

Role of Metal Cocatalysts in the Photocatalytic Production of Hydrogen from Water Revisited

Published as part of *Energy & Fuels special issue* “2025 Pioneers in Energy Research: Prashant Kamat”.

Francisco Zaera*



Cite This: *Energy Fuels* 2025, 39, 2422–2434



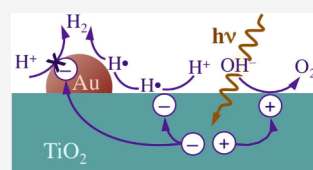
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The use of photocatalysts to promote the production of molecular hydrogen from water, following the so-called water splitting reaction, continues to be a promising route for the green production of fuels. The molecular basis of this photocatalysis is the photoexcitation of electrons from the valence band of semiconductors to their conduction band, from which they can be transferred to chemical reactants, protons in the case of water, to promote a reduction reaction. The mechanism by which such a process takes place has been studied extensively using titanium oxide, a simple material that fulfills most requirements for water splitting. However, photocatalysis with TiO_2 tends to be highly inefficient; a cocatalyst, commonly a late transition metal (Au, Pt) in nanoparticle form, needs to be added to facilitate the production of H_2 . The metal is widely believed to help with the scavenging of the excited electrons from the conduction band of the semiconductor in order to prevent their recombination with the accompanying hole formed in the valence band, a step that cancels the initial photon absorption and competes with the photolytic chemical reduction. Here we review and analyze the molecular basis for that mechanism and argue for an alternative explanation, that the role of the metal is to help with the recombination of the atomic hydrogen atoms produced by proton reduction on the semiconductor surface instead. First, we summarize what is known about the electronic structure of these photocatalysts and how the electronic levels need to line up for the reduction of protons in water to be feasible. Next, we review the current understanding of the dynamics of the steps associated with the absorption of photons, the de-excitation via electron–hole pair recombination and fluorescence decay, and the electronic transitions that lead to proton reduction, and contrast those with the rates of the chemical steps required to produce molecular hydrogen. The following section addresses the changes introduced by the addition of the metal cocatalyst, comparatively evaluating its role as either an electron scavenger or a promoter of the recombination of hydrogen atoms. A discussion of the viable chemical mechanisms for the latter pathway is included. Finally, we briefly mention other associated aspects of this photocatalysis, including the possible promotion of H_2 production with visible light via resonant excitation of the surface plasmon of Au nanoparticles, the use of single-metal (Au, Pt) atom catalysts and of yolk–shell nanostructures, and the reduction of organic molecules. We end with a brief personal perspective on the possible generality of the concepts introduced in this Critical Review.



INTRODUCTION

Heterogeneous catalysis is central to most chemical industries and also contributes to the production and processing of fuels and to environmental remediation. The essence of catalysis is that it opens an alternative pathway for the reaction at hand with an overall lower activation barrier to help increase the conversion rate. Nevertheless, many catalyzed chemical reactions are endothermic and therefore still require considerable amounts of energy. In most processes, this energy is provided thermally, via heating of the reaction mixture, but it would be highly desirable to be able to use greener and more efficient energy sources. In some cases electrocatalysts may be implemented for this purpose, but, ideally, the required energy could be harvested directly from the sun.

To that end, there has been an increased interest in the design of appropriate photocatalysts. For instance, much work has been directed recently to the development of photocatalysts to convert carbon dioxide to carbon monoxide and/or a mixture of

organic feedstocks.^{1,2} Another photocatalytic process that has generated great interest is the production of molecular hydrogen (and molecular oxygen) from water, a reaction often referred to as water splitting, because H_2 is a feedstock for other industrial conversions and can also be used as a clean fuel.^{3–7} The implementation of these ideas is still a work in progress, and further advances could benefit from a better understanding of the chemistry involved at the molecular level. In this Critical Review we address a specific aspect of such photocatalysis,

Received: December 13, 2024

Revised: January 21, 2025

Accepted: January 21, 2025

Published: January 29, 2025



namely, the role of metals, which are added as cocatalysts, in the photocatalysis of water splitting.

■ ELECTRONIC STRUCTURE OF PHOTOCATALYSTS

The main element in most photocatalysts is a semiconductor material, to which additional cocatalysts are added as needed (Figure 1a). Semiconductors are capable of absorbing photons

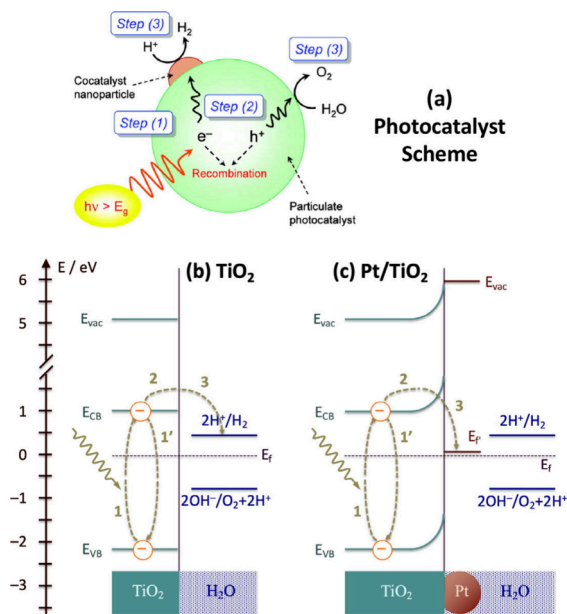


Figure 1. Basics of photocatalysis. (a) Schematic representation of the major components and processes associated with semiconductor photocatalysts. Reproduced from ref 26 with permission. Copyright 2007 American Chemical Society. (b) Electronic band structure and transitions associated with the photoreduction of water to H_2 using pure titanium oxide. (c) Equivalent electronic information for a titanium oxide photocatalyst modified with a metal (Pt) cocatalyst.

with higher energy than their bandgap, that is, the energy difference between the edges of their valence and conduction bands ($E_{\text{bg}} = E_{\text{CB}} - E_{\text{VB}}$), and potentially convert them into either electrical or chemical energy.^{6,8,9} A prototypical photocatalyst for basic studies is titanium oxide: although that oxide has a wide bandgap and cannot absorb any of the visible radiation coming from the sun, making it less than ideal for most practical applications,¹⁰ it has been characterized more extensively than other materials.^{1,11–17} As such, this Critical Review will focus on TiO_2 as the main component of photocatalysts for the production of hydrogen from water, to derive basic concepts applicable to other materials.

The electronic structure of titanium oxide and the electronic transitions associated with water-splitting photocatalysis are summarized in Figure 1b. Versions of this diagram can be found in multiple publications, but a detailed quantitative placing of the individual energy levels is usually given in approximate form because those are quite sensitive to the exact structure of the material and to the surrounding environment.^{18,19} In Figure 1b we attempted to provide numbers for the case of anatase, the most common form of crystalline titanium oxide. The position of the top of the valence band, E_{VB} , was taken from photoelectron yield measurements²⁰ and optical absorption, fluorescence, and valence band studies²¹ to be -7.25 eV below the vacuum level (E_{vac}). Given that the bandgap of anatase has been reported to be $E_{\text{bg}} = 3.13$ eV (based on ultraviolet

photoelectron spectroscopy—UPS—measurements),²² the bottom of the conduction band is then estimated at $E_{\text{CB}} = 4.12$ eV below the vacuum level; this is the electron affinity of TiO_2 . The same UPS data were used to determine the work function of anatase to be $\phi = 5.1$ eV, placing the conduction band about 1 eV above the Fermi level (E_{f}). The E_{CB} and ϕ values have been confirmed by quantum mechanics calculations,^{23,24} and the placement of the conduction band above the Fermi level is also consistent with theoretical estimates.²⁵

With respect to the splitting of water, electrochemical measurements provide the value for the potential needed to convert H_2O to H_2 and O_2 at 1.23 eV. The placement of the energy levels of the proton reduction and hydroxide oxidation half-reactions depends on the pH of the solution (it increases by 59 meV per unit of pH), but the former has been estimated to align somewhere between 0.4 and 0.6 above the Fermi level of TiO_2 at pH = 0 (under the standard hydrogen electrode, SHE, conditions).^{27–29} The key conclusion from an analysis of these energy levels is that the conduction band of titanium oxide lies above the hydrogen reduction potential, which means that the excited electrons from photon absorption by the semiconductor can be transferred to protons within the water phase to produce H_2 . Similarly, the energy of the valence band of titanium oxide is much lower than the energy of oxidation of water, so electrons can flow freely from water to the solid as O_2 is produced once photoexcitation has taken place.

