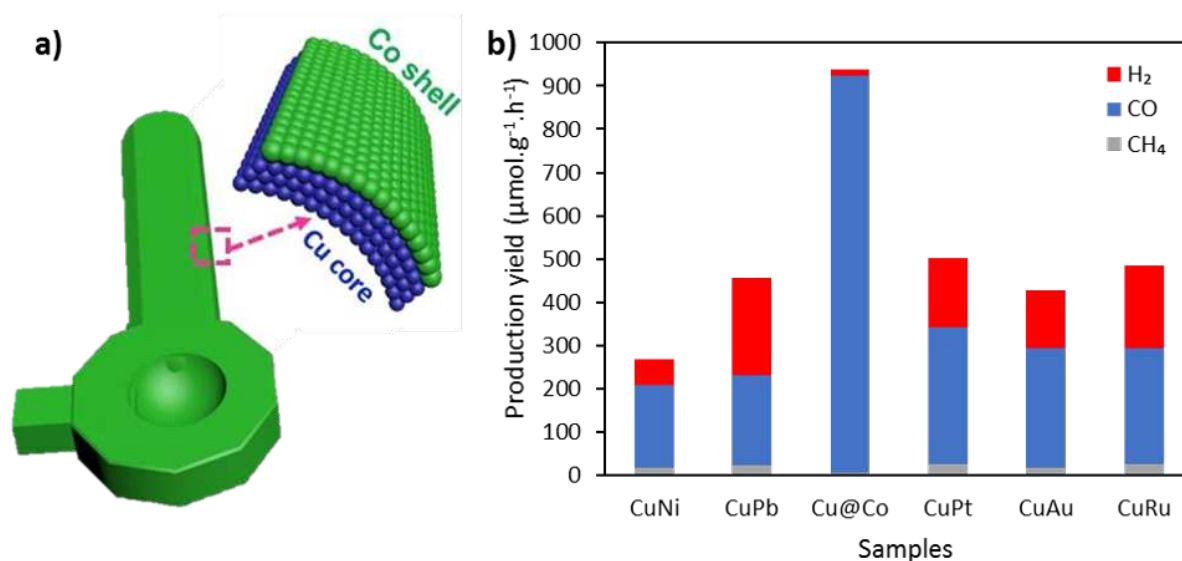
Recently, dagger-axe like  $\text{Cu@Co}$  core-shell photocatalysts were designed (Fig. 10a), yielding stable rates of 920  $\mu\text{mol CO} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  with a CO selectivity of 98% under UV-VIS illumination (150  $\text{mW} \cdot \text{cm}^{-2}$ ). The activity exceeded the rates for  $\text{CuCo}$  (741  $\mu\text{mol CO} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ ) and other alloys ( $\text{Cu@Co} > \text{CuCo} > \text{CuPt} > \text{CuAu} > \text{CuRu} > \text{CuPb} > \text{CuNi}$ ) (Fig. 10b). This was attributed to enhanced  $\text{CO}_2$  adsorption and better charge separation and migration. Remarkably, considerable amounts of  $\text{CH}_4$  and especially  $\text{H}_2$  were formed for the other alloys (up to ~50% for  $\text{CuPb}$ ) [94]. Both may be regarded as unwanted here. For instance,  $\text{H}_2$  formation reduces the number of protons which are needed for the proton-assisted formation of CO (eq. 9). Pt is both a good catalyst for  $\text{H}_2$  evolution (see 3.2.1), but also for  $\text{CO}_2$  conversion [248]. To ensure selectivity towards  $\text{CH}_4$ , Zhai *et al.* applied  $\text{Cu}_2\text{O}$  shells, leading to more than doubling of the  $\text{CH}_4$  selectivity to 85%. Besides, alloying with Cu aiming at high-indexed facets

may also improve CH<sub>4</sub> selectivity. Lang *et al.* revealed that the (730) facets of PtCu concave nanocubes loaded on C<sub>3</sub>N<sub>4</sub> nanosheets had more low-coordinated active sites, compared to (100) facets. This increased the CO<sub>2</sub> adsorption and activation [267]. Note that the selectivity towards CO or CH<sub>4</sub> can also be adjusted by changing or adding a metal [194]. A good example of this is the study of Han *et al.* [269]. They demonstrated that their Au@Pd@MOF-74 photocatalyst with a selectivity of ~100% for CO, produced CH<sub>4</sub> with a selectivity of 84% after addition of Pt on the outer shell [269].

On the other hand, H<sub>2</sub> can be used as a reagent, instead of water, in the reverse water gas shift (rWGS) reaction in order to generate CO from CO<sub>2</sub> (eq. 10).



Halas' group rationally designed Al@Cu<sub>2</sub>O antenna-reactor NPs (see 2.2.1) [270]. These systems, based on sustainable, broadly absorbing Al, gave external quantum efficiencies of 0.35%, exceeding hybrid Ag [264] and Au systems [270]. Furthermore, outstanding CO selectivity (> 99%) could be achieved at low temperature and high light intensity (up to 10 W.cm<sup>-2</sup>), greatly exceeding the values attained by the thermally driven rWGS (50-97%) [270]. Finally, also CH<sub>4</sub> can be used as reductant for CO<sub>2</sub>. This process is better known as dry reforming of methane (DRM) and produces syngas (eq. 11).



**Fig. 10** a) Dagger-axe like Cu@Co core-shell photocatalyst, with b) its production yields for CH<sub>4</sub> (grey), CO (blue) and H<sub>2</sub> (red) after UV-VIS illumination (150 mW.cm<sup>-2</sup>), compared to those for other bimetallic alloys. Adapted with permission from [94]. Copyright 2021 Elsevier

For years, this reaction has been performed at temperatures of 800-1000 °C [259]. Liu *et al.* opened up this photocatalytic application by observing DRM activity by plasmonic Au catalysts under VIS light irradiation and lower temperature (500°C) [271]. Later, they also introduced real hybrid examples such as PdAu alloys [272]. Recently, Zhou *et al.* proposed bimetallic CuRu as plasmonic antenna-single site reactor systems, able to operate at room temperature. Under 19.2 W.cm<sup>-2</sup> white light illumination, these photocatalysts converted CH<sub>4</sub> with rates exceeding 200 µmol.g<sup>-1</sup>.s<sup>-1</sup>, producing syngas with an excellent selectivity (>99%) and stability (50 h). Proper alloying is of paramount importance here, since the presence of single Ru atoms leads to less coking, less rWGS and decreases the activation barriers [273]. The required high intensities of both rWGS and DRM are also a drawback of this process. They are about 2 orders of magnitude higher than for conventional CO<sub>2</sub> photoreductions with H<sub>2</sub>O. In Table 2, the disclosed reaction conditions (reagents, intensities, *etc.*) are summarized, together with the

achieved activity, selectivity and stability for several recent CO<sub>2</sub> reduction studies. An accurate mutual comparison remains difficult here as well for the same reason as for water splitting.

Table 2 Several recent CO<sub>2</sub> conversion studies using plasmonic hybrid nanostructures, given with their reaction conditions, activity, selectivity and reaction time of which at least 90% of its mentioned activity is retained ( $t_{>90\%}$ )

Photocatalyst	Light (intensity) <sup>a</sup>	Reaction medium (temperature, pressure) <sup>a</sup>	Activity (species) [ $\mu\text{mol.g}^{-1}.\text{h}$ ]	Selectivity (species) [%]	$t_{>90\%}$ [h]	Ref.
<b>Ag@TiO<sub>2</sub></b>	Solar (NA <sup>b</sup> )	CO <sub>2</sub> and H <sub>2</sub> O vapor (0.5%) (25°C)	4.9 (CH <sub>4</sub> )	>94 (CH <sub>4</sub> )	3	[86]
<b>Au@TiO<sub>2</sub> (20nm)-Au</b>	UV-VIS (NA)	1.5% CO <sub>2</sub> and 0.6% H <sub>2</sub> O in ultrapure He (5°C, 0.15 MPa)	~0.83 (CH <sub>4</sub> ) ~0.69 (CO) ~10 (H <sub>2</sub> )	~8 (CH <sub>4</sub> ) ~7 (CO) ~85 (H <sub>2</sub> )	6	[85]
<b>Au@TiO<sub>2</sub> (20nm)</b>	UV-VIS (NA)	1.5% CO <sub>2</sub> and 0.6% H <sub>2</sub> O in ultrapure He (5°C, 0.15 MPa)	~0.30 (CH <sub>4</sub> ) ~0.32 (CO) ~10 (H <sub>2</sub> )	~3 (CH <sub>4</sub> ) ~4 (CO) ~93 (H <sub>2</sub> )	2	[85]
<b>Inverse opal TiO<sub>2</sub>-supported Au@CdS</b>	UV-VIS (320-780 nm, 100 mW.cm <sup>-2</sup> )	99.999% CO <sub>2</sub> passed through H <sub>2</sub> O bubbler (25°C, 0.1 MPa)	41.6 (CH <sub>4</sub> )	98.6 (CH <sub>4</sub> )	2	[263]
<b>Pt/TiO<sub>2</sub>/Au (18 nm)@SiO<sub>2</sub></b>	365 nm + 530 nm (NA)	H <sub>2</sub> O saturated CO <sub>2</sub> (0.1040 MPa)	3.0 (CH <sub>4</sub> )	NA	2	[265]
<b>Ag@Re<sub>n</sub>-MOF</b>	VIS (400-700 nm, NA)	Trimethylamine:acetonitrile (1:20) and CO <sub>2</sub> (0.1013 MPa)	~163 <sup>c</sup> (CO)	NA	50	[264]
<b>Hierarchical urchin-like yolk@ TiO<sub>2</sub>-xH<sub>x</sub> shell decorated with core-shell Au@Pd</b>	UV-VIS (NA)	99.9% CO <sub>2</sub> bubbled through H <sub>2</sub> O (15 °C)	18 (CH <sub>4</sub> )	94 (CH <sub>4</sub> )	7	[262]
<b>Dagger-axe-like Cu@Co</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT <sup>b</sup> , 0.1013 MPa)	920 (CO)	98 (CO)	12	[94]
<b>CuCo alloy</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT, 0.1013 MPa)	741 (CO)	90 (CO)	12	[94]
<b>CuNi alloy</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT, 0.1013 MPa)	~187 (CO)	~69 (CO)	12	[94]
<b>CuPb alloy</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT, 0.1013 MPa)	~243 (CO)	~53 (CO)	12	[94]
<b>CuPt alloy</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT, 0.1013 MPa)	~290 (CO)	~57 (CO)	12	[94]

<b>CuAu alloy</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT, 0.1013 MPa)	~280 (CO)	~65 (CO)	12	[94]
<b>CuRu alloy</b>	UV-VIS (150 mW.cm <sup>-2</sup> )	H <sub>2</sub> O:lactic acid (2:1) and CO <sub>2</sub> (RT, 0.1013 MPa)	~262 (CO)	~54 (CO)	12	[94]
<b>Au@Pd@MOF-74</b>	UV-VIS (NA)	800 ppm CO <sub>2</sub> , sprayed H <sub>2</sub> O in N <sub>2</sub>	2.5 (CO)	~100 (CO)	5	[269]
<b>Pt/Au@Pd@MOF-74</b>	UV-VIS (NA)	800 ppm CO <sub>2</sub> , sprayed H <sub>2</sub> O in N <sub>2</sub>	2.5 (CH <sub>4</sub> ) 0.5 (CO)	84 (CH <sub>4</sub> ) 16 (CO)	5	[269]
<b>Al@Cu<sub>2</sub>O</b>	UV-VIS (400-850 nm, 10 W.cm <sup>-2</sup> )	10 sccm CO <sub>2</sub> :H <sub>2</sub> (1:1) (no external heating, ~155 °C <sup>d</sup> )	360 μmol.cm <sup>-2</sup> .h <sup>-1</sup> (CO)	99.3 (CO)	0.28	[270]
<b>NiAu/SiO<sub>2</sub></b>	Green light (520 nm, 68.4 W.cm <sup>-2</sup> )	CO <sub>2</sub> :H <sub>2</sub> :N <sub>2</sub> (1:4:1) (450°C)	34% CO <sub>2</sub> conversion	77 (CH <sub>4</sub> )	NA	[266]
<b>AuCu/TiO<sub>2</sub></b>	Solar (1 W.cm <sup>-2</sup> )	CO <sub>2</sub> bubbled through water (RT-60°C, 1.9 atm)	2200 (CH <sub>4</sub> )	97 (CH <sub>4</sub> )	6	[268]
<b>PtCu concave nanocubes with (730) high-index facets/C<sub>3</sub>N<sub>4</sub></b>	UV-VIS (100 mW.cm <sup>-2</sup> )	CO <sub>2</sub> (0.15 MPa)	7.47 (CH <sub>4</sub> )	90.6 (CH <sub>4</sub> )	4	[267]
<b>Pd<sub>90</sub>Au<sub>10</sub>/Al<sub>2</sub>O<sub>3</sub></b>	VIS (0.21 W.cm <sup>-2</sup> )	20 mL.min <sup>-1</sup> CO <sub>2</sub> :CH <sub>4</sub> (1:1)	~32 x 10 <sup>3</sup> (CH <sub>4</sub> ) ~48 x 10 <sup>3</sup> (CO)	~100 (syngas)	3	[272]
<b>Cu<sub>19,9</sub>Ru<sub>0,1</sub></b>	White light (19.2 W.cm <sup>-2</sup> )	8 sccm CH <sub>4</sub> , 8 sccm CO <sub>2</sub> (RT)	~0.78 x 10 <sup>6</sup> (CH <sub>4</sub> )	>99 (syngas)	>50	[273]

<sup>a</sup> if known

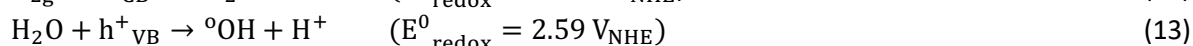
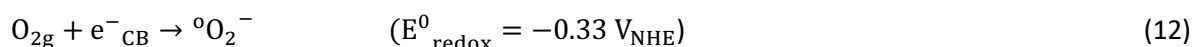
<sup>b</sup> NA and RT are resp. the abbreviations for not available and room temperature

<sup>c</sup> based on Re weight

<sup>d</sup> temperature because of high intensity irradiation, no additional heating

### 3.2.3 Pollutant degradation

Degradation of air- and water-based pollutants is one of the most widely studied subjects within photocatalysis. Air pollution abatement studies often focus on simple inorganic (*e.g.* NO<sub>x</sub> and SO<sub>x</sub>) or volatile organic compounds (VOCs) (*e.g.* formaldehyde). Water-based research on the other hand, mostly deals with more complex compounds such as dyes, pharmaceuticals, and pesticides [9]. The mechanism for photocatalytic degradation of pollutants in air and water is driven by ROS. Species like super oxide anion and hydroxyl radicals are generated by the redox reactions of oxygen and water with the e<sup>-</sup><sub>CB</sub> and h<sup>+</sup><sub>VB</sub> (eq. 12-13) [4, 238]. These ROS can oxidize pollutants, due to their high redox potentials (Fig. 9).



### 3.2.3.1 Water purification

Dye degradation is the most widely studied application in photocatalytic water purification. However, a major point of attention in this regard, which is regrettably often overlooked, is that such compounds may themselves act as photosensitizers, possibly leading to confounding results [274]. Hence, careful setup and control experiments are required [9]. Alternatively, VIS-transparent molecules like phenol or naphthol can be used. Mostly SCs modified with multi-metal core-shell [275–279] or alloys [280–282, 284–286] (Au, Ag, Cu, Pd, Co, Ni *etc.*) have been investigated. For the degradation of phenol, core-shell Au@Pd deposited on TiO<sub>2</sub> yielded 5.4 times faster phenol degradation under VIS light ( $\lambda > 420$  nm) than the alloy on TiO<sub>2</sub> ( $3.8 \mu\text{M}\cdot\text{min}^{-1}$  vs.  $0.7 \mu\text{M}\cdot\text{min}^{-1}$ ). It was claimed that Pd at the surface was more favorable due to its stronger ability to generate charge carriers, compared to Au [280]. Furthermore, it is even suggested that for some SCs (such as narrow band gap SCs), Janus configurations may even be more beneficial. For example, Janus Au-SnS<sub>2</sub> (2.1-2.4 eV) displays the highest apparent reaction rates ( $k_{\text{app}}$ ) for the degradation of methyl orange under VIS light ( $0.240 \text{ min}^{-1}$  vs.  $0.072 \text{ min}^{-1}$  for core-shell Au@SnS<sub>2</sub> and  $0.060 \text{ min}^{-1}$  for sole SnS<sub>2</sub> for suspensions containing  $0.625 \text{ g}\cdot\text{L}^{-1}$ ). This could be explained by an increased VIS light extinction, while the red-shift experienced by core-shell NPs is so large ( $>100$  nm) that the absorption maximum reaches the NIR spectral region [287]. On the other hand, alloying may still yield superior results compared to combined deposition of separate monometallic plasmonic NPs. Zielińska-Jurek *et al.* found phenol degradation rates of  $3.54 \mu\text{M}\cdot\text{min}^{-1}$  for Au<sub>0.5</sub>Ag<sub>1.5</sub> on TiO<sub>2</sub> under VIS light illumination ( $\lambda > 450$  nm) while comparable Au and Ag samples yielded significantly lower rates (*resp.*  $0.35$  and  $1.26 \mu\text{M}\cdot\text{min}^{-1}$ ). Hence, they underlined the necessity of contact between the metals for efficient charge separation [282]. Nevertheless, the authors also observed that the dominant Ag species is Ag<sub>2</sub>O [282]. Working in an aqueous environment raises important stability issues regarding corrosion and dissolution [9]. The latter will be discussed more in detail in section 3.2.4. To increase the stability, several solutions have emerged. For instance, embedment in Ag halide yielded stable AuAg@AgBr photocatalysts [288]. The material roughly retained its initial 2-naphthol degradation activity (100% degradation after 15 min of illumination with VIS light ( $\lambda > 420$  nm), for a starting concentration of  $10 \mu\text{M}$  and a catalyst loading of  $1 \text{ g}\cdot\text{L}^{-1}$ ) after five consecutive reaction cycles. No signs of Ag<sup>+</sup> or Br<sup>-</sup> leaching were detected with ion chromatography and inductively coupled plasma spectroscopy [288]. Another interesting option to stabilize the NPs can be found in the field of aerobic oxidation. Sugano *et al.* showed that oxidized Cu in AuCu alloys could be regenerated by Au, as confirmed by EPR spectroscopy. Requirements for this are an e<sup>-</sup> donor (*e.g.* alcohols) and a sufficiently high Au content, *i.e.* Au<sub>0.7</sub>Cu<sub>0.3</sub> [289].

