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### REVIEW

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### Plasmonic metal-semiconductor photocatalysts and photoelectrochemical cells: a review

The incorporation of plasmonic metals into semiconductors is a promising route to improve the performance of photocatalysts and photoelectrochemical cells. This article summarizes the three major mechanisms of plasmonic energy transfer from a metal to a semiconductor, including light scattering/trapping, plasmon-induced resonance energy transfer (PIRET) and hot electron injection (also called direct electron

transfer (DET)). It also discusses the rational design of plasmonic metal-semiconductor heterojunctions

based on the underlying plasmonic energy transfer mechanisms. Moreover, this article highlights the

applications of plasmonic photocatalysts and photoelectrochemical cells in solar water splitting, carbon

dioxide reduction and environmental pollutant decomposition.

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### 1. Introduction

Photocatalysts have been widely used in solar-to-fuel conversion, environmental remediation, organic compound transformation and synthesis, and photodynamic therapy. Since energy shortage and environmental disruption are becoming a global concern, special attention is being paid to photocatalysts that convert solar energy into chemical energy in fuels by directly splitting water or by reducing  $CO_2$ .<sup>1,2</sup> So far, no single

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trochemical cells for solar energy harvesting, (ii) batteries and supercapacitors for energy storage, and (iii) biosensors and lab-onchips for health care and environment monitoring. semiconductor photocatalyst has been commercially available to catalyze water-splitting reactions with an energy conversion efficiency larger than 10% under "one sun" radiation, which is the benchmark for commercialization of solar photocatalytic systems.<sup>3</sup> This benchmark has not been achieved because current photocatalysts suffer from insufficient light absorption, inefficient charge separation, high charge recombination rates and high costs. The energetic requirements of the reaction have put a constraint on the band gap of the semiconductor. For water splitting, the optimal band gap is 1.9-2.3 eV.<sup>2</sup> However, most narrow band gap semiconductors are not stable during photocatalytic reactions.<sup>4,5</sup> Wide band gap metal oxide semiconductors such as TiO<sub>2</sub> are stable, but can only absorb ultraviolet (UV) light, leading to a low solar-to-fuel energy conversion efficiency.<sup>6,7</sup> An alternative solution to this problem is to integrate two different materials together to form heterojunction-based photocatalysts or photoelectrodes.<sup>2</sup>

The formation of heterojunctions by coupling plasmonic nanostructures with semiconductors can greatly enhance the activity of photocatalysts by plasmonic energy transfer from the metal nanostructure to the semiconductor. Localized surface plasmon resonance (LSPR) is generated on the surface of illuminated metal nanostructures, such as gold, silver, copper and aluminum. Plasmonics has proved particularly promising in extending the light absorption range of semiconductors because metal nanostructures act as tunable light antennas across the full solar radiation spectrum. Interest in plasmonic photocatalysis was triggered in the mid-2000s and it has been receiving increasing attention during the last decade. 3185 papers have been published since 1990 according to the statistical data generated by the author from the Web of Science® with the relevant keywords. Most of these papers were published after 2010 and the number of papers has increased rapidly from 2010 till now.

Plasmonic metal nanoparticles alone can act as photocatalysts,<sup>8</sup> which is beyond the scope of this article. This article will focus on plasmonic metal-semiconductor heterojunctions. Recently, several review articles were published in this field and gave an overview of the plasmonic concepts and the plasmonic enhancement processes.<sup>9-17</sup> The present article gives a comprehensive review of the field. It will give a summary of the three major mechanisms of plasmonic energy transfer from a metal to a semiconductor, including light scattering/trapping, plasmon-induced resonance energy transfer (PIRET) and hot electron injection. It will place an emphasis on the rational design of materials based on the plasmonic energy transfer mechanisms. In addition, it will highlight the applications of heterojunctions in solar water splitting, carbon dioxide reduction and environmental pollutant decomposition.

# 2. Progress in plasmonic photocatalysts and photoelectrochemical cells

In 1971, Endriz and Spicer observed that a photoemission peak occurred at energies near the surface plasma frequency of an aluminum film with a rough surface, and the peak intensity was strongly dependent on the surface roughness.<sup>18,19</sup> The observed photoemission was claimed to be one-electron excitations from the decay of excited plasmons.<sup>19</sup> In the early 1990s, Kostecki and Augustynski demonstrated the plasmoninduced photoelectrochemical activity of a rough Ag film electrode.<sup>20,21</sup> The CO<sub>2</sub> reduction photocurrent was maximized at ~360 nm, corresponding to the energy of surface plasmons of Ag.<sup>21</sup> In 2004, Tian and Tatsuma revealed that the incident photon-to-current efficiency (IPCE) of the Ag and Au nanoparticle (NP)-decorated TiO<sub>2</sub> electrode matched the shape of localized surface plasmon resonance (LSPR) of metallic NPs.<sup>22</sup> In 2005, they provided direct evidence of the plasmonic hot electron injection from Au NPs to TiO2.23 In 2005, Schaadt et al. showed enhanced optical absorption in the semiconductor by LSPR of metal nanoparticles.<sup>24</sup> In 2006, Derkacs et al. improved the performance of amorphous silicon solar cells via plasmon-induced light scattering from metallic NPs.<sup>25</sup> To the best of my knowledge, Awazu et al. for the first time used the term "plasmonic photocatalysis" in 2008,26 and demonstrated the plasmon-enhanced photocatalytic decomposition of methylene blue with Ag NPs embedded in TiO<sub>2</sub>. In 2008, Zhu's group reported the visible-light photocatalytic oxidation of formaldehyde and methanol in air by gold nanoparticles dispersed on SiO<sub>2</sub> and ZrO<sub>2</sub> supports.<sup>27</sup> In December 2010, García's group reported solar hydrogen generation from water with 1.87 nm sized gold NP-decorated TiO2 particles, and proposed that the hot electrons were injected into the conduction band of TiO2.28 In 2011, Brongersma's group demonstrated a plasmon-enhanced photocurrent with large Au@SiO2 NPs embedded in the hematite film photoanode in a photoelectrochemical cell (PEC) via the LSPR-associated light scattering process.<sup>29</sup> In 2012, Wu, Cushing and co-workers discovered the mechanism of plasmon-induced resonance energy transfer (PIRET) from a metal to a semiconductor,<sup>30</sup> and further developed the PIRET theory in a follow-up paper,<sup>31</sup> showing that PIRET is characteristic of a coherent energy transfer process. In 2012, Moskovits's group showed simultaneous hydrogen and oxygen evolution with a gold nanorod-based photocatalyst, and claimed that oxygen evolution was ascribed to the plasmonic hot hole injection into the cobalt-based catalyst.<sup>32,33</sup> In 2013, Wu, Cushing and co-workers demonstrated the propagating surface plasmon polariton (SPP)-enhanced solar water splitting in a PEC with a gold nanohole-hematite nanorod array photoanode.<sup>34</sup> In 2013, Govorov et al. employed quantum theory to predict the injection of plasmonic hot carriers from a metal nanostructure into a semiconductor.<sup>35</sup> In 2015, Wu, Cushing and co-workers clarified that there were three major mechanisms of energy transfer from a plasmonic metal to a semiconductor including light scattering/trapping, PIRET and hot electron injection. These three processes can be tracked in a time-resolved manner and controlled by the dephasing time. Following this, a theoretical approach has been developed to predict the theoretical maximum efficiency of solar energy conversion in plasmonic metal-semiconductor heterojunctions.<sup>36</sup> Some of the important developments on plasmonic photocatalysts and photoelectrochemical cells are highlighted in this section to the best of my knowledge. More contributions to this active field of research are described in the following sections.

# 3. Roles of plasmon in solar energy conversion

# 3.1 Motivation for the incorporation of plasmonic nanostructures into semiconductors

Semiconductors must meet the requirement of band energetics in order to perform photocatalysis.<sup>2,37</sup> The conduction band and the valence band levels must straddle the redox potentials of photochemical reactions. From the viewpoint of thermodynamics, a minimum potential of 1.23 V is required to split water completely into hydrogen and oxygen at 298 K. If a single semiconductor is employed as the particulate photocatalyst or as the photoelectrode in a PEC for water splitting, the minimum band gap of the semiconductor should be 1.23 eV plus the required overpotentials associated with thermodynamic and kinetic losses. Hence the ideal band gap of a single semiconductor is 1.9-2.3 eV for solar water splitting.<sup>2,37</sup> This indicates that a single semiconductor even with an ideal band gap can only absorb sunlight in the spectral range of less than 644 nm (Fig. 1a). In fact, most of the semiconductors, which are stable during solar water splitting, have band gaps larger than the ideal value. For example, the band gap of anatase  $TiO_2$  is 3.2 eV, which makes it only absorb ultraviolet (UV) light, which accounts for <5% of the whole solar radiation (Fig. 1c). Therefore, single semiconductor-based photocatalysts or photoelectrodes cannot meet the need for high-efficiency



Fig. 1 (a) The light-absorption spectral range of a single semiconductor in the solar spectrum; (b) multiple plasmonic photosensitizers used for harvesting the full solar spectrum; (c) the absorbance of two typical semiconductors, and (d) the ideal band gap of a single semiconductor for water splitting. (a)–(c) are adapted from ref. 38 with permission from the Electrochemical Society.

solar energy conversion. An alternative route to extend the light absorption of photocatalysts or photoelectrodes is by the use of photosensitizers such as organic dyes and inorganic quantum dots. Unfortunately, organic dyes suffer from a narrow lightabsorption band and poor stability under solar radiation. The electron transfer rate from inorganic quantum dots to a semiconductor is relatively slow and inefficient. Also, many inorganic quantum dots are toxic and unstable during solar water splitting. In contrast, plasmonic metal nanostructures exhibit tunable broad light absorption bands and large absorption cross-sections<sup>9</sup> and have great potential for use in the photosensitization of semiconductors. In addition, plasmonic metal nanostructures can be used for light management (light scattering and trapping) in semiconductor-based devices.

