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Overall water splitting and hydrogen peroxide synthesis by gold nanoparticle-based plasmonic photocatalysts

Gold nanoparticle-based plasmonic photocatalysts can be driven by excitation of the localized surface plasmon resonance. Among them, hot-electron transfer-type photocatalysts have recently attracted interest as promising solar-to-chemical converters owing to the wide spectral response from visible-to-infrared light. This Minireview highlights recent studies on two kinds of artificial photosynthesis - water splitting and H2O2 synthesis from water and oxygen - using hot-electron transfer-type plasmonic photocatalysts with particular emphasis placed on the electrocatalysis of Au nanoparticles.

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Overall water splitting and hydrogen peroxide synthesis by gold nanoparticle-based plasmonic photocatalysts

Hiroaki Tada

Plasmonic photocatalysts driven by the localized surface plasmon resonance excitation of gold nanoparticles (Au NPs) can be efficient solar-to-chemical converters due to their wide spectral response. This review article highlights recent studies on plasmonic water splitting and \( \text{H}_2\text{O}_2 \) synthesis from water and oxygen (O\(_2\)) with a particular emphasis placed on the electrocatalysis of Au NPs. The Introduction (Section 1) points to the importance of the establishment of solar hydrogen and oxygen cycles involving hydrogen (H\(_2\)) and hydrogen peroxide (H\(_2\)O\(_2\)) as the key compound, respectively, for realizing a 'sustainable society'. Section 2 deals with the basic action mechanisms of Au NP-based plasmonic photocatalysts. Section 3 treats the electrocatalytic activity of Au NPs for the half-reactions involved in the reactions. Section 4 describes recent advances in the plasmonic overall water splitting (4.1) and H\(_2\)O\(_2\) synthesis (4.2). Finally, a summary is presented with the possible development direction in Section 5.

1. Introduction

Hydrogen (H\(_2\)) and hydrogen peroxide (H\(_2\)O\(_2\)) are basic feedstocks in chemical industries, and their use will expand more and more in future due to their environmental benignity. Presently, most H\(_2\) is produced by steam reforming of methane at 700–800 °C using a Ni-based catalyst, while H\(_2\)O\(_2\) is industrially produced by the anthraquinone auto-oxidation involving multiple steps.\(^1\) Both processes consume large amounts of energy and are undesirable from both environmental and economic aspects. Unambiguously, overall water splitting is the ideal process for H\(_2\) production (reaction (1)), while the synthesis of H\(_2\)O\(_2\) from water and oxygen (O\(_2\)) as well as the direct synthesis from H\(_2\) and O\(_2\) (ref. 2) is very beneficial (reaction (2)).

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2 \Delta G^0 = +237.13 \text{ kJ mol}^{-1} \quad (1)
\]

where \( \Delta G^0 \) is the standard Gibbs energy of reaction.

\[
\text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}_2 \Delta G^0 = +115.8 \text{ kJ mol}^{-1} \quad (2)
\]

External energy must be supplied to drive the energetically up-hill reactions. Utilization of thermal energy as the driving force is impossible for both the reactions because only 2% of water is decomposed even at 2000 °C, and H\(_2\)O\(_2\) is vulnerable to heat. In principle, reactions (1) and (2) can be driven by photons with energy larger than 1.23 eV and 0.54 eV, respectively, under mild conditions. These considerations motivate one to develop photocatalysts for reactions (1) and (2) by effectively utilizing the visible-to-near infrared light abundantly present in sunlight. If such production of H\(_2\) and H\(_2\)O\(_2\) is achieved, input of H\(_2\) into H\(_2\)-O\(_2\) fuel cells and input of H\(_2\)O\(_2\) into one-compartment fuel cells\(^a\)\(^b\) and photofuel cells\(^7\) would generate electric energy to complete the solar hydrogen cycle (Scheme 1a) and solar oxygen cycle (Scheme 1b), respectively. So far, many semiconductor

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\(^{a}\) Solar hydrogen cycle and (b) solar oxygen cycle.