Another challenge associated with photocatalytic water purification using suspended particles systems is catalyst recycling. As a solution, the introduction of magnetic shells has been proposed for facile post-recovery. Reduced graphene oxide (rGO) modified with Au@magnetic Ni lost less than 17% of its initial activity in the sunlight driven degradation of phenol after 5 consecutive cycles. Besides, this loss was mostly attributed to a loss of surface sites [276]. Similar results were obtained for Ag/AgBr@Fe<sub>2</sub>O<sub>3</sub> for methyl orange degradation [290]. However, magnetic oxides tend to be unstable, especially in acidic waste waters [277]. Therefore, Su *et al.* developed triple shelled Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> photocatalysts. The extra inert SiO<sub>2</sub> layer inhibited the e<sup>-</sup>/h<sup>+</sup> transfer from TiO<sub>2</sub> to Fe<sub>3</sub>O<sub>4</sub> and avoided strong Fabry-Perot oscillations [277]. Note furthermore that due to this interlayer the transfer of hot electrons is prevented (see 3.1), which is often considered the dominant plasmonic effect in plasmon-enhanced photocatalytic water purification [275, 291]. On the other hand, the near-field enhancement mechanism benefits from the higher refractive index of the iron oxide (2.42) [277]. Other solutions include the fixation of the catalyst onto membranes [292] or even water-floatable structures [293]. Recently, Kaur *et al.* successfully applied the latter concept by incorporating Cr doped TiO<sub>2</sub> modified with plasmonic TiN@SiO<sub>2</sub> core-shell NPs on highly solar transparent and water permeable alginate networks. These floatable networks, mimicking natural Marimo algae, allowed a 3.3-fold enhanced

methylene blue (MB) degradation activity under 1 Sun solar light ( $k_{app}$  of  $0.30 \text{ min}^{-1}$  vs.  $0.09 \text{ min}^{-1}$  for the non-plasmonic equivalent,  $2 \text{ g catalyst.L}^{-1}$ ) [293].

Bathla *et al.*, pointed out the superiority of core-shell nanostructures over alloys due to multiple reasons such as an accelerated interfacial charge transfer and synergistic adsorption and photocatalysis effects of certain atomic groups at the surface [294]. Nonetheless, complete mineralization remains often difficult for plasmon-enhanced photocatalysts [9]. A final water pollutant class are inorganic ions (*e.g.* As, Cr species *etc.*). By appropriately choosing the metal and SC (with sufficiently energetic CB), simultaneous oxidation of organic pollutants and reduction of inorganic contaminants is possible [277]. These concurrent oxidations are often necessary. The less toxic  $\text{Cr}^{\text{III}}$  tends to quickly re-oxidize if the  $\text{h}^+$  are not effectively scavenged [295]. Patnaik *et al.* observed an increased  $\text{Cr}^{\text{VI}}$  removal after adding  $20 \text{ mg.L}^{-1}$  phenol. The  $\text{Cr}^{\text{VI}}$  conversion after 2 h of UV-VIS illumination for their alloyed AuPd on  $\text{g-C}_3\text{N}_4$  photocatalysts ( $1 \text{ g.L}^{-1}$ ) raised from 64% to 91.6% [285]. Rationally designed plasmonic hybrids could further circumvent this issue due to their good charge separation. Metal@SC Janus NPs, where the metal functions as an electron sink and the redox reactions take place at different locations, would thus be interesting in that regard. Unfortunately, actual plasmonic Janus NPs studies for  $\text{Cr}^{\text{VI}}$  removal are still lacking to date.

Lastly, it is noteworthy that hybrid plasmonic NPs are also gradually being applied for other main classes of water pollutants like persistent pesticides [281, 296], endocrine disrupting chemicals [290], pharmaceuticals or other contaminants of emerging concern (CECs) [292, 297]. Table 3 displays a summary of selected exemplary plasmonic hybrid studies on both CECs and less persistent compounds. A true comparison remains also here difficult due to the lack of standardization.

Table 3 Several recent water pollution abatement studies using plasmonic hybrid nanostructures, given with their reaction conditions and apparent rate constant ( $k_{app}$ )

Photocatalyst	Light (intensity) <sup>a</sup>	Reaction medium (temperature, pH) <sup>a</sup>	$k_{app}$ [ $\text{h}^{-1}$ ]	Ref.
$\text{Co}_{1.7}\text{Pd}/\text{BiVO}_3$	VIS ( $\geq 400 \text{ nm}$ , NA)	$0.2 \text{ mM}$ phenol; $0.8 \text{ mg catalyst.mL}^{-1}$ (RT)	$50.2^{\text{b1}}$	[298]
AuPd/mesoporous silica modified $\text{g-C}_3\text{N}_4$	UV-VIS (NA)	$10 \text{ mg Cr}^{\text{VI}}.\text{L}^{-1}$ ; $20 \text{ mg phenol.L}^{-1}$ ; $1 \text{ mg catalyst.mL}^{-1}$ (pH 5.7)	$0.528$ ( $\text{Cr}$ ) <sup>b2</sup> $1.074$ (phenol) <sup>b2</sup>	[285]
AuPd/rGO	Natural sunlight (NA)	$0.5 \text{ mM}$ phenol; $0.5 \text{ mg catalyst.mL}^{-1}$ (pH 6)	$0.576^{\text{b2}}$	[299]
AuPd/Amberlyst® resin	VIS (400-700 nm, NA)	$10 \text{ ppm}$ parathion, $25 \text{ mg catalyst.mL}^{-1}$ ( $20^\circ\text{C}$ )	$\sim 1.14$	[296]
AuPd/ $\text{TiO}_2$ film	UV (365 nm, $0.4 \text{ mW.cm}^{-2}$ )	$10 \text{ mg}$ malathion. $\text{L}^{-1}$	$0.948^{\text{b1}}$	[281]
AuCu/ $\text{TiO}_2$ /reduced graphene oxide	UV-VIS (380 – 697 nm, NA)	$0.5 \text{ mM}$ 2-nitrophenol; $0.3 \text{ mg catalyst.L}^{-1}$ (pH 6.8)	$\sim 1.2^{\text{b2,c}}$	[286]
$1.5 \text{ wt\% Au}_{0.1}\text{Ag}_{0.9}/\text{TiO}_2$ on CA	VIS ( $>420 \text{ nm}$ , NA)	$5 \text{ mg}$ tetracycline. $\text{L}^{-1}$ ; $0.05 \text{ MPa}$ transmembrane pressure ( $25^\circ\text{C}$ )	$0.7656^{\text{b2}}$	[292]
Au@Ag/TNT	Simulated sunlight ( $100 \text{ mW.cm}^{-2}$ )	$8 \text{ mM}$ MB; $0.33 \text{ mg catalyst.mL}^{-1}$	$1.746^{\text{b2}}$	[275]
Au@Ni/rGO	Natural sunlight	$0.08 \text{ mM}$ phenol; $1 \text{ mg catalyst.mL}^{-1}$ (pH 7)	$0.4173^{\text{b2}}$	[276]

	(0.75-0.85 mW.cm <sup>-2</sup> )			
<b>Au@Pd/TiO<sub>2</sub></b>	UV-VIS (62 mW.cm <sup>-2</sup> for 310-380 nm range)	0.21 mM phenol; 5 mg catalyst.mL <sup>-1</sup>	~0.714 <sup>b2</sup>	[280]
<b>Ag/AgBr@Fe<sub>2</sub>O<sub>3</sub></b>	VIS (>420 nm, NA)	10 mg bisphenol A.L <sup>-1</sup> ; 1 mg catalyst.mL <sup>-1</sup> (30°C)	~0.35 <sup>b1</sup>	[290]
<b>TiN@SiO<sub>2</sub>@Cr-TiO<sub>2</sub> embedded in Ca-alginate beads</b>	Simulated sunlight (100 mW.cm <sup>-2</sup> )	0.01 mM MB; 2 mg catalyst.mL <sup>-1</sup>	18 <sup>b2</sup>	[293]
<b>Au@SnS<sub>2</sub></b>	VIS (400-780 nm, NA)	40 mg MO.L <sup>-1</sup> ; 0.625 mg catalyst.L <sup>-1</sup> (RT)	4.32 <sup>b2</sup>	[287]
<b>Janus Au-SnS<sub>2</sub></b>	VIS (400-780 nm, NA)	40 mg MO.L <sup>-1</sup> ; 0.625 mg catalyst.L <sup>-1</sup> (RT)	14.4 <sup>b2</sup>	[287]

<sup>a</sup> if known

<sup>b1</sup> concentrations measured by high pressure liquid chromatography (HPLC) or <sup>b2</sup> colorimetric means

<sup>c</sup> after normalization for prior adsorption phase

### 3.2.3.2 Air purification

Important reactions in the domain of air purification are the degradation of VOCs (*e.g.* benzene, formaldehyde *etc.*), CO oxidation, and conversion of inorganic gaseous molecules like NO<sub>x</sub> and SO<sub>x</sub>. The foremost majority of metal-modified SC-based air purification studies make use of binary or ternary composites of metal NPs deposited on the SC surface, with the aim of reducing charge carrier recombination. As mentioned above, the use of single plasmonic NPs in environmental remediation is not in the scope of the present overview, but is discussed thoroughly in the review of Wang *et al.* [9]. The rest of this subsection will again focus on studies involving more complex, hybrid materials.

A major difference with liquid pollutant research is that air purification studies more often make use of continuous flow systems dealing with low concentrations. This results in low residence times and underlines the importance of a large surface area [300]. Hence, in VOC removal studies, high-surface area substrates like graphene oxide (GO), rGO, MOFs, zeolites ... are modified with single plasmon NPs and SCs, forming binary or ternary heterostructures [301–303]. The past decade, also true plasmonic hybrids entered the field, often in combination with sensing purposes [304, 305]. For example, Wang *et al.* developed Janus Au nanorod@ZnO@ZIF-8 formaldehyde detectors [304]. Due to the ZIF-8, these structures could achieve a surface area up to 924 m<sup>2</sup>.g<sup>-1</sup>. They also noticed a continuous stream of non-toxic formic acid upon VIS light irradiation, pointing out its detection and removal potential. Au@SnO<sub>2</sub> core-shell configurations showed to be promising for acetaldehyde detection and removal as well [305]. For the latter, Zeng *et al.* constructed 2 μm Ag NW@TiO<sub>2</sub> core-shell catalysts. These were able to degrade 72% of the initial 500 ppm acetaldehyde in a contact time of only 4.8 min under 20 mW.cm<sup>-2</sup> 260 W fluorescent light irradiation. The photocatalysts remained stable for 15 weeks and greatly outperformed pristine TiO<sub>2</sub> (37%) [300]. Further boosting of metal@SC structures has been done by extra modification of the SC shell. Gao *et al.* incorporated Pd atoms in the ceria lattice of Ag@CeO<sub>2</sub> NPs, hereby increasing the oxygen dissociative adsorption capacity and the number of oxygen vacancies. Together with the LSPR effect and good charge separation efficiencies, these structures yielded toluene removal rates of ~50% under VIS light at 89°C (500 ppm, 160 mW.cm<sup>-2</sup>, 0.1 g catalyst). This value was about ten times the activity for bare Ag@CeO<sub>2</sub> NPs at the same reaction temperature [306]. Also without crystalline SCs, active photocatalysts can be designed. The Ag@C systems of Sun *et al.* were found to be superior to N-doped TiO<sub>2</sub> for the degradation of acetaldehyde (89% vs. 31% under VIS light, 0.1 g catalyst) [307]. Alloys finally, are less studied than their core-shell equivalents.

Wysocka et al. studied different alloys (CuAg, AgPt, CuPt) on TiO<sub>2</sub> for the degradation of toluene under 460 nm light-emitting diode (LED) light. The synergistic effect of Pt was pointed out here, improving the interfacial charge transfer. Hence, higher toluene degradation rates were achieved (rate constants of 2.60 and 2.15 min<sup>-1</sup> for AgPt- and CuPt-TiO<sub>2</sub>, respectively, vs. 0.79 min<sup>-1</sup> for CuAg-Pt) [308].

The photocatalytic degradation of VOCs like toluene is generally not a selective process, and may yield a myriad of byproducts, going from various oxidized benzene derivatives to smaller aldehydes [308]. Several of these may be toxic, although by rational design of the hybrid structure, such compounds may be eliminated. The addition of Pd on TiO<sub>2</sub> surfaces may for instance remove surface -OH groups. This promotes the activation of oxygen to °OH radicals. In the toluene degradation reaction, these directly attack the methyl group, avoiding the formation of toxic methyl-phenolic compounds [309]. Another issue is the formation of CO which may poison the catalysts, especially when Pt particles are involved. High electron densities favor strong binding of CO to the metal [310]. In electrocatalysis, single Pt atom PtCu alloys with a cationic nature are hence applied [311]. Also plasmon induced heating, leading to the decomposition of surface carbonates may be helpful, but these often require intensities in the order of W.cm<sup>2</sup> [312]. Still, Li et al. managed to design efficient antenna-reactor complexes consisting of Ag@SiO<sub>2</sub>/Pt core-shell/satellite configurations for the selective oxidation of CO. High quantum yields of 7-10% for VIS light were reported for intermediate size Ag antennas. 25 nm Ag cores proved to be the most optimal trade-off between near-field enhancement on the Pt surface, scattering and absorption by Ag [313].

An important inorganic pollutant is NO, leading to smog, acid rain and health issues. For its removal, the use of non-noble plasmonic Bi has recently been investigated. This low cost semimetal has a work function of 4.22-4.25 eV [314]. Therefore, it may well inject electrons in the CB of most SCs. To protect the relatively big Bi cores (100-200 nm), Chen et al. applied 5 nm amorphous Bi<sub>2</sub>O<sub>3</sub> shells. These systems yielded a maximal NO removal efficiency of 26.4% using Xe light source (400 ppb, 0.1 g catalyst) [315]. The use of amorphous layers may on the other hand also introduce recombination centers [316]. Thus, Zhang et al. transformed this shell into a crystalline Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> shell by a facile secondary hydrothermal treatment. The NO removal efficiency upon 28.5 mW.cm<sup>-2</sup> UV-VIS light irradiation increased from 12.3% for Bi@Bi<sub>2</sub>O<sub>3</sub> to 34.1% for Bi@Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> NPs due to the lower hot electron transfer resistance [316]. Similar activities are noticed for Bi shells, considering the amount of photocatalyst (0.2 g). Bi<sub>4</sub>MoO<sub>9</sub>@Bi systems attained 55.4% NO removal due to the LSPR effect of Bi and the oxygen vacancies (OVs) in the SC. Bi and the OVs also display a synergistic effect to prevent the formation of toxic NO<sub>2</sub> dimers (N<sub>2</sub>O<sub>4</sub>) (eq. 14) [317].



The enhanced ROS formation from O<sub>2</sub> by the LSPR effect of Bi and the direct oxidation of NO by h<sup>+</sup>, together with the reaction of O<sub>2</sub> with the OVs, avoids the formation of N<sub>2</sub>O<sub>4</sub>, as shown by *in-situ* diffuse reflectance infrared Fourier transform spectroscopy. Finally, the bismuth oxides can also be used as substrates for Ag@AgCl NPs, showing again similar removal rates (~50% for 0.2 g catalyst) [318]. These values can be compared due to a similar setup. A broader comparison between studies can be found in Table 4. However, due to the frequent lacking of reported intensity data, a true mutual comparison is again hampered.

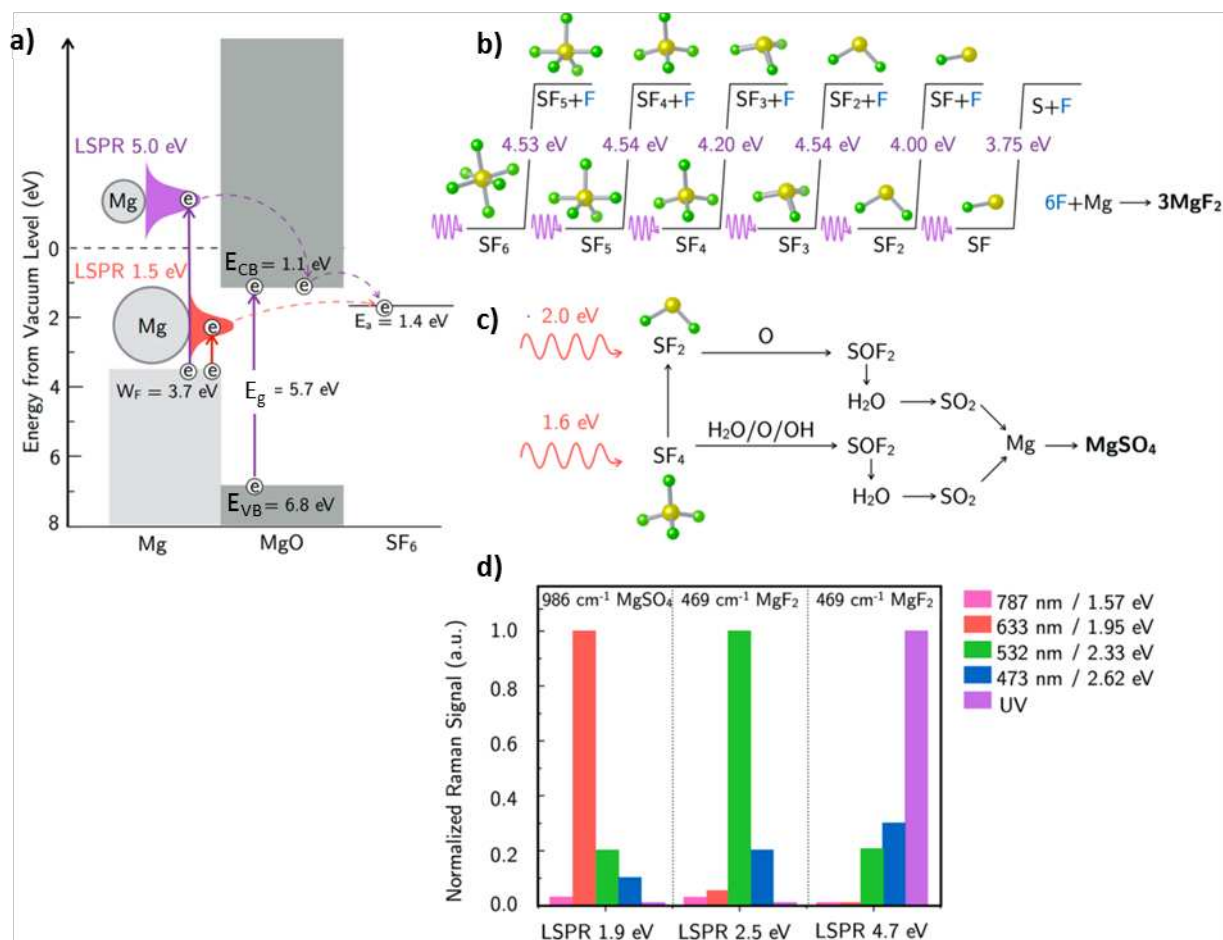
An interesting final example of air pollution abatement by plasmonic hybrids is the degradation of SF<sub>6</sub> by Mg@MgO core-shell catalysts [319]. SF<sub>6</sub> is a greenhouse gas with a global warming potential of 24,000 times that of CO<sub>2</sub>. Plasmonic Mg@MgO can degrade this compound to both MgF<sub>2</sub> and MgSO<sub>4</sub>. Fascinatingly, the final product is determined by the LSPR effect (Fig. 11a). For Mg with a diameter of 30 nm, LSPR is induced by highly energetic illumination (UV, >3 eV). The generated free electrons are



then tunneled to SF<sub>6</sub>. This well-known electron-scavenger dissociates subsequently in SF<sub>5</sub> and F radicals (eq. 15)



The former may undergo a cascade dissociation reaction, yielding S. F<sup>-</sup> reacts at the Mg/MgO surface, forming MgF<sub>2</sub> and MgO<sub>x</sub>F<sub>y</sub> (Fig. 11b). For Mg nanostructures with a diameter of 50-100 nm, photons with a lower energy content of 1.5-2 eV are able to induce LSPR. Hence, SF<sub>4</sub> and SF<sub>2</sub> radicals are formed which can react with moisture and O- or OH-sites on MgO, leading to SO<sub>2</sub>. The latter adsorbs on acidic Mg<sup>2+</sup> sites producing MgSO<sub>3</sub>. This compound is further oxidized to MgSO<sub>4</sub> (Fig. 11c). This wavelength dependency was verified by using different light sources for Mg nanostructures with different LSPR maxima, showing that for hybrids with LSPR at 4.7 eV under UV light (160-400 nm, 3.1-7.75 eV) MgF<sub>2</sub> was the dominant product. On the contrary, for structures with LSPR at 1.9 eV (632 nm) MgSO<sub>4</sub> was the main product under 1.95 eV (633 nm) laser irradiation (Fig. 11d). The Mg species could at last be regenerated in a few seconds using a hydrogen plasma afterglow process at room temperature [319].