# 3.2 Mechanisms of plasmon-enhanced solar energy conversion

For detailed concepts and principles of plasmonics the reader can refer to my previous paper.<sup>39</sup> Solar energy can be converted into a large amount of plasmonic energy in a plasmonic nanostructure. However, it is extremely difficult for a plasmon alone to achieve a high efficiency in solar energy conversion due to the short lifetime of excited intraband transitions. In contrast, it is highly feasible to achieve a high energy-conversion efficiency by using a well-designed plasmonic metal–semiconductor heterojunction, in which the plasmonic metal serves as a light antenna and transfers plasmonic energy to the semiconductor, enhancing photoconversion in the semiconductor both above and below the band gap.<sup>36</sup>

When plasmonic metal nanostructures are used in photocatalysts or photoelectrodes, plasmons can modulate photocatalysis *via* the following effects: (i) strong light absorption, (ii) intensive far-field light scattering, (iii) a strong near-field electromagnetic field, (iii) abundant hot carrier generation and (iv) plasmonic heating effects. These effects may alter the key physical and chemical processes in a semiconductor such as light absorption, charge separation, migration and recombination as well as charge injection into the redox species in the electrolyte. In the last decade, significant progress has been made on the effects of plasmon on the light absorption and charge separation in semiconductors. So far, few studies have been performed on the effects of plasmons on charge migration and recombination in semiconductors as well as charge injection into redox species.

Previous papers have described the mechanisms of plasmon-enhanced photoconversion in semiconductors in detail.<sup>9,38,40</sup> Hence this article just highlights some important aspects. Plasmonic energy in a metal can be transferred to a semiconductor through three major mechanisms (Fig. 2): (i) light scattering/trapping, (ii) plasmon-induced resonance energy transfer (PIRET), and (iii) hot electron injection, also named direct electron transfer (DET).

Light scattering/trapping. For colloidal metal particles, the LSPR extinction band comes from the overall contribution of both light absorption and scattering. The light scattering contribution is dominant in the LSPR band for a large metal particle (typically larger than 50 nm in diameter). When large plasmonic metal nanoparticles are integrated with a semiconductor to form a metal-semiconductor heterojunction, incident light can be scattered by the metal nanoparticles to penetrate the semiconductor (Fig. 2(a)), leading to an increase in photon flux in the semiconductor.<sup>24,25</sup> Because this scattering effect enhances the light absorption and charge separation in the active semiconductor component, it is also called "light trapping". Besides the LSPR mode, the SPP mode can also be used for light trapping.<sup>34</sup> The SPP is the electron oscillation that generates electromagnetic near-field propagation on the surface of planar metal films or nanostructures. It is worth noting that the light absorption spectral range of solar energy devices cannot be extended by utilizing the plasmonic light scattering effect. To enable the light trapping effect, the scattering photon's energy must be larger than the band gap of the semiconductor. To maximize the light trapping effect, it is better to create a broadband plasmonic band that is overlapping with the absorption band of the semiconductor completely or to a large extent.

Plasmonic light absorption and scattering of metal nanostructures are strongly dependent on the size and shape of metal nanoparticles as well as the dielectric properties of the surrounding medium. The discrete dipole approximation (DDA) and the finite difference time domain (FDTD) methods can be used to thoroughly simulate the interaction of electromagnetic radiation with nanostructures to quantitatively investigate the light absorption and scattering of nanostructures with different sizes, shapes, compositions and aggregation states. For the simple case of a metal sphere, simple equations are available for the calculation of the cross-sections of scattering ( $C_{\rm sca}$ ) and absorption ( $C_{\rm abs}$ ) as follows:<sup>41</sup>

$$C_{\rm sca} = \frac{8}{3}\pi k^4 r^6 \left| \frac{\varepsilon - \varepsilon_{\rm m}}{\varepsilon + 2\varepsilon_{\rm m}} \right|^2 \tag{1}$$

$$C_{\rm abs} = 4\pi k r^3 lm \left[ \frac{\varepsilon - \varepsilon_{\rm m}}{\varepsilon + \varepsilon_{\rm m}} \right]$$
(2)



Fig. 2 Three mechanisms of plasmonic energy transfer from a metal to a semiconductor. (a) Light scattering; (b) PIRET; (c) hot electron injection; (d) evolution of the plasmon after being excited by light, adapted from ref. 36 with permission from the Royal Society of Chemistry.

where  $k = 2\pi/\lambda$ ,  $\lambda$  is the wavelength, r is the radius of the particle,  $\varepsilon$  is the relative permittivity of the metal particle, and  $\varepsilon_{\rm m}$  is the relative permittivity of the surrounding medium.  $l_{\rm m}$  denotes the imaginary component of relative permittivity. It can be seen from the above equations that light absorption is dominant and scattering is negligible for a small particle. The ratio ( $C_{\rm sca}/C_{\rm abs}$ ) increases with the dependence on  $r^3$ , leading to the dominance of light scattering in a large metal particle.

Hot electron injection. The non-radiative dissipation of plasmon energy can generate hot carriers via Landau damping, including both intra- and inter-band transitions of electrons, which have a higher energy than that achieved by thermal excitation. The hot electrons, which have energy higher than the Schottky barrier at the metal-semiconductor interface, can be directly injected into the conduction band of the semiconductor, 22,23 as shown in Fig. 2(c). It is worth noting that the hot electrons injected from a plasmonic metal into a thin semiconductor exhibit a non-thermal energetic distribution with energy up to the plasmon frequency. In other words, the electrons injected into the semiconductor can still be considered as hot carriers with an energetic level above the conduction band level. In contrast, for a dye-sensitized semiconductor, the photogenerated electrons in the semiconductor, which are transferred from the conduction band of organic dyes, are quickly thermalized to the conduction band edge. Also, it has been observed that in a plasmonic Au/TiO<sub>2</sub> photoelectrode, the hot electron injected into TiO<sub>2</sub> has a lifetime two orders of magnitude longer than that of electrons that are photogenerated by the interband transition in TiO<sub>2</sub>.<sup>42</sup>

In short, the hot electrons transferred from the excited plasmonic metal could have a higher thermodynamic driving force for the photocatalytic redox reaction, and a lower charge recombination as compared to those electrons that are directly photogenerated *via* inter-band transitions in the semiconductor. To maximize the hot electron injection effect, it is essential to keep intimate contact between the metal and the semiconductor. The hot electron injection process is inefficient in a metal-metal/semiconductor heterojunction with an ohmic contact interface due to severe back electron transfer and charge recombination.

Generally, photoemission from a bulk metal to a semiconductor can be explained by Fowler's theory,<sup>43</sup> assuming an isotropic electron momentum distribution in the metal. This assumption is no longer valid for small nanoparticles with dimensions less than the electron mean free path,  $d_{\lambda}$  (*e.g.*,  $d_{\lambda}$  = 40 nm for Au and  $d_{\lambda}$  = 50 nm for Ag at energies near the Fermi energy<sup>44,45</sup>). To quantitatively predict hot electron generation in plasmonic metal nanoparticles and injection into the semiconductor, Govorov's group<sup>35,46,47</sup> and Kumarasinghe's group<sup>48,49</sup> have developed a single-electron model, assuming a non-interacting electron gas confined under a uniform background potential in metals. Their theories show that hot electron generation and injection are strongly sensitive to the size and shape of nanoparticles as well as the presence of "hot spots".

**PIRET.** Excitation of plasmons in a metal can generate a strong dipole. Plasmonic energy in the metal can be non-radia-tively transferred to the semiconductor *via* the dipole-dipole

interaction in the near-field, generating electron-hole pairs in the semiconductor,<sup>30,31</sup> as shown in Fig. 2(b). The PIRET process can occur even in the presence of an insulating space layer up to ~25 nm thick between the plasmonic metal and the semiconductor. The PIRET efficiency is strongly dependent on two factors: (i) the distance between the energy donor (metal) and the energy acceptor (semiconductor), and (ii) the spectral overlap between the plasmonic resonance band and the semiconductor's absorption band. PIRET is a blue-shift energy transfer process, which is different from the Förster resonance energy transfer (FRET) that is a red-shift energy transfer process. Thus plasmonic nanostructures can be used as photosensitizers for semiconductors, which can significantly extend the light absorption spectral range of solar energy devices. In addition, PIRET is a coherent energy transfer process. Stokes shift is absent in PIRET but present in FRET. Moreover, for Type-II semiconductor heterojunctions or dye-sensitized semiconductor systems, there is a stringent band alignment requirement in order to allow electron transfer across the interface. In contrast, there is no such requirement for band alignment to enable a PIRET process.