The excited state of semiconductors upon absorbing photons of higher energy than their bandgap leads to the creation of excited electron–hole (e^-h^+) pairs (Step 1 in Figure 1). The electrons then diffuse toward the surface (Step 2) and are used to reduce the reactant, converting H^+ into H^\bullet in the case of water splitting, for instance (Step 3), while the holes can accept electrons from the chemical being oxidized, H_2O in water splitting, to facilitate its conversion to O_2 (also Step 3).^{9,26} Semiconductors with bandgaps smaller than that of titanium oxide are desirable in order to be able to use a wider range of the solar spectrum for H_2 production, but the position of the bandgap of any alternative material still needs to be optimized so that the E_{CB} and E_{VB} levels straddle the H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox potentials. Other criteria for the selection of photocatalysts include a high light-absorption coefficient and good structural and chemical stability; many promising light-harvesting semiconductors such as Si, GaAs, InP, and metal chalcogenides, for instance, have small bandgaps but are prone to self-oxidation by photogenerated holes and corrosion by water and are therefore not good choices.³⁰ Finally, it is desirable for the photocatalytic material to display small overpotentials for the promotion of the two water splitting half-reactions, because those need to be added to the redox potential of the reaction, hence increasing the minimum viable bandgap energy and diminishing the fraction of the solar spectrum that can be absorbed and used to promote a chemical reaction. The search for semiconductors that fulfill all these conditions is one of the most active areas of photocatalysis,^{7,26,29,31–33} but will not be discussed further in this Critical Review.

■ DYNAMICS OF LIGHT ABSORPTION, FLUORESCENCE DECAY, AND ELECTRONIC TRANSITIONS. METAL COCATALYST

Semiconductors that fulfill all of the characteristics listed above can still display poor photocatalytic activity because the excited e^-h^+ pairs resulting from photon absorption may prefer to recombine, via nonradiative or, more commonly, radiative

(fluorescence) steps before they can be harvested for chemical conversions. The dynamics of the different processes involved in the photocatalytic promotion of reduction reactions such as the conversion of protons to hydrogen gas have been studied extensively with a variety of techniques, primarily time-resolved optical spectroscopies. The main challenge here is that there is a gross mismatch in time scales between the electronic transitions within the solid, which occurs in the picosecond to nanosecond range, and those associated with the interfacial charge transfer and subsequent chemical processes, which can take from milliseconds to seconds (Figure 2).^{13,14,34–38} Photocatalytic

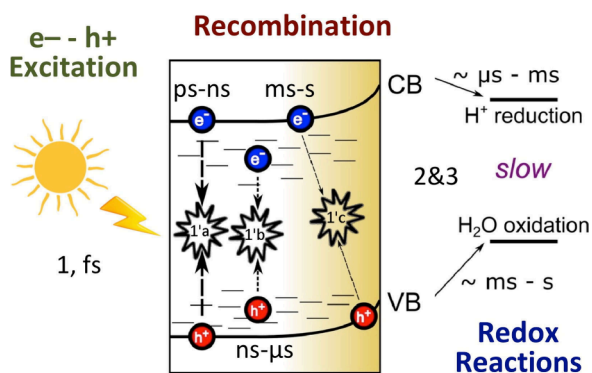


Figure 2. Time scales of the electronic steps relevant to photocatalytic processes and to water splitting in particular. Adapted from ref 37 with permission. Copyright 2017 Elsevier Ltd.

reactions have in general low quantum efficiencies, but not low enough to explain such large differences in time scales. It has been argued that the lifetime of the excited $e^- - h^+$ pairs may be increased by augmenting the charge separation processes, relying, for instance, on the creation of new heterojunctions or surface defects.^{15,39–42} However, the trapping of charges also reduces their mobility, possibly preventing them from reaching the surface and becoming available for the promotion of redox chemistry. What has become apparent is that the kinetic competition between charge separation and bulk recombination can determine the efficiency of the photocatalytic process.¹⁵

Fortunately, the $e^- - h^+$ recombination in titania is relatively slow to begin with, occurring in approximately 6 ns, because the valence and conduction bands are mainly composed of O 2p and Ti 3d orbitals, respectively, and therefore are already spatially separated.¹⁵ Furthermore, the lifetime of the trapped holes can be extended even more, to the millisecond time scale, in the presence of electron acceptors such as late transition metals, typically Pt or Au nanoparticles (NPs).^{13–15,37,43,44} Several explanations have been advanced for the changes in electronic dynamics induced by the addition of these metal cocatalysts, but the most accepted model by far is based on an electron transfer from the semiconductor to the metal upon the two phases coming in contact with each other and the accompanying generation of a Schottky barrier at the semiconductor/metal interface.^{14,45,46} As an example, the electronic structure of a Pt/TiO₂ interface is schematically shown in Figure 1c. All vacuum, conduction, and valence bands of the semiconductor bend upward to match the vacuum level of the metal, which has a higher work function than titanium oxide, approximately 5.65 eV in the case of Pt^{47,48} (versus 5.1 eV for TiO₂).²⁰ The ensuing Schottky barrier was reported in one case to be somewhere between 0.3 and 0.4 eV in height on the basis of Kelvin-probe force microscopy (KPFM) measurements, but more realistic

numbers range from 0.6 to 1.6 eV depending on the nature of the interface.^{46–49} Regardless of the exact value of that barrier, though, what is clear is that the Fermi level of the metal lies approximately 1 eV below the conduction band of the semiconductor, making the transfer of the excited photoelectrons from TiO₂ to Pt (or another metal) energetically favorable. It has been argued that this process aids a further charge separation upon illumination and therefore increases the lifetime of the photon absorption excitation.

The fact that the photoillumination of semiconductor/metal interfaces leads to significant charge transfer from the former phase to the latter has been corroborated experimentally. In one case, the photoluminescence signal of the titanium oxide was reported to be attenuated by the addition of Au or Ag NPs,^{50,51} and a blue shift in the absorption spectrum upon illumination was seen as well due to an increase in the surface plasmon frequency of the electron gas in the metal NPs.^{44,52,53} In fact, continuous illumination leads to a new steady-state with a net accumulation of extra charge in the metal NPs, of up to 66 electrons per NP for Ag@TiO₂ core-shell photocatalysts with Ag cores 3–4 nm in diameter,⁵² and to an accompanying shift upward in the energy of the Fermi level of the system, by a few tens of meV depending on the size of the NPs.^{46,54–56} However, although this electron migration from the semiconductor to the metal NPs consumes the reduced centers that initially form on the surface of the former after photon absorption (Ti³⁺ in titanium oxide), the process is not complete (according to results from EPR and XPS measurements),^{15,57,58} and some Ti³⁺ sites are still available on the surface of the TiO₂, potentially active for the reduction of protons. In addition, the time mismatch mentioned above between electronic transitions and chemical conversions applies here as well: transient bleaching of the surface plasmon of the metal NPs occurs in time scales on the order of picoseconds, whereas other steps in the water-splitting process, including hole oxidation, take hundreds of microseconds.^{44,59}

Several attempts have been reported to directly identify differences in the dynamics of the electronic transitions relevant to photocatalysis between pure and metal-modified titanium oxide samples using time-resolved spectroscopies, but the results have been, in our opinion, inconclusive. Some early reports with Pt claimed that the picosecond decay of the $e^- - h^+$ excitation measured in transient absorption, transient photoluminescence, or time-resolved microwave conductivity experiments is faster when a metal is added to the semiconductor.^{43,60–62} However, the reported differences have often been small, and some of those experiments were carried out using high laser intensities, where carrier annihilation effects become important. Also, the early studies have not always used directly comparable samples with versus without metal to eliminate the effect of other contributing factors. In contrast, studies from our laboratory directly contrasting the fluorescence dynamics of TiO₂, Au/TiO₂, and Pt/TiO₂ photocatalysts could not detect measurable differences at any of the time scales probed, from subnanoseconds to microseconds.^{63,64} This was in fact the case when using either commercial P25 titanium oxide (a mixture of anatase and rutile phases) or homemade Au@Void@TiO₂ yolk-shell catalysts (the catalysts reported in Figure 3), and also for catalysts with various metal loadings. A previous study had shown that the measured fluorescence lifetimes are sensitive to the crystallinity of the titanium oxide phase,⁶⁵ but the same values were obtained (for the same TiO₂ crystallinity) with pure versus Au-modified catalysts; Au does not appear to appreciably