**Fig. 11** a) Energy band diagram of Mg@MgO core-shell NPs for the decomposition of SF<sub>6</sub>. W<sub>F</sub> - work function of Mg and E<sub>g</sub> - electron affinity energy level of SF<sub>6</sub>. Reaction scheme of the plasmon-catalyzed decomposition of SF<sub>6</sub> to b) MgF<sub>2</sub> and c) MgSO<sub>4</sub>. d) Raman signal for different Mg@MgO nanostructures with various LSPR maxima, i.e. at 1.9, 2.5 and 4.7 eV. Adapted with permission from [319]. Copyright (2020) American Chemical Society

Due to the ability of photocatalytic materials to degrade pollutants, coating them on walls is a facile way of simultaneously purifying the air and keeping the walls clean. In particular, in combination with the superhydrophilic properties of SCs like TiO<sub>2</sub>. Such surfaces can be called self-cleaning surfaces. The photocatalytic coating can be applied on ceramics, glass as well as fabrics. Verbruggen et al. investigated the use of TiO<sub>2</sub> modified with Au<sub>x</sub>Ag<sub>1-x</sub> alloy NPs [59, 128, 139]. By applying a protective

LbL polymer shell around the bimetallic NPs, the activity also remained the same after 1 month of ageing [139]. Another successful stabilization method is the full embedment of Au NPs within the TiO<sub>2</sub> film. Recently, Peeters *et al.* showed that these systems effectively lead to self-cleaning activity enhancement (+29% for 1 wt.% of Au compared to pristine TiO<sub>2</sub> upon 1 sun AM1.5G illumination) [320].

Table 4: Several recent air purification studies using plasmonic hybrid nanostructures, given with their reaction conditions and attained pollutant conversion (with the time needed to achieve these values)

Photocatalyst	Light (intensity) <sup>a</sup>	Reaction medium	Conversion [%] (time needed)	Ref.
0.5 wt.% Ag NW@TiO <sub>2</sub>	UV-VIS (20 mW.cm <sup>-2</sup> )	500 ppm CH <sub>3</sub> CHO; 20 mL.min <sup>-1</sup> , 0.1 g catalyst,	72 <sup>b1</sup> (~120 min)	[300]
Ag@C	VIS (>420nm, NA)	100 ppm CH <sub>3</sub> CHO; N <sub>2</sub> ; 0.1 g catalyst	89 <sup>b1</sup> (65 min)	[307]
Au@SnO <sub>2</sub> on ceramic foam	UV (365 nm, NA)	500 ppm CH <sub>3</sub> CHO	~100 <sup>b1</sup> (~120 min)	[305]
Au@truncated wedge-shaped TiO <sub>2</sub>	VIS (NA)	100 ppm CH <sub>3</sub> CHO; air; 250 mL.min <sup>-1</sup> ; RH of 60%; 0.05 g catalyst; 25°C	~91 <sup>b1</sup> (210 min)	[321]
CuNi NWs-TiO <sub>2</sub>	VIS (NA)	500 ppm CH <sub>3</sub> CHO; 20 mL.min <sup>-1</sup> ; total volume of 0.3 L; 0.1 g catalyst	56 <sup>b1</sup> (~75 min)	[322]
Ag@CeO <sub>2</sub> with Pd incorporated in the shell lattice	VIS (400-800 nm, 160 mW.cm <sup>-2</sup> )	500 ppm toluene; 20% O <sub>2</sub> ; N <sub>2</sub> ; 33.3 mL.min <sup>-1</sup> ; 0.1 g catalyst; 89°C	50 <sup>b1</sup> (NA)	[306]
Ag@CeO <sub>2</sub>	VIS (400-800 nm, 160 mW.cm <sup>-2</sup> )	500 ppm toluene; 20% O <sub>2</sub> ; N <sub>2</sub> ; 33.3 mL.min <sup>-1</sup> ; 0.1 g catalyst; 89°C	<5 <sup>b1</sup> (NA)	[306]
Au/hedgehog-shaped TiO <sub>2</sub> microspheres@CuO	VIS (490-760 nm, NA)	0.3 vol% CO; 0.3 vol% O <sub>2</sub> ; He; 100 mL.min <sup>-1</sup> ; 0.5 g catalyst	~80 <sup>b1</sup> (NA)	[323]
Bi@amorphous Bi <sub>2</sub> O <sub>3</sub>	(300 W Xe light, no filter)	400 ppb NO; air; 3 L.min <sup>-1</sup> ; total volume of 4.5 L; 0.1 g catalyst	26.4 <sup>b2</sup> (~10 min)	[315]
Bi@crystalline Bi <sub>2</sub> O <sub>3</sub> CO <sub>3</sub>	VIS (28.5 mW.cm <sup>2</sup> )	400 ppb NO; air; 3 L.min <sup>-1</sup> ; total volume of 4.5 L; RH <sup>c</sup> of 25%; 0.1 g catalyst; 25°C	34.1 <sup>b2</sup> (~30 min)	[316]
Bi <sub>4</sub> MoO <sub>9</sub> @Bi	VIS (>420 nm, NA)	550 ppb NO; air; RH <sup>c</sup> of 55%; 2.415 mL.min <sup>-1</sup> ; total volume of 4.5 L; 0.2 g catalyst	55.4 <sup>b2</sup> (NA)	[324]
Ag/AgCl on La(OH) <sub>3</sub>	VIS (>420 nm, 0.16 W.cm <sup>-2</sup> )	550 ppb NO; air; 2.415 L.min <sup>-1</sup> ; total volume of 4.5 L; 0.1 g catalyst	55% (~30 min)	[325]
Ag/AgCl on BiOCl/Bi <sub>12</sub> O <sub>17</sub> Cl <sub>2</sub>	VIS (>420 nm, NA)	500 ppb NO; air; RH <sup>c</sup> of 55%; 2.4 L.min <sup>-1</sup> ; total volume of 4.5 L; 0.2 g catalyst	49.5 <sup>b2</sup> (~30 min)	[318]

<sup>a</sup> if known

<sup>b1</sup> concentrations measured by GC or <sup>b2</sup> chemiluminescence NO<sub>x</sub> analyzer

<sup>c</sup> RH refers to relative humidity.

### 3.2.4 Disinfection

Initially, hybrid plasmonic nanostructures were not introduced in the disinfection research field for their photocatalytic activity, but mainly in view of other properties. For instance, Au@drug complexes were studied extensively for their photothermal effect or for imaging purposes. Composites with Ag are more common, due to the inherent antimicrobial activity of Ag, even in darkness [326, 327]. However, the photocatalytic property holds tremendous promise as well, especially towards antibiotic resistant strains. The photocatalytically formed oxidative species may induce peroxidation of cell membrane phospholipids, direct DNA damage and coenzyme A oxidation, which inhibit respiratory activity and result in cell death [328]. For more in-depth explanations on photocatalytic antimicrobial mechanisms, we gladly refer to the excellent reviews of Markowska-Szczupak *et al.* [329] and Endo and Kowalska [328].

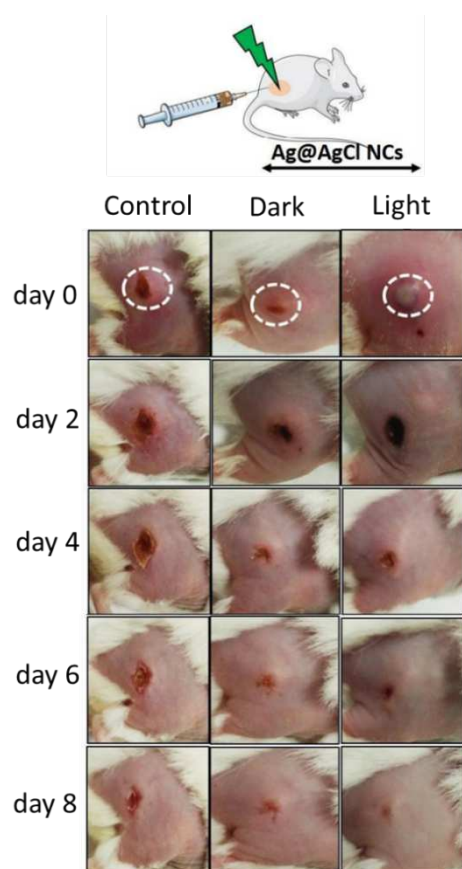
Ag@metal oxide core-shell hybrids are frequently studied in this context [330–333]. An overview of several recent studies can be found in Table 5. In order to make a distinction between photocatalytic effects and the pure antimicrobial properties of metals, both the activity in dark and upon illumination are given. Unfortunately, due to the lack of standardized experimental parameters, mutual comparison between different studies is again problematic. Inorganic hybrids do not suffer from enzymatic degradation and benefit from more light absorption compared to complexes with organic photosensitizers [333]. Very few disinfection studies deal with plasmonic multi-metal alloys (e.g. alloying Ag with Cu or Pt) [284, 327]. On the other hand, core-shell configurations have shown to be more stable in harsh oxidative environments [330]. Though the release of Ag<sup>+</sup> is considered beneficial for antibacterial purposes [284], it might be important that no (toxic) ions such as Ag<sup>+</sup> or metal ions from the SC leach into the treated water. Das *et al.* demonstrated with Atomic Absorption Spectroscopy (AAS) for both their Ag@ZnO and Ag@SnO<sub>2</sub>@ZnO photocatalysts that no detectable amounts of Ag<sup>+</sup>, Zn<sup>2+</sup> or Sn<sup>4+</sup> [330–332]. Besides, they showed a superior activity compared to the pure SCs. Ag@ZnO degraded *V. cholera* bacteria 9-10 times better under natural sunlight than ZnO or TiO<sub>2</sub> [332]. Similar results were obtained for *E. coli* [331]. Ag@SnO<sub>2</sub>@ZnO was even capable of completely disinfecting 10<sup>7</sup> colony forming units (CFU).mL<sup>-1</sup> of multidrug resistant *Bacillus* species in 3.5h under natural sunlight (~79 mW.cm<sup>-2</sup> [330]. Here, H<sub>2</sub>O<sub>2</sub> was revealed as the dominant oxidative species. However other disinfection studies point out O<sub>2</sub><sup>•</sup> as major oxidant. Interestingly, the use of Ag@AgCl hybrids enables the use of reactive chlorine species (RCS), next to ROS. When AgCl absorbs light, Ag<sup>+</sup> is reduced, while Cl<sup>•</sup> is formed (eq. 16) [333].



With  $h$  Planck's constant and  $\nu$  the frequency of the incoming light.

Recently, Thangudu *et al.* showed *in vivo* that the implementation of Ag@AgCl NCs as nanomedicine allowed complete reepithelization of subcutaneous abscesses in mice for both multidrug resistant gram-positive as well as gram-negative bacteria (Fig. 12) [333]. Note that most disinfection studies deal with bacteria while also other organisms such as fungi may cause harm. The photocatalytic microbial inactivation efficiency is not the same for all microorganisms and seems to follow a pattern correlated to the cell complexity (easiest degradation of gram-negative bacteria > gram positive bacteria >> fungi (yeast) > fungi (mold)). By using synergistic effects of a well-designed plasmonic hybrid, also effective fungi destruction can be achieved [334]. In 2019, Mendez Medrano *et al.* modified TiO<sub>2</sub> with Ag@CuO core-shell nanostructures. Due to the combined effects of the Ag plasmon-enhanced ROS generation, the narrow band gap of CuO (1.7 eV), the penetration of the catalyst in the cell membrane and the presence of germicidal Ag<sup>+</sup> and Cu<sup>+</sup> ions, high antifungal activity was obtained. This included growth

inhibition for *Aspergillus melleus* and *Penicillium chrysogenum*, but also significant inhibition of sporulation and mycotoxin or sclerotia containing droplets [334].



**Fig. 12** Images of the MRSA infected mice at different days. 100  $\mu\text{L}$  of 1  $\text{mg}\cdot\text{mL}^{-1}$  Ag@AgCl NCs was injected under-skin for both the 'dark' and 'light' experiment. For the latter, the infected region was irradiated with 532 nm laser light for 10 min ( $250 \text{ mW}\cdot\text{cm}^{-2}$ .) Republished with permission of Royal Society of Chemistry, from [333]; permission conveyed through Copyright Clearance Center, Inc.

Finally, since wastewater disinfection often makes use of suspended particulate systems, significant catalyst losses may be encountered [330, 332]. Rationally designed core-shell structures, consisting of a Ag/AgBr core and a magnetic  $\text{Fe}_2\text{O}_3$  shell, were therefore applied for disinfection purposes [290]. Plasmonic hybrids are recently also being incorporated in membrane matrices. The presence of the plasmonic photocatalysts mitigates membrane (bio)fouling. Li *et al.* designed cellulose acetate (CA) membranes modified with  $\text{Au}_{0.1}\text{Ag}_{0.9}\text{-TiO}_2$  NRs, yielding *E. coli* degradation efficiencies of 98.5% after 30 min of VIS light irradiation ( $\lambda > 420 \text{ nm}$ ) [292].

Table 5: Several recent disinfection studies using plasmonic hybrid nanostructures, given with their reaction conditions and apparent rate constant both with and without illumination (resp.  $k_{\text{app}}$  and  $k_{\text{app, dark}}$ )

Photocatalyst	Light (intensity) <sup>a</sup>	Reaction medium (temperature, pH) <sup>a</sup>	$k_{\text{app}}^{\text{b}}$ ( $k_{\text{app, dark}}$ ) [ $\text{h}^{-1}$ ]	Ref.
AgCu-TiO <sub>2</sub>	VIS (>450 nm, NA)	<i>E. coli</i> (K12); $1.5 \times 10^8$ CFU.mL <sup>-1</sup> ; 0.9% NaCl; 7.14 mg catalyst.mL <sup>-1</sup>	$\sim -1.6$ ( $\sim -1.3$ )	[327]
AgPt-TiO <sub>2</sub>	VIS (>450 nm, NA)	<i>E. coli</i> (K12); $1.5 \times 10^8$ CFU.mL <sup>-1</sup> ; 0.9 NaCl; 7.14 mg catalyst.mL <sup>-1</sup>	$\sim -0.9$ ( $\sim -0.7$ )	[327]

<b>AgPt-TiO<sub>2</sub></b>	400 nm (0.63 mW.cm <sup>-2</sup> )	<i>P. chrysogenum</i> ; 9.6 x 10 <sup>3</sup> CFU.cm <sup>-2</sup> ; 2.4 mg.cm <sup>-2</sup>	-0.66 (-0.56)	[308]
<b>CuAg-TiO<sub>2</sub></b>	400 nm (0.63 mW.cm <sup>-2</sup> )	<i>P. chrysogenum</i> ; 9.6 x 10 <sup>3</sup> CFU.cm <sup>-2</sup> ; 2.4 mg.cm <sup>-2</sup>	-0.66 (-0.45)	[308]
<b>AgCu-β-NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup>@TiO<sub>2</sub></b>	NIR (> 800 nm)	<i>S. aureus</i> ; 1 x 10 <sup>9</sup> CFU.mL <sup>-1</sup> ; 1.67 mg catalyst.mL <sup>-1</sup>	-0.245 (~0)	[284]
<b>Ag@SnO<sub>2</sub>@ZnO</b>	Natural sunlight (~79 mW.cm <sup>-2</sup> )	<i>Bacillus sp.</i> ; 1 x 10 <sup>-7</sup> CFU.mL <sup>-1</sup> ; 0.9% NaCl; 0.5 mg catalyst.mL <sup>-1</sup> (35 °C, pH 6.8)	~-1.90 (~0.01)	[330]
<b>Ag@ZnO</b>	Natural sunlight (NA)	<i>E. coli</i> ; 5 x 10 <sup>6</sup> CFU.mL <sup>-1</sup> ; 0.9% NaCl; 2 mg.L <sup>-1</sup> (35°C)	~-4.64 (~0.03)	[331]
<b>Ag@ZnO</b>	Natural sunlight (NA)	<i>S. aureus</i> ; 5 x 10 <sup>6</sup> CFU.mL <sup>-1</sup> ; 0.9% NaCl; 3 mg.L <sup>-1</sup> (35°C)	~-2.45 (~0.20)	[331]
<b>Ag@ZnO</b>	Natural sunlight (NA)	<i>V. cholera</i> ; 4 x 10 <sup>5</sup> CFU.mL <sup>-1</sup> ; 0.5 mg catalyst.L <sup>-1</sup> (35-65°C)	-2.1 (NA) (35°C) -7.74 (NA) (65°C)	[332]
<b>Ag@AgCl NCs</b>	532 nm (250 mW.cm <sup>-2</sup> )	MRSA; ~1 x 10 <sup>8</sup> CFU.mL <sup>-1</sup> ; 0.01 mg catalyst.mL <sup>-1</sup>	~-1.8 <sup>c</sup> (~0.1 <sup>c</sup> )	[333]
<b>Ag@AgCl NCs</b>	532 nm (250 mW.cm <sup>-2</sup> )	<i>E. coli</i> ; 0.01 mg catalyst.mL <sup>-1</sup>	~-8.5 <sup>c</sup> (-7.2 <sup>c</sup> )	[333]
<b>Ag core in lipid shell layer with incorporated tris(bipyridine)-ruthenium(II)</b>	430 nm (9.76 mW.cm <sup>-2</sup> )	<i>Arthrobacter sp.</i> ; 10 <sup>8</sup> bacteria and 10 <sup>10</sup> NPs (1:100) (RT)	-7.03 (~0)	[335]
<b>Ag core in lipid shell layer with incorporated tris(bipyridine)-ruthenium(II)</b>	430 nm (9.76 mW.cm <sup>-2</sup> )	<i>E. coli.</i> ; 10 <sup>8</sup> bacteria and 10 <sup>10</sup> NPs (1:100) (RT)	-3.93 (~0)	[335]
<b>Ag@Cu<sub>2</sub>O</b>	VIS (400-700 nm, NA)	<i>S. aureus</i> ; 1 x 10 <sup>7</sup> CFU.mL <sup>-1</sup> ; 0.0568 mg.mL <sup>-1</sup>	-0.14 <sup>c</sup> (NA)	[336]
<b>Ag@Cu<sub>2</sub>O</b>	VIS (400-700 nm, NA)	<i>E. coli</i> ; 1 x 10 <sup>7</sup> CFU.mL <sup>-1</sup> ; 0.0568 mg.mL <sup>-1</sup>	-0.17 <sup>c</sup> (~-0.03 <sup>c</sup> )	[336]
<b>Au<sub>0.1</sub>Ag<sub>0.9</sub>-TiO<sub>2</sub> NRs - CA</b>	VIS (>420 nm, NA)	<i>E. coli</i> ; 1 x 10 <sup>6-7</sup> CFU.mL <sup>-1</sup> ;	~-3.7 (-0.59)	[292]

<sup>a</sup> if known

<sup>b</sup>  $k_{app}$  follows the Chick-Watson disinfection model and is determined by the slope of  $\log(N/N_0)$  in function of the time where  $N$  and  $N_0$  are resp. the actual and initial CFU. CFUs were counted by conventional colony counting methods.