For PIRET from a metal to a semiconductor, the energy transfer rate can be calculated as  $^{30}$ 

$$k_{\text{transfer}} = \frac{1}{\tau_{\text{donor}}} \left(\frac{R_0}{R}\right)^6 \tag{3}$$

where  $\tau_{donor}$  is the radiative lifetime of the energy donor, and  $R_0$  (given in angstroms) can be calculated as

$$R_0 = 0.2108 (\kappa^2 \Phi_0 n^{-4} J)^{1/6} \tag{4}$$

where  $\kappa$  is an orientation factor usually taken as 2/3, *n* is the refractive index,  $\Phi_0$  is the quantum yield of the donor, and *J* is the normalized overlap integral between the donor spectrum (*F*<sub>D</sub>) and the acceptor spectrum ( $\varphi_A$ ):

$$J = \int F_{\rm D}(\lambda) \times \varphi_{\rm A}(\lambda) \times \lambda^4 \mathrm{d}\lambda.$$
 (5)

**Occurrence and balance of three plasmonic enhancement processes.** The plasmonic enhancement mechanisms can be best understood from progression of the plasmon after excitation,<sup>9,36,50–52</sup> as shown schematically in Fig. 2(d). Initially, light excites the plasmons (collective electron oscillations) in the metal.

(i) The collective electron oscillations can create a large combined dipole moment, concentrating incident energy in the near field, yielding a large absorption cross section of plasmons. The intense local field of the plasmon can non-radiatively excite interband transitions in the semiconductor through PIRET, enhancing the carrier generation near the band edge. Plasmons will then decay in either a radiative or a non-radiative way.

(ii) The electron oscillations can collectively depolarize as radiative scatter with a large cross section. The plasmon's farfield scattering can increase light trapping in the semiconductor at energies above the band edge. (iii) The collective nature of the plasmon ceases in less than 20–30 fs, with the electron oscillations becoming out of phase from each other (dephasing) and converting the collective oscillations non-radiatively to a population of individual hot carriers *via* Landau damping. The hot electrons or holes can be transferred to a semiconductor. The metal–semiconductor interface and plasmons can influence the charge carrier lifetime.

(iv). After Lamdau damping, hot carriers will be relaxed close to the thermal energy *via* electron–phonon scattering in 100 fs to 1 ps. Subsequently hot carriers will be relaxed to the Fermi level, emitting heat in 1 ps to 10 ns.

The plasmonic enhancement mechanisms are rooted in the balance of near-field dipole-dipole interaction, light scattering, and hot carrier responses to incident light.<sup>36</sup> Therefore, the plasmon's dephasing time, as determined by radiative and non-radiative damping mechanisms, directly determines which step in the plasmon's evolution is dominant in the enhancement of a semiconductor. Taking a plasmonic NP as an example, it can be reflected by the change in the plasmon's optical response with the particle size.<sup>36,50-52</sup> For large metal NPs, the resonance energy is usually red-shifted from the metal-specific interband dampening energy. This allows the plasmon to stay collective longer, approaching dephasing times of the bulk metal, leading to large scattering-induced efficiencies. As the size of the metal NP is reduced to ~15 nm, surface scattering and interband damping increase while radiative scattering decreases, and the near-field primarily dominates the optical response as exemplified by surfaceenhanced Raman scattering (SERS). Further reducing the NP's size to ~3 nm almost completely damps the plasmon, and makes the resonance behavior disappear. The light absorption only heats the metal.

The plasmonic DET and PIRET processes can be controlled by the spectral overlap and the physical contact between the metal and the semiconductor.<sup>53</sup> For example, PIRET occurs in the Ag@SiO<sub>2</sub>@TiO<sub>2</sub> core–shell nanoparticles due to the spectra overlap between Ag and TiO<sub>2</sub>.<sup>53</sup> DET takes place in the Au@TiO<sub>2</sub> core–shell nanoparticles given by the intimate contact between Au and TiO<sub>2</sub>. However, neither DET nor PIRET happens in the Au@SiO<sub>2</sub>@TiO<sub>2</sub> core–shell nanoparticles due to the presence of an insulating space layer at the interface and due to the lack of spectral overlap; the plasmon cannot enhance the photoconversion of TiO<sub>2</sub> although the Au core absorbs light strongly by LSPR.

The three above-mentioned mechanisms (light trapping, DET and PIRET) enhance the photoconversion in the semiconductor by modulating the light absorption and the charge separation processes in the semiconductor. In addition, plasmons may affect the charge migration and recombination processes in a semiconductor. Indeed it was observed that charge carriers photogenerated in the plasmonic Au–Fe<sub>2</sub>O<sub>3</sub> photoelectrode exhibited longer lifetimes and lower charge recombination rates than those in Fe<sub>2</sub>O<sub>3</sub> alone.<sup>34</sup>

In metal-semiconductor heterojunctions, the metal nanostructures may play multiple roles including surface catalysis,

surface passivation, Fermi level equilibration and plasmonic enhancement.<sup>54</sup> One cannot simply claim that the enhancement of photocatalytic activity or photocurrent is solely due to the plasmonic enhancement effect of metal nanostructures. The plasmonic enhancement role of a metal nanostructure can be distinguished from other enhancement effects by experimental methods.54

#### Rational design of plasmonic 4. metal-semiconductor heterojunctions

Photocatalytic systems fall into two categories based on the configuration:<sup>2</sup> (i) photoelectrochemical cells (PEC) and (ii) particulate photocatalysts. PECs generally have higher energy conversion efficiency and are more convenient for separating H<sub>2</sub> and O<sub>2</sub> products. Particulate photocatalytic systems are simpler and inexpensive. In a PEC, a photoactive semiconductor is immobilized on a planar electric contact as a photoelectrode, which provides more flexibility for the incorporation of a plasmonic metal nanostructure into a semiconductor. In particular, 2D or 3D plasmonic architectures can be used to generate SPP mode in a photoelectrode.

The predicted theoretical maximum efficiency of solar energy conversion indicates that there is plenty of room to improve the performance of plasmonic metal-semiconductor heterojunctions.<sup>36</sup> However, the interaction between the plasmonic metal and the semiconductor could be very weak if simply mixing small plasmonic metal nanoparticles with semiconductor particles or randomly depositing plasmonic metal nanoparticles on the semiconductor surface.<sup>54</sup> Consequently, a plasmon makes little contribution to the overall solar energy conversion although plasmonic metal nanostructures are capable of harvesting light. It is important to construct plasmonic metal-semiconductor composites according to the "device-by-design" strategy, that is, a plasmonic device must enable one or more efficient plasmonic energy transfer mechanisms from the metal to the semiconductor in the composite, as shown in Fig. 3.<sup>36</sup> It is worth noting that the band gap of a semiconductor is an important parameter when designing a plasmonic metal-semiconductor heterojunction because it is a critical factor governing the plasmonic coupling between the metal and the semiconductor.<sup>36</sup> The band gap of a semiconductor can modulate the PIRET efficiency or the light trapping effectiveness. Moreover, it can directly determine which plasmonic energy transfer mechanism is dominant in the enhancement of photoconversion in the semiconductor. When a semiconductor with a band gap larger than 3.1 eV is coupled with a metal with the plasmon resonance band in the visiblelight or near-infrared light range, only hot electron injection can be used for the transfer of plasmonic energy, leading to very limited plasmonic enhancement of photoconversion in the semiconductor. It is recommended to select a semiconductor with a band gap of less than 2.5 eV to couple with a metal antenna with the plasmon resonance band in the visible-light or near-infrared light range, which will allow the



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Fig. 3 Schematic illustration of photoconversion enhancement in semiconductors by each plasmonic energy transfer mechanism. Reprinted from ref. 36 with permission from the Royal Society of Chemistry.

utilization of all three major plasmonic energy transfer mechanisms.<sup>36</sup> This provides a route to reach the theoretical maximum efficiency of solar energy conversion.

#### 4.1 Design of heterojunctions based on the light trapping mechanism

The light scattering mechanism cannot be used to extend the light absorption spectral range of semiconductors. Instead, it can be employed to increase the optical path length. Light scattering is effective in enhancement when dephasing of the plasmon is close to the bulk metal and the plasmon's energy is larger than the band gap of the photoactive semiconductor (Fig. 3). In particular, the light trapping mechanism is significantly important to the indirect band gap semiconductors or to the photoactive materials that have a short minority-charge diffusion length. To enable photo-generation of electron-hole pairs in the indirect band gap semiconductors such as Si and Ge, the energy of incident photons must be larger than the sum of the band gap plus the energy due to the phonon's momentum. Hence silicon-based photoactive components are typically hundreds of microns thick due to their low light absorption coefficient. Otherwise, much of the incident light will simply pass through a thin film of Si. If a semiconductor has a short minority-charge diffusion length, it must be very thin along the charge carrier migration direction to allow more photogenerated charge carriers to migrate to the surface of the photocatalyst or the photoelectrode. Otherwise, many photogenerated charge carriers are recombined due to their short lifetime in a thick film. In short, for thin film-based semiconductors with indirect band gaps or with a poor minoritycarrier diffusion length, the light scattering mechanism of plasmonic metals can be used to extend the optical path length in photocatalysts or photoelectrodes.