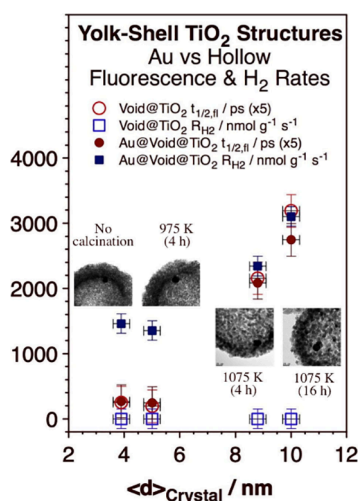


Figure 3. Average fluorescence lifetimes ($t_{1/2,n}$, red circles) and rates of H₂ photoproduction (R_{H_2} , blue squares) versus titanium oxide grain average size ($\langle d \rangle_{Crystal}$) for hollow (Void@TiO₂, open symbols) and Au-containing (Au@Void@TiO₂, filled symbols) yolk-shell nanostructures.⁶⁴ Increased crystallinity was achieved by increasing the severity of the final calcination step during the synthesis of these materials, as indicated in the figure. TEM close-up images of the titanium oxide shells are also included to better visualize the crystallite sizes of the different catalysts. The fluorescence lifetimes clearly increase with increasing TiO₂ crystallite size but are similar for the hollow versus Au-containing catalysts. On the other hand, H₂ can be produced from the photocatalytic reduction of water only if Au NPs are added to these nanostructures.

vary the e^-h^+ recombination dynamics (Figure 3). On the other hand, although a good correlation was established between the fluorescence lifetime of the Au/TiO₂ photocatalysts (which in our yolk-shell catalysts could be tuned by controlling the calcination temperature during their synthesis) and the efficiency of the hydrogen production rate, the latter was only detected if Au NPs were added (Figure 3); the metal is needed for the H₂ photogeneration.⁶³

In addition to the role of noble-metal cocatalysts as agents to improve charge separation within the semiconductor particle and discharge photogenerated electrons across the interface, it has been suggested that they may also provide a pathway for the reduction of protons to hydrogen with low overpotential during water-splitting processes.^{44,66,67} There is no doubt that, from an empirical point of view, the addition of noble-metal NP cocatalysts enhances the production of water in these water-splitting processes.^{57,59,64,68–70} Moreover, previous studies have suggested that colloidal NPs of metals such as Pt may promote hydrogen generation by intercepting a photochemically reduced methyl viologen cation radical (MV^{+•}).^{71,72} Transient photon absorption experiments using semiconductor photocatalysts (CdSe in this case) with versus without Pt NPs, where the evolution of the semiconductor excitation and the concentration of the MV^{+•} species were followed independently, highlighted a fast oxidation pathway that opens up for MV^{+•} via electron transfer to the metal.⁴⁴ However, that work did not explore the effect of such parallel electron transfer pathway on hydrogen production. Regardless of how the excited electrons arrive to the Pt NPs from the semiconductor, a further electron transfer from the metal to the chemical reactants (protons) in the liquid phase may be energetically uphill (Figure 1c) and therefore not spontaneous, even if the Fermi level of the metal is (marginally,

by 20–60 meV)^{54,55} raised by the semiconductor-to-metal charge transfer induced by illumination. This is an aspect of the metal promotion of water splitting with photocatalysts that has not been properly discussed in the literature. We argue that electron transfer from the semiconductor to the metal upon photoactivation may be facile but also possibly a dead end that does not aid in the reduction of protons to molecular hydrogen.

A recent study provides direct evidence that the electrons trapped on the metal NPs may not be the ones that contribute to the production of H₂.⁷³ In a unique setup, the authors of that work synchronized the periodicity of their photocatalyst excitation, which was modulated at frequencies in the kHz range using a chopper, with the Michelson interferometer used for FTIR spectroscopy probing of the surface under reaction conditions (Figure 4). This way, they were able to suppress the

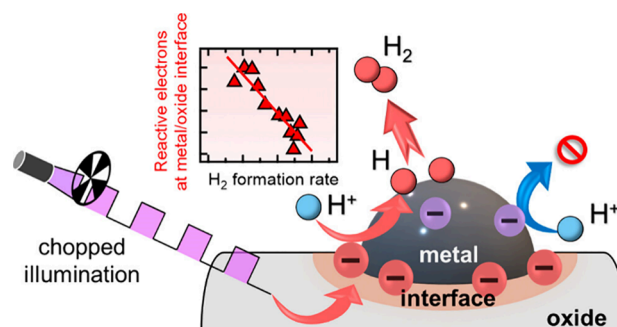


Figure 4. Schematic illustration of the experimental setup used to study the correlation between the photoexcitation of electrons in metal-NP-modified semiconductor oxide photocatalysts and the generation of H₂. Also shown is the mechanism suggested for that reaction. It is proposed that photogenerated excited electrons migrate to the oxide sites adjacent to the metal NP and are transferred to protons from the water above to produce H[•] atoms; those atoms then recombine on the metal surface to produce H₂. The diagram also explicitly indicates that the direct participation of excited electrons transferred from the semiconductor to the metal do not participate in this chemistry. The inset provides results indicating a direct correlation between the amount of reactive electrons accumulated at the metal-oxide interface and the rate of H₂ production. Reproduced with permission from ref 73. Copyright 2024 American Chemical Society.

contribution from thermally excited electrons and correlate the number of reactive photogenerated electrons with the photocatalytic evolution of hydrogen (Figure 4, inset). The authors concluded that the free electrons in the metal cocatalysts are not directly involved in the reduction reaction. Instead, a correlation was identified between the H₂ production rate and the number of electrons shallowly trapped in the in-gap states of the oxide, which is enhanced upon the loading of the metal cocatalysts. The main conclusion of this work was that the metal-induced semiconductor surface states formed at the periphery of the metal cocatalyst play a key role in the photocatalytic hydrogen evolution reaction (Figure 4).

■ ROLE OF METAL AS PROMOTER OF HYDROGEN ATOM RECOMBINATION

The fact that the time-resolved spectroscopic evidence for the metal acting as a quencher of the e^-h^+ recombination pathway is not conclusive, together with the unfavorable alignment of the Fermi level of the titanium oxide/metal photocatalysts below the hydrogen reduction potential, brings into question the generally accepted model of the role of the metal as providing the sites for

the reduction of H^+ to H_2 . In fact, it is important to realize that this reaction actually consists of at least two distinct steps: the reduction of protons to neutral atomic hydrogen (hydrogen radicals or related species) and the subsequent recombination of two hydrogen radicals to make molecular hydrogen. This subtlety is important, because late transition metals are certainly very effective at promoting the second of those steps, the coupling of hydrogen atoms to yield H_2 .⁷⁴ We argue that, in fact, this may be the main contribution of the metal NP cocatalysts to the water-splitting process. What may be in question is whether the reduction of protons takes place at titanium oxide or metal sites; we have advanced the idea that it may happen on the TiO_2 surface.^{63,75–79}