<sup>c</sup> calculated from cell viability/bacteriostasis data, derived from the following equation (eq. 17) [336]:

$$\text{Bacteriostasis (\%)} = \frac{(A-B)}{A \times 100\%} = 100\% - \text{Cell viability} \quad (17)$$

With  $A$  and  $B$  resp. the number of bacteria in control circumstances and in the experimental samples.

## 4. Conclusion and Outlook

Despite significant photocatalytic activity enhancements that have been obtained by a myriad of well-considered hybrid material combinations, we feel the achieved efficiencies still leave ample room for improvement. Additional optimization may be achieved by further rational design of such plasmonic hybrid NPs. For instance, Halas' group is investigating core-shell [270] or single atom alloy [273] plasmonic antenna-reactor systems, trying to optimize the activity, selectivity and stability. Nevertheless, also the combination of core-shell and Janus NPs that could possibly yield effective photocatalytic antenna-reactor systems, remains rather unexplored to date. Conversely, also less complex rational design may yield significant improvements. For example, based on a thorough understanding of the dominant underlying plasmon-mediated mechanism(s), better matching of the structure to the mechanism could boost the overall performance. Hot spot engineering by adjusting the spacing layers in core-shell configurations seems promising in that regard [5], especially since sub-nanometer control of both insulating as well as conductive shell layers is proven to be practically feasible using facile and versatile techniques [21, 84]. It should be noted furthermore that a fundamental, theoretical understanding of these processes remains crucial. Utilizing theoretical tools such as DFT and Finite-Difference Time-Domain (FDTD) simulations, is key to identify the loopholes and get the most efficient structure and materials. For example, simulations have pointed out the potential of plasmonic atomic clusters. Yet, the application of such clusters is still underexplored, due to the lack of experimental validation. This remains difficult, since these clusters tend to aggregate, complicating further hybridization into even more advanced materials. Small changes in the number of atoms may already yield significant changes in kinetics and thermodynamics [185–187], pointing out the importance of an accurate synthesis method. Solving this, an extra research line may be developed.

While the fabrication of hybrid plasmonic nanomaterials enables many opportunities, the progressive degree of hybrid complexity may not hamper the eventual scale-up of the catalyst synthesis. Hence, research towards simplifying protocols is still very advantageous for the scientific community. One example is the improvement shown by Asapu *et al.* for the LbL stabilization strategy, leading to a faster and cheaper synthesis of metal@polymer NPs [21, 84]. Generally, to further improve synthesis methods, we also feel there is still underexplored potential in using microreactor-based techniques.

Given the fact that sunlight is free, the incorporation of more solar active metals with an activity ranging from UV up until NIR light, is a key research line. An interesting example provided in that sense was the four times nanogapped Au-Ag core with a CdS shell, yielding such a broad absorption band [113]. However, noble metals and CdS are not sustainable. Hence, it is more promising to use relatively non-toxic, abundant Al of which the LSPR can be tuned between ~250-650 nm [111]. Also other more sustainable plasmonic materials such as Cu, Bi and Mg deserve extra attention. It is even claimed by several pioneers in the plasmonics field, that Al and Mg will be at the center of studies in the near future [28, 111]. Nonetheless, special care should then be taken with respect to long-term stability. Core-shell configurations with protective shells might provide a solution to that end. More stable nanostructures would also allow their introduction in more harsh reaction environments. It would for instance enable to make the shift from photocatalytic H<sub>2</sub> production from (scarce) fresh water to abundant seawater or wastewater as sustainable technology [234]. Considering their activity, the use of core-shell NPs seems also more promising than their alloy counterparts, due to the straightforward charge separation between light absorbing plasmonic cores and reactive shells. However, interesting results are also booked in the field of Janus configurations and deserve further exploration.

Finally, to elucidate the most promising materials, we strongly advertise the use of more standardized photocatalytic activity measurements. In order to compare among different studies, as a minimum,

the spectral output of the light source and especially the absolute irradiance incident on the sample, should be documented in each report. Following the proposed research opportunities, significant progress still lies ahead.

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## Conflict of Interest Statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

## References

1. Artioli G, Angelini I, Polla A (2008) Crystals and phase transitions in protohistoric glass materials. *Phase Transitions* 81:233–252. <https://doi.org/10.1080/01411590701514409>
2. Bobin O, Schvoerer M, Ney C, et al (2003) The role of copper and silver in the colouration of metallic luster decorations (Tunisia, 9th century; Mesopotamia, 10th century; Sicily, 16th century): A first approach. *Color Res Appl* 28:352–359. <https://doi.org/https://doi.org/10.1002/col.10183>
3. Freestone I, Meeks N, Sax M, Higgitt C (2007) The Lycurgus Cup — A Roman nanotechnology. *Gold Bull* 40:270–277. <https://doi.org/10.1007/BF03215599>
4. Verbruggen SW (2015) TiO<sub>2</sub> photocatalysis for the degradation of pollutants in gas phase: From morphological design to plasmonic enhancement. *J Photochem Photobiol C Photochem Rev* 24:64–82. <https://doi.org/10.1016/j.jphotochemrev.2015.07.001>
5. Linic S, Christopher P, Ingram DB (2011) Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat Mater* 10:911–921
6. Atwater HA, Polman A (2010) Plasmonics for improved photovoltaic devices. *Nat Mater* 9:205
7. Anker JN, Hall WP, Lyandres O, et al (2009) Biosensing with plasmonic nanosensors. In: *Nanoscience and Technology*. Co-Published with Macmillan Publishers Ltd, UK, pp 308–319
8. Barbillon G (2020) Latest Novelties on Plasmonic and Non-Plasmonic Nanomaterials for SERS Sensing. *Nanomater*. 10
9. Wang D, Pillai SC, Ho S-H, et al (2018) Plasmonic-based nanomaterials for environmental remediation. *Appl Catal B Environ* 237:721–741. <https://doi.org/10.1016/j.apcatb.2018.05.094>
10. Statista (2021) Annual global CO<sub>2</sub> emissions from 2000 to 2019. <https://www.statista.com/statistics/276629/global-co2-emissions/>. Accessed 21 Sep 2021
11. Fuel Cells and Hydrogen Joint Undertaking (FCH) (2019) Hydrogen Roadmap Europe - a Sustainable Pathway for the European Energy Transition
12. Sharma G, Kumar A, Sharma S, et al (2019) Novel development of nanoparticles to bimetallic nanoparticles and their composites: A review. *J King Saud Univ - Sci* 31:257–269. <https://doi.org/10.1016/j.jksus.2017.06.012>
13. Major KJ, De C, Obare SO (2009) Recent Advances in the Synthesis of Plasmonic Bimetallic

- Nanoparticles. *Plasmonics* 4:61–78. <https://doi.org/10.1007/s11468-008-9077-8>
14. Kavitha R, Kumar SG (2020) Review on bimetallic-deposited TiO<sub>2</sub>: preparation methods, charge carrier transfer pathways and photocatalytic applications. *Chem Pap* 74:717–756. <https://doi.org/10.1007/s11696-019-00995-4>
  15. Sytwu K, Vadai M, Dionne JA (2019) Bimetallic nanostructures: combining plasmonic and catalytic metals for photocatalysis. *Adv Phys X* 4:1619480. <https://doi.org/10.1080/23746149.2019.1619480>
  16. Srinoi P, Chen Y-T, Vittur V, et al (2018) Bimetallic Nanoparticles: Enhanced Magnetic and Optical Properties for Emerging Biological Applications. *Appl. Sci.* 8
  17. Chen T, Rodionov VO (2016) Controllable Catalysis with Nanoparticles: Bimetallic Alloy Systems and Surface Adsorbates. *ACS Catal* 6:4025–4033. <https://doi.org/10.1021/acscatal.6b00714>
  18. Ahn J, Kim J, Qin D (2020) Orthogonal deposition of Au on different facets of Ag cuboctahedra for the fabrication of nanoboxes with complementary surfaces. *Nanoscale* 12:372–379. <https://doi.org/10.1039/C9NR08420G>
  19. Gloag L, Benedetti TM, Cheong S, et al (2018) Three-Dimensional Branched and Faceted Gold–Ruthenium Nanoparticles: Using Nanostructure to Improve Stability in Oxygen Evolution Electrocatalysis. *Angew Chemie Int Ed* 57:10241–10245. <https://doi.org/https://doi.org/10.1002/anie.201806300>
  20. Zhang Q, Kusada K, Wu D, et al (2018) Selective control of fcc and hcp crystal structures in Au–Ru solid-solution alloy nanoparticles. *Nat Commun* 9:510. <https://doi.org/10.1038/s41467-018-02933-6>
  21. Asapu R, Claes N, Bals S, et al (2017) Silver-polymer core-shell nanoparticles for ultrastable plasmon-enhanced photocatalysis. *Appl Catal B Environ* 200:31–38. <https://doi.org/10.1016/j.apcatb.2016.06.062>
  22. Ni Y, Kan C, He L, et al (2019) Alloyed Au-Ag nanorods with desired plasmonic properties and stability in harsh environments. *Photonics Res* 7:558–565. <https://doi.org/10.1364/PRJ.7.000558>
  23. Blommaerts N, Vanrompay H, Nuti S, et al (2019) Unraveling Structural Information of Turkevich Synthesized Plasmonic Gold–Silver Bimetallic Nanoparticles. *Small* 15:1902791. <https://doi.org/https://doi.org/10.1002/smll.201902791>
  24. Davey WP (1925) Precision Measurements of the Lattice Constants of Twelve Common Metals. *Phys Rev* 25:753–761. <https://doi.org/10.1103/PhysRev.25.753>
  25. Combettes S, Lam J, Benzo P, et al (2020) How interface properties control the equilibrium shape of core–shell Fe–Au and Fe–Ag nanoparticles. *Nanoscale* 12:18079–18090. <https://doi.org/10.1039/D0NR04425C>
  26. Lohse SE, Burrows ND, Scarabelli L, et al (2014) Anisotropic Noble Metal Nanocrystal Growth: The Role of Halides. *Chem Mater* 26:34–43. <https://doi.org/10.1021/cm402384j>
  27. Jacobson CR, Solti D, Renard D, et al (2020) Shining Light on Aluminum Nanoparticle Synthesis. *Acc Chem Res* 53:2020–2030. <https://doi.org/10.1021/acs.accounts.0c00419>
  28. Ringe E (2020) Shapes, Plasmonic Properties, and Reactivity of Magnesium Nanoparticles. *J Phys Chem C* 124:15665–15679. <https://doi.org/10.1021/acs.jpcc.0c03871>



29. Thota S, Wang Y, Zhao J (2018) Colloidal Au–Cu alloy nanoparticles: synthesis, optical properties and applications. *Mater Chem Front* 2:1074–1089. <https://doi.org/10.1039/C7QM00538E>
30. Zhang J, Yu Y, Zhang B (2020) Synthesis and characterization of size controlled alloy nanoparticles. *Phys Sci Rev* 5:. <https://doi.org/doi:10.1515/psr-2018-0046>
31. Zhao H, Qi W, Zhou X, et al (2018) Composition-controlled synthesis of platinum and palladium nanoalloys as highly active electrocatalysts for methanol oxidation. *Chinese J Catal* 39:342–349. [https://doi.org/10.1016/S1872-2067\(18\)63020-7](https://doi.org/10.1016/S1872-2067(18)63020-7)
32. Leteba GM, Lang CI (2013) Synthesis of Bimetallic Platinum Nanoparticles for Biosensors. *Sensors* 13
33. Gu J, Lan G, Jiang Y, et al (2015) Shaped Pt–Ni nanocrystals with an ultrathin Pt-enriched shell derived from one-pot hydrothermal synthesis as active electrocatalysts for oxygen reduction. *Nano Res* 8:1480–1496. <https://doi.org/10.1007/s12274-014-0632-7>
34. Xia Y, Gilroy KD, Peng H-C, Xia X (2017) Seed-Mediated Growth of Colloidal Metal Nanocrystals. *Angew Chemie Int Ed* 56:60–95. <https://doi.org/10.1002/anie.201604731>
35. Emam HE (2019) Arabic Gum as Bio-Synthesizer for Ag–Au Bimetallic Nanocomposite Using Seed-Mediated Growth Technique and Its Biological Efficacy. *J Polym Environ* 27:210–223. <https://doi.org/10.1007/s10924-018-1331-3>
36. Dong P, Wu Y, Guo W, Di J (2013) Plasmonic Biosensor Based on Triangular Au/Ag and Au/Ag/Au Core/Shell Nanoprisms onto Indium Tin Oxide Glass. *Plasmonics* 8:1577–1583. <https://doi.org/10.1007/s11468-013-9574-2>
37. Sutter E, Zhang B, Sutter P (2020) DNA-Mediated Three-Dimensional Assembly of Hollow Au–Ag Alloy Nanocages as Plasmonic Crystals. *ACS Appl Nano Mater* 3:8068–8074. <https://doi.org/10.1021/acsanm.0c01528>
38. Yue X, Hou J, Zhao H, et al (2020) Au–Ag alloy nanoparticles with tunable cavity for plasmon-enhanced photocatalytic H<sub>2</sub> evolution. *J Energy Chem* 49:1–7. <https://doi.org/10.1016/j.jechem.2020.01.005>
39. Sui N, Yue R, Wang Y, et al (2019) Boosting methanol oxidation reaction with Au@AgPt yolk-shell nanoparticles. *J Alloys Compd* 790:792–798. <https://doi.org/10.1016/j.jallcom.2019.03.196>
40. Kamat GA, Yan C, Osowiecki WT, et al (2020) Self-Limiting Shell Formation in Cu@Ag Core–Shell Nanocrystals during Galvanic Replacement. *J Phys Chem Lett* 11:5318–5323. <https://doi.org/10.1021/acs.jpcllett.0c01551>
41. Reboul J, Li ZY, Yuan J, et al (2021) Synthesis of small Ni-core–Au-shell catalytic nanoparticles on TiO<sub>2</sub> by galvanic replacement reaction. *Nanoscale Adv* 3:823–835. <https://doi.org/10.1039/D0NA00617C>
42. Wang Z, Ai B, Wang Y, et al (2019) Hierarchical Control of Plasmonic Nanochemistry in Microreactor. *ACS Appl Mater Interfaces* 11:35429–35437. <https://doi.org/10.1021/acsami.9b10917>
43. Sebastian V, Smith CD, Jensen KF (2016) Shape-controlled continuous synthesis of metal nanostructures. *Nanoscale* 8:7534–7543. <https://doi.org/10.1039/C5NR08531D>
44. Chen P-C, Liu G, Zhou Y, et al (2015) Tip-Directed Synthesis of Multimetallic Nanoparticles. *J Am Chem Soc* 137:9167–9173. <https://doi.org/10.1021/jacs.5b05139>

45. Neumeister A, Jakobi J, Rehbock C, et al (2014) Monophasic ligand-free alloy nanoparticle synthesis determinants during pulsed laser ablation of bulk alloy and consolidated microparticles in water. *Phys Chem Chem Phys* 16:23671–23678. <https://doi.org/10.1039/C4CP03316G>
46. Prymak O, Jakobi J, Rehbock C, et al (2018) Crystallographic characterization of laser-generated, polymer-stabilized 4 nm silver-gold alloyed nanoparticles. *Mater Chem Phys* 207:442–450. <https://doi.org/10.1016/j.matchemphys.2017.12.080>
47. Vegard L (1921) Die Konstitution der Mischkristalle und die Raumfüllung der Atome. *Zeitschrift für Phys* 5:17–26. <https://doi.org/10.1007/BF01349680>
48. Petkov V, Shastri S, Shan S, et al (2013) Resolving Atomic Ordering Differences in Group 11 Nanosized Metals and Binary Alloy Catalysts by Resonant High-Energy X-ray Diffraction and Computer Simulations. *J Phys Chem C* 117:22131–22141. <https://doi.org/10.1021/jp408017v>
49. Bozzolo G, Garcés JE, Derry GN (2007) Atomistic modeling of segregation and bulk ordering in Ag–Au alloys. *Surf Sci* 601:2038–2046. <https://doi.org/10.1016/j.susc.2007.02.035>
50. Nguyen CM, Frias Batista LM, John MG, et al (2021) Mechanism of Gold–Silver Alloy Nanoparticle Formation by Laser Coreduction of Gold and Silver Ions in Solution. *J Phys Chem B* 125:907–917. <https://doi.org/10.1021/acs.jpcc.0c10096>
51. Zhang D, Gökce B, Barcikowski S (2017) Laser Synthesis and Processing of Colloids: Fundamentals and Applications. *Chem Rev* 117:3990–4103. <https://doi.org/10.1021/acs.chemrev.6b00468>
52. Liao W, Lan S, Gao L, et al (2017) Nanocrystalline high-entropy alloy (CoCrFeNiAl<sub>0.3</sub>) thin-film coating by magnetron sputtering. *Thin Solid Films* 638:383–388. <https://doi.org/10.1016/j.tsf.2017.08.006>
53. Li B, Huang L, Zhou M, et al (2014) Preparation and spectral analysis of gold nanoparticles using magnetron sputtering and thermal annealing. *J Wuhan Univ Technol Sci Ed* 29:651–655. <https://doi.org/10.1007/s11595-014-0973-9>
54. Atef N, Emara SS, Eissa DS, et al (2021) Well-dispersed Au nanoparticles prepared via magnetron sputtering on TiO<sub>2</sub> nanotubes with unprecedentedly high activity for water splitting. *Electrochem Sci Adv* 1:e2000004. <https://doi.org/10.1002/elsa.202000004>
55. Sun L, Yuan G, Gao L, et al (2021) Chemical vapour deposition. *Nat Rev Methods Prim* 1:5. <https://doi.org/10.1038/s43586-020-00005-y>
56. Harvey E, Ghantasala M (2006) 12 - Nanofabrication. In: Hannink RHJ, Hill AJBT-NC of M (eds). Woodhead Publishing, pp 303–330
57. Bakrania SD, Rathore GK, Wooldridge MS (2009) An investigation of the thermal decomposition of gold acetate. *J Therm Anal Calorim* 95:117–122. <https://doi.org/10.1007/s10973-008-9173-1>
58. Hirayama Y, Takagi K (2019) Evaluation of compositional homogeneity of Fe-Co alloy nanoparticles prepared by thermal plasma synthesis. *J Alloys Compd* 792:594–598. <https://doi.org/10.1016/j.jallcom.2019.04.083>
59. Verbruggen SW, Keulemans M, Goris B, et al (2016) Plasmonic ‘rainbow’ photocatalyst with broadband solar light response for environmental applications. *Appl Catal B Environ* 188:147–153. <https://doi.org/10.1016/j.apcatb.2016.02.002>
60. Samal AK, Polavarapu L, Rodal-Cedeira S, et al (2013) Size Tunable Au@Ag Core–Shell