When a LSPR mode is used for light scattering enhancement of photoconversion in a semiconductor, the particle size and shape of metal particles may have a significant effect on the light scattering effect. As shown in eqn (1) and (2), large particles (typically > 50 nm in size) can be used for light scattering. Also, nanorods are more effective in light scattering than nanospheres, nanocubes and nanostars. In addition,

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light scattering becomes stronger as the aspect ratio of nanorods increases. In short, long metal nanorods are favorably used in LSPR-associated light scattering.

In addition to the LSPR mode, the SPP mode can also be used for light trapping. Periodic arrays of nanoholes, grooves and gratings are usually made to generate propagating SPP. The key to the success of light trapping with SPP is to enable strong plasmonic coupling between the metal nanostructure and the semiconductor. Wu's group fabricated a gold nanohole array pattern and then grew a vertically aligned hematite nanorod array onto the gold nanoholes as the photoanode in a PEC (Fig. 4). The gold nanohole array pattern generated strong SPP, leading to extraordinary light transmission through the nanoholes.<sup>34</sup> This launched a propagating waveguide mode inside the nanorods (Fig. 4(d)), which greatly enhanced the light absorption in hematite nanorods.

A recent study shows that the photocurrent in the  $TiO_2$  film can be enhanced by the light trapping effects of SPP combined with LSPR.<sup>55</sup> In this nanostructure, a mirror consisting of a 100 nm thick Au film with a 1 nm thick Cr adhesion layer was deposited on indium-doped tin oxide (ITO)-coated glass. A 120–190 nm thick  $TiO_2$  film was then deposited over the Au mirror. Finally, the short-range ordered Au nano-discs (about 35 nm high and 90 nm in diameter on average) were deposited on the top surface of the  $TiO_2$  film. In this structure, light scattering from the Au nano-discs was strong. The Fabry–Perot cavity modes occurred in the  $TiO_2$  film due to multiple reflections between the mirror and the Au nano-discs. The interplay between the LSPR of Au nano-discs and the cavity modes significantly enhanced the light absorption in the  $TiO_2$  film, leading to an increase in the photocurrent by a factor of 2–10 as compared to the counterpart without the Au mirror.

# 4.2 Design of heterojunctions based on the hot electron injection mechanism

The hot electron injection mechanism can be used for the plasmonic enhancement of wide band gap semiconductors when the plasmon exhibits a small energy, and the plasmon dephasing balances the light absorption intensity and line width (Fig. 3). In the case when the LSPR peak is away from the light absorption band edge of the semiconductor, hot electron injection is the only possible mechanism for enhancing photoconversion in the semiconductor because both the PIRET and the light scattering processes are disabled in this case. The typical material system of such a case is the Au nanoparticle-decorated TiO<sub>2</sub> system, in which the hot electron injection is the only possible plasmonic enhancement mechanism.<sup>53</sup>

The particle size of a metal has a significant effect on the hot electron generation and injection. Most of the hot carriers photogenerated in large metal particles have very small excitation energies. For smaller metal particles, the hot carriers shift to higher energetic levels due to the stronger quantum surface effect.<sup>35</sup> Also, given that plasmonic hot electrons have a very short lifetime, a small size allows the hot electrons to reach the metal-semiconductor interface before decay. On the other hand, for small nanoparticles, the plasmon decays mainly through non-radiative energy transfer to the electron



**Fig. 4** A plasmonic  $Au-Fe_2O_3$  photoanode for solar hydrogen generation showing strong light trapping and PIRET enhancement. (a) Schematic illustration of a hematite nanorod array coupled to a Au nanohole array; (b) photocurrent density vs. applied bias; (c) SPP and LSPR enhancement; (d) SPP-induced light trapping. Reprinted from ref. 34 with permission from Macmillan Publishers Limited.

gas rather than radiative decay.<sup>56</sup> But if the particle size is too small (typically less than 3 nm), its light absorption capability is very weak due to surface damping. It is estimated that 10–20 nm is the optimal size for gold nanoparticles to maximize the hot electron generation and injection efficiencies.<sup>35</sup>

The hot electron generation and injection processes are highly dependent on the shape of plasmonic nanoparticles. The theoretical calculation results reveal that the rate of hot electron injection from the metallic nanorods is several orders of magnitude higher than that from the spherical counterparts.<sup>48</sup> The rate of hot electron injection to the semiconductor increases with an increase in the aspect ratio of the nanorod, and decreases with an increase in the volume of the nanorod keeping the aspect ratio constant. Misawa's group fabricated a Au-TiO<sub>2</sub> photoanode, in which a gold nanorod array pattern was deposited on the surface of a  $TiO_2$  film (Fig. 5). The hot electrons were injected into TiO2 and transferred to the Pt counter electrode via a wire for hydrogen evolution. It was proposed that hot holes might be trapped in the surface states near the Au-TiO2-water interface, which oxidize water molecules.<sup>57</sup> The Au photosensitizer has extended the light absorption spectral range of the photoanode to 1100 nm. The incident photon-to-electron conversion efficiency (IPCE) corresponding to the plasmonic water splitting reached about 1.2-2.2%, which was one order of magnitude higher than that induced by plasmonic Au nanospheres reported previously. In addition, Zhang et al. decorated the Ag nanoprisms and the Ag



Fig. 5 A gold nanorod-TiO<sub>2</sub> photoanode enabling hot electron injection. (a) SEM image of the photoanode; (b) IPCE and product selectivity curve. Reprinted from ref. 57 with permission from the American Chemical Society.

nanospheres on the ZnO nanorods as the photoanode for solar water splitting.<sup>58</sup> The photocurrent density of the Ag nanoprism-ZnO at 0.5 V (vs. Ag|AgCl) was 3.1 and 10 times larger than that of the Ag nanosphere-ZnO and the ZnO nanorod alone, respectively. This was due to the fact the sharp tips on the Ag nanoprisms generated strong "hot spots".

Plasmonic "hot spots" occur on the corners and tips of nanoparticles such as nanoneedles, nanocones, nanocubes, nanoprisms or nanostars or inside the narrow gaps between neighboring nanoparticles. "Hot spots" lead to a strong enhancement of the localized electromagnetic field, and break the linear momentum of the electrons, which enhances the hot electron generation.<sup>59</sup> Hence nanocubes and nanostars are suitable for the plasmonic enhancement of photoconversion in a semiconductor based on the hot electron injection process. Recently, a new "on-wire" lithography technique was used to synthesize Au nanorod dimers, in which a tunable gap from 7 nm to 28 nm was present between two nanorods in a diameter of 43 nm.<sup>60</sup> The electromagnetic fields in the 7 nmgap "hot spots" in the nanorod dimers were three orders of magnitude greater than those of the nanosphere counterparts, and about 50 times greater than that of the rod segment alone. Such Au nanorod dimers were embedded into anatase TiO<sub>2</sub> sheets to form a unique plasmonic Au-TiO<sub>2</sub> composite.

The metal-semiconductor interface is another factor governing the hot electron injection efficiency. It has been reported that the Schottky barrier height and the defect states near the interface affect the hot electron injection process.<sup>61</sup> Strong near-field coupling at the interface of the plasmonic metal and the semiconductor can promote the hot electron transfer, which was confirmed in the long-range ordered Ag nanowire grating pattern on a TiO<sub>2</sub> film,<sup>62</sup> and in the periodic Au nanowire grating pattern on a TiO<sub>2</sub> film.<sup>63</sup> The experimental results showed that there was strong light–matter coupling between confined photons on a semiconductor waveguide and LSPR on the metal nanowires. Strong coupling of particle plasmons and waveguide modes reduced the radiative decay rate, and increased the rate of hot electron injection to the supporting semiconductor waveguide.

So far, the sole utilization of the hot electron injection process has not resulted in high solar energy conversion efficiency in the plasmonic metal-semiconductor heterojunctions. One of the reasons is that only a small portion of the hot electrons can be harvested to allow injection into the conduction band of the semiconductor via the "sequential excitation-charge-transfer" process<sup>23,64</sup> although a large number of plasmonic hot electrons are generated during plasmon decay. One possible route to improve the hot electron transfer efficiency is by the "direct excitation of an interfacial chargetransfer transition" wherein the wavefunctions of the plasmon are hybridized with those of the semiconductor.65,66 However, the "direct excitation of an interfacial charge-transfer transition" process is rarely observed in the metal-inorganic semiconductor heterojunctions although a similar chemical interface damping (CID) process<sup>67-69</sup> is often observed in hybrid metal-organic molecule systems.

## 4.3 Design of heterojunctions based on the PIRET mechanism

As mentioned above, the PIRET efficiency is dependent on the spectral overlap and the gap between the metal and the semiconductor. In addition, the dipole moment of the plasmon is better to be aligned spatially with that of the semiconductor.<sup>9</sup> Interfacial damping also needs to be considered. For example, Au@SiO<sub>2</sub>@Cu<sub>2</sub>O sandwich particles with a SiO<sub>2</sub> spacer layer showed a higher PIRET efficiency than Au@Cu2O particles with direct contact between Au and Cu<sub>2</sub>O because interfacial damping happened at the Au-Cu<sub>2</sub>O interface.<sup>31</sup> Furthermore, if a semiconductor is located inside the plasmonic "hot spots", the PIRET process can be enhanced because the dipole moment becomes larger due to the stronger near-field inside the "hot spots".9 Generally speaking, PIRET can achieve the highest efficiency of solar energy conversion among the three major plasmonic enhancement mechanisms (Fig. 3). In particular, PIRET can effectively enhance the photoconversion in semiconductors with the weak light absorption states near the band edge or with relatively low charge mobility.