Titanium oxide can certainly reduce other ions: examples include Co^{3+} (Co^{3+}/Co^{2+} reduction potential = +1.82 V versus NHE), Ce^{4+} (Ce^{4+}/Ce^{3+} reduction potential = +1.44 V versus NHE), $Cr_2O_7^{2-}$ (Cr^{6+}/Cr^{3+} reduction potential = +1.33 V versus NHE), IO_3^- (I^{7-}/I_2 reduction potential = +1.08 V versus NHE), Hg^{2+} (Hg^{2+}/Hg^0 reduction potential = +0.854 V versus NHE), Ag^+ (Ag^+/Ag^0 reduction potential = +0.799 V versus NHE), Fe^{3+} (Fe^{3+}/Fe^{2+} reduction potential = +0.771 V versus NHE), and UO_2^{2+} (U^{6+}/U^{4+} reduction potential = +0.27 V versus NHE).^{63,80–84} This type of photoactivity from titanium oxide is well-known, as it is in some instances exploited to remove contaminants from water.^{85,86} In all of the cases cited above the reduction is easier to induce than with H^+ (the reduction potentials are positive with respect to NHE), but they still illustrate the fact that titanium oxide is capable of promoting reduction reactions by itself upon illumination, without the addition of metal cocatalysts. It should also be mentioned that, in the case of IO_3^- at least, the rate of H_2 photoproduction was measured to be the same, within experimental error, with pure versus Pt-modified titanium oxide; the Pt cocatalyst does not seem to help that reaction.⁶³ It may very well be that TiO_2 can photocatalytically produce H^\bullet radicals (or a related intermediate) from water but not be capable of promoting the recombination of those atoms into molecular hydrogen.⁶²

In order to separate the possible photoreducing and thermal catalysis contributions of the metal to the enhancement of the conversion of protons to H_2 in water, we have carried out experiments with other materials as cocatalysts capable of providing one of those functionalities but not the other.⁶³ The data are summarized in Figure 5. All catalysts were tested for both hydrogen photoproduction (using methanol as a sacrificial agent for the oxidation half-reaction) and hydrogen recombination activity, following the isotopic scrambling of $H_2 + D_2$ gas mixtures. In terms of the cocatalyst used, these were graphitic carbon, which can easily accept electrons from the conduction band of titanium oxide but is not good at promoting the hydrogen recombination reaction, nickel oxide, with which the opposite is true, and gold and platinum, both noble metals good at both functions. It was found that the rates of H_2 photoproduction and H-D isotope scrambling (our proxy for the atomic hydrogen recombination step) correlate well with each other across this series of catalysts. Moreover, it should be noted that if the role of the cocatalyst were to trap the photoexcited electrons and reduce protons, high H_2 photoproduction would have been expected with the C/TiO_2 catalyst but not with the NiO/TiO_2 counterpart (the NiO cocatalyst case has also been reported by others),⁸⁷ yet the opposite was seen in these experiments. These data are consistent with the metal producing H_2 from H^\bullet intermediates formed at the titanium oxide surface.

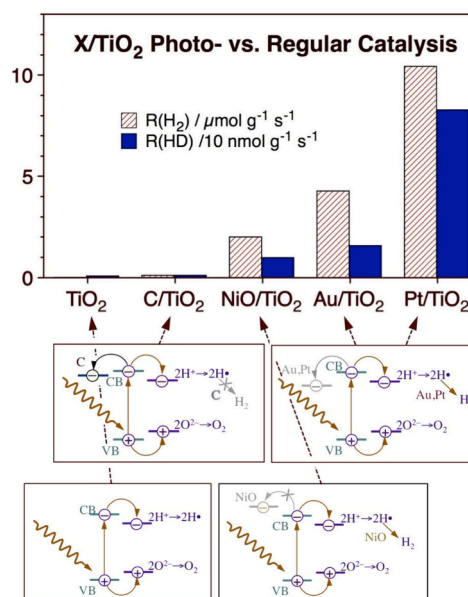


Figure 5. Rates of H_2 photoproduction (red hatched bars) and of HD production via the room-temperature scrambling of $H_2 + D_2$ gas mixtures, both measured by using titania by itself and with added carbon, nickel oxide, gold, or platinum NP cocatalysts. Schematic representations of the electronic transitions associated with the photocatalysis are shown at the bottom for all cases. The correlation between the two rates suggests that it is the atomic hydrogen recombination step that requires the assistance of the cocatalyst.⁶³

Additional experiments were carried out where the metal (Au) NPs were shielded from making an electrical contact with the semiconductor surface by coating them with a thin silica layer (in a core–shell nanostructure).⁶³ It was shown that indeed, in these $Au@SiO_2/TiO_2$ catalysts, the silica shell electrically isolates the metal and prevents the shift of the plasmon resonance peak expected from charging of the metal NP via the transfer of electrons from the titanium oxide support upon illumination. On the other hand, the resulting new catalysts were shown to still promote both the photocatalytic production of H_2 and the gas-phase H–D isotope scrambling of $H_2 + D_2$ mixtures. These observations further support the idea that the main role of metal cocatalysts in the photocatalytic production of H_2 from water is the promotion of hydrogen atom recombination rather than the scavenging of photoexcited electrons.

REACTION MECHANISM

The nature of the species that form on the semiconductor (titanium oxide) surface upon photoexcitation and proton reduction is difficult to ascertain. As mentioned above, some authors have identified, on the basis of experiments using EPR and XPS, the transient formation of reduced (Ti^{3+}) centers.^{15,57,58} However, the role of those species in the production of hydrogen has not been established. One possibility is the formation of $Ti^{3+} \cdot H^+$ polarons at the surface. DFT calculations have estimated the energy level for the formation of such intermediate to be approximately 0.82 eV below the conduction band of anatase and a bond energy for the $Ti^{4+} - H^\bullet$ surface species produced after a charge transfer step of 1.7 eV.⁸⁸ The latter value may seem high,^{88,89} but a recent publication has reported results from a clever experiment showing that photoexcitation of titanium oxide exposed to water

vapor can in fact produce and eject hydrogen radicals.⁹⁰ The schematics of the setup used and a summary of the data obtained in that work are shown in Figure 6. A flow reactor was designed

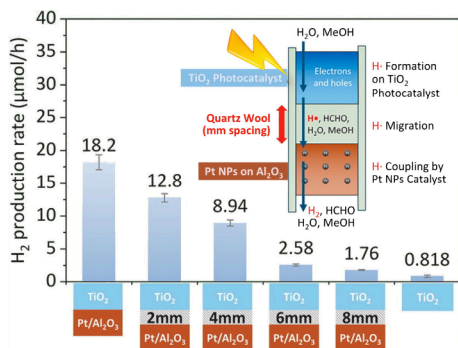


Figure 6. Rates of H₂ photoproduction from water vapor (spiked with methanol as a sacrificial oxidation agent) using the two-stage reactor depicted in the inset where the pure titanium oxide and supported Pt phases were physically spaced so that the photocatalytic production of atomic hydrogen and its recombination to form H₂ could be probed separately. An intermediate space filled with quartz wool was used to determine the distance over which the hydrogen radicals could travel, which turned out to be on the order of several millimeters. Adapted from ref 90 with permission. Copyright 2024 Hydrogen Energy Publications LLC. Published by Elsevier Ltd.

with two physically separated regions, the first containing pure titanium oxide, at a level that could be irradiated with UV light (a xenon lamp) and a second downstream from the first and separated by quartz wool filled with an alumina-supported Pt catalyst. Flowing a gas mixture of water and methanol in an argon carrier through this reactor with the lamp turned on resulted in the detection of molecular hydrogen. Because in this arrangement the semiconductor and metal phases lie apart from each other, it was concluded that hydrogen radicals need to be generated at the TiO₂ photocatalyst, migrate through the quartz wool layer, and recombine to yield H₂ on the Pt NPs. By varying

the length of the inert middle (quartz wool) region, it was determined that the atomic hydrogen radicals could travel and survive distances on the order of several millimeters. This report provides direct evidence for the viability of the model where the role of the metal cocatalyst is primarily to assist in the atomic-hydrogen recombination and not in the charge separation step.