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photocatalysts for water splitting have been intensively studied; however, a band gap larger than \( \sim 2.5 \) eV is usually necessary because of the large overpotentials for water splitting, particularly the water oxidation reaction (WOR).\(^9\) The same is true for the synthesis of \( \text{H}_2\text{O}_2 \) from water and \( \text{O}_2 \) by semiconductor photocatalysts including graphitic carbon nitride (g-C\(_2\)N\(_4\))\(^{10-13} \) and bismuth vanadate.\(^{14} \) On the other hand, the research on Au NP-based plasmonic photocatalysts with strong and broad absorption in the visible-to-near infrared region due to the localized surface plasmon resonance (LSPR) is rapidly progressing.\(^{15-22} \) The great advantage of plasmonic photocatalysts over semiconductor ones is the availability of “hot carriers” generated by the absorption of such low-energy-photons for chemical reactions,\(^{15,17,18,21} \) which is a prerequisite for achieving high solar-to-chemical conversion efficiency.

This article reviews recent advances in the plasmonic overall water splitting and \( \text{H}_2\text{O}_2 \) synthesis from water and \( \text{O}_2 \). This field is still in its infancy, but I believe that this article would contribute to the acceleration and future development in the very important and fascinating topics.

2. Action mechanisms of plasmonic photocatalysts

Plasmonic photocatalysts can be categorized into the hot-electron transfer (HET)-type\(^{23,24} \) and the local electric field-enhanced (LEFE)-type\(^{25-28} \) or the plasmon-resonant energy-transfer-type.\(^{29} \) Here the basic action mechanisms of the HET- and LEFE-type plasmonic photocatalysts are explained for the typical hetero-nanostructures of Au NP-loaded semiconductors (Au/semiconductor) and Au NP-incorporated semiconductors (Au@semiconductor) including Au NP (core)-semiconductor (shell) nanohybrids, respectively.

2.1 Hot-electron transfer mechanism

The excitation of the LSPR of Au NP generates excited carriers referred to as “hot carriers” having sufficient energy to drive chemical reactions through the non-radiative decay process or the Landau damping with an efficiency of \( \phi_{\text{HCG}} \).\(^{21} \) In the HET-type (Fig. 1), the hot electrons are transferred to the conduction band (CB) of a semiconductor.\(^{25,24} \) The CB-electrons cause a reduction reaction on the semiconductor surface, while an oxidation reaction is induced by the holes left in Au NPs. In this case, solar-to-chemical conversion efficiency \( \phi_{\text{STC}} \) can be provided by multiplication of the efficiencies of light harvesting by the plasmonic metal \( \phi_{\text{LHEPM}} \), \( \phi_{\text{HCG}} \), hot-electron injection from the plasmonic metal to semiconductor \( \phi_{\text{INJ(Au\rightarrow SEM)}} \), charge separation \( \phi_{\text{CS}} \), and redox reaction efficiency \( \phi_{\text{redox}} \) (eqn (3)).

\[
\phi_{\text{STC(LEFE)}} = \phi_{\text{LHEPM}} \times \phi_{\text{HCG}} \times \phi_{\text{INJ(Au\rightarrow SEM)}} \times \phi_{\text{CS}} \times \phi_{\text{redox}} \quad (4)
\]

Fig. 1 Hot electron transfer mechanism.

2.2 Local electromagnetic field-enhanced mechanism

On the other hand, in the LEFE-type (Fig. 2), redox reactions are caused by the band gap excitation of a semiconductor. In this case, the active optical antenna effect of Au NPs enhances the LHE of the semiconductor.\(^{20} \) The local electric field enhancement of Au NPs increases the rate of electron-hole generation in the semiconductor, further promoting the charge separation.\(^{26-31} \) Thus, the \( \phi_{\text{STC}} \) is expressed by multiplication of the efficiencies of light harvesting by Au@semiconductor \( \phi_{\text{LHEAu@SEM}} \), carrier generation \( \phi_{\text{CG}} \), \( \phi_{\text{CS}} \), and \( \phi_{\text{redox}} \) (eqn (4)).