PIRET was observed in various heterojunction systems such as Au-Fe<sub>2</sub>O<sub>3</sub>,<sup>34</sup> Au@Cu<sub>2</sub>O, Au@SiO<sub>2</sub>@Cu<sub>2</sub>O,<sup>30,31</sup> Ag@TiO<sub>2</sub>,<sup>53</sup> Ag@SiO<sub>2</sub>@TiO<sub>2</sub>,<sup>70</sup> Ag@SiO<sub>2</sub>-BiVO<sub>4</sub>,<sup>71</sup> Ag@SiO<sub>2</sub>-CdS,<sup>72</sup> Ag@SiO<sub>2</sub>-C<sub>3</sub>N<sub>4</sub><sup>73</sup> and Au-La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> doped with nitrogen.<sup>74</sup> Wu's group synthesized a plasmonic Au@Pt-La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>/reduced graphene oxide (rGO) sheet for solar hydrogen generation as shown in Fig. 6.<sup>74</sup> The LTO nanoplates were supported on the rGO sheet; and the Au and Pt nanoparticles were dispersed on the LTO nanoplates. Fig. 6(b) shows that the absorption band edge of La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (LTO) was cut off at 350 nm, and the LSPR band was centered at 550 nm. It can be seen from the curve labeled with "Au-Pt-LTO/rGO" in Fig. 6(b) that there was no overlap between the LSPR band of Au nanoparticle and the absorption band of pristine LTO. Consequently, the incorporation of Au nanoparticles onto the pristine LTO did not contribute to IPCE (the curve of "Au-Pt-LTO/rGO"). In contrast, N-doping reduced the band gap to 2.25 eV, extending the absorption band edge to 550 nm. This resulted in spectral overlap between the Au nanoparticles and the N-doped LTO (see the curves labeled "Au@Pt-NLTO" and "Au@Pt-NLTO/ rGO" in Fig. 6(b)), leading to an increase in IPCE up to 600 nm (Fig. 6(b) and (d)). This result shows that only PIRET was responsible for IPCE enhancement near and above the band edge of N-doped LTO and neither light trapping nor hot electron injection was involved in the IPCE enhancement.

# 4.4 Design of heterojunctions based on multiple or hybrid enhancement mechanisms

To further enhance the solar energy conversion efficiency, plasmonic metal–semiconductor heterojunctions can be rationally designed to enable multiple plasmonic energy transfer mechanisms. In the Ag@Cu<sub>2</sub>O core–shell nanoparticles shown in Fig. 7,<sup>75</sup> the presence of the LSPR band of nanoparticles extended the light absorption spectral range over the entire visible-light region (Fig. 7(b)). The LSPR band can be tuned, showing a red-shift with an increase in the Cu<sub>2</sub>O shell thickness.<sup>75</sup> The plasmonic energy was transferred from Ag to Cu<sub>2</sub>O *via* both PIRET and DET simultaneously (Fig. 7(c)), generating



**Fig. 6** Au@Pt-NLTO/rGO photocatalyst enabling PIRET enhancement of solar hydrogen generation. (a) Schematic illustration of a photocatalyst; (b) UV-visible spectra; (c) IPCE curves; (d) quantification of PIRET enhancement. Reprinted from ref. 74 with permission from the American Chemical Society.



**Fig. 7** Ag@Cu<sub>2</sub>O core-shell nanoparticles showing hybrid plasmonic enhancement mechanisms. (a) Schematic illustration of a photocatalyst; (b) UV-visible spectra; (c) PIRET plus DET enhancement; (d) action spectrum of photocatalytic activity. Reprinted from ref. 75 with permission from the American Chemical Society.

electrons and holes in Cu<sub>2</sub>O. As a result, the photocatalytic activity of Ag@Cu<sub>2</sub>O nanoparticles in the visible-light region, which was ascribed to the plasmonic enhancement effect, was comparable to that in the UV-light region that was due to the contribution of  $Cu_2O$  alone (Fig. 7(d)). It is worth noting that the core-shell structure is favorable for strong plasmonic interaction between the metal and the semiconductor, and facilitates both the PIRET and the hot electron injection processes. An additional example shows that the largest plasmonic enhancement of solar energy conversion in a metal-semiconductor can be achieved by combining PIRET with light reradiation to increase photoconversion near the band edge of the semiconductor. In the plasmonic Au nanohole array-Fe<sub>2</sub>O<sub>3</sub> nanorod array photoanode (Fig. 4), both the SPP mode at around 475 nm and a LSPR at 650 nm were excited simultaneously under the simulated solar radiation.<sup>34</sup> As a result, both the SPP-induced light trapping and the LSPR-associated PIRET processes occurred simultaneously (Fig. 4(c)). Accordingly, the photocurrent of the plasmonic Au-Fe<sub>2</sub>O<sub>3</sub> photoanode exhibited a 10-fold increase in the photocurrent at a bias of 0.23 V (versus Ag|AgCl) under simulated solar radiation as compared to the  $Fe_2O_3$  photoanode (Fig. 4(b)).

Plasmonic-photonic hybrid nanostructures have also been demonstrated for efficient enhancement. Zhang et al. have developed a Au-TiO<sub>2</sub> bi-layer structure photoanode for photoelectrochemical water splitting.<sup>76</sup> A vertically aligned TiO<sub>2</sub> nanorod array was first grown on a conducting substrate; and a TiO<sub>2</sub> photonic crystal with an inverse opal structure was supported on the top of the TiO<sub>2</sub> nanorod array; finally 10 nm sized Au nanoparticles were deposited on the surface of TiO<sub>2</sub>. When the LSPR band matched the photonic band gap of the photonic crystal, the LSPR effect was intensified considerably, which increased the hot electron generation in the Au nanoparticles, and promoted the hot electron injection to TiO<sub>2</sub>. As a result, the PEC with the optimized Au-TiO<sub>2</sub> photoanode achieved a photoconversion efficiency of 0.71% in water splitting under the simulated sunlight illumination. In addition, an inverse opal of BiVO4 photonic crystal was decorated with the Au nanoparticles as a photoanode for photoelectrochemical water splitting.<sup>77</sup> The PEC with such a plasmonic-photonic photoanode exhibited a photocurrent density of 3.1 mA cm<sup>-2</sup> at 1.23 V (vs. RHE) under solar radiation (one sun@AM 1.5G), which was more than 4 times higher than the planar photoanode. An additional plasmonic-photonic hybrid nanostructure was a wafer-scale Au-TiO<sub>2</sub> photonic crystal, in which the plasmonic energy transferred from Au to TiO<sub>2</sub> through the hot electron injection mechanism.<sup>78</sup> A vertically aligned Al<sub>2</sub>O<sub>3</sub> nanotube array was supported on a conductive substrate. A 75 nm thick  $TiO_2$  layer was deposited on the  $Al_2O_3$  surface; and Au was then deposited over TiO2. Broad-band light absorption appeared above the absorption band edge of TiO<sub>2</sub>, which came from four basic modes: (i) cavity mode with the electric field of incident light trapped inside the cavity; (ii) gap mode with light coupled to the gaps between cavities; (iii) waveguide mode with light coupled inside metal-insulator-metal structure; and (iv) SPP mode with light confined at the Au-TiO<sub>2</sub>

interface. The photonic structure enhanced the light absorption of Au, and the enhanced electromagnetic field could increase the hot electron generation in Au.

# 5. Applications of plasmonic photocatalysts and photoelectrochemical cells

In the metal-semiconductor photocatalysts and photoelectrochemical cells, the plasmonic metal serves as light antenna and/or photosensitizer, which can concentrate and trap light, and extend the light absorption spectral range. This opens new avenues to apply the photocatalysts and photoelectrochemical cells to several fields.

#### 5.1 Solar water splitting

Au, Ag, Cu and Al are the most common plasmonic metals. None of them have catalytic activity toward either water reduction or water oxidation. Also, plasmonic hot holes have short lifetime, which makes it difficult to oxidize water directly. Hence plasmonic metals such as Au, Ag, Cu and Al typically are not used for direct photocatalytic water splitting. Instead, they are incorporated with semiconductors to form metal-semiconductor heterojunctions to perform solar water splitting. Gold nanostructures have been used as photosensitizers for wide band gap semiconductors such as TiO<sub>2</sub><sup>28,61</sup> and ZnO<sup>79</sup> to extend the light absorption spectral range to the visible-light region,28,80 and even to the near-infrared region up to 1100 nm.<sup>81</sup> Fig. 8 shows a plasmonic metal-semiconductor photocatalyst that was able to produce hydrogen and oxygen simultaneously by splitting water.<sup>82</sup> A cobalt-based oxygen evolution catalyst was deposited on the transverse surface of a Au nanorod. Pt-decorated TiO2 was deposited on the end of nanorod. There was a gap between the oxygen evolution catalyst and TiO<sub>2</sub>, which promoted the separation of hot electron and hot holes. Plasmonic hot electrons were injected to TiO<sub>2</sub> and then migrated to the Pt surface for water reduction. Hot holes were injected to the oxygen evolution catalyst to drive water oxidation. Each nanorod autonomously produced  $5 \times 10^{13}$  H<sub>2</sub> molecules per  $cm^2$  s under illumination of one sun (AM 1.5G).