The mechanism of the photocatalytic production of hydrogen from water is perhaps different in the presence of liquid water because the stability of atomic hydrogen or any other intermediate is bound to depend strongly on its interaction with that media, but the possibility of generating a version of reduced hydrogen atoms on the titanium oxide surface is still likely under such conditions. Some understanding of the photocatalytic production of molecular hydrogen have been extracted from experiments using infrared absorption spectroscopy (IR)^{41,91} and quantum mechanics calculations.^{92,93} The reaction is likely to start with the formation of a reduced surface structure, versions of which include the addition of the hydrogen atom to an oxygen bridge site (Ti⁴⁺–O(H)–Ti⁴⁺),⁹⁴ a surface hydroxide group on a reduced titanium ion (likely a Ti³⁺–OH group),^{13,95} a water molecule covalently bonded to a titanium surface site (Ti⁴⁺–OH₂),⁹⁶ and a “loosely coupled proton/electron pair distributed across the titania surface hydroxyl” (Ti³⁺–OH₂⁺).⁹⁷ The formation of such excited intermediate in water, whatever its form, happens even in the dark,^{98–100} but appears to be enhanced by the absorption of photons. In fact, some of these surface species may act as electron or hole traps, extending the lifetime of the photoexcitation to a time scale of up to minutes,^{13,101–103} and may correspond to the first intermediate where reduced hydrogen atoms are bound to the surface of the catalyst.

On the basis of results from DFT calculations it has been established that, on defect-free titanium oxide, about 5% of adsorbed water dissociates on surface oxygen atoms to form surface OH groups.⁹³ These calculations have concluded that single hydrogen atoms preferentially adsorb on top of bridging 2-fold coordinated oxygen atoms, possibly forming the Ti⁴⁺–

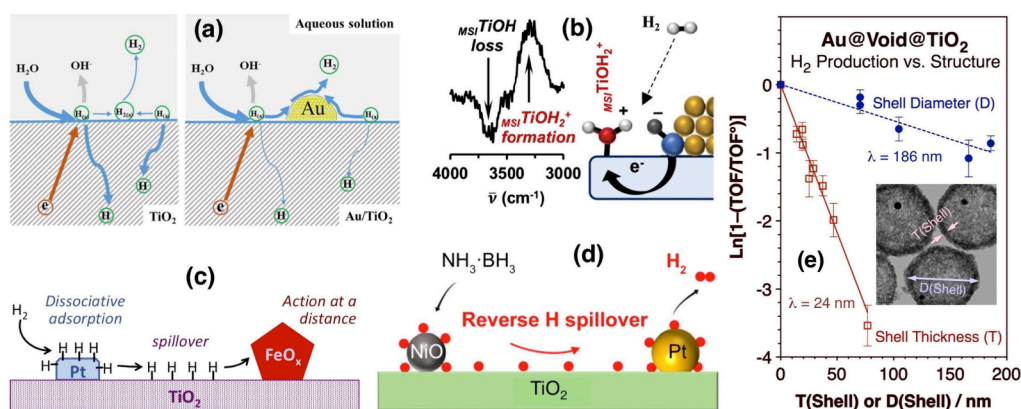


Figure 7. Examples of studies supporting the reduction of protons on semiconductor surfaces and the migration of the resulting intermediates to metal NPs. (a) Proposed steps during the electrolytic reduction of water on TiO₂ (left) versus Au/TiO₂ (right) electrodes. The thicknesses of the several arrows indicate the relative importance of the different steps. Reproduced from ref 105 with permission. Copyright 2021 The Authors, published by Elsevier B.V. (b) Left: IR data highlight the protonation of hydroxyl groups (MSITiOH, seen as an IR signal loss) to MSITiOH₂⁺ (for which the IR signal increases) upon the heterolytic adsorption of H₂ on Au/TiO₂, following the mechanism depicted on the right. Reproduced from ref 91 with permission. Copyright 2021 American Chemical Society. (c) Schematic representation of the spillover of hydrogen atoms produced via H–H activation at Pt NPs and their migration to iron oxide NPs, where reduction of the oxide takes place.¹⁰⁶ (d) Similar hydrogen spillover scheme using NiO sites to hydrolyze ammonia borane and Pt NPs to produce H₂. Adapted from ref 108 with permission. Copyright 2022, The Authors, published by Springer Nature. (e) Hydrogen photoproduction turnover frequencies (TOFs) as a function of the diameter (*D*) and thickness (*T*) of the titanium oxide shells in Au@Void@TiO₂ yolk–shell nanostructures.¹⁰⁹

O(H)–Ti⁴⁺ mentioned above, with an adsorption energy of between approximately 1.5 and 2.3 eV depending on the crystalline form of the oxide and the orientation of the facet exposed.⁹² The migration of those hydrogen atoms into the bulk was found to be quite favorable, occurring even below room temperature, but, although diffusion of these atoms on the surface was estimated to exhibit an activation barrier of about 1.4 eV, twice as large as that for migration into the bulk, it is a process that may be also favorable if it involves surface OH species.⁹² A dynamic equilibrium where a pair of short-lived hydroxyl groups form on the TiO₂ surface via a water-assisted proton transfer may be a viable mechanism for this hydrogen surface mobility.⁹³ The feasibility of the reverse spillover of hydrogen atoms from metal NPs to oxide supports, where they bind to O²⁻ ions, has been supported using DFT as well.¹⁰⁴ On the other hand, although the production of H₂ from recombination of surface hydrogen atoms on TiO₂ was estimated to be exothermic by 0.95 eV (in anatase), the activation barrier was calculated at more than 2 eV, possibly too high to compete with other pathways (or with de-excitation back to H⁺ + TiO₂).⁹² The energy landscape that emerges from these studies suggests that, from an energetic point of view, the most probable way by which hydrogen gas is produced in this photocatalysis is via the initial formation of a version of atomic hydrogen on the surface followed by migration to the metal NPs, where recombination to yield H₂ is facile.

Several experimental studies have also provided indirect evidence to support the model of proton reduction on the semiconductor surface followed by migration of the resulting intermediates to the metal NP for recombination and H₂ formation. In one case, the electrolytic reduction of water in alkaline media was tested using cyclic voltammetry, explicitly contrasting the performance of titanium oxide electrodes pure versus modified with Au NPs.¹⁰⁵ The data indicated that with pure TiO₂ the atomic hydrogen produced by reduction at high cathodic potentials diffuses into the bulk of the electrode, but that if Au NPs are added H₂ production is observed instead. These results were explained on the basis of the migration (spillover) of the H[•] species produced on the TiO₂ surface to the Au NPs, where they recombine to form H₂ (Figure 7a). In a different study, IR was used to follow the adsorption and activation of H₂ on Au/TiO₂.⁹¹ As shown in the left side of Figure 7b, the spectra revealed both the loss of nonprotonated hydroxyl groups (_{MSI}TiOH) and the creation of protonated hydroxyl species (_{MSI}TiOH₂⁺) at the metal–semiconductor interface (MSI) upon exposure of the catalyst to molecular hydrogen. The authors of that work claimed that after the heterolytic dissociation of the H–H bond at the MSI (right side of Figure 7b) the resulting hydrogen atoms spill over into the titanium oxide surface; a microscopic reversibility sequence in which H[•] migration from TiO₂ to the metal/TiO₂ interface is followed by recombination to produce H₂ would explain the photocatalysis discussed here.⁹⁷ The ability of hydrogen atoms to spill over and migrate on titanium oxide surfaces has been further demonstrated by a couple of separate experiments, in one case using Pt NPs to produce the H[•] species from H₂ and iron oxide NPs to detect them as the oxide is reduced to metallic iron (a reaction followed by X-ray absorption spectroscopy – XPS–) (Figure 7c),^{106,107} and in the other by generating H[•] species via ammonia borane hydrolysis at NiO sites and collecting H₂ at Pt NPs (Figure 7d).¹⁰⁸ We have reported different characteristic lengths for the photoproduction of H₂ from water with Au@Void@TiO₂ yolk–shell nanostructures as

a function of shell thickness (*T*) versus shell diameter (*D*) (Figure 7e): the first was associated with the mean free path of the initial excited electron as it travels to the surface, whereas the second, which is almost an order of magnitude larger, is likely to reflect the average distance traveled by the hydrogen atom intermediates before they reach the Au NPs.¹⁰⁹ In all three cases, traveling distances of at least tens of nanometers were measured for atomic hydrogen on TiO₂. It is even possible to promote the reduction of TiO₂ itself with H₂ activated by Pt NPs to create Ti³⁺ and color centers.^{110,111} Finally, it has been recently claimed that H₂ photoproduction on modified titanium oxide catalysts can be optimized by tuning the electronic properties of the metal NPs (via alloying) to optimize the energetics of the atomic hydrogen recombination step.¹¹²