- Nanoparticles: Synthesis and Surface-Enhanced Raman Scattering Properties. *Langmuir* 29:15076–15082. <https://doi.org/10.1021/la403707j>
61. Boltersdorf J, Leff AC, Forcherio GT, Baker DR (2021) Plasmonic Au–Pd Bimetallic Nanocatalysts for Hot-Carrier-Enhanced Photocatalytic and Electrochemical Ethanol Oxidation. *Cryst.* 11
  62. Etchegoin PG, Le Ru EC, Meyer M (2006) An analytic model for the optical properties of gold. *J Chem Phys* 125:164705. <https://doi.org/10.1063/1.2360270>
  63. Balamurugan B, Maruyama T (2005) Evidence of an enhanced interband absorption in Au nanoparticles: Size-dependent electronic structure and optical properties. *Appl Phys Lett* 87:143105. <https://doi.org/10.1063/1.2077834>
  64. Kolwas K, Derkachova A (2020) Impact of the Interband Transitions in Gold and Silver on the Dynamics of Propagating and Localized Surface Plasmons. *Nanomater.* 10
  65. Borah R, Verbruggen SW (2020) Silver–Gold Bimetallic Alloy versus Core–Shell Nanoparticles: Implications for Plasmonic Enhancement and Photothermal Applications. *J Phys Chem C* 124:12081–12094. <https://doi.org/10.1021/acs.jpcc.0c02630>
  66. Ponzellini P, Giovannini G, Cattarin S, et al (2019) Metallic Nanoporous Aluminum–Magnesium Alloy for UV-Enhanced Spectroscopy. *J Phys Chem C* 123:20287–20296. <https://doi.org/10.1021/acs.jpcc.9b04230>
  67. Pujari A, Thomas T (2021) Aluminium nanoparticles alloyed with other earth-abundant plasmonic metals for light trapping in thin-film a-Si solar cells. *Sustain Mater Technol* 28:e00250. <https://doi.org/10.1016/j.susmat.2021.e00250>
  68. Kim D, Resasco J, Yu Y, et al (2014) Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles. *Nat Commun* 5:4948. <https://doi.org/10.1038/ncomms5948>
  69. Liu Y, Walker ARH (2010) Monodisperse Gold–Copper Bimetallic Nanocubes: Facile One-Step Synthesis with Controllable Size and Composition. *Angew Chemie Int Ed* 49:6781–6785. <https://doi.org/https://doi.org/10.1002/anie.201001931>
  70. Henkel A, Jakab A, Brunklaus G, Sönnichsen C (2009) Tuning Plasmonic Properties by Alloying Copper into Gold Nanorods. *J Phys Chem C* 113:2200–2204. <https://doi.org/10.1021/jp810433e>
  71. De Marchi S, Núñez-Sánchez S, Bodelón G, et al (2020) Pd nanoparticles as a plasmonic material: synthesis, optical properties and applications. *Nanoscale* 12:23424–23443. <https://doi.org/10.1039/D0NR06270G>
  72. Sugawa K, Tahara H, Yamashita A, et al (2015) Refractive Index Susceptibility of the Plasmonic Palladium Nanoparticle: Potential as the Third Plasmonic Sensing Material. *ACS Nano* 9:1895–1904. <https://doi.org/10.1021/nn506800a>
  73. Cortie MB, McDonagh AM (2011) Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles. *Chem Rev* 111:3713–3735. <https://doi.org/10.1021/cr1002529>
  74. Peng Z, Yang H (2008) Ag–Pt alloy nanoparticles with the compositions in the miscibility gap. *J Solid State Chem* 181:1546–1551. <https://doi.org/10.1016/j.jssc.2008.03.013>
  75. Zhu X, Guo Q, Sun Y, et al (2019) Optimising surface d charge of AuPd nanoalloy catalysts for enhanced catalytic activity. *Nat Commun* 10:1428. <https://doi.org/10.1038/s41467-019-09421-5>

76. Valenti M, Venugopal A, Tordera D, et al (2017) Hot Carrier Generation and Extraction of Plasmonic Alloy Nanoparticles. *ACS Photonics* 4:1146–1152. <https://doi.org/10.1021/acsp Photonics.6b01048>
77. Kadkhodazadeh S, Nugroho FAA, Langhammer C, et al (2019) Optical Property–Composition Correlation in Noble Metal Alloy Nanoparticles Studied with EELS. *ACS Photonics* 6:779–786. <https://doi.org/10.1021/acsp Photonics.8b01791>
78. Lee C, Park Y, Park JY (2019) Hot electrons generated by intraband and interband transition detected using a plasmonic Cu/TiO<sub>2</sub> nanodiode. *RSC Adv* 9:18371–18376. <https://doi.org/10.1039/C9RA02601K>
79. Keast VJ, Barnett RL, Cortie MB (2014) First principles calculations of the optical and plasmonic response of Au alloys and intermetallic compounds. *J Phys Condens Matter* 26:305501. <https://doi.org/10.1088/0953-8984/26/30/305501>
80. Rossi TP, Erhart P, Kuisma M (2020) Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure. *ACS Nano* 14:9963–9971. <https://doi.org/10.1021/acsnano.0c03004>
81. Ma J, Zhang X, Gao S (2021) Tunable electron and hole injection channels at plasmonic Al–TiO<sub>2</sub> interfaces. *Nanoscale* 13:14073–14080. <https://doi.org/10.1039/D1NR03697A>
82. Huang H, Zhang L, Lv Z, et al (2016) Unraveling Surface Plasmon Decay in Core–Shell Nanostructures toward Broadband Light-Driven Catalytic Organic Synthesis. *J Am Chem Soc* 138:6822–6828. <https://doi.org/10.1021/jacs.6b02532>
83. van der Hoeven JES, Jelic J, Olthof LA, et al (2021) Unlocking synergy in bimetallic catalysts by core–shell design. *Nat Mater*. <https://doi.org/10.1038/s41563-021-00996-3>
84. Asapu R, Claes N, Ciocarlan R-G, et al (2019) Electron Transfer and Near-Field Mechanisms in Plasmonic Gold-Nanoparticle-Modified TiO<sub>2</sub> Photocatalytic Systems. *ACS Appl Nano Mater* 2:4067–4074. <https://doi.org/10.1021/acsnm.9b00485>
85. Pougina A, Dodekatos G, Dilla M, et al (2018) Au@TiO<sub>2</sub> Core–Shell Composites for the Photocatalytic Reduction of CO<sub>2</sub>. *Chem – A Eur J* 24:12416–12425. <https://doi.org/10.1002/chem.201801796>
86. Hong D, Lyu L-M, Koga K, et al (2019) Plasmonic Ag@TiO<sub>2</sub> Core–Shell Nanoparticles for Enhanced CO<sub>2</sub> Photoconversion to CH<sub>4</sub>. *ACS Sustain Chem Eng* 7:18955–18964. <https://doi.org/10.1021/acssuschemeng.9b04345>
87. Mondal I, Gonuguntla S, Pal U (2019) Photoinduced Fabrication of Cu/TiO<sub>2</sub> Core–Shell Heterostructures Derived from Cu-MOF for Solar Hydrogen Generation: The Size of the Cu Nanoparticle Matters. *J Phys Chem C* 123:26073–26081. <https://doi.org/10.1021/acs.jpcc.9b07171>
88. Prodan E, Radloff C, Halas NJ, Nordlander P (2003) A Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science* (80- ) 302:419 LP – 422. <https://doi.org/10.1126/science.1089171>
89. Kamimura S, Yamashita S, Abe S, et al (2017) Effect of core@shell (Au@Ag) nanostructure on surface plasmon-induced photocatalytic activity under visible light irradiation. *Appl Catal B Environ* 211:11–17. <https://doi.org/10.1016/j.apcatb.2017.04.028>
90. Wang Y, Zhang Q, Wang Y, et al (2021) Ultrastable Plasmonic Cu-Based Core–Shell Nanoparticles. *Chem Mater* 33:695–705. <https://doi.org/10.1021/acs.chemmater.0c04059>

91. Joplin A, Hosseini Jebeli SA, Sung E, et al (2017) Correlated Absorption and Scattering Spectroscopy of Individual Platinum-Decorated Gold Nanorods Reveals Strong Excitation Enhancement in the Nonplasmonic Metal. *ACS Nano* 11:12346–12357. <https://doi.org/10.1021/acsnano.7b06239>
92. Song HM, Moosa BA, Khashab NM (2012) Water-dispersable hybrid Au–Pd nanoparticles as catalysts in ethanol oxidation, aqueous phase Suzuki–Miyaura and Heck reactions. *J Mater Chem* 22:15953–15959. <https://doi.org/10.1039/C2JM32702C>
93. Wang F, Li C, Chen H, et al (2013) Plasmonic Harvesting of Light Energy for Suzuki Coupling Reactions. *J Am Chem Soc* 135:5588–5601. <https://doi.org/10.1021/ja310501y>
94. Lai H, Xiao W, Wang Y, et al (2021) Plasmon-induced carrier separation boosts high-selective photocatalytic CO<sub>2</sub> reduction on dagger-axe-like Cu@Co core–shell bimetal. *Chem Eng J* 417:129295. <https://doi.org/10.1016/j.cej.2021.129295>
95. Kuo C-S, Lyu L-M, Sia R-F, et al (2020) Ultrathin Octahedral CuPt Nanocages Obtained by Facet Transformation from Rhombic Dodecahedral Core–Shell Nanocrystals. *ACS Sustain Chem Eng* 8:10544–10553. <https://doi.org/10.1021/acssuschemeng.0c03256>
96. Tsai C-H, Chen S-Y, Song J-M, et al (2015) Effect of Ag Templates on the Formation of Au-Ag Hollow/Core-Shell Nanostructures. *Nanoscale Res Lett* 10:438. <https://doi.org/10.1186/s11671-015-1141-7>
97. Yang Y, Liu J, Fu Z-W, Qin D (2014) Galvanic Replacement-Free Deposition of Au on Ag for Core–Shell Nanocubes with Enhanced Chemical Stability and SERS Activity. *J Am Chem Soc* 136:8153–8156. <https://doi.org/10.1021/ja502472x>
98. Mendoza C, Désert A, Chateau D, et al (2020) Au nanobipyramids@mSiO<sub>2</sub> core–shell nanoparticles for plasmon-enhanced singlet oxygen photooxygenations in segmented flow microreactors. *Nanoscale Adv* 2:5280–5287. <https://doi.org/10.1039/D0NA00533A>
99. Mostafa AM, Mwafy EA, Awwad NS, Ibrahim HA (2021) Au@Ag core/shell nanoparticles prepared by laser-assisted method for optical limiting applications. *J Mater Sci Mater Electron* 32:14728–14739. <https://doi.org/10.1007/s10854-021-06028-9>
100. Cha SK, Mun JH, Chang T, et al (2015) Au–Ag Core–Shell Nanoparticle Array by Block Copolymer Lithography for Synergistic Broadband Plasmonic Properties. *ACS Nano* 9:5536–5543. <https://doi.org/10.1021/acsnano.5b01641>
101. Forcherio GT, Baker DR, Boltersdorf J, et al (2018) Targeted Deposition of Platinum onto Gold Nanorods by Plasmonic Hot Electrons. *J Phys Chem C* 122:28901–28909. <https://doi.org/10.1021/acs.jpcc.8b07868>
102. van der Hoeven JES, Deng T-S, Albrecht W, et al (2021) Structural Control over Bimetallic Core–Shell Nanorods for Surface-Enhanced Raman Spectroscopy. *ACS Omega* 6:7034–7046. <https://doi.org/10.1021/acsomega.0c06321>
103. Spitaleri L, Nicotra G, Zimbone M, et al (2019) Fast and Efficient Sun Light Photocatalytic Activity of Au\_ZnO Core–Shell Nanoparticles Prepared by a One-Pot Synthesis. *ACS Omega* 4:15061–15066. <https://doi.org/10.1021/acsomega.9b01850>
104. Huang J, He Y, Wang L, et al (2017) Bifunctional Au@TiO<sub>2</sub> core–shell nanoparticle films for clean water generation by photocatalysis and solar evaporation. *Energy Convers Manag* 132:452–459. <https://doi.org/10.1016/j.enconman.2016.11.053>
105. Hartman T, Weckhuysen BM (2018) Thermally Stable TiO<sub>2</sub>- and SiO<sub>2</sub>-Shell-Isolated Au

- Nanoparticles for In Situ Plasmon-Enhanced Raman Spectroscopy of Hydrogenation Catalysts. *Chem – A Eur J* 24:3733–3741. <https://doi.org/https://doi.org/10.1002/chem.201704370>
106. Kamarudheen R, Kumari G, Baldi A (2020) Plasmon-driven synthesis of individual metal@semiconductor core@shell nanoparticles. *Nat Commun* 11:3957. <https://doi.org/10.1038/s41467-020-17789-y>
  107. Eom H, Jung J-Y, Shin Y, et al (2014) Strong localized surface plasmon resonance effects of Ag/TiO<sub>2</sub> core-shell nanowire arrays in UV and visible light for photocatalytic activity. *Nanoscale* 6:226–234. <https://doi.org/10.1039/C3NR04388F>
  108. Seong S, Park I-S, Jung YC, et al (2019) Synthesis of Ag-ZnO core-shell nanoparticles with enhanced photocatalytic activity through atomic layer deposition. *Mater Des* 177:107831. <https://doi.org/10.1016/j.matdes.2019.107831>
  109. Liz-Marzán LM, Giersig M, Mulvaney P (1996) Synthesis of Nanosized Gold-Silica Core-Shell Particles. *Langmuir* 12:4329–4335. <https://doi.org/10.1021/la9601871>
  110. Huang MH, Rej S, Chiu C-Y (2015) Facet-Dependent Optical Properties Revealed through Investigation of Polyhedral Au-Cu<sub>2</sub>O and Bimetallic Core-Shell Nanocrystals. *Small* 11:2716–2726. <https://doi.org/https://doi.org/10.1002/sml.201403542>
  111. Knight MW, King NS, Liu L, et al (2014) Aluminum for Plasmonics. *ACS Nano* 8:834–840. <https://doi.org/10.1021/nn405495q>
  112. Ma X, Zhao K, Tang H, et al (2014) New Insight into the Role of Gold Nanoparticles in Au@CdS Core-Shell Nanostructures for Hydrogen Evolution. *Small* 10:4664–4670. <https://doi.org/https://doi.org/10.1002/sml.201401494>
  113. Ma L, Chen Y-L, Yang D-J, et al (2020) Multi-interfacial plasmon coupling in multigap (Au/AgAu)@CdS core-shell hybrids for efficient photocatalytic hydrogen generation. *Nanoscale* 12:4383–4392. <https://doi.org/10.1039/C9NR09696E>
  114. Lee C, Shin K, Lee YJ, et al (2018) Effects of shell thickness on Ag-Cu<sub>2</sub>O core-shell nanoparticles with bumpy structures for enhancing photocatalytic activity and stability. *Catal Today* 303:313–319. <https://doi.org/10.1016/j.cattod.2017.08.016>
  115. Bai X, Zong R, Li C, et al (2014) Enhancement of visible photocatalytic activity via Ag@C<sub>3</sub>N<sub>4</sub> core-shell plasmonic composite. *Appl Catal B Environ* 147:82–91. <https://doi.org/10.1016/j.apcatb.2013.08.007>
  116. Ning X, Lu G (2020) Photocorrosion inhibition of CdS-based catalysts for photocatalytic overall water splitting. *Nanoscale* 12:1213–1223. <https://doi.org/10.1039/C9NR09183A>
  117. Monga A, Bathla A, Pal B (2017) A Cu-Au bimetallic co-catalysis for the improved photocatalytic activity of TiO<sub>2</sub> under visible light radiation. *Sol Energy* 155:1403–1410. <https://doi.org/10.1016/j.solener.2017.07.084>
  118. Li A, Zhu W, Li C, et al (2019) Rational design of yolk-shell nanostructures for photocatalysis. *Chem Soc Rev* 48:1874–1907. <https://doi.org/10.1039/C8CS00711J>
  119. Sun H, He Q, Zeng S, et al (2017) Controllable growth of Au@TiO<sub>2</sub> yolk-shell nanoparticles and their geometry parameter effects on photocatalytic activity. *New J Chem* 41:7244–7252. <https://doi.org/10.1039/C7NJ01491K>
  120. Wang Y, Yang C, Chen A, et al (2019) Influence of yolk-shell Au@TiO<sub>2</sub> structure induced photocatalytic activity towards gaseous pollutant degradation under visible light. *Appl Catal B Environ* 251:57–65. <https://doi.org/10.1016/j.apcatb.2019.03.056>

121. Yang H, Li M, Li S, et al (2020) A critical structured TiO<sub>2</sub> with enhanced photocatalytic activity during the formation of yolk-shell structured TiO<sub>2</sub>. *J Mater Sci Mater Electron* 31:2–9. <https://doi.org/10.1007/s10854-018-9986-z>
122. Zhao B, Guo X, Zhao W, et al (2017) Facile synthesis of yolk-shell Ni@void@SnO<sub>2</sub>(Ni<sub>3</sub>Sn<sub>2</sub>) ternary composites via galvanic replacement/Kirkendall effect and their enhanced microwave absorption properties. *Nano Res* 10:331–343. <https://doi.org/10.1007/s12274-016-1295-3>
123. Li A, Zhang P, Chang X, et al (2015) Gold Nanorod@TiO<sub>2</sub> Yolk-Shell Nanostructures for Visible-Light-Driven Photocatalytic Oxidation of Benzyl Alcohol. *Small* 11:1892–1899. <https://doi.org/https://doi.org/10.1002/sml.201403058>
124. Wang W, Efrima S, Regev O (1998) Directing Oleate Stabilized Nanosized Silver Colloids into Organic Phases. *Langmuir* 14:602–610. <https://doi.org/10.1021/la9710177>
125. Tzhayik O, Sawant P, Efrima S, et al (2002) Xanthate Capping of Silver, Copper, and Gold Colloids. *Langmuir* 18:3364–3369. <https://doi.org/10.1021/la015653n>
126. Heinz H, Pramanik C, Heinz O, et al (2017) Nanoparticle decoration with surfactants: Molecular interactions, assembly, and applications. *Surf Sci Rep* 72:1–58. <https://doi.org/10.1016/j.surfrep.2017.02.001>
127. Turkevich J, Stevenson PC, Hillier J (1951) a Study of the Nucleation and Growth Processes I N the Synthesis of. *Discuss Faraday Soc* 55:. <https://doi.org/10.1039/DF9511100055>
128. Verbruggen SW, Keulemans M, Filippousi M, et al (2014) Plasmonic gold–silver alloy on TiO<sub>2</sub> photocatalysts with tunable visible light activity. *Appl Catal B Environ* 156–157:116–121. <https://doi.org/10.1016/j.apcatb.2014.03.027>
129. Cao M, Liu Q, Chen M, et al (2017) Dispersing hydrophilic nanoparticles in nonaqueous solvents with superior long-term stability. *RSC Adv* 7:25535–25541. <https://doi.org/10.1039/C7RA03472E>
130. Xing S, Tan LH, Yang M, et al (2009) Highly controlled core/shell structures: tunable conductive polymer shells on gold nanoparticles and nanochains. *J Mater Chem* 19:3286–3291. <https://doi.org/10.1039/B900993K>
131. Chen J-Y, Wu H-C, Chiu Y-C, Chen W-C (2014) Plasmon-Enhanced Polymer Photovoltaic Device Performance Using Different Patterned Ag/PVP Electrospun Nanofibers. *Adv Energy Mater* 4:1301665. <https://doi.org/10.1002/aenm.201301665>
132. Yu S, Wilson AJ, Heo J, Jain PK (2018) Plasmonic Control of Multi-Electron Transfer and C–C Coupling in Visible-Light-Driven CO<sub>2</sub> Reduction on Au Nanoparticles. *Nano Lett* 18:2189–2194. <https://doi.org/10.1021/acs.nanolett.7b05410>
133. Kvítek L, Panáček A, Soukupová J, et al (2008) Effect of Surfactants and Polymers on Stability and Antibacterial Activity of Silver Nanoparticles (NPs). *J Phys Chem C* 112:5825–5834. <https://doi.org/10.1021/jp711616v>
134. Lisunova M, Mahmoud M, Holland N, et al (2012) The unusual fluorescence intensity enhancement of poly(p-phenyleneethynylene) polymer separated from the silver nanocube surface by H-bonded LbL shells. *J Mater Chem* 22:16745–16753. <https://doi.org/10.1039/C2JM32450D>
135. Schneider G, Decher G (2004) From Functional Core/Shell Nanoparticles Prepared via Layer-by-Layer Deposition to Empty Nanospheres. *Nano Lett* 4:1833–1839. <https://doi.org/10.1021/nl0490826>