Ag NPs possess a LEFE factor much greater than that of Au NPs, and for example, Ag NP-incorporated AgX \( (X = \text{Cl, Br, and I}) \) can be a promising plasmonic photocatalyst.\(^{32} \) Excellent review papers on Ag-based plasmonic photocatalysts have recently been published;\(^{13,14} \) however, the photocatalytic reaction is almost limited to the decomposition of organic dyes. It should also be stressed that most features of plasmonic photocatalysts or the wide spectral response can be obtained only for the HET-type. Also, in both types, the reduction in the overpotentials for the redox reactions is pivotal to enhance the photocatalytic activity.

2.3 Photothermal and light-scattering effects

As the secondary effects, photothermal conversion and light scattering can enhance the activity of plasmonic photocatalysts. Generally, radiative damping is the dominant decay mechanism for large Au NPs larger than 50 nm for dipolar plasmon resonances, while nonradiative damping is the dominant decay mechanism for small Au NPs.\(^{35} \)

Strong light absorption due to the LSPR of Au NPs followed by nonradiative energy dissipation causes a rise in temperature
of the surroundings. Particularly, under high-power irradiation, this photothermal effect may boost \( \Phi_{\text{STC}} \) for the HET-type and LEFE-type plasmonic photocatalysts through the increases in \( \Phi_{\text{redox}} \) shown in eqn (3) and (4). The LSPR extinction band for plasmonic metal NPs consists of the contributions from light absorption and scattering. When the size of Au particles exceeds 50 nm, light scattering becomes dominant. In the LEFE-type plasmonic photocatalysts, light scattering effectively increases to enhance the rate of photogenerated charge carriers in the semiconductor. Thus, the light-scattering effect can boost the \( \Phi_{\text{STC}} \) through the increase in LHE shown in eqn (4). However, the light scattering effect would be usually negligible because the particle size of Au NPs used in most studies on plasmonic photocatalysts is significantly smaller than 50 nm.

3. Electrocatalytic activity of gold nanoparticles

The oxidation half-reaction common in overall water splitting and \( \text{H}_2\text{O}_2 \) synthesis from water and \( \text{O}_2 \) is the WOR (reaction in the reverse direction of reaction (5)), where \( E^0 \) is the standard electrode potential with respect to the standard hydrogen electrode (SHE).

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^0 = +1.23 \text{ V} \tag{5}
\]

On the other hand, the reduction half-reactions in the former and latter are the hydrogen evolution reaction (HER, reaction (6)) and the two-electron oxygen reduction reaction (ORR) (reaction (7)), respectively. The key aspect in \( \text{H}_2\text{O}_2 \) synthesis is to restrict the four-electron ORR (reaction (5)), which is thermodynamically more favored than the two-electron ORR. The selectivity for electrochemical \( \text{H}_2\text{O}_2 \) formation can be quantitatively determined using the rotating ring disk technique.

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E^0 = 0 \text{ V} \tag{6}
\]

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad E^0 = +0.695 \text{ V} \tag{7}
\]

The electrocatalytic activities of Au NPs for these reactions are described below.