OTHER RELATED PHOTOCATALYTIC HYDROGEN-PRODUCTION SYSTEMS

One limitation of using semiconductors with wide bandgaps such as titanium oxide as photocatalysts is that they can only absorb UV radiation and therefore are inefficient if the source for photoactivation is sunlight. However, if Au or Ag NPs are used as cocatalysts, those can absorb visible light, which excite their surface plasmon. Some research groups have tried to exploit that process to harness low-energy photons for chemical conversions, including the production of hydrogen from water.^{113,114} Several mechanisms have been discussed in relation to the way the initial photoexcitation of the metal NPs may be transferred to the reactants to promote chemical conversions, including plasmon resonance energy transfer (PRET), near field electromagnetic enhancement, and scattering and photothermal heating effects,^{15,46,115–117} but perhaps the most commonly cited pathway is a simple generation of hot electrons at the metal NPs and their transfer to the conduction band of the semiconductor, where the reduction step is alleged to take place (Figure 8). A couple of considerations must be taken into account in connection with this mechanism. First, the energy of

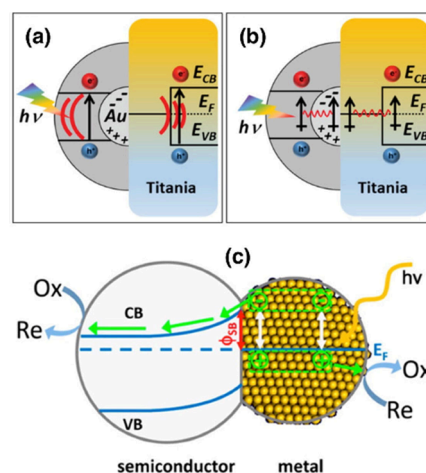


Figure 8. Proposed mechanisms for photocatalysis based on excitation of the surface plasmon of metal NPs. (a) Near-field electromagnetic enhancement of absorption; (b) plasmon resonant energy transfer (PRET); (c) hot-electron formation and transfer to the conduction band of the semiconductor. The need to promote the accompanying oxidation reaction at the metal site is highlighted in the latter case. Reproduced with permission from refs 116, copyright 2021 The Authors, Small published by Wiley-VCH GmbH, and ref 15, copyright 2014 American Chemical Society.

the absorbed photons is quite low, which means that to complete the redox process a sacrificial agent with a very low reduction potential is required. Sacrificial agents such as methanol are in fact used in most water-splitting studies, especially with titanium oxide, because the overpotential for O₂ production from water is quite high,^{5,67,118} but in the case of surface-plasmon-excitation photocatalysis the demand on this added reactant is particularly onerous. The second factor is that because the reduction step is supposed to occur at the surface of the semiconductor, the yields in the case of H₂ production from water are expected to be quite low unless a way to efficiently spill over the H[•] intermediates back to the metal is possible. In the end, several studies have shown that the contribution of the plasmonic effect to the photocatalytic production of H₂ from water is in most instances negligible.^{75,119,120}

From the point of view of the design of photocatalysts, there has been an interest in recent years in maximizing the use of the metal, which often is an expensive noble metal such as Au or Pt, by reducing the size of their NPs. The ultimate limit in this case is single atoms dispersed on the semiconductor support, an approach that has become a hot area of research in recent years.^{121–125} Some studies have been carried out to use such single-atom catalysts (SACs) for the photocatalytic splitting of water,^{126–128} but a full understanding of how these catalysts operate is still not available. One issue that has been seldom mentioned here is the fact that single metal atoms dispersed on oxide supports tend to be in an oxidized, not metallic, state. In the case of Pt on either titanium oxide or cerium oxide, +2 and +4 oxidation states have been detected by XPS, X-ray absorption spectroscopies (XAS), and CO titrations using IR, and also estimated from DFT calculations;^{129–134} the exact oxidation state depends on the facet of the oxide exposed and the coordination of the surface atoms (basal planes versus defect sites). In addition, because these are discrete ions rather than metal NPs, their electronic levels are sharp; density-of-state (DOS) calculations have placed the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of these Pt single atoms (actually ions), the equivalent to the valence and conduction bands, at between -1.0 and -0.2 eV and between $+0.2$ and $+0.7$ eV relative to the Fermi level, respectively.^{129,134,135} The latter seems to fall in between the conduction band of titanium oxide and the reduction potential for the H⁺/H₂ conversion, better aligned than in the case of metal NPs for electron trapping and subsequent proton reduction at the Pt atom site (the conventional photocatalysis model), which may be the reason for the better performance for H₂ production from water seen in some studies with SAC-Pt/TiO₂ when contrasted with regular NP-Pt/TiO₂ counterparts.^{134–136} On the other hand, the ability of these Pt single atoms to promote the recombination of hydrogen atoms is likely to be diminished:¹³⁷ high activation barriers, on the order of 1 eV, have been calculated for this process with DFT,¹³⁸ and an almost complete suppression of H₂ + D₂ isotope scrambling activity has been seen experimentally when transitioning from NP-Pt/TiO₂ to SAC-Pt/TiO₂.¹³⁹ This means that the H[•] dimerization step may become the bottleneck in photocatalysis with SCAs. It should be indicated that recent DFT calculations have shown that single-atom catalysts can bind two H atoms and form a dihydrogen metal complex, a possible precursor state to H₂ desorption.¹⁴⁰ Yet, that work did not directly probe the kinetics (activation barrier) of the final H[•] recombination step.

Another approach that has been explored in terms of the design of nanostructures for photocatalysis is the use of core–

shell or yolk–shell constructs: Au (or Pt) NPs, for instance, can be trapped inside titanium oxide shells to make either Au@TiO₂ or Au@Void@TiO₂ photocatalysts.^{116,141–144} As we have already illustrated in Figures 3 and 7e, the use of yolk–shell nanostructures affords great control on geometrical and structural parameters such as shell diameter and thickness, metal NP diameter, and degree of crystallinity of the oxide in the shell.^{63–65,109,145–153} In another example, research using Au@Void@Cu₇S₄ nanostructures demonstrated that control over the size of the void space can improve mass transport kinetics across the shell and enhance photocatalytic activity for hydrogen production, and that these photocatalysts exhibit efficient charge transfer and strong surface plasmon resonance (SPR)-mediated near-field effects.¹⁵⁴ Similar claims were made with Au@Void@TiO₂ photocatalysts.¹⁵⁵ In general, though, in most studies, the use of these and other complex nanostructures has not been properly justified.

Finally, the same principles and constructs discussed above for photocatalytic water splitting have been used for the conversion of organic reactants. For instance Au/TiO₂ has been used to photocatalytically produce H₂ from oxalic acid.⁷⁷ In that case, bare titanium oxide was also photoactive, but the addition of a metal cocatalyst led to an increase in activity (more with Pt than with Au). Moreover, the absence of photoactivity when only visible light was used, combined with results from comparison experiments using pure Au versus Au–Pt alloys, indicated the absence of any contribution from the surface plasmon excitation mechanism. Photoreforming of other oxygenates to produce H₂ has been reported as well, with other organic acids as well as with various alcohols.⁷⁸ One caveat here is that the experiments with organic feedstocks have been carried out using aqueous solutions, which means that in reality the reduction reaction may be the same as with pure water, namely, a conversion of protons to H₂. It should be emphasized that, in most studies of the “water splitting” process, a sacrificial agent, typically methanol or ethanol, is used to facilitate the oxidation half-reaction because O₂ production from water exhibits a high overpotential; by bypassing that step it is then possible to focus on the hydrogen reduction side of the reaction.¹¹⁸ In order to truly photocatalytically split water a second cocatalyst is needed to facilitate the O₂ evolution reaction; oxides of metals such as Co, Fe, Ni, Mn, Ru, and Ir have proven to be good choices for this purpose.^{6,30,156–158} Much research has been carried out to better understand and improve the oxidation half-reaction, but further discussion of that work is beyond the objectives of our Critical Review.