136. Schneider G, Decher G (2008) Functional Core/Shell Nanoparticles via Layer-by-Layer Assembly. Investigation of the Experimental Parameters for Controlling Particle Aggregation and for Enhancing Dispersion Stability. *Langmuir* 24:1778–1789. <https://doi.org/10.1021/la7021837>
137. Claes N, Asapu R, Blommaerts N, et al (2018) Characterization of silver-polymer core–shell nanoparticles using electron microscopy. *Nanoscale* 10:9186–9191. <https://doi.org/10.1039/C7NR09517A>
138. Yu X, Lei DY, Amin F, et al (2013) Distance control in-between plasmonic nanoparticles via biological and polymeric spacers. *Nano Today* 8:480–493. <https://doi.org/https://doi.org/10.1016/j.nantod.2013.09.001>
139. Dingenen F, Blommaerts N, Van Hal M, et al (2021) Layer-by-Layer-Stabilized Plasmonic Gold-Silver Nanoparticles on TiO<sub>2</sub>: Towards Stable Solar Active Photocatalysts. *Nanomater.* 11
140. Liang L, Lam SH, Ma L, et al (2020) (Gold nanorod core)/(poly(3,4-ethylene-dioxythiophene) shell) nanostructures and their monolayer arrays for plasmonic switching. *Nanoscale* 12:20684–20692. <https://doi.org/10.1039/D0NR05502F>
141. Yang K, Li Y, Huang K, et al (2014) Promoted effect of PANI on the preferential oxidation of CO in the presence of H<sub>2</sub> over Au/TiO<sub>2</sub> under visible light irradiation. *Int J Hydrogen Energy* 39:18312–18325. <https://doi.org/10.1016/j.ijhydene.2014.09.053>
142. Jeon J-W, Ledin PA, Geldmeier JA, et al (2016) Electrically Controlled Plasmonic Behavior of Gold Nanocube@Polyaniline Nanostructures: Transparent Plasmonic Aggregates. *Chem Mater* 28:2868–2881. <https://doi.org/10.1021/acs.chemmater.6b00882>
143. Wang X, Shen Y, Xie A, Chen S (2013) One-step synthesis of Ag@PANI nanocomposites and their application to detection of mercury. *Mater Chem Phys* 140:487–492. <https://doi.org/10.1016/j.matchemphys.2013.03.058>
144. Jiang N, Zhuo X, Wang J (2018) Active Plasmonics: Principles, Structures, and Applications. *Chem Rev* 118:3054–3099. <https://doi.org/10.1021/acs.chemrev.7b00252>
145. Lu W, Jiang N, Wang J (2017) Active Electrochemical Plasmonic Switching on Polyaniline-Coated Gold Nanocrystals. *Adv Mater* 29:1604862. <https://doi.org/10.1002/adma.201604862>
146. Magnozzi M, Brasse Y, König TAF, et al (2020) Plasmonics of Au/Polymer Core/Shell Nanocomposites for Thermoresponsive Hybrid Metasurfaces. *ACS Appl Nano Mater* 3:1674–1682. <https://doi.org/10.1021/acsanm.9b02403>
147. Pastoriza-Santos I, Kinnear C, Pérez-Juste J, et al (2018) Plasmonic polymer nanocomposites. *Nat Rev Mater* 3:375–391. <https://doi.org/10.1038/s41578-018-0050-7>
148. Seh ZW, Liu S, Low M, et al (2012) Janus Au-TiO<sub>2</sub> Photocatalysts with Strong Localization of Plasmonic Near-Fields for Efficient Visible-Light Hydrogen Generation. *Adv Mater* 24:2310–2314. <https://doi.org/10.1002/adma.201104241>
149. Tong F, Lou Z, Liang X, et al (2020) Plasmon-induced dehydrogenation of formic acid on Pd-dotted Ag@Au hexagonal nanoplates and single-particle study. *Appl Catal B Environ* 277:119226. <https://doi.org/10.1016/j.apcatb.2020.119226>
150. Liu L, Dao TD, Kodiyath R, et al (2014) Plasmonic Janus-Composite Photocatalyst Comprising Au and C–TiO<sub>2</sub> for Enhanced Aerobic Oxidation over a Broad Visible-Light Range. *Adv Funct Mater* 24:7754–7762. <https://doi.org/10.1002/adfm.201402088>
151. Wen L, Xu R, Cui C, et al (2018) Template-Guided Programmable Janus Heteronanostructure



- Arrays for Efficient Plasmonic Photocatalysis. *Nano Lett* 18:4914–4921.  
<https://doi.org/10.1021/acs.nanolett.8b01675>
152. Robotjazi H, Lou M, Clark BD, et al (2020) Site-Selective Nanoreactor Deposition on Photocatalytic Al Nanocubes. *Nano Lett* 20:4550–4557.  
<https://doi.org/10.1021/acs.nanolett.0c01405>
  153. Zhang H, Lam SH, Guo Y, et al (2021) Selective Deposition of Catalytic Metals on Plasmonic Au Nanocups for Room-Light-Active Photooxidation of o-Phenylenediamine. *ACS Appl Mater Interfaces*. <https://doi.org/10.1021/acsami.1c03806>
  154. Albrecht W, Bladt E, Vanrompay H, et al (2019) Thermal Stability of Gold/Palladium Octopods Studied in Situ in 3D: Understanding Design Rules for Thermally Stable Metal Nanoparticles. *ACS Nano* 13:6522–6530. <https://doi.org/10.1021/acsnano.9b00108>
  155. Ben-Shahar Y, Banin U (2016) Hybrid Semiconductor–Metal Nanorods as Photocatalysts. *Top Curr Chem* 374:54. <https://doi.org/10.1007/s41061-016-0052-0>
  156. Lee SW, Hong JW, Lee H, et al (2018) The surface plasmon-induced hot carrier effect on the catalytic activity of CO oxidation on a Cu<sub>2</sub>O/hexoctahedral Au inverse catalyst. *Nanoscale* 10:10835–10843. <https://doi.org/10.1039/C8NR00555A>
  157. Liu L, Yang H, Ren X, et al (2015) Au–ZnO hybrid nanoparticles exhibiting strong charge-transfer-induced SERS for recyclable SERS-active substrates. *Nanoscale* 7:5147–5151. <https://doi.org/10.1039/C5NR00491H>
  158. Daware K, Kasture M, Kalubarme R, et al (2019) Detection of toxic metal ions Pb<sup>2+</sup> in water using SiO<sub>2</sub>@Au core-shell nanostructures: A simple technique for water quality monitoring. *Chem Phys Lett* 732:136635. <https://doi.org/10.1016/j.cplett.2019.136635>
  159. Reguera J, Flora T, Winckelmans N, et al (2020) Self-assembly of Janus Au:Fe<sub>3</sub>O<sub>4</sub> branched nanoparticles. From organized clusters to stimuli-responsive nanogel suprastructures. *Nanoscale Adv* 2:2525–2530. <https://doi.org/10.1039/D0NA00102C>
  160. Yang L, Yan Z, Yang L, et al (2020) Photothermal conversion of SiO<sub>2</sub>@Au nanoparticles mediated by surface morphology of gold cluster layer. *RSC Adv* 10:33119–33128. <https://doi.org/10.1039/D0RA06278B>
  161. Li W, Guo Y, Zhang P (2010) General Strategy to Prepare TiO<sub>2</sub>-Core Gold-Shell Nanoparticles as SERS-Tags. *J Phys Chem C* 114:7263–7268. <https://doi.org/10.1021/jp908160m>
  162. Elmoula MA, Panaitescu E, Phan M, et al (2009) Controlled attachment of gold nanoparticles on ordered titania nanotube arrays. *J Mater Chem* 19:4483–4487. <https://doi.org/10.1039/B903197A>
  163. Gurbatov SO, Modin E, Puzikov V, et al (2021) Black Au-Decorated TiO<sub>2</sub> Produced via Laser Ablation in Liquid. *ACS Appl Mater Interfaces* 13:6522–6531. <https://doi.org/10.1021/acsami.0c20463>
  164. Tang KY, Chen JX, Legaspi EDR, et al (2021) Gold-decorated TiO<sub>2</sub> nanofibrous hybrid for improved solar-driven photocatalytic pollutant degradation. *Chemosphere* 265:129114. <https://doi.org/10.1016/j.chemosphere.2020.129114>
  165. Liu T, Li Y (2016) Plasmonic solar desalination. *Nat Photonics* 10:361–362. <https://doi.org/10.1038/nphoton.2016.97>
  166. Dhiman M, Maity A, Das A, et al (2019) Plasmonic colloidosomes of black gold for solar energy harvesting and hotspots directed catalysis for CO<sub>2</sub> to fuel conversion. *Chem Sci* 10:6594–

6603. <https://doi.org/10.1039/C9SC02369K>
167. Efremova M V., Nalench YA, Myrovali E, et al (2018) Size-selected Fe<sub>3</sub>O<sub>4</sub>-Au hybrid nanoparticles for improved magnetism-based theranostics. *Beilstein J Nanotechnol* 9:2684–2699. <https://doi.org/10.3762/bjnano.9.251>
168. Zhou L, Zhang H, Bao H, et al (2018) Decoration of Au Nanoparticles on MoS<sub>2</sub> Nanospheres: From Janus to Core/Shell Structure. *J Phys Chem C* 122:8628–8636. <https://doi.org/10.1021/acs.jpcc.8b01216>
169. Chen P, Hu J, Yin M, et al (2021) MoS<sub>2</sub> Nanoflowers Decorated with Au Nanoparticles for Visible-Light-Enhanced Gas Sensing. *ACS Appl Nano Mater*. <https://doi.org/10.1021/acsanm.1c00847>
170. Ponnuvelu D V, Dhakshinamoorthy J, Prasad AK, et al (2020) Geometrically Controlled Au-Decorated ZnO Heterojunction Nanostructures for NO<sub>2</sub> Detection. *ACS Appl Nano Mater* 3:5898–5909. <https://doi.org/10.1021/acsanm.0c01053>
171. Kim J-H, Mirzaei A, Kim HW, Kim SS (2019) Realization of Au-decorated WS<sub>2</sub> nanosheets as low power-consumption and selective gas sensors. *Sensors Actuators B Chem* 296:126659. <https://doi.org/10.1016/j.snb.2019.126659>
172. Dunklin JR, Lafargue P, Higgins TM, et al (2018) Monolayer-enriched production of Au-decorated WS<sub>2</sub> Nanosheets via Defect Engineering. *MRS Adv* 3:2435–2440. <https://doi.org/10.1557/adv.2018.350>
173. Ahmad MZ, Sadek AZ, Yaacob MH, et al (2013) Optical characterisation of nanostructured Au/WO<sub>3</sub> thin films for sensing hydrogen at low concentrations. *Sensors Actuators B Chem* 179:125–130. <https://doi.org/10.1016/j.snb.2012.09.102>
174. Karthick Raj AG, Murugan C, Pandikumar A (2021) Efficient photoelectrochemical reduction of carbon dioxide into alcohols assisted by photoanode driven water oxidation with gold nanoparticles decorated titania nanotubes. *J CO<sub>2</sub> Util* 52:101684. <https://doi.org/10.1016/j.jcou.2021.101684>
175. Gao Z, Ye H, Tang D, et al (2017) Platinum-Decorated Gold Nanoparticles with Dual Functionalities for Ultrasensitive Colorimetric in Vitro Diagnostics. *Nano Lett* 17:5572–5579. <https://doi.org/10.1021/acs.nanolett.7b02385>
176. Noel K, Wang X (2019) Pt-decorated Au Nanoparticles: Highly Active Catalyst for Formic Acid Oxidation. *ECS Trans* 16:639–645. <https://doi.org/10.1149/1.2981899>
177. Zhao Z, Heck KN, Limpornpipat P, et al (2019) Hydrogen-generating behavior of Pd-decorated gold nanoparticles via formic acid decomposition. *Catal Today* 330:24–31. <https://doi.org/10.1016/j.cattod.2018.06.044>
178. Kang Y, Ye X, Chen J, et al (2013) Engineering Catalytic Contacts and Thermal Stability: Gold/Iron Oxide Binary Nanocrystal Superlattices for CO Oxidation. *J Am Chem Soc* 135:1499–1505. <https://doi.org/10.1021/ja310427u>
179. Shibuta M, Yamamoto K, Ohta T, et al (2021) Confined Hot Electron Relaxation at the Molecular Heterointerface of the Size-Selected Plasmonic Noble Metal Nanocluster and Layered C<sub>60</sub>. *ACS Nano* 15:1199–1209. <https://doi.org/10.1021/acs.nano.0c08248>
180. Liao TW, Verbruggen SW, Claes N, et al (2018) TiO<sub>2</sub> films modified with au nanoclusters as self-cleaning surfaces under visible light. *Nanomaterials* 8:1–9. <https://doi.org/10.3390/nano8010030>

181. Attia Y, Samer M (2017) Metal clusters: New era of hydrogen production. *Renew Sustain Energy Rev* 79:878–892. <https://doi.org/10.1016/j.rser.2017.05.113>
182. Zheng J, Zhang C, Dickson RM (2004) Highly Fluorescent, Water-Soluble, Size-Tunable Gold Quantum Dots. *Phys Rev Lett* 93:77402. <https://doi.org/10.1103/PhysRevLett.93.077402>
183. Fitzgerald JM, Narang P, Craster R V, et al (2016) Quantum plasmonics. *Proc IEEE* 104:2307–2322
184. Bozhevolnyi SI, Khurgin JB (2017) The case for quantum plasmonics. *Nat Photonics* 11:398–400. <https://doi.org/10.1038/nphoton.2017.103>
185. Van Dao D, Cipriano LA, Di Liberto G, et al (2021) Plasmonic Au nanoclusters dispersed in nitrogen-doped graphene as a robust photocatalyst for light-to-hydrogen conversion. *J Mater Chem A* 9:22810–22819. <https://doi.org/10.1039/D1TA05445G>
186. Wiegold S, Nienhaus L, Knoller FL, et al (2017) Plasmonic support-mediated activation of 1 nm platinum clusters for catalysis. *Phys Chem Chem Phys* 19:30570–30577. <https://doi.org/10.1039/C7CP04882C>
187. Joo SH, Park JY, Renzas JR, et al (2010) Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation. *Nano Lett* 10:2709–2713. <https://doi.org/10.1021/nl101700j>
188. Rong H, Ji S, Zhang J, et al (2020) Synthetic strategies of supported atomic clusters for heterogeneous catalysis. *Nat Commun* 11:5884. <https://doi.org/10.1038/s41467-020-19571-6>
189. Palmer RE, Cai R, Vernieres J (2018) Synthesis without Solvents: The Cluster (Nanoparticle) Beam Route to Catalysts and Sensors. *Acc Chem Res* 51:2296–2304. <https://doi.org/10.1021/acs.accounts.8b00287>
190. Zhang J, Li Z, Zheng K, Li G (2018) Synthesis and characterization of size-controlled atomically precise gold clusters. *Phys Sci Rev* 3:. <https://doi.org/10.1515/psr-2017-0083>
191. Li J, Ye W, Chen C (2019) Chapter 5 - Removal of toxic/radioactive metal ions by metal-organic framework-based materials. In: Chen CBT-IS and T (ed) *Emerging Natural and Tailored Nanomaterials for Radioactive Waste Treatment and Environmental Remediation*. Elsevier, pp 217–279
192. Hamoud HI, Douma F, Lafjah M, et al (2022) Size-Dependent Photocatalytic Activity of Silver Nanoparticles Embedded in ZX-Bi Zeolite Supports. *ACS Appl Nano Mater* 5:3866–3877. <https://doi.org/10.1021/acsanm.1c04484>
193. Liao Y, Li J, Thomas A (2017) General Route to High Surface Area Covalent Organic Frameworks and Their Metal Oxide Composites as Magnetically Recoverable Adsorbents and for Energy Storage. *ACS Macro Lett* 6:1444–1450. <https://doi.org/10.1021/acsmacrolett.7b00849>
194. Blommaerts N, Hoeven N, Arenas Esteban D, et al (2021) Tuning the turnover frequency and selectivity of photocatalytic CO<sub>2</sub> reduction to CO and methane using platinum and palladium nanoparticles on Ti-Beta zeolites. *Chem Eng J* 410:128234. <https://doi.org/10.1016/j.cej.2020.128234>
195. El-Roz M, Telegeiev I, Mordvinova NE, et al (2018) Uniform Generation of Sub-nanometer Silver Clusters in Zeolite Cages Exhibiting High Photocatalytic Activity under Visible Light. *ACS Appl Mater Interfaces* 10:28702–28708. <https://doi.org/10.1021/acsmi.8b09634>
196. Robotjazi H, Weinberg D, Swearer DF, et al (2019) Metal-organic frameworks tailor the properties of aluminum nanocrystals. *Sci Adv* 5:eaav5340.