3.1 Electrocatalytic activity for the water oxidation reaction

Misawa and co-workers first showed that the WOR occurs on an Au nanorod-loaded \( \text{TiO}_2 \) electrode under illumination of visible and even near infrared light. We studied the electrocatalytic activity of Au/\( \text{TiO}_2 \) films coated on a fluorine-doped tin oxide photoanode (Au/\( \text{TiO}_2/\text{FTO} \)) for the WOR in a three-electrode photoelectrochemical (PEC) cell with the structure of photoanode|0.1 mol dm\(^{-3}\) \( \text{NaClO}_4 \) aqueous solution|Ag/AgCl (reference electrode)|glassy carbon (cathode) under illumination of simulated sunlight (AM 1.5 one sun, \( \lambda > 430 \text{ nm} \)). Fig. 3a shows the time courses for \( \text{O}_2 \) generation in aqueous solution. \( \text{TiO}_2/\text{FTO} \) is inactive for the WOR under these conditions. In the Au/\( \text{TiO}_2/\text{FTO} \) system, \( \text{O}_2 \) concentration increases in proportion to irradiation time. Also, the rate of \( \text{O}_2 \) generation increases with a decrease in Au particle size (\( d_{\text{Au}} \)). Garcia and co-workers also reported the same trend in an Au/\( \text{TiO}_2 \) particulate system. Fig. 3b shows the action spectrum of the incident photon-to-current efficiency (IPCE) for the Au/\( \text{TiO}_2/\text{FTO} \) photoanode cell. Surprisingly, the IPCE rises at excitation energy \( (h\nu) \approx 1.5 \text{ eV} \). As the wavelength of incident light shortens, the IPCE increases with a peak near the LSPR peak. A similar action spectrum was reported for the WOR in a PEC cell employing Au/\( \text{SrTiO}_3 \) as the photoanode. Also, the electrocatalytic activity of Au/\( \text{TiO}_2 \) for the WOR can be dramatically enhanced by the formation of a Pb shell on the Au NPs.

Scheme 2 shows the energy diagram of the Au/\( \text{TiO}_2 \) plasmonic anode with the intraband transition via the surface plasmon decay. The excitation by photons with \( h\nu = 1.5 \text{ eV} \) promotes the electrons with energy below the Fermi energy \( (E_F) \) to high energy levels within the 6sp-band. The hot electrons are injected into the CB of \( \text{TiO}_2 \), while the hot holes oxidize water. In this manner, the rise in the IPCE at \( h\nu \approx 1.5 \text{ eV} \) can be explained by the intraband-transition mechanism, and in this scheme, the WOR by the hot holes would determine the rate of the reaction.

3.2 Electrocatalytic activity for the hydrogen evolution reaction

The electrocatalytic activity of bulk-state metal electrodes for the HER can be correlated to the M–H bond energy. A clear
volcano-shaped curve in the plots of electrocatalytic activity for the HER vs. Gibbs energy of metal–H bond formation indicates that the group of metals with moderate M–H bond energy have high levels of activity for the HER. Among metal electrodes, Au possesses a high electrocatalytic activity for the HER following some rare metals (Pt, Re, Rh, and Ir). Then, to evaluate the electrocatalytic activity of Au NPs, the Au/TiO2-photocatalyzed H2 generation from ethanol aqueous solution was carried out under UV-light irradiation in the absence of O2. UV-light irradiation of Au/TiO2 excites the electrons in the valence band (VB) of TiO2 to the CB (eqn (8)). The CB-electrons in TiO2 are effectively transferred to Au NPs with a large work function to be accumulated in them (eqn (9)).47 The VB-holes in TiO2 easily oxidize ethanol to yield acetaldehyde and protons (eqn (10)). On the other hand, the electrons accumulated in Au NPs reduce water to H2 (eqn (11)). Accordingly, the photocatalytic activity can be a good indicator of the electrocatalytic activity of Au NPs for the HER.

\[
\text{Au/TiO}_2 + h\nu (\lambda_{\text{ex}} < 400 \text{ nm}) \rightarrow \text{Au/TiO}_2(e^- \cdots h^+) \quad (8)
\]

\[
\text{Au/TiO}_2(e^- \cdots h^+) \rightarrow \text{Au}(e^-)/\text{TiO}_2(h^+) \quad (9)
\]

\[
\begin{align*}
\text{Au}(2e^-)/\text{TiO}_2(2h^+) + \text{C}_2\text{H}_5\text{OH} & \rightarrow \\
& \text{Au}(2e^-)/\text{TiO}_2 + \text{CH}_3\text{CHO} + 2\text{H}^+ \quad (10)
\end{align*}
\]

\[
\text{Au}(2e^-)/\text{TiO}_2 + 2\text{H}^+ \rightarrow \text{Au/TiO}_2 + \text{H}_2 \quad (11)
\]