CONCLUDING REMARKS

The focus of this Critical Review has been the molecular details of the photocatalytic production of H₂ from water, with an emphasis on the role that metal cocatalysts play in enhancing the activity of that process. It is widely accepted that metals help scavenge the excited electrons produced from photon absorption by the semiconductor that comprises the heart of the photocatalyst, hence preventing rapid de-excitation via recombination with the accompanying hole photogenerated in the valence band. We here have argued that although this electron transfer does take place, it is probably a side process by which those electrons get trapped below the energy level required for the reduction of protons at the water/solid interface. Instead, it is perhaps more likely for the protons to be directly reduced at the titanium oxide surface and for the

metal to then facilitate the recombination of the resulting hydrogen atoms to yield H₂.

If applicable, how general may this alternative mechanism be? For one, it is straightforward to assume that it would apply to other semiconductors used as photocatalysts. This includes the many semiconductor materials that have been tested for the photosplitting of water using visible light since those also have their conduction band placed at energy levels comparable to that of titanium oxide; this is a requirement if the photogenerated excited electrons are to be able to be transferred to protons in solution. In addition, it is easy to imagine the need of cocatalysts for the promotion of various other thermal chemistries, with other feedstocks, following the photoformation of the initial reduced intermediates on the surface of the semiconductor in order to convert them into the final products. In this vein, it is worth remembering that H₂ photoproduction, like many other photocatalytic processes, requires multiple electron-transfer steps; in this case, two separate protons need to each accept one electron from the surface to be converted to neutral hydrogen atoms (or associated surface species). The oxygen-evolution step that completes the redox photoconversion of water to H₂ + O₂ is even more demanding, requiring four electrons. Because photon absorption by photocatalysts typically produces one single excited e⁻-h⁺ pair at a time (unless high photon fluxes from powerful lasers are used), the expectation is for each photoexcitation plus electron transfer to require the creation of a chemical intermediate on the surface in order to “trap” it until the next photoexcitation can be added. For oxygen production from water, for instance, the formation of hydroxo radicals, peroxides, and superoxides have all been proposed.^{103,159} The oxidation of the alcohols or organic acids used as sacrificial agents in the studies on the hydrogen evolution reaction also yield several surface intermediates such as formates and alkoxides on the way to the production of CO₂.

The thermal chemistry that follows the surface intermediates produced via the photoreduction of either the initial reactant or any of the previously produced adsorbed species may potentially occur on the spot at the same site of the reduction. However, the semiconductors used as photocatalyst may not be particularly effective promoters of those steps, as we have argued here may be the case with the photoproduction of H₂ from water. In such instances, a cocatalyst may be required. On the positive side, the incorporation of cocatalysts also offers a way to add specific chemistry to the overall photocatalytic process and perhaps to direct it toward the selective generation of interesting products. This is certainly a desirable approach in the case of the photocatalytic reduction of CO₂, for instance, where it may be relatively easy to produce CO but more beneficial to make other value-added products such as alcohols.^{160–162} In fact, the same approach can be used in electrocatalysis: selective complex catalytic processes may be designed so that either photons or voltages are employed to generate hard-to-produce or energy-demanding intermediates, which then migrate to other surface sites in order to follow additional thermal (and selective) chemistry.^{163–165} We believe that the design of bifunctional photocatalysts where the initial photoexcitation and reduction step at the main semiconductor surface is followed by additional thermal chemistry at sites on added cocatalysts specifically chosen to drive selective and possibly complex chemistry is a promising and underdeveloped approach. We hope that the discussion presented above provides enough incentive for research groups to explore this idea.

AUTHOR INFORMATION

Corresponding Author

Francisco Zaera – Department of Chemistry and UCR Center for Catalysis, University of California, Riverside, California 92521, United States; orcid.org/0000-0002-0128-7221; Email: zaera@ucr.edu

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.energyfuels.4c06100>

Notes

The author declares no competing financial interest.

Biography

Francisco Zaera is the Hartland H. Schmidt Founder's Chair and a Distinguished Professor in Chemistry at UCR. He was until recently Senior Editor of The Journal of Physical Chemistry Letters. He has authored ~450 articles and has received several international awards, including the ACS Olah, Adamson, and Inaugural Exceptional Achievements in Catalysis Awards, the NACS Emmett Award, and a Humboldt Research Award for Senior Scientists. He is a Fellow of the ACS, AVS, and AAAS.

ACKNOWLEDGMENTS

Funding for the writing of this Critical Review was provided by a grant from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Transformations Division, Catalysis Science Program, under award no. DE-SC0023119. We also wish to thank Dr. Jeroen Anton van Bokhoven for providing us with a draft of Figure 7c.

REFERENCES

- (1) Ola, O.; Maroto-Valer, M. M. Review of Material Design and Reactor Engineering on TiO₂ Photocatalysis for CO₂ Reduction. *J. Photochem. Photobiol., C* **2015**, *24*, 16–42.
- (2) Kumaravel, V.; Bartlett, J.; Pillai, S. C. Photoelectrochemical Conversion of Carbon Dioxide (CO₂) into Fuels and Value-Added Products. *ACS Energy Lett.* **2020**, *5* (2), 486–519.
- (3) Bahnemann, D. Photocatalytic Water Treatment: Solar Energy Applications. *Sol. Energy* **2004**, *77* (5), 445–459.
- (4) Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K. A Review and Recent Developments in Photocatalytic Water-Splitting Using for Hydrogen Production. *Renewable Sustainable Energy Rev.* **2007**, *11* (3), 401–425.
- (5) Xing, J.; Fang, W. Q.; Zhao, H. J.; Yang, H. G. Inorganic Photocatalysts for Overall Water Splitting. *Chem.-Asian J.* **2012**, *7* (4), 642–657.
- (6) Takata, T.; Domen, K. Particulate Photocatalysts for Water Splitting: Recent Advances and Future Prospects. *ACS Energy Lett.* **2019**, *4* (2), 542–549.
- (7) Costantino, F.; Kamat, P. V. Do Sacrificial Donors Donate H₂ in Photocatalysis? *ACS Energy Lett.* **2022**, *7* (1), 242–246.
- (8) Kamat, P. V. Semiconductor Surface Chemistry as Holy Grail in Photocatalysis and Photovoltaics. *Acc. Chem. Res.* **2017**, *50* (3), 527–531.
- (9) Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2020**, *120* (2), 919–985.
- (10) Osterloh, F. E. Inorganic Materials as Catalysts for Photochemical Splitting of Water. *Chem. Mater.* **2008**, *20* (1), 35–54.
- (11) Carp, O.; Huisman, C. L.; Reller, A. Photoinduced Reactivity of Titanium Dioxide. *Prog. Solid State Chem.* **2004**, *32* (1–2), 33–177.
- (12) Chen, X.; Mao, S. S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**, *107* (7), 2891–2959.
- (13) Fujishima, A.; Zhang, X.; Tryk, D. A. TiO₂ Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63* (12), 515–582.