<https://doi.org/10.1126/sciadv.aav5340>

197. Shevchenko E V, Talapin D V, Kotov NA, et al (2006) Structural diversity in binary nanoparticle superlattices. *Nature* 439:55–59. <https://doi.org/10.1038/nature04414>
198. Ye X, Chen J, Diroll BT, Murray CB (2013) Tunable Plasmonic Coupling in Self-Assembled Binary Nanocrystal Superlattices Studied by Correlated Optical Microspectroscopy and Electron Microscopy. *Nano Lett* 13:1291–1297. <https://doi.org/10.1021/nl400052w>
199. Swearer DF, Zhao H, Zhou L, et al (2016) Heterometallic antenna–reactor complexes for photocatalysis. *Proc Natl Acad Sci* 113:8916 LP – 8920. <https://doi.org/10.1073/pnas.1609769113>
200. Ciraci C, Hill RT, Mock JJ, et al (2012) Probing the Ultimate Limits of Plasmonic Enhancement. *Science* (80- ) 337:1072 LP – 1074. <https://doi.org/10.1126/science.1224823>
201. Ma X-C, Dai Y, Yu L, Huang B-B (2016) Energy transfer in plasmonic photocatalytic composites. *Light Sci Appl* 5:e16017. <https://doi.org/10.1038/lsa.2016.17>
202. Linsebigler AL, Lu GQ, Yates JT (1995) Photocatalysis on TiO<sub>2</sub> Surfaces - Principles, Mechanisms, and Selected Results. *Chem Rev* 95:735–758
203. Mubeen S, Lee J, Singh N, et al (2013) An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat Nanotechnol* 8:247–251. <https://doi.org/10.1038/nnano.2013.18>
204. Brown L V., Zhao K, King N, et al (2013) Surface-Enhanced Infrared Absorption Using Individual Cross Antennas Tailored to Chemical Moieties. *J Am Chem Soc* 135:3688–3695. <https://doi.org/10.1021/ja312694g>
205. Chen X-J, Cabello G, Wu D-Y, Tian Z-Q (2014) Surface-enhanced Raman spectroscopy toward application in plasmonic photocatalysis on metal nanostructures. *J Photochem Photobiol C Photochem Rev* 21:54–80. <https://doi.org/10.1016/j.jphotochemrev.2014.10.003>
206. Burda C, Chen X, Narayanan R, El-Sayed MA (2005) Chemistry and Properties of Nanocrystals of Different Shapes. *Chem Rev* 105:1025–1102. <https://doi.org/10.1021/cr030063a>
207. Hodak JH, Martini I, Hartland G V. (1998) Spectroscopy and Dynamics of Nanometer-Sized Noble Metal Particles. *J Phys Chem B* 102:6958–6967. <https://doi.org/10.1021/jp9809787>
208. Lehmann J, Merschdorf M, Pfeiffer W, et al (2000) Surface Plasmon Dynamics in Silver Nanoparticles Studied by Femtosecond Time-Resolved Photoemission. *Phys Rev Lett* 85:2921–2924. <https://doi.org/10.1103/PhysRevLett.85.2921>
209. Kale MJ, Avanesian T, Christopher P (2014) Direct Photocatalysis by Plasmonic Nanostructures. *ACS Catal* 4:116–128. <https://doi.org/10.1021/cs400993w>
210. Kim C, Suh BL, Yun H, et al (2017) Surface Plasmon Aided Ethanol Dehydrogenation Using Ag–Ni Binary Nanoparticles. *ACS Catal* 7:2294–2302. <https://doi.org/10.1021/acscatal.7b00411>
211. Petek H (2012) Photoexcitation of adsorbates on metal surfaces: One-step or three-step. *J Chem Phys* 137:091704. <https://doi.org/10.1063/1.4746801>
212. Mukherjee S, Libisch F, Large N, et al (2013) Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H<sub>2</sub> on Au. *Nano Lett* 13:240–247. <https://doi.org/10.1021/nl303940z>
213. Boerigter C, Campana R, Morabito M, Linic S (2016) Evidence and implications of direct charge excitation as the dominant mechanism in plasmon-mediated photocatalysis. *Nat Commun* 7:10545. <https://doi.org/10.1038/ncomms10545>

214. Zhao H, Zheng X, Feng X, Li Y (2018) CO<sub>2</sub> Reduction by Plasmonic Au Nanoparticle-Decorated TiO<sub>2</sub> Photocatalyst with an Ultrathin Al<sub>2</sub>O<sub>3</sub> Interlayer. *J Phys Chem C* 122:18949–18956. <https://doi.org/10.1021/acs.jpcc.8b04239>
215. Gomes Silva C, Juárez R, Marino T, et al (2011) Influence of Excitation Wavelength (UV or Visible Light) on the Photocatalytic Activity of Titania Containing Gold Nanoparticles for the Generation of Hydrogen or Oxygen from Water. *J Am Chem Soc* 133:595–602. <https://doi.org/10.1021/ja1086358>
216. Torimoto T, Horibe H, Kameyama T, et al (2011) Plasmon-Enhanced Photocatalytic Activity of Cadmium Sulfide Nanoparticle Immobilized on Silica-Coated Gold Particles. *J Phys Chem Lett* 2:2057–2062. <https://doi.org/10.1021/jz2009049>
217. Tu W, Zhou Y, Li H, et al (2015) Au@TiO<sub>2</sub> yolk–shell hollow spheres for plasmon-induced photocatalytic reduction of CO<sub>2</sub> to solar fuel via a local electromagnetic field. *Nanoscale* 7:14232–14236. <https://doi.org/10.1039/C5NR02943K>
218. Hirakawa T, Kamat P V (2005) Charge separation and catalytic activity of Ag@TiO<sub>2</sub> core-shell composite clusters under UV-irradiation. *J Am Chem Soc* 127:3928–34. <https://doi.org/10.1021/ja042925a>
219. Clavero C (2014) Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nat Photonics* 8:95–103. <https://doi.org/10.1038/nphoton.2013.238>
220. Subramanian V, Wolf EE, Kamat P V (2004) Catalysis with TiO<sub>2</sub>/gold nanocomposites. Effect of metal particle size on the Fermi level equilibration. *J Am Chem Soc* 126:4943–4950
221. Li J, Cushing SK, Meng F, et al (2015) Plasmon-induced resonance energy transfer for solar energy conversion. *Nat Photonics* 9:601–607. <https://doi.org/10.1038/nphoton.2015.142>
222. Ingram DB, Christopher P, Bauer JL, Linic S (2011) Predictive Model for the Design of Plasmonic Metal/Semiconductor Composite Photocatalysts. *ACS Catal* 1:1441–1447
223. Borah R, Verbruggen SW (2019) Coupled Plasmon Modes in 2D Gold Nanoparticle Clusters and Their Effect on Local Temperature Control. *J Phys Chem C* 123:. <https://doi.org/10.1021/acs.jpcc.9b09048>
224. Yu S, Wilson AJ, Kumari G, et al (2017) Opportunities and Challenges of Solar-Energy-Driven Carbon Dioxide to Fuel Conversion with Plasmonic Catalysts. *ACS Energy Lett* 2:2058–2070. <https://doi.org/10.1021/acseenergylett.7b00640>
225. Kreibitz U, Vollmer M (1995) *Optical Properties of Metal Clusters*. Springer-Verlag Berlin Heidelberg
226. Baffou G, Quidant R, Girard C (2010) Thermoplasmonics modeling: A Green's function approach. *Phys Rev B* 82:165424. <https://doi.org/10.1103/PhysRevB.82.165424>
227. Baffou G, Berto P, Bermúdez Ureña E, et al (2013) Photoinduced Heating of Nanoparticle Arrays. *ACS Nano* 7:6478–6488. <https://doi.org/10.1021/nn401924n>
228. Ni G, Miljkovic N, Ghasemi H, et al (2015) Volumetric solar heating of nanofluids for direct vapor generation. *Nano Energy* 17:290–301. <https://doi.org/10.1016/j.nanoen.2015.08.021>
229. Priebe JB, Karnahl M, Junge H, et al (2013) Water reduction with visible light: synergy between optical transitions and electron transfer in Au-TiO<sub>2</sub> catalysts visualized by in situ EPR spectroscopy. *Angew Chem Int Ed Engl* 52:11420–4. <https://doi.org/10.1002/anie.201306504>

230. Caretti I, Keulemans M, Verbruggen SW, et al (2015) Light-Induced Processes in Plasmonic Gold/TiO<sub>2</sub> Photocatalysts Studied by Electron Paramagnetic Resonance. *Top Catal* 58:776–782. <https://doi.org/10.1007/s11244-015-0419-4>
231. Awazu K, Fujimaki M, Rockstuhl C, et al (2008) A plasmonic photocatalyst consisting of silver nanoparticles embedded in titanium dioxide. *J Am Chem Soc* 130:1676–1680
232. Sun S, Rasskazov IL, Carney PS, et al (2020) Critical Role of Shell in Enhanced Fluorescence of Metal–Dielectric Core–Shell Nanoparticles. *J Phys Chem C* 124:13365–13373. <https://doi.org/10.1021/acs.jpcc.0c03415>
233. Asapu R, Ciocarlan R-G, Claes N, et al (2017) Plasmonic Near-Field Localization of Silver Core–Shell Nanoparticle Assemblies via Wet Chemistry Nanogap Engineering. *ACS Appl Mater Interfaces* 9:41577–41585. <https://doi.org/10.1021/acsami.7b13965>
234. Dingenen F, Verbruggen SW (2021) Tapping hydrogen fuel from the ocean: A review on photocatalytic, photoelectrochemical and electrolytic splitting of seawater. *Renew Sustain Energy Rev* 142:110866. <https://doi.org/10.1016/j.rser.2021.110866>
235. Habisreutinger SN, Schmidt-Mende L, Stolarczyk JK (2013) Photocatalytic Reduction of CO<sub>2</sub> on TiO<sub>2</sub> and Other Semiconductors. *Angew Chemie Int Ed* 52:7372–7408. <https://doi.org/https://doi.org/10.1002/anie.201207199>
236. Yang J-L, He Y-L, Ren H, et al (2021) Boosting Photocatalytic Hydrogen Evolution Reaction Using Dual Plasmonic Antennas. *ACS Catal* 11:5047–5053. <https://doi.org/10.1021/acscatal.1c00795>
237. Tran PD, Wong LH, Barber J, Loo JSC (2012) Recent advances in hybrid photocatalysts for solar fuel production. *Energy Environ Sci* 5:5902–5918. <https://doi.org/10.1039/C2EE02849B>
238. Koppenol WH, Stanbury DM, Bounds PL (2010) Electrode potentials of partially reduced oxygen species, from dioxygen to water. *Free Radic Biol Med* 49:317–322. <https://doi.org/10.1016/j.freeradbiomed.2010.04.011>
239. Ha E, Lee LYS, Man H-W, et al (2015) Morphology-Controlled Synthesis of Au/Cu<sub>2</sub>FeSnS<sub>4</sub> Core–Shell Nanostructures for Plasmon-Enhanced Photocatalytic Hydrogen Generation. *ACS Appl Mater Interfaces* 7:9072–9077. <https://doi.org/10.1021/acsami.5b00715>
240. Bhunia K, Chandra M, Khilari S, Pradhan D (2019) Bimetallic PtAu Alloy Nanoparticles-Integrated g-C<sub>3</sub>N<sub>4</sub> Hybrid as an Efficient Photocatalyst for Water-to-Hydrogen Conversion. *ACS Appl Mater Interfaces* 11:478–488. <https://doi.org/10.1021/acsami.8b12183>
241. Bian H, Nguyen NT, Yoo J, et al (2018) Forming a Highly Active, Homogeneously Alloyed AuPt Co-catalyst Decoration on TiO<sub>2</sub> Nanotubes Directly During Anodic Growth. *ACS Appl Mater Interfaces* 10:18220–18226. <https://doi.org/10.1021/acsami.8b03713>
242. Rahul TK, Mohan M, Sandhyarani N (2018) Enhanced Solar Hydrogen Evolution over In Situ Gold–Platinum Bimetallic Nanoparticle-Loaded Ti<sup>3+</sup> Self-Doped Titania Photocatalysts. *ACS Sustain Chem Eng* 6:3049–3059. <https://doi.org/10.1021/acssuschemeng.7b02898>
243. Gesesse GD, Wang C, Chang BK, et al (2020) A soft-chemistry assisted strong metal–support interaction on a designed plasmonic core–shell photocatalyst for enhanced photocatalytic hydrogen production. *Nanoscale* 12:7011–7023. <https://doi.org/10.1039/C9NR09891G>
244. Ngaw CK, Xu Q, Tan TTY, et al (2014) A strategy for in-situ synthesis of well-defined core–shell Au@TiO<sub>2</sub> hollow spheres for enhanced photocatalytic hydrogen evolution. *Chem Eng J* 257:112–121. <https://doi.org/10.1016/j.cej.2014.07.059>

245. Lou Z, Fujitsuka M, Majima T (2016) Pt–Au Triangular Nanoprisms with Strong Dipole Plasmon Resonance for Hydrogen Generation Studied by Single-Particle Spectroscopy. *ACS Nano* 10:6299–6305. <https://doi.org/10.1021/acsnano.6b02494>
246. Gao M, Connor PKN, Ho GW (2016) Plasmonic photothermic directed broadband sunlight harnessing for seawater catalysis and desalination. *Energy Environ Sci* 9:3151–3160. <https://doi.org/10.1039/C6EE00971A>
247. Hung S-F, Yu Y-C, Suen N-T, et al (2016) The synergistic effect of a well-defined Au@Pt core–shell nanostructure toward photocatalytic hydrogen generation: interface engineering to improve the Schottky barrier and hydrogen-evolved kinetics. *Chem Commun* 52:1567–1570. <https://doi.org/10.1039/C5CC08547K>
248. Nasrallah H, Douma F, Hamoud HI, El-Roz M (2021) Chapter 5 - Metal nanoparticles in photocatalysis: Advances and challenges. In: Nguyen V-H, Vo D-VN, Nanda SBT-NP (eds). Elsevier, pp 119–143
249. Pandit S, Kunwar S, Pandey P, Lee J (2019) Improved LSPR Properties of Ag–Pt and Pt Nanoparticles: A Systematic Study on Various Configurations and Compositions of NPs via the Solid-State Dewetting of Ag–Pt Bilayers. *Met.* 9
250. Sui M, Kunwar S, Pandey P, Lee J (2019) Strongly confined localized surface plasmon resonance (LSPR) bands of Pt, AgPt, AgAuPt nanoparticles. *Sci Rep* 9:16582. <https://doi.org/10.1038/s41598-019-53292-1>
251. Xiao J-D, Han L, Luo J, et al (2018) Integration of Plasmonic Effects and Schottky Junctions into Metal–Organic Framework Composites: Steering Charge Flow for Enhanced Visible-Light Photocatalysis. *Angew Chemie Int Ed* 57:1103–1107. <https://doi.org/https://doi.org/10.1002/anie.201711725>
252. Liu Y, Sun Z, Hu YH (2021) Bimetallic cocatalysts for photocatalytic hydrogen production from water. *Chem Eng J* 409:128250. <https://doi.org/10.1016/j.cej.2020.128250>
253. Ding J, Li X, Chen L, et al (2018) Photocatalytic hydrogen production over plasmonic AuCu/CaIn<sub>2</sub>S<sub>4</sub> composites with different AuCu atomic arrangements. *Appl Catal B Environ* 224:322–329. <https://doi.org/10.1016/j.apcatb.2017.10.045>
254. Zhang P, Zeng G, Song T, et al (2019) Design of plasmonic CuCo bimetal as a nonsemiconductor photocatalyst for synchronized hydrogen evolution and storage. *Appl Catal B Environ* 242:389–396. <https://doi.org/10.1016/j.apcatb.2018.10.020>
255. Naya S, Kume T, Akashi R, et al (2018) Red-Light-Driven Water Splitting by Au(Core)–CdS(Shell) Half-Cut Nanoegg with Heteroepitaxial Junction. *J Am Chem Soc* 140:1251–1254. <https://doi.org/10.1021/jacs.7b12972>
256. Wu B, Liu D, Mubeen S, et al (2016) Anisotropic Growth of TiO<sub>2</sub> onto Gold Nanorods for Plasmon-Enhanced Hydrogen Production from Water Reduction. *J Am Chem Soc* 138:1114–1117. <https://doi.org/10.1021/jacs.5b11341>
257. Zheng Z, Tachikawa T, Majima T (2014) Single-Particle Study of Pt-Modified Au Nanorods for Plasmon-Enhanced Hydrogen Generation in Visible to Near-Infrared Region. *J Am Chem Soc* 136:6870–6873. <https://doi.org/10.1021/ja502704n>
258. Han C, Wu L, Ge L, et al (2015) AuPd bimetallic nanoparticles decorated graphitic carbon nitride for highly efficient reduction of water to H<sub>2</sub> under visible light irradiation. *Carbon N Y* 92:31–40. <https://doi.org/10.1016/j.carbon.2015.02.070>

259. Verma R, Belgamwar R, Polshettiwar V (2021) Plasmonic Photocatalysis for CO<sub>2</sub> Conversion to Chemicals and Fuels. *ACS Mater Lett* 3:574–598. <https://doi.org/10.1021/acsmaterialslett.1c00081>
260. Inoue T, Fujishima A, Konishi S, Honda K (1979) Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* 277:637–638. <https://doi.org/10.1038/277637a0>
261. Yu S, Jain PK (2019) Plasmonic photosynthesis of C<sub>1</sub>–C<sub>3</sub> hydrocarbons from carbon dioxide assisted by an ionic liquid. *Nat Commun* 10:2022. <https://doi.org/10.1038/s41467-019-10084-5>
262. Ziarati A, Badiei A, Luque R, et al (2020) Visible Light CO<sub>2</sub> Reduction to CH<sub>4</sub> Using Hierarchical Yolk@shell TiO<sub>2</sub>-xH<sub>2</sub>O Modified with Plasmonic Au–Pd Nanoparticles. *ACS Sustain Chem Eng* 8:3689–3696. <https://doi.org/10.1021/acssuschemeng.9b06751>
263. Wei Y, Jiao J, Zhao Z, et al (2015) Fabrication of inverse opal TiO<sub>2</sub>-supported Au@CdS core–shell nanoparticles for efficient photocatalytic CO<sub>2</sub> conversion. *Appl Catal B Environ* 179:422–432. <https://doi.org/10.1016/j.apcatb.2015.05.041>
264. Choi KM, Kim D, Rungtaweeworanit B, et al (2017) Plasmon-Enhanced Photocatalytic CO<sub>2</sub> Conversion within Metal–Organic Frameworks under Visible Light. *J Am Chem Soc* 139:356–362. <https://doi.org/10.1021/jacs.6b11027>
265. Bera S, Lee JE, Rawal SB, Lee WI (2016) Size-dependent plasmonic effects of Au and Au@SiO<sub>2</sub> nanoparticles in photocatalytic CO<sub>2</sub> conversion reaction of Pt/TiO<sub>2</sub>. *Appl Catal B Environ* 199:55–63. <https://doi.org/10.1016/j.apcatb.2016.06.025>
266. Stanley JNG, García-García I, Perfrement T, et al (2019) Plasmonic effects on CO<sub>2</sub> reduction over bimetallic Ni–Au catalysts. *Chem Eng Sci* 194:94–104. <https://doi.org/10.1016/j.ces.2018.04.003>
267. Lang Q, Yang Y, Zhu Y, et al (2017) High-index facet engineering of PtCu cocatalysts for superior photocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub>. *J Mater Chem A* 5:6686–6694. <https://doi.org/10.1039/C7TA00737J>
268. Neațu Ș, Maciá-Agulló JA, Concepción P, Garcia H (2014) Gold–Copper Nanoalloys Supported on TiO<sub>2</sub> as Photocatalysts for CO<sub>2</sub> Reduction by Water. *J Am Chem Soc* 136:15969–15976. <https://doi.org/10.1021/ja506433k>
269. Han Y, Xu H, Su Y, et al (2019) Noble metal (Pt, Au@Pd) nanoparticles supported on metal organic framework (MOF-74) nanoshuttles as high-selectivity CO<sub>2</sub> conversion catalysts. *J Catal* 370:70–78. <https://doi.org/10.1016/j.jcat.2018.12.005>
270. Robotjazi H, Zhao H, Swearer DF, et al (2017) Plasmon-induced selective carbon dioxide conversion on earth-abundant aluminum-cuprous oxide antenna-reactor nanoparticles. *Nat Commun* 8:27. <https://doi.org/10.1038/s41467-017-00055-z>
271. Liu H, Meng X, Dao TD, et al (2015) Conversion of Carbon Dioxide by Methane Reforming under Visible-Light Irradiation: Surface-Plasmon-Mediated Nonpolar Molecule Activation. *Angew Chemie* 127:11707–11711. <https://doi.org/10.1002/ange.201504933>
272. Liu H, Li M, Dao TD, et al (2016) Design of PdAu alloy plasmonic nanoparticles for improved catalytic performance in CO<sub>2</sub> reduction with visible light irradiation. *Nano Energy* 26:398–404. <https://doi.org/10.1016/j.nanoen.2016.05.045>
273. Zhou L, Martinez JMP, Finzel J, et al (2020) Light-driven methane dry reforming with single