Idriss and co-workers reported Au/TiO2-photocatalyzed H2 generation from an aqueous solution of ethanol.48 The authors showed that UV-light irradiation of Au/anatase TiO2 and Au/rutile TiO2 yields H2, while each unmodified TiO2 is inactive. Interestingly, the activity of Au/anatase TiO2 is significantly higher than that of Au/rutile TiO2 at the same Au loading, further exceeding the activity of Pt/TiO2.

3.3 Electrocatalytic activity for the oxygen reduction reaction

In bulk-state electrodes, the two-electron ORR preferentially proceeds on Au, while the four-electron ORR occurs on Pt.49 The photocatalytic activity of metal NP-loaded TiO2 (M/TiO2, M = Au and Pt) for the ORR was carried out in aerated ethanol aqueous solution under UV-light irradiation (M/TiO2, M = Au and Pt).50 In this case, the electrons in metal NPs can be used for the two-electron and/or four-electron ORR (reactions (12) and (13)), and the photocatalytic activity can be a good indicator of the electrocatalytic activity of metal NPs for the ORR.

\[
\begin{align*}
\text{M}(2e^-)/\text{TiO}_2 + \text{O}_2 + 2\text{H}^+ & \rightarrow \text{M/TiO}_2 + \text{H}_2\text{O}_2 \quad (12) \\
\text{M}(4e^-)/\text{TiO}_2 + \text{O}_2 + 4\text{H}^+ & \rightarrow \text{M/TiO}_2 + 2\text{H}_2\text{O} \quad (13)
\end{align*}
\]

Fig. 4a shows the comparison of the photocatalytic activity of TiO2, Au/TiO2, and Pt/TiO2 for the two-electron ORR. In the TiO2 system, only micromolar H2O2 is generated as previously reported.51–53 Loading Pt NPs on TiO2 increases the saturated H2O2 concentration to ~1 mmol dm⁻³. Strikingly, Au/TiO2 exhibits much higher activity than Pt/TiO2, and the H2O2 concentration reaches ~6 mmol dm⁻³ at irradiation time = 24 h. To gain information about the origin of the great difference of the activity, density functional theory (DFT) simulations were performed for model systems (Au28/(TiO2)32 and Pt28/(TiO2)32).54 Fig. 4b shows the comparison of the adsorption energy of the sequentially reduced O2 species and the optimized structures. The one-electron ORR to OOHa(ad) is an energetically large downhill process, and the structure is the same in each system. In the two-electron ORR, the OOHa(ad) can be reduced to HOOH in the Au28/(TiO2)32 system, whereas H2OHa(ad) and OHa(ad) are produced with the O–O bond cleavage in the Pt28/(TiO2)32 system. In the electrode systems, the selectivity for electro-chemical H2O2 formation was reported to be 6.3% for Au/TiO2 and <0.1% for Pt/TiO2.55 These experimental and theoretical calculation results indicate that the Au NP catalyst is a good electrocatalyst for the two-electron ORR, while Pt NPs accelerate the four-electron ORR.

4. Photocatalytic reactions

Usually, the photocatalytic activity can be evaluated using the external quantum yield (φex) defined by eqn (1).

\[
\phi_{\text{ex}} = \frac{n \times \text{ (number of product molecules)}}{\text{number of incident photons}} \quad (14)
\]

where \( n = 2 \) for the HER (product = H2) and the 2-electron ORR (product = H2O2), and \( n = 4 \) for the WOR (O2).