It is worth noting that the absorption band edge of anatase  $TiO_2$  is generally cut off at 386 nm while the LSPR peak of Au nanoparticles is typically  $\geq$ 520 nm. Consequently the hot carrier injection is the only plasmonic energy transfer mechanism in the Au-undoped  $TiO_2$  heterojunctions. Since there is no spectral overlap between the absorption spectrum of  $TiO_2$  and the LSPR band of Au, both PIRET and light trapping cannot occur in the Au-undoped  $TiO_2$  heterojunctions. Keeping this in mind, it is not surprising that plasmon leads to limited enhancement of solar energy conversion efficiency in the Au-undoped  $TiO_2$  heterojunctions. Replacing Au with Ag can result in larger plasmonic enhancement because Ag has stronger LSPR than Au, and its LSPR band is overlapped with that of  $TiO_2$ . Hence both light trapping and PIRET can be used



**Fig. 8** A plasmonic photocatalyst for autonomous  $H_2$  and  $O_2$  generation. (a) Schematic illustration of a photocatalyst, (b) TEM image of a photocatalyst, and (c) the charge transfer pathway. Reprinted from ref. 82 with permission from Macmillan Publishers Limited.

for enhancing photoconversion in  $TiO_2$ . For example, a plasmonic Ag– $TiO_2$  photoanode was prepared by assembling the Ag nanoparticles onto the anodic  $TiO_2$  nanotube array.<sup>83</sup> The hydrogen evolution rate of the Ag– $TiO_2$  nanotube array was 3.3 times as that of the  $TiO_2$  nanotube array alone.

 $Fe_2O_3$  (~2.2 eV), BiVO<sub>4</sub> (~2.4) and WO<sub>3</sub> (~2.7 eV) have smaller band gaps as compared to TiO2 and ZnO. All three plasmonic energy transfer mechanisms could occur, which provides great flexibility in design plasmonic photocatalysts and photoelectrodes. The n-type Fe<sub>2</sub>O<sub>3</sub> has a very short minority-charge carrier diffusion length (~10 nm). Hence a thin film of Fe<sub>2</sub>O<sub>3</sub> is typically made for photoelectrodes. In this case, light trapping and PIRET are very helpful to photoconversion. When small Au nanoparticles are incorporated into Fe<sub>2</sub>O<sub>3</sub>, PIRET is the dominant plasmonic enhancement mechanism. When large Au nanospheres or nanorods are used, light trapping is enabled. Yang's group made a gold nanopillar array (300 nm in lateral size, 300 nm high and 700 nm in pitch) on the substrate, and then coated the nanopillar array with a Fe<sub>2</sub>O<sub>3</sub> film.<sup>84</sup> The photocurrent of the plasmonic Au-Fe<sub>2</sub>O<sub>3</sub> photoelectrode was 40% higher than that of the planar  $Fe_2O_3$  film at 1.5 V vs. RHE (reversible hydrogen electrode).

Pan's group modified the surface of a Fe<sub>2</sub>O<sub>3</sub> film photoanode with a large number of randomly distributed gold nanorods (12 nm in diameter and 45 nm long).<sup>85</sup> Light scattering from the Au nanorods contributed to the plasmonic enhancement of the photocurrent. BiVO4 has a modest light absorption capability, especially near the absorption band edge. Hence the surface of a BiVO4 film photoanode was decorated with 30% coverage of the Ag(a)SiO<sub>2</sub> core-shell nanoparticles.<sup>71</sup> The photocurrent was enhanced by a factor of ~2.5 at 1.23 V vs. RHE under illumination of one sun (AM 1.5G). Far-field light scattering was claimed to be the major photocurrent enhancement mechanism, and the near-field PIRET can be an additional enhancement mechanism. Solarska et al. incorporated polyoxometalate-capped Au nanoparticles into a WO<sub>3</sub> film for solar water splitting.86 The photocurrent plateau of the Au-polyoxometalate-WO<sub>3</sub> photoanode was 200% of that of the bare WO3 photoanode. The LSPR band of Au nanoparticles was overlapping with the absorption band of WO3, which indicated the near-field plasmonic enhancement of the photocurrent.

Plasmonic hot holes generally are not directly involved in water oxidation. Instead, water oxidation by hot holes needs the assistance of an oxygen evolution catalyst. A recent study on the Au–TiO<sub>2</sub> heterojunction showed that hot holes were accumulated near the Au–TiO<sub>2</sub> interface, which was considered the active site for plasmonic water oxidation.<sup>87</sup> On the other hand, LSPR can activate the oxygen evolution catalyst, as shown in the Au NP-decorated Ni(OH)<sub>2</sub> nanosheet catalyst.<sup>88</sup> This result revealed that excitation of LSPR resulted in a 4-fold enhancement of the oxygen evolution activity of the Au–Ni (OH)<sub>2</sub> nanosheet, and reduced the overpotential from 330 mV to 270 mV at a current density of 10 mA cm<sup>-2</sup>, which was even lower than the values of the benchmark IrO<sub>2</sub> and RuO<sub>2</sub> catalysts.

As mentioned in section 3.2, when metal nanoparticles on the semiconductor surface are immersed in a liquid electrolyte, the Fermi level equilibration occurs,<sup>54</sup> which will elevate the Fermi level and increase the efficiency of electron injection into the redox molecules, reducing the charge recombination.<sup>89</sup> Under steady-state illumination, the photogenerated electrons could be accumulated on both the semiconductor and the metal. The excess electrons can be transferred from the semiconductor to the metal nanoparticle, and then be injected rapidly into the solvent. This will reduce the accumulation of electrons in the semiconductor, lowering the charge recombination rate. The Fermi Level Equilibration effect is applied not only to water splitting but also to other redox reactions as described in sections 5.2 and 5.3.

#### 5.2 Sunlight-driven carbon dioxide reduction

Many methods have been developed to convert  $CO_2$  into fuels.<sup>90,91</sup> These methods include hetero-catalytic reduction, bio-catalytic conversion, electrochemical reduction and photocatalytic conversion. Conversion of  $CO_2$  into liquid fuels with heterocatalysts such as Cu/ZnO/ZrO<sub>2</sub> typically occurs at high temperature (>350 °C), which is energy-intensive. Bio-catalytic conversion of  $CO_2$  with an enzyme typically requires expensive co-factors, and its reaction proceeds slowly. Moreover, the stability of an enzyme is of concern during long-term operation. Electrochemical reduction of  $CO_2$  consumes a lot of energy, and exhibits poor thermodynamic efficiency and low current efficiency. Conversion of  $CO_2$  into liquid fuels typically undergoes uphill reactions. Hence extra energy is needed to enable the reactions at high temperature. In contrast, the uphill reactions can proceed at ambient temperature with the assistance of photocatalysts.

The electrochemical potential for the single-electron reduction of  $CO_2$  to the anion radical  $CO_2^-$  is -1.9 eV vs. NHE (Normal Hydrogen Electrode) at neutral pH.92 No semiconductor has suitable band energetics to fulfil the thermodynamic requirements for such a process. Therefore, photocatalytic CO<sub>2</sub> reduction typically proceeds with multiple electron processes with the involvement of protons. Water is an alternative proton source. Thus CO<sub>2</sub> can be converted into hydrocarbon compounds with water as the reducing agent. In this case, however, production of hydrocarbon compounds from CO<sub>2</sub> competes with the generation of hydrogen from water. Because the electrochemical potentials of CO<sub>2</sub> reduction are more negative than water reduction, semiconductors or cocatalysts that are able to reduce CO<sub>2</sub> can also reduce water into hydrogen. Hence it is necessary to suppress the hydrogen generation by selecting catalysts and controlling the operating parameters. Plasmonic materials such as Au, Ag and Cu can act as heterogeneous catalysts for CO<sub>2</sub> reduction. Hence these

materials not only assist photoconversion but also alter the reaction pathway, the selectivity and the kinetics. It is worth noting that the reduction of  $CO_2$  into different hydrocarbon compounds has different electrochemical potentials. From the thermodynamics viewpoint, different hydrocarbon compounds could be produced if the energetic levels of the photogenerated electrons are different.

Cronin's group studied the photocatalytic reduction of CO<sub>2</sub> and water with a plasmonic Au-TiO<sub>2</sub> composite.<sup>93</sup> When the LSPR of Au was excited by the incident light, the photocatalytic activity of Au-TiO<sub>2</sub> increased by 24 fold. It was interesting to note that the reaction products were dependent on the photoconversion process in the Au-TiO2 composite. Under 532 nm laser illumination, only the Au-TiO<sub>2</sub> heterojunctions showed photocatalytic activity toward CO<sub>2</sub> conversion to CH<sub>4</sub> (Fig. 9) while TiO<sub>2</sub> or Au alone was inactive. This indicated that there was no direct injection of hot electrons into  $CO_2$  although the LSPR of Au was excited. It can be seen from Fig. 9(b) that the energetic levels of the photogenerated electrons were likely to be between -0.244 eV and -0.32 eV. The authors claimed that photogenerated electrons from the conduction band of TiO<sub>2</sub> were responsible for CO<sub>2</sub> reduction to CH<sub>4</sub>. In my personal opinion, hot electrons, which were transferred to the conduction band of TiO<sub>2</sub>, might be involved in CO<sub>2</sub> reduction into CH<sub>4</sub>. In contrast, under the 254 nm laser illumination, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, HCHO and CH<sub>3</sub>OH were identified as the photocatalysis products with the Au NP alone or with the Au-TiO<sub>2</sub> composite



**Fig. 9** A Au–TiO<sub>2</sub> photoanode for photocatalytic CO<sub>2</sub> reduction; (a) the reaction product under a 532 nm laser; (b) the band energetics under a 532 nm laser; (c) the reaction product under a 532 nm laser; (d) the band energetics under a 254 nm laser. Reprinted from ref. 93 with permission from the American Chemical Society.