- atomic site antenna-reactor plasmonic photocatalysts. *Nat Energy* 5:61–70. <https://doi.org/10.1038/s41560-019-0517-9>
274. Yan X, Ohno T, Nishijima K, et al (2006) Is methylene blue an appropriate substrate for a photocatalytic activity test? A study with visible-light responsive titania. *Chem Phys Lett* 429:606–610. <https://doi.org/10.1016/j.cplett.2006.08.081>
  275. Misra M, Singh N, Gupta RK (2017) Enhanced visible-light-driven photocatalytic activity of Au@Ag core-shell bimetallic nanoparticles immobilized on electrospun TiO<sub>2</sub> nanofibers for degradation of organic compounds. *Catal Sci Technol* 7:570–580. <https://doi.org/10.1039/C6CY02085B>
  276. Darabdhara G, Das MR (2019) Dual responsive magnetic Au@Ni nanostructures loaded reduced graphene oxide sheets for colorimetric detection and photocatalytic degradation of toxic phenolic compounds. *J Hazard Mater* 368:365–377. <https://doi.org/10.1016/j.jhazmat.2019.01.010>
  277. Su J, Zhang Y, Xu S, et al (2014) Highly efficient and recyclable triple-shelled Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> photocatalysts for degradation of organic pollutants and reduction of hexavalent chromium ions. *Nanoscale* 6:5181–5192. <https://doi.org/10.1039/C4NR00534A>
  278. Tanaka A, Hashimoto K, Kominami H (2011) Gold and Copper Nanoparticles Supported on Cerium(IV) Oxide—A Photocatalyst Mineralizing Organic Acids under Red Light Irradiation. *ChemCatChem* 3:1619–1623. <https://doi.org/https://doi.org/10.1002/cctc.201100158>
  279. Tanaka A, Fuku K, Nishi T, et al (2013) Functionalization of Au/TiO<sub>2</sub> Plasmonic Photocatalysts with Pd by Formation of a Core-Shell Structure for Effective Dechlorination of Chlorobenzene under Irradiation of Visible Light. *J Phys Chem C* 117:16983–16989. <https://doi.org/10.1021/jp403855p>
  280. Cybula A, Priebe JB, Pohl M-M, et al (2014) The effect of calcination temperature on structure and photocatalytic properties of Au/Pd nanoparticles supported on TiO<sub>2</sub>. *Appl Catal B Environ* 152–153:202–211. <https://doi.org/10.1016/j.apcatb.2014.01.042>
  281. Yu H, Wang X, Sun H, Huo M (2010) Photocatalytic degradation of malathion in aqueous solution using an Au-Pd-TiO<sub>2</sub> nanotube film. *J Hazard Mater* 184:753–758. <https://doi.org/10.1016/j.jhazmat.2010.08.103>
  282. Zielińska-Jurek A, Kowalska E, Sobczak JW, et al (2011) Preparation and characterization of monometallic (Au) and bimetallic (Ag/Au) modified-titania photocatalysts activated by visible light. *Appl Catal B Environ* 101:504–514. <https://doi.org/10.1016/j.apcatb.2010.10.022>
  283. Jiang T, Jia C, Zhang L, et al (2015) Gold and gold-palladium alloy nanoparticles on heterostructured TiO<sub>2</sub> nanobelts as plasmonic photocatalysts for benzyl alcohol oxidation. *Nanoscale* 7:209–217. <https://doi.org/10.1039/C4NR05905K>
  284. Zhang Y, Wang L, Kong X, et al (2018) Novel Ag-Cu bimetallic alloy decorated near-infrared responsive three-dimensional rod-like architectures for efficient photocatalytic water purification. *J Colloid Interface Sci* 522:29–39. <https://doi.org/10.1016/j.jcis.2018.02.005>
  285. Patnaik S, Sahoo DP, Parida KM (2020) Bimetallic co-effect of Au-Pd alloyed nanoparticles on mesoporous silica modified g-C<sub>3</sub>N<sub>4</sub> for single and simultaneous photocatalytic oxidation of phenol and reduction of hexavalent chromium. *J Colloid Interface Sci* 560:519–535. <https://doi.org/10.1016/j.jcis.2019.09.041>
  286. Wen H, Long Y, Han W, et al (2018) Preparation of a novel bimetallic AuCu-P25-rGO ternary nanocomposite with enhanced photocatalytic degradation performance. *Appl Catal A Gen*

- 549:237–244. <https://doi.org/10.1016/j.apcata.2017.09.028>
287. Fu R, Li L, Li X, et al (2021) Photogenerated carrier separation and localized surface plasmon resonance in SnS<sub>2</sub>@AuNPs Janus heterostructures for enhanced visible light catalysis. *Mater Chem Phys* 267:124702. <https://doi.org/10.1016/j.matchemphys.2021.124702>
288. Naya S, Tada H (2020) Au–Ag alloy nanoparticle-incorporated AgBr plasmonic photocatalyst. *Sci Rep* 10:19972. <https://doi.org/10.1038/s41598-020-77062-6>
289. Sugano Y, Shiraishi Y, Tsukamoto D, et al (2013) Supported Au–Cu Bimetallic Alloy Nanoparticles: An Aerobic Oxidation Catalyst with Regenerable Activity by Visible-Light Irradiation. *Angew Chemie Int Ed* 52:5295–5299. <https://doi.org/10.1002/anie.201301669>
290. Huang S, Xu Y, Chen Z, et al (2015) A core–shell structured magnetic Ag/AgBr@Fe<sub>2</sub>O<sub>3</sub> composite with enhanced photocatalytic activity for organic pollutant degradation and antibacterium. *RSC Adv* 5:71035–71045. <https://doi.org/10.1039/C5RA13403J>
291. Zhou N, Polavarapu L, Gao N, et al (2013) TiO<sub>2</sub> coated Au/Ag nanorods with enhanced photocatalytic activity under visible light irradiation. *Nanoscale* 5:4236–4241. <https://doi.org/10.1039/C3NR00517H>
292. Li W, Li B, Meng M, et al (2019) Bimetallic Au/Ag decorated TiO<sub>2</sub> nanocomposite membrane for enhanced photocatalytic degradation of tetracycline and bactericidal efficiency. *Appl Surf Sci* 487:1008–1017. <https://doi.org/10.1016/j.apsusc.2019.05.162>
293. Kaur M, Shinde SL, Ishii S, et al (2020) Marimo-Bead-Supported Core–Shell Nanocomposites of Titanium Nitride and Chromium-Doped Titanium Dioxide as a Highly Efficient Water-Floatable Green Photocatalyst. *ACS Appl Mater Interfaces* 12:31327–31339. <https://doi.org/10.1021/acsami.0c03781>
294. Bathla A, Younis SA, Pal B, Kim K-H (2021) Recent progress in bimetallic nanostructure impregnated metal-organic framework for photodegradation of organic pollutants. *Appl Mater Today* 24:101105. <https://doi.org/10.1016/j.apmt.2021.101105>
295. Testa JJ, Grela MA, Litter MI (2004) Heterogeneous Photocatalytic Reduction of Chromium(VI) over TiO<sub>2</sub> Particles in the Presence of Oxalate: Involvement of Cr(V) Species. *Environ Sci Technol* 38:1589–1594. <https://doi.org/10.1021/es0346532>
296. Mohammadi P, Sheibani H (2019) Evaluation, of the bimetallic photocatalytic performance of Resin–Au–Pd nanocomposite for degradation of parathion pesticide under visible light. *Polyhedron* 170:132–137. <https://doi.org/10.1016/j.poly.2019.05.030>
297. Chen Q, Xin Y, Zhu X (2015) Au-Pd nanoparticles-decorated TiO<sub>2</sub> nanobelts for photocatalytic degradation of antibiotic levofloxacin in aqueous solution. *Electrochim Acta* 186:34–42. <https://doi.org/10.1016/j.electacta.2015.10.095>
298. Zhang K, Liu Y, Deng J, et al (2018) Co–Pd/BiVO<sub>4</sub>: High-performance photocatalysts for the degradation of phenol under visible light irradiation. *Appl Catal B Environ* 224:350–359. <https://doi.org/10.1016/j.apcatb.2017.10.044>
299. Darabdhara G, Boruah PK, Borthakur P, et al (2016) Reduced graphene oxide nanosheets decorated with Au–Pd bimetallic alloy nanoparticles towards efficient photocatalytic degradation of phenolic compounds in water. *Nanoscale* 8:8276–8287. <https://doi.org/10.1039/C6NR00231E>
300. Zeng Q, Xie X, Wang X, et al (2018) Enhanced photocatalytic performance of Ag@TiO<sub>2</sub> for the gaseous acetaldehyde photodegradation under fluorescent lamp. *Chem Eng J* 341:83–92.

- <https://doi.org/10.1016/j.cej.2018.02.015>
301. Wang Z, Yan S, Sun Y, et al (2017) Bi metal sphere/graphene oxide nanohybrids with enhanced direct plasmonic photocatalysis. *Appl Catal B Environ* 214:148–157. <https://doi.org/10.1016/j.apcatb.2017.05.040>
  302. Wang W, Zhang D, Sun P, et al (2021) High efficiency photocatalytic degradation of indoor formaldehyde by Ag/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite catalyst with ZSM-5 as the carrier. *Microporous Mesoporous Mater* 322:111134. <https://doi.org/10.1016/j.micromeso.2021.111134>
  303. Haldorai Y, Kim B-K, Jo Y-L, Shim J-J (2014) Ag@graphene oxide nanocomposite as an efficient visible-light plasmonic photocatalyst for the degradation of organic pollutants: A facile green synthetic approach. *Mater Chem Phys* 143:1452–1461. <https://doi.org/10.1016/j.matchemphys.2013.11.065>
  304. Wang D, Li Z, Zhou J, et al (2017) Simultaneous Detection and Removal of Formaldehyde at Room Temperature: Janus Au@ZnO@ZIF-8 Nanoparticles. *Nano-Micro Lett* 10:4. <https://doi.org/10.1007/s40820-017-0158-0>
  305. Tripathy SK, Mishra A, Jha SK, et al (2013) Synthesis of thermally stable monodispersed Au@SnO<sub>2</sub> core–shell structure nanoparticles by a sonochemical technique for detection and degradation of acetaldehyde. *Anal Methods* 5:1456–1462. <https://doi.org/10.1039/C3AY26549H>
  306. Gao J, Si Z, Xu Y, et al (2019) Pd–Ag@CeO<sub>2</sub> Catalyst of Core–Shell Structure for Low Temperature Oxidation of Toluene Under Visible Light Irradiation. *J Phys Chem C* 123:1761–1769. <https://doi.org/10.1021/acs.jpcc.8b09060>
  307. Sun S, Wang W, Zhang L, et al (2009) Ag@C core/shell nanocomposite as a highly efficient plasmonic photocatalyst. *Catal Commun* 11:290–293. <https://doi.org/10.1016/j.catcom.2009.09.026>
  308. Wysocka I, Markowska-Szczupak A, Szveda P, et al (2019) Gas-phase removal of indoor volatile organic compounds and airborne microorganisms over mono- and bimetal-modified (Pt, Cu, Ag) titanium(IV) oxide nanocomposites. *Indoor Air* 29:979–992. <https://doi.org/https://doi.org/10.1111/ina.12595>
  309. Wu Q, Ye J, Qiao W, et al (2021) Inhibit the formation of toxic methylphenolic by-products in photo-decomposition of formaldehyde–toluene/xylene mixtures by Pd cocatalyst on TiO<sub>2</sub>. *Appl Catal B Environ* 291:120118. <https://doi.org/10.1016/j.apcatb.2021.120118>
  310. Yang K, Huang K, He Z, et al (2014) Promoted effect of PANI as electron transfer promoter on CO oxidation over Au/TiO<sub>2</sub>. *Appl Catal B Environ* 158–159:250–257. <https://doi.org/10.1016/j.apcatb.2014.04.028>
  311. Liu J, Lucci FR, Yang M, et al (2016) Tackling CO Poisoning with Single-Atom Alloy Catalysts. *J Am Chem Soc* 138:6396–6399. <https://doi.org/10.1021/jacs.6b03339>
  312. Novello P, Varanasi C V, Liu J (2019) Effects of Light on Catalytic Activities and Lifetime of Plasmonic Au Catalysts in the CO Oxidation Reaction. *ACS Catal* 9:578–586. <https://doi.org/10.1021/acscatal.8b03166>
  313. Li K, Hogan NJ, Kale MJ, et al (2017) Balancing Near-Field Enhancement, Absorption, and Scattering for Effective Antenna–Reactor Plasmonic Photocatalysis. *Nano Lett* 17:3710–3717. <https://doi.org/10.1021/acs.nanolett.7b00992>
  314. Jupnik H (1941) Photoelectric Properties of Bismuth. *Phys Rev* 60:884–889.

<https://doi.org/10.1103/PhysRev.60.884>

315. Chen M, Li Y, Wang Z, et al (2017) Controllable Synthesis of Core–Shell Bi@Amorphous Bi<sub>2</sub>O<sub>3</sub> Nanospheres with Tunable Optical and Photocatalytic Activity for NO Removal. *Ind Eng Chem Res* 56:10251–10258. <https://doi.org/10.1021/acs.iecr.7b02497>
316. Zhang P, Rao Y, Huang Y, et al (2021) Transformation of amorphous Bi<sub>2</sub>O<sub>3</sub> to crystal Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> on Bi nanospheres surface for photocatalytic NO<sub>x</sub> oxidation: Intensified hot-electron transfer and reactive oxygen species generation. *Chem Eng J* 420:129814. <https://doi.org/10.1016/j.cej.2021.129814>
317. Li F, Dong B, Feng S (2019) Bi shell-BiOI core microspheres modified TiO<sub>2</sub> nanotube arrays photoanode: Improved effect of Bi shell on photoelectrochemical hydrogen evolution in seawater. *Int J Hydrogen Energy* 44:29986–29999. <https://doi.org/10.1016/j.ijhydene.2019.09.210>
318. Zhang W, Dong X, Liang Y, et al (2018) Ag/AgCl nanoparticles assembled on BiOCl/Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> nanosheets: Enhanced plasmonic visible light photocatalysis and in situ DRIFTS investigation. *Appl Surf Sci* 455:236–243. <https://doi.org/10.1016/j.apsusc.2018.05.171>
319. Gutiérrez Y, Giangregorio MM, Palumbo F, et al (2020) Sustainable and Tunable Mg/MgO Plasmon-Catalytic Platform for the Grand Challenge of SF<sub>6</sub> Environmental Remediation. *Nano Lett* 20:3352–3360. <https://doi.org/10.1021/acs.nanolett.0c00244>
320. Peeters H, Keulemans M, Nuyts G, et al (2020) Plasmonic gold-embedded TiO<sub>2</sub> thin films as photocatalytic self-cleaning coatings. *Appl Catal B Environ* 267:118654. <https://doi.org/10.1016/j.apcatb.2020.118654>
321. Wu X-F, Song H-Y, Yoon J-M, et al (2009) Synthesis of Core–Shell Au@TiO<sub>2</sub> Nanoparticles with Truncated Wedge-Shaped Morphology and Their Photocatalytic Properties. *Langmuir* 25:6438–6447. <https://doi.org/10.1021/la900035a>
322. Zhu S, Xie X, Chen S-C, et al (2017) Cu-Ni nanowire-based TiO<sub>2</sub> hybrid for the dynamic photodegradation of acetaldehyde gas pollutant under visible light. *Appl Surf Sci* 408:117–124. <https://doi.org/10.1016/j.apsusc.2017.02.217>
323. Yang K, Huang K, Lin L, et al (2015) Superior preferential oxidation of carbon monoxide in hydrogen-rich stream under visible light irradiation over gold loaded hedgehog-shaped titanium dioxide nanospheres: Identification of copper oxide decoration as an efficient promoter. *J Power Sources* 284:194–205. <https://doi.org/10.1016/j.jpowsour.2015.03.003>
324. He W, Sun Y, Jiang G, et al (2018) Defective Bi<sub>4</sub>MoO<sub>9</sub>/Bi metal core/shell heterostructure: Enhanced visible light photocatalysis and reaction mechanism. *Appl Catal B Environ* 239:619–627. <https://doi.org/10.1016/j.apcatb.2018.08.064>
325. Xiao X, Zhang W, Yu J, et al (2016) Mechanistic understanding of ternary Ag/AgCl@La(OH)<sub>3</sub> nanorods as novel visible light plasmonic photocatalysts. *Catal Sci Technol* 6:5003–5010. <https://doi.org/10.1039/C6CY00262E>
326. Ding X, Zhang L, Gao Y (2017) Insights into electrolyte effects on photoactivities of dye-sensitized photoelectrochemical cells for water splitting. *J Energy Chem* 26:476–480. <https://doi.org/10.1016/j.jechem.2016.11.022>
327. Wysocka I, Kowalska E, Ryl J, et al (2019) Morphology, Photocatalytic and Antimicrobial Properties of TiO<sub>2</sub> Modified with Mono- and Bimetallic Copper, Platinum and Silver Nanoparticles. *Nanomater.* 9

328. Endo-Kimura M, Kowalska E (2020) Plasmonic Photocatalysts for Microbiological Applications. *Catal.* 10
329. Markowska-Szczupak A, Ulfing K, Morawski AW (2011) The application of titanium dioxide for deactivation of bioparticulates: An overview. *Catal Today* 169:249–257. <https://doi.org/10.1016/j.cattod.2010.11.055>
330. Das S, Misra AJ, Habeeb Rahman AP, et al (2019) Ag@SnO<sub>2</sub>@ZnO core-shell nanocomposites assisted solar-photocatalysis downregulates multidrug resistance in *Bacillus* sp.: A catalytic approach to impede antibiotic resistance. *Appl Catal B Environ* 259:118065. <https://doi.org/10.1016/j.apcatb.2019.118065>
331. Das S, Ranjana N, Misra AJ, et al (2017) Disinfection of the Water Borne Pathogens *Escherichia coli* and *Staphylococcus aureus* by Solar Photocatalysis Using Sonochemically Synthesized Reusable Ag@ZnO Core-Shell Nanoparticles. *Int. J. Environ. Res. Public Heal.* 14
332. Das S, Sinha S, Suar M, et al (2015) Solar-photocatalytic disinfection of *Vibrio cholerae* by using Ag@ZnO core-shell structure nanocomposites. *J Photochem Photobiol B Biol* 142:68–76. <https://doi.org/10.1016/j.jphotobiol.2014.10.021>
333. Thangudu S, Kulkarni SS, Vankayala R, et al (2020) Photosensitized reactive chlorine species-mediated therapeutic destruction of drug-resistant bacteria using plasmonic core-shell Ag@AgCl nanocubes as an external nanomedicine. *Nanoscale* 12:12970–12984. <https://doi.org/10.1039/D0NR01300E>
334. Méndez-Medrano MG, Kowalska E, Endo-Kimura M, et al (2019) Inhibition of Fungal Growth Using Modified TiO<sub>2</sub> with Core@Shell Structure of Ag@CuO Clusters. *ACS Appl Bio Mater* 2:5626–5633. <https://doi.org/10.1021/acsabm.9b00707>
335. An X, Naowarajna N, Liu P, Reinhard BM (2020) Hybrid Plasmonic Photoreactors as Visible Light-Mediated Bactericides. *ACS Appl Mater Interfaces* 12:106–116. <https://doi.org/10.1021/acsami.9b14834>
336. Feng H, Wang W, Wang W, et al (2021) Charge transfer channels of silver @ cuprous oxide heterostructure core-shell nanoparticles strengthen high photocatalytic antibacterial activity. *J Colloid Interface Sci* 601:531–543. <https://doi.org/10.1016/j.jcis.2021.05.113>