4.1 Overall water splitting

Moskovits and co-workers were the first to show plasmonic overall water splitting using TiO2-capped Au nanorods with Pt as the hydrogen evolution catalyst on TiO2 and a Co-based oxygen evolution catalyst on Au (φex = ~0.1%).55 The Au/TiO2–NiOx plasmonic photocatalyst has also been reported to be capable of splitting water with φex = 0.013% at hν = 2.1 eV.56 As shown in Scheme 2, the low CB minimum of TiO2 (E_{CBM} = −4.1 eV for rutile TiO2 and −3.9 eV for anatase TiO2 at pH 7 vs. vacuum level) which is insufficient for the HER (E_{CBM} = −4.02 eV at pH 7) is mainly responsible for the limited efficiencies. On
the CB of CdS generated by the LSPR excitation can be efficiently injected into the CB of CdS through the large area and high-quality junction. The high-energy electrons in the CB of CdS enable a smooth HER, while the hot holes left in Au NPs oxidize water with the aid of the electrocatalytic activity for the WOR. Importantly, selective excitation of the Au NP-LSPR suppresses the photodissolution of CdS so far hampering its use as a water splitting photocatalyst.

Tan and co-workers have recently prepared a Pt NP-loaded TiO2 hierarchical nano-architecture (Pt/TiO2-HA), showing that it has a high level of visible-light activity for overall water splitting ($\phi_{ex} = 0.23\%$ at $h_\gamma = 2.25\text{ eV}$). The authors postulated the HET mechanism described in Section 2.1 for the Pt/TiO2-HA photocatalyst, where Au and TiO2 act as oxidation and reduction sites, respectively (Fig. 1). We have shown that visible-light irradiation of small- ($d_{Au} \approx 2\text{ nm}$) and large- ($d_{Au} \approx 10\text{ nm}$) Au NP-loaded TiO2 referred to as bimodal (BM)-Au/TiO2 induces the interfacial electron transfer from small Au NPs to large Au NPs through the CB of TiO2. This phenomenon was rationalized in terms of the entropic driving force for the interfacial electron transfer.

Scheme 3 illustrates the basic reaction scheme of water splitting by the HC-Au@CdS plasmonic photocatalyst. HC-Au@CdS efficiently absorbs sunlight. The hot-electrons generated by the LSPR excitation can be effectively injected into the CB of CdS through the large area and high-quality junction. The high-energy electrons in the CB of CdS enable a smooth HER, while the hot holes left in Au NPs oxidize water with the aid of the electrocatalytic activity for the WOR. Importantly, selective excitation of the Au NP-LSPR suppresses the photodissolution of CdS so far hampering its use as a water splitting photocatalyst.

4.2 Hydrogen peroxide synthesis

Au/TiO2 plasmonic photocatalysts have been applied to various important oxidations. This is probably because the electrocatalytic activity of Au NPs for the reduction reaction cannot be utilized in the usual HET-type Au/TiO2 plasmonic photocatalyst, where Au and TiO2 act as oxidation and reduction sites, respectively (Fig. 1). We have shown that visible-light irradiation of small- ($d_{Au} \approx 2\text{ nm}$) and large- ($d_{Au} \approx 10\text{ nm}$) Au NP-loaded TiO2 referred to as bimodal (BM)-Au/TiO2 induces the interfacial electron transfer from small Au NPs to large Au NPs through the CB of TiO2. This phenomenon was rationalized in terms of the entropic driving force for the interfacial electron transfer.

Scheme 3 Schematic representation of water splitting by the HC-Au@CdS/TiO2 plasmonic photocatalyst.