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as the photocatalyst while only  $CH_4$  was reduced from  $CO_2$  if  $TiO_2$  alone served as a photocatalyst (Fig. 9(c)). This suggested that the electrons, which were photogenerated from the interband transition in Au, can directly reduce  $CO_2$  into  $CH_4$ ,  $C_2H_6$ , HCHO and  $CH_3OH$  in the absence of  $TiO_2$  (Fig. 9(d)). The photocatalytic activity was enhanced in the presence of  $TiO_2$  but the reaction selectivity was not changed. In short, the selectivity of photocatalytic  $CO_2$  reduction is dependent on the energetic levels of the photogenerated electrons.

The dependence of selectivity on the energetics of plasmonic hot electrons has been confirmed by Liu's group.<sup>94</sup> They prepared the Rh-Al<sub>2</sub>O<sub>3</sub> photocatalyst, in which the plasmonic 37 nm Rh nanocubes were supported on the Al<sub>2</sub>O<sub>3</sub> particles. The photocatalytic CO<sub>2</sub> reduction activity of Rh-Al<sub>2</sub>O<sub>3</sub> was compared to that of the Au-Al<sub>2</sub>O<sub>3</sub> system. Only CO was produced on the plasmonic Au nanoparticles under both dark conditions and white light illumination. For the unheated Rh nanoparticles on Al<sub>2</sub>O<sub>3</sub>, CH<sub>4</sub> was generated with a selectivity of >86% and >98% under the illumination of blue and ultraviolet light-emitting diodes (LEDs), respectively. The high selectivity toward CH<sub>4</sub> generation disappeared under dark conditions. In both the Rh-Al<sub>2</sub>O<sub>3</sub> and Au-Al<sub>2</sub>O<sub>3</sub> systems, the hot electrons were unlikely to get injected into the conduction band of Al<sub>2</sub>O<sub>3</sub> because Al<sub>2</sub>O<sub>3</sub> is an insulating material with a large band gap. Hence the photocatalytic CO<sub>2</sub> reduction selectivity was determined by the energetics of hot electrons and the follow-up transfer of hot electrons from the metal to the reactants or to intermediates. According to the density functional theory (DFT) calculation results, the selectivity of the plasmonic Rh nanoparticles toward photocatalytic CO<sub>2</sub> reduction to CH<sub>4</sub> was due to the fact that the energetics of hot electrons were well aligned with that of the anti-bonding orbital of CHO (the critical reaction intermediate), leading to the activation of CO<sub>2</sub> methanation.

Cu, Rh and Al were also supported on the semiconductors in addition to Au as a plasmonic photocatalyst for  $CO_2$ reduction. Columnar Cu nanostructures with tunable lengths were directly grown on a porous  $TiO_2$  film.<sup>95</sup> The Cu columns with a length of >160 nm on  $TiO_2$  extended the light absorption to ~600 nm. The methane production rate for Cu– $TiO_2$ was more than 160 times higher than that for the  $TiO_2$  film alone under illumination of one sun (AM 1.5G) when  $CO_2$  and  $H_2O$  were used as the reactants. In addition, it has been reported that the support of the Cu– $TiO_2$  composite on the molecular sieve promoted the photocatalytic reduction of  $CO_2$ selectively to oxalic acid in addition to methanol, acetic acid and traces of methane,<sup>96</sup> which was due to the enhanced adsorption of  $CO_2$ , water and product on the molecular sievebased photocatalyst.

The chemical composition of plasmonic metals on the semiconductor can be tuned to improve the selectivity of the photocatalyst toward CO<sub>2</sub> reduction. Garcia's group has deposited Au–Cu alloy nanoparticles onto P25 TiO<sub>2</sub> particles.<sup>97</sup> The Au–Cu/TiO<sub>2</sub> photocatalyst (Au/Cu ratio of 1:2) showed a plasmonic band centered at 570 nm. The Au–Cu alloy nanoparticles played a dual role, that is, their LSPR not only

extended the light absorption of photocatalysts to the visiblelight range, but also improved the selectivity of photocatalysts. The results showed that the selectivity of conduction band electrons for methane formation was about 97% when CO<sub>2</sub> and H<sub>2</sub>O were employed as the reactants. In contrast, the Cu-TiO<sub>2</sub> photocatalyst showed a similar methane selectivity but a lower activity while Au/TiO2 exhibited activity toward hydrogen evolution. Tahir et al. developed the Cu-In/TiO<sub>2</sub> photocatalyst, which showed a LSPR band at around 600 nm.98 CO was the main product for the 0.2 wt% Au-3.5 wt% In/TiO<sub>2</sub> photocatalyst with H<sub>2</sub> as the reducing agent, achieving a CO selectivity of 99% and a CO<sub>2</sub> conversion of 9.5% at the CO<sub>2</sub>/H<sub>2</sub> feed ratio of 1.5. The CO production on co-metals Au-In/TiO2 was 1.3 times higher than that of Au/TiO<sub>2</sub>, 4.39 times higher than that of In/TiO<sub>2</sub>, and 76 times higher than that of the monolithic TiO<sub>2</sub> photocatalyst. Recently, Xiong's group prepared the Pd<sub>7</sub>Cu<sub>1</sub>-TiO<sub>2</sub> photocatalyst for CO<sub>2</sub> reduction.<sup>99</sup> Isolation of Cu atoms in the Pd lattice offered paired Cu-Pd sites for enhanced CO<sub>2</sub> adsorption, and suppressed the H<sub>2</sub> evolution, and elevated the d-band center of Cu sites for the promoted  $CO_2$  activation, which enhanced the  $CO_2$  conversion into  $CH_4$ , leading to 96% selectivity toward CH4 production. On the other hand, the facet index of plasmonic metals has an influence on the photocatalytic activity toward CO<sub>2</sub> reduction. Lang et al. deposited PtCu alloy nanocrystals on C<sub>3</sub>N<sub>4</sub> nanosheets for photocatalytic CO2 reduction with CO2 and H2O as the reactants.<sup>100</sup> The rate of CH<sub>4</sub> production over the PtCu alloy concave nanocubes with (730) facets on C<sub>3</sub>N<sub>4</sub> was 3 times higher than that over the PtCu nanocubes with (100) facets on  $C_3N_4$ ; and the selectivity for  $CH_4$  production also increased from 85.9% to 90.6%.

In the early stage of plasmonic CO<sub>2</sub> photocatalyst development, wide band gap semiconductors such as TiO<sub>2</sub> were selected as the support of plasmonic metallic NPs. More effort should be made to explore semiconductors with smaller band gaps. The semiconductor support affects not only the solar energy conversion efficiency but also the selectivity of products. Robatjazi *et al.* have demonstrated an Al/Al<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O photocatalyst in which plasmonic Al served as a light antenna to enhance the visible-light absorption, and Cu<sub>2</sub>O acted as the active site for CO<sub>2</sub> reduction.<sup>101</sup> Recently, Choi *et al.* coated the metal–organic framework (MOF) onto Ag nanocubes for photocatalytic CO<sub>2</sub> reduction.<sup>102</sup> Incorporation of Ag nanocubes with MOF enhanced the CO<sub>2</sub>-to-CO conversion by 7 fold under visible-light irradiation, showing stability up to 48 h.

When utilizing hot electrons for direct  $CO_2$  reduction, attention must be paid to hot holes. Hot holes must be extracted in order to keep the charge balance in a plasmonic metal. On the other hand, hot holes can be used to oxidize chemicals to provide the proton source for  $CO_2$  reduction. For example, alcohol can be used as a hot-hole scavenger in an aqueous solution and is oxidized to protons.<sup>103,104</sup>

#### 5.3 Removal of environmental pollutants

There are four prevailing types of pollutants in the environment, namely pathogens (bacteria, fungi and viruses), hydro-

carbon compounds (especially persistent organic pollutants, POPs), inorganic anions (nitrite, nitrate and phosphates) and heavy metals. Pollutants can be cleaned up by several methods such as sedimentation, screening, filtration, distillation, chemical oxidation, aeration and biotechnology. Compared to these conventional environment remediation methods, photocatalysis is an inexpensive and sustainable technique, and is able to clean up a wide range of pollutants utilizing sunlight.

Photocatalysts are used to inactivate pathogens, to decompose hydrocarbon compounds even into carbon dioxide, to convert nitrate and nitrite into nitrogen, and to transform toxic heavy metal ions into less or non-toxic forms. From the viewpoint of thermodynamics, the minimum electrochemical potential for decomposition or conversion of pollutants, in many cases, is less or much less than that (1.23 V) required for splitting water. Theoretically, it can achieve a high solar energy conversion efficiency during photocatalytic removal of pollutants and it is less demanding in the band energetics of semiconductors, providing more flexibility in the selection of photocatalyst materials. In addition, the selectivity of products generally is not an issue for the photocatalytic decomposition of hydrocarbon compounds. Plasmonic metals in photocatalysts can serve as either light antennas and/or surface catalysts. It is proposed that there are three major plasmon-modulated reaction pathways with different charge transfer processes when decomposing pollutants with plasmonic metal-semiconductor photocatalysts (Fig. 10).

(i). Pollutants are decomposed on the surface of plasmonic metals by the emitted plasmonic hot carriers. Pollutants can be decomposed *via* the direct hot carrier transfer from the plasmonic metal to adsorbates, leading to either hot electron-mediated reduction or hot hole-mediated oxidation half-reactions (Fig. 10(a)). Alternatively, hot electrons can be captured by the surface adsorbed oxygen to form the superoxide radical  $(O_2^-)$ , and hot holes can react with OH<sup>-</sup> to form the hydroxyl radical ('OH).

(ii). Pollutants are decomposed on the metal surface *via* the chemical interface damping (CID) effect. When CID occurs, photogeneration of charge carriers does not take place solely in the metal. Instead, the charge carriers in the metal are excited directly to the LUMO (Lowest Unoccupied Molecular Orbital) level of the absorbed molecules (Fig. 10(b)).

(iii). Pollutants are decomposed on the semiconductor surface by the reactions. First, incident light excites plasmons. Next, the plasmonic energy is transferred from the metal to the semiconductor through at least one of three mechanisms (light scattering, PIRET and hot electron injection) to induce or enhance the charge separation in the semiconductor. The electrons in the semiconductor can be captured by the surface adsorbed oxygen to form the superoxide radical ( $O_2^-$ ), and the holes can react with OH<sup>-</sup> to form the hydroxyl radical ('OH). The superoxide radical and the hydroxyl radical typically are the active species that decompose pollutants. In some cases, the electron and the holes can directly act as the active species to decompose pollutants (Fig. 10(c)).



**Fig. 10** Schematic reaction pathways for compound decomposition or transformation by plasmonic photocatalysts. (a) Reactions on the metal surface *via* hot carrier injection; (b) reactions on the metal surface *via* chemical interface damping; (c) reactions on the semiconductor surface after the plasmonic energy transfer to the semiconductor.

The first reaction pathway in Fig. 10(a) has been observed. In 2008, Chen et al. prepared Au nanoparticles supported on SiO<sub>2</sub> and ZrO<sub>2</sub>, respectively.<sup>105</sup> Excitation of the LSPR of Au nanoparticles caused the decomposition of HCHO into CO<sub>2</sub>. Given that SiO<sub>2</sub> is an insulating material, the three major mechanisms (light trapping, PIRET and hot electron injection) cannot happen. Hence it was likely that HCHO was decomposed on the Au surface by plasmonic hot carriers, as shown in Fig. 10(a). In addition, Chen et al. have demonstrated decomposition of methyl orange by the Au NP-mesoporous carbon blended with a Nafion® polymer under outdoor sunlight radiation.<sup>106</sup> Fourier transform infrared spectroscopy (FTIR) analysis showed that hydroxyl groups (OH<sup>-</sup>) were generated during photo-induced decomposition. The incorporation of carbon with Au NPs could promote charge transport, facilitating the processes shown in Fig. 10(a). Hu et al. used the plasmonic Ag-AgI/Al<sub>2</sub>O<sub>3</sub> photocatalyst to decompose pesticides and herbicides such as 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and trichlorophenol (TCP) under irradiation with visible light or simulated sunlight.<sup>107</sup> It was postulated that excitation of the LSPR of the Ag NPs led to the generation of holes (h<sup>+</sup>) and

superoxide radicals  $(O_2^-)$ , which were the main active species in the degradation reaction.

The third reaction pathway in Fig. 10(c) is popular in plasmonic photocatalysis toward pollution removal. Ma's group prepared doped NaYF<sub>4</sub> core@porous-TiO<sub>2</sub>-shell microspheres and loaded Au NPs into the pores of TiO2 shell for the decomposition of methyl orange.<sup>108</sup> Under visible-light irradiation, the upconversion NaYF<sub>4</sub> core was not photo-active, but the LSPR of Au nanoparticles was excited, leading to the injection of hot electrons into TiO<sub>2</sub>. Under excitation by a near-infrared (NIR) diode laser light (980 nm), the core-shell nanoparticles showed photocatalytic activity toward methyl orange decomposition. It was claimed that the NIR light excited the upconversion luminescence (in the UV-visible light range) of the doped NaYF<sub>4</sub> core. Subsequently, the upconverted UV emission could directly lead to electron-hole generation in TiO<sub>2</sub>. Meanwhile, the upconverted green emission could excite the LSPR of Au nanoparticles. As a result, the plasmonic hot electrons were transferred from Au to TiO<sub>2</sub>, leading to methyl orange decomposition, as shown in Fig. 10(c). In addition, Xiang et al. have prepared Ag-TiO<sub>2</sub> nanocomposite hollow spheres.<sup>109</sup> This structure increased the specific area of the photocatalyst and made the Ag NP well dispersed. The plasmonic Ag-TiO<sub>2</sub> photocatalyst showed 2-fold higher photocatalysis efficiency than Degussa P-25 TiO<sub>2</sub> toward Rhodamine decomposition. Moreover, Su et al. synthesized R Ag@Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> core-triple shell nanoparticles for the photo-reduction of hexavalent chromium ions in waste water.<sup>110</sup> The Ag nanoparticles were employed for plasmonic enhancement of photocatalysis, and the magnetic Fe<sub>3</sub>O<sub>4</sub>containing photocatalyst can be collected and separated by applying an external magnetic field for recycling.

### 6. Remarks and perspectives

Plasmonic photocatalysts and photoelectrochemical cells emerged ten years ago and hold great promise in the future. Significant progress has been made in understanding the underlying mechanisms of plasmonic energy transfer from a metal to a semiconductor. More effort needs to be made to understand how the chemical composition, microstructure, and electronic structure of metals and semiconductors modulate the efficiency of plasmonic energy transfer, which is necessary for the rational design of high-performance plasmonic metal-semiconductor heterojunctions for solar energy conversion.

When Au nanoparticles are placed on the surface of a semiconductor, other enhancement mechanisms such as surface catalysis, surface passivation, and Fermi level equilibration effects, rather than plasmonic enhancement mechanisms will take part in the performance enhancement of photocatalysts. One cannot simply claim that the performance improvement is solely due to the plasmonic effect. Furthermore, one should also avoid the simple claim that the plasmonic enhancement of photoconversion is exclusively ascribed to the hot electron injection. Instead, careful studies should be conducted to separate all these possible mechanisms. Indeed these mechanisms that coexist with plasmonic enhancement can be separated by experiments.<sup>54</sup>

Most importantly, future studies should place emphasis on the development of plasmonic photocatalysts and photoelectrochemical cells that are able to achieve a high solar energy conversion efficiency to meet the practical need. Random mixing of metal nanoparticles with a semiconductor will, in most cases, lead to weak plasmonic interaction between the metal and the semiconductor, showing weak plasmonic enhancement of photoconversion. Instead, plasmonic metalsemiconductor heterojunctions should be constructed according to the "device-by-design" approach. That is, heterojunctions should be designed and optimized based on the plasmonic energy transfer mechanisms including light trapping, PIRET and hot electron injection. There is plenty of room to reach the theoretical maximum efficiency of plasmonic metalsemiconductor heterojunctions.

Many attempts have been made to design plasmonic metalsemiconductor heterojunctions by utilizing hot electron injection mechanisms. However, utilizing currently known hot electron injection mechanisms to enhance solar energy conversion will only result in very limited improvement in the efficiency unless a new, more efficient hot carrier transfer pathway is found. Instead, PIRET and light trapping can achieve much higher plasmonic energy transfer efficiency than the hot electron injection process. Hence more effort is needed to design heterojunctions based on PIRET and light trapping. In addition, metal nanostructures can play other roles alongside plasmonic enhancement. Plasmonic enhancement combined with other improvement effects of metal nanostructures can be considered to be an efficient way to maximize the solar energy conversion efficiency.

Many papers have reported plasmonic photocatalysts based on Au–TiO<sub>2</sub> composites over the last decade. The Au–TiO<sub>2</sub> composite serves as a model system from which we have learned a lot about the plasmonic enhancement of photoconversion. However, coupling Au with undoped TiO<sub>2</sub> can achieve very limited plasmonic enhancement due to the intrinsic shortcomings of this composite. In the future, more effort is needed to explore new material systems for heterojunctions. One of the promising systems is a visible-light or near-infrared plasmonic metal nanostructure coupled to a semiconductor with a band gap of around 2.0 eV because this heterojunction system provides great flexibility in enabling three major plasmonic energy transfer mechanisms (light trapping, PIRET and DET),<sup>36</sup> and maximizing the solar energy conversion efficiency.

Gold is a stable and strong plasmonic material. However, it is expensive to mass produce commercial plasmonic devices. Copper nanoparticles exhibit a LSPR band in the visible-light range (typically > 570 nm); the plasmon resonance peak of copper can be tuned to the near-infrared range by creating periodic nano-array patterns. Copper is inexpensive but unstable, and generally exhibits a relatively weak plasmon resonance band. It is significant to develop the stable copperbased plasmonic nanostructure with strong plasmon resonance bands of LSPR or SPP.

### Conflicts of interest

There are no conflicts to declare.

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