Fig. 5 (a) The comparison of the H2 evolution rate for HC-Au/TiO2 generation in the absence (red) and presence of 4% C2H5OH (green) under irradiation of visible-light ($\lambda_{ex} > 430\text{ nm}$, light intensity integrated from 420 to 485 nm = 4.0 mW cm$^{-2}$) at 298 K. (b) Photocatalytic activity of S-Au/TiO2, L-Au/TiO2, BM-Au/TiO2, and BM-Au/TiO2-CO2$^2$ for the reduction of O2 to H2O2 in an aqueous solution containing 4% HCOOH (pH 1.7) in the dark and under irradiation of visible-light ($\lambda_{ex} > 430\text{ nm}$, light intensity integrated from 420 to 485 nm = 4.0 mW cm$^{-2}$) at 298 K. Figures are taken from ref. 68.
pathway to increase the yield of H₂O₂. An effective way is the surface-fluorination of TiO₂ (ref. 70 and 71) enabling the production of H₂O₂ at a millimolar level under UV-light irradiation.²⁴

\[ \text{Ti}_x\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{Ti}_x\text{OOH} + \text{H}_2\text{O} \]  
(15)

where the subscript s denotes the surface atom.

\[ \text{Ti}_x\text{OOH} + 2\text{H}^+ + 2e^-_{\text{CB}} \rightarrow \text{Ti}_x\text{OH} + \text{H}_2\text{O} \]  
(16)

Then, the effect of the surface modification of BM-Au/TiO₂ with carbonate ions (BM-Au/TiO₂–CO₃²⁻) on the photocatalytic activity was examined. As shown in Fig. 6b, the surface modification drastically increases the photocatalytic activity, and the \( \phi_{\text{ex}} \) reached 5.4% at \( \hbar\omega = 2.3 \text{ eV} \). In the H₂O₂ synthesis from water and O₂ using semiconductor photocatalysts, a \( \phi_{\text{ex}} \) value of 0.24% at \( \hbar\omega = 2.95 \text{ eV} \) was reported for Au/BiVO₄.¹⁴ Importantly, Shiraishi and co-workers have found that g-C₃N₄ possesses an extremely high selectivity of ~90% for electrochemical H₂O₂ formation,¹⁰ and the efficiency of photocatalytic H₂O₂ synthesis was greatly improved by using it as the photocatalyst \( (\phi_{\text{ex}} = 2.6\% \text{ at } \hbar\omega = 2.95 \text{ eV}) \). In a holey defective g-C₃N₄ photocatalytic system, an extremely high \( \phi_{\text{ex}} \) value of ~16% was achieved in the presence of 2-propanol as an electron donor at \( \hbar\omega = 3.26 \text{ eV} \).¹³

The high photocatalytic activity of BM-Au/TiO₂ for H₂O₂ synthesis from water and O₂ can be rationalized as follows (Scheme 4). Visible-light irradiation of BM-Au/TiO₂ gives rise to the net electron transport from small Au NPs to large Au NPs, accumulating electrons and holes in large and small Au NPs, respectively. As a result, water is oxidized on small Au NPs (Fig. 3a), while the two-electron ORR occurs on large Au NPs. Eventually, the high photocatalytic activity of BM-Au/TiO₂ for H₂O₂ synthesis can stem from the effective charge separation through the interfacial electron transfer from small Au NPs to large Au NPs, the former’s excellent electrocatalytic activity for the WOR, and the low catalytic activity of the small and large Au NPs for H₂O₂ decomposition.²⁸ Further, the surface modification with CO₃²⁻ ions of BM-Au/TiO₂ is effective in suppressing the reductive decomposition of H₂O₂ to increase its yield.

From a viewpoint of organic synthesis, BM-Au/TiO₂ has also paved a way for the application of plasmonic photocatalysts in reductive chemical transformations. As an example, Table 1 summarizes the BM-Au/TiO₂ photoreduction of nitrobenzene and its derivatives.⁶⁷ BM-Au/TiO₂ exhibits a high level of visible-light activity for the one-step synthesis of azobenzenes from nitrobenzenes at 25 °C with a high yield of >95% and selectivity >99%, whereas unimodal Au/TiO₂ is photocatalytically inactive.

5. Summary and perspectives

H₂ and H₂O₂ are not only basic chemical feedstocks but also the key compounds for the energy cycles. A big challenge in chemistry is the development of highly active photocatalysts for the overall water splitting and H₂O₂ synthesis from water and O₂. The HET-type Au NP-based plasmonic photocatalysts can generate “hot carriers” with potential to drive the energetically uphill reactions through the excitation by low-energy photons which the usual semiconductor photocatalysts cannot utilize. The overall water splitting and H₂O₂ synthesis comprise the half-reactions of the WOR, HER, and two-electron ORR. Au NPs possess high levels of electrocatalytic activities for these reactions strongly depending on the size, shape, and composition.⁷⁴ Consequently, the Au NP-based HET-type plasmonic photocatalyst can be a very promising solar-to-chemical converter.

However, there is plenty of room for the enhancement of the photocatalytic activity by the judicious selection of semiconductors and the optimization of Au NPs corresponding to the targeted reaction. First, the information about the influence of the band structure of semiconductors on the activity is a prerequisite for the rational design of plasmonic photocatalysts. Second, the bimetallization of Au NPs has great potential for improving the photocatalytic activity, while the effects of Au NP-size and shape on the activity have been reviewed.²³ Alloying of Au NPs with Pd⁷³ and Pt,⁷⁶ and Pd/Pt-shell formation on the surface of Au NPs⁷⁷ have been reported to boost the activity of the Au/TiO₂ plasmonic photocatalyst for the HER from water containing methanol as a sacrificial electron.

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Table 1  BM-Au/TiO₂ photocatalyzed reduction of nitrobenzenes<sup>a</sup>

| Substrate Product | Time | Conversion | Selectivity |
|------------------|------|------------|-------------|
| C₆H₅NO₂         | 12 h | 95%        | >99%        |
| C₆H₅(NO₂)₂      | 24 h | >99%       | >99%        |
| C₆H₅NO₂         | 20 h | 98%        | >99%        |
| C₆H₅(NO₂)₂      | 24 h | >99%       | >99%        |
| C₆H₅(NO₂)₂      | 12 h | >99%       | >99%        |

*Reaction conditions: BM-Au/TiO₂ 10 mg, nitrobenzene (10 mM) solution (10 mL, 2-propanol) with KOH (10 mM), visible-light (\( \lambda_{\text{ex}} > 430 \text{ nm}, 10 \text{ mW cm}^{-2} \)) irradiation at 25 °C under anaerobic conditions. The table is taken from ref. 67.*

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Scheme 4  Schematic representation of H₂O₂ synthesis from water and O₂ by the BM-Au/TiO₂ plasmonic photocatalyst.
donor. These effects would partly result from the excellent electrocatalytic activity of Pt and Pd for the HER. Third, as a common subject in heteronanostructured photocatalysts, the importance of devising a general mechanism for enhancing the charge separation between the components should also be stressed. An effective approach to achieve this is the formation of an atomically commensurate heteroepitaxial junction. In addition, the construction of multi-component plasmonic photocatalysts is also very promising. Recently, three-component plasmonic photocatalysts such as Au and Pt NP-codeposited TiO₂ (ref. 80) and Au/TiO₂-graphitic carbon nitride [g-C₃N₄]²⁺ have been reported to show much higher photocatalytic activity than Au/TiO₂ for the HER from methanol aqueous solution. The effective charge separation through the interfacial electron transfer from Au NPs to Pt NPs in the former system, and from g-C₃N₄ to TiO₂ in the latter system would be responsible for the high photocatalytic activities. Meanwhile, the research on the catalysis of supported Au NPs for various reactions is intensively and constantly continued.²¹ I anticipate that the combination of the research on the catalysis of Au NPs and Au NP-based plasmonic photocatalysts can effect further development of various “green” processes for solar-to-chemical transformations.

Conflicts of interest
There are no conflicts to declare.

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