- (14) Henderson, M. A. A Surface Science Perspective on Photo-catalysis. *Surf. Sci. Rep.* **2011**, *66* (6–7), 185–297.
- (15) Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D. W. Understanding TiO₂ Photocatalysis: Mechanisms and Materials. *Chem. Rev.* **2014**, *114* (19), 9919–9986.
- (16) Ge, M.; Cai, J.; Iocozzia, J.; Cao, C.; Huang, J.; Zhang, X.; Shen, J.; Wang, S.; Zhang, S.; Zhang, K.-Q.; et al. A Review of TiO₂ Nanostructured Catalysts for Sustainable H₂ Generation. *Int. J. Hydrogen Energy* **2017**, *42* (12), 8418–8449.
- (17) Kausar, F.; Varghese, A.; Pinheiro, D.; Devi K R, S. Recent Trends in Photocatalytic Water Splitting Using Titania Based Ternary Photocatalysts-A Review. *Int. J. Hydrogen Energy* **2022**, *47* (53), 22371–22402.
- (18) Mansfeldova, V.; Zlamalova, M.; Tarabkova, H.; Janda, P.; Vorokhta, M.; Piliat, L.; Kavan, L. Work Function of TiO₂ (Anatase, Rutile, and Brookite) Single Crystals: Effects of the Environment. *J. Phys. Chem. C* **2021**, *125* (3), 1902–1912.
- (19) Zabara, M. A.; Yazar Kaplan, B.; Alkan Gürsel, S.; Yürüm, A. Facet-Dependent Interfacial and Photoelectrochemical Properties of TiO₂ Nanoparticles. *Adv. Mater. Interfaces* **2023**, *10* (31), 2300555.
- (20) Fujisawa, J.-i.; Eda, T.; Hanaya, M. Comparative Study of Conduction-Band and Valence-Band Edges of TiO₂, SrTiO₃, and BaTiO₃ by Ionization Potential Measurements. *Chem. Phys. Lett.* **2017**, *685*, 23–26.
- (21) Toyoda, T.; Yindeesuk, W.; Okuno, T.; Akimoto, M.; Kamiyama, K.; Hayase, S.; Shen, Q. Electronic Structures of Two Types of TiO₂ Electrodes: Inverse Opal and Nanoparticulate Cases. *RSC Adv.* **2015**, *5* (61), 49623–49632.
- (22) Gutmann, S.; Wolak, M. A.; Conrad, M.; Beerbom, M. M.; Schlaf, R. Effect of Ultraviolet and X-Ray Radiation on the Work Function of TiO₂ Surfaces. *J. Appl. Phys.* **2010**, *107* (10), 103705.
- (23) Xiong, G.; Shao, R.; Droubay, T. C.; Joly, A. G.; Beck, K. M.; Chambers, S. A.; Hess, W. P. Photoemission Electron Microscopy of TiO₂ Anatase Films Embedded with Rutile Nanocrystals. *Adv. Funct. Mater.* **2007**, *17* (13), 2133–2138.
- (24) Scanlon, D. O.; Dunnill, C. W.; Buckeridge, J.; Shevlin, S. A.; Logsdail, A. J.; Woodley, S. M.; Catlow, C. R. A.; Powell, M. J.; Palgrave, R. G.; Parkin, I. P.; et al. Band Alignment of Rutile and Anatase TiO₂. *Nat. Mater.* **2013**, *12* (9), 798–801.
- (25) Cheng, J.; Sprik, M. Alignment of Electronic Energy Levels at Electrochemical Interfaces. *Phys. Chem. Chem. Phys.* **2012**, *14* (32), 11245–11267.
- (26) Maeda, K.; Domen, K. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem. C* **2007**, *111* (22), 7851–7861.
- (27) Grätzel, M. Photoelectrochemical Cells. *Nature* **2001**, *414* (6861), 338–344.
- (28) Wang, K.; Peng, T.; Wang, Z.; Wang, H.; Chen, X.; Dai, W.; Fu, X. Correlation between the H₂ Response and Its Oxidation over TiO₂ and N Doped TiO₂ under UV Irradiation Induced by Fermi Level. *Appl. Catal., B* **2019**, *250*, 89–98.
- (29) Huang, H.; Pradhan, B.; Hofkens, J.; Roeffaers, M. B. J.; Steele, J. A. Solar-Driven Metal Halide Perovskite Photocatalysis: Design, Stability, and Performance. *ACS Energy Lett.* **2020**, *5* (4), 1107–1123.
- (30) Wang, Z.; Li, C.; Domen, K. Recent Developments in Heterogeneous Photocatalysts for Solar-Driven Overall Water Splitting. *Chem. Soc. Rev.* **2019**, *48* (7), 2109–2125.
- (31) Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. *Chem. Soc. Rev.* **2009**, *38* (1), 253–278.
- (32) Sivula, K.; van de Krol, R. Semiconducting Materials for Photoelectrochemical Energy Conversion. *Nat. Rev. Mater.* **2016**, *1* (2), 15010.
- (33) Ismael, M. A Review and Recent Advances in Solar-to-Hydrogen Energy Conversion Based on Photocatalytic Water Splitting over Doped-TiO₂ Nanoparticles. *Sol. Energy* **2020**, *211*, 522–546.
- (34) Fox, M. A.; Lindig, B.; Chen, C. C. Transients Generated Upon Photolysis of Colloidal Titanium Dioxide in Acetonitrile Containing Organic Redox Couples. *J. Am. Chem. Soc.* **1982**, *104* (21), 5828–5829.
- (35) Serpone, N.; Lawless, D.; Khairutdinov, R.; Pelizzetti, E. Subnanosecond Relaxation Dynamics in TiO₂ Colloidal Sols (Particle Sizes Rp = 1.0–13.4 nm). Relevance to Heterogeneous Photocatalysis. *J. Phys. Chem.* **1995**, *99* (45), 16655–16661.
- (36) Colombo, D. P., Jr; Bowman, R. M. Femtosecond Diffuse Reflectance Spectroscopy of TiO₂ Powders. *J. Phys. Chem.* **1995**, *99* (30), 11752–11756.
- (37) Godin, R.; Kafizas, A.; Durrant, J. R. Electron Transfer Dynamics in Fuel Producing Photosystems. *Curr. Opin. Electrochem.* **2017**, *2* (1), 136–143.
- (38) Qian, R.; Zong, H.; Schneider, J.; Zhou, G.; Zhao, T.; Li, Y.; Yang, J.; Bahnemann, D. W.; Pan, J. H. Charge Carrier Trapping, Recombination and Transfer During TiO₂ Photocatalysis: An Overview. *Catal. Today* **2019**, *335*, 78–90.
- (39) Kuznetsov, A. I.; Kameneva, O.; Alexandrov, A.; Bityurin, N.; Marteau, P.; Chhor, K.; Sanchez, C.; Kanaev, A. Light-Induced Charge Separation and Storage in Titanium Oxide Gels. *Phys. Rev. E* **2005**, *71* (2), 021403.
- (40) Di Valentin, C.; Pacchioni, G.; Selloni, A. Electronic Structure of Defect States in Hydroxylated and Reduced Rutile TiO₂ (110) Surfaces. *Phys. Rev. Lett.* **2006**, *97* (16), 166803.
- (41) Panayotov, D. A.; Burrows, S. P.; Yates, J. T.; Morris, J. R. Mechanistic Studies of Hydrogen Dissociation and Spillover on Au/TiO₂: IR Spectroscopy of Coadsorbed CO and H-Donated Electrons. *J. Phys. Chem. C* **2011**, *115* (45), 22400–22408.
- (42) Gupta, N. M. Factors Affecting the Efficiency of a Water Splitting Photocatalyst: A Perspective. *Renewable Sustainable Energy Rev.* **2017**, *71*, 585–601.
- (43) Iwata, K.; Takaya, T.; Hamaguchi, H.-o.; Yamakata, A.; Ishibashi, T.-a.; Onishi, H.; Kuroda, H. Carrier Dynamics in TiO₂ and Pt/TiO₂ Powders Observed by Femtosecond Time-Resolved near-Infrared Spectroscopy at a Spectral Region of 0.9–1.5 μm with the Direct Absorption Method. *J. Phys. Chem. B* **2004**, *108* (52), 20233–20239.
- (44) Kamat, P. V. Manipulation of Charge Transfer across Semiconductor Interface. A Criterion That Cannot Be Ignored in Photocatalyst Design. *J. Phys. Chem. Lett.* **2012**, *3* (5), 663–672.
- (45) Disdier, J.; Herrmann, J.-M.; Pichat, P. Platinum/Titanium Dioxide Catalysts. A Photoconductivity Study of Electron Transfer from the Ultraviolet-Illuminated Support to the Metal and of the Influence of Hydrogen. *J. Chem. Soc. Faraday Trans. 1* **1983**, *79* (3), 651–660.
- (46) Panayotov, D. A.; Morris, J. R. Surface Chemistry of Au/TiO₂: Thermally and Photolytically Activated Reactions. *Surf. Sci. Rep.* **2016**, *71* (1), 77–271.
- (47) Hossein-Babaei, F.; Lajvardi, M. M.; Alaei-Sheini, N. The Energy Barrier at Noble Metal/TiO₂ Junctions. *Appl. Phys. Lett.* **2015**, *106* (8), 083503.
- (48) Michalas, L.; Khiat, A.; Stathopoulos, S.; Prodromakis, T. Electrical Characteristics of Interfacial Barriers at Metal–TiO₂ Contacts. *J. Phys. D: Appl. Phys.* **2018**, *51* (42), 425101.
- (49) Tachikawa, T.; Minohara, M.; Hikita, Y.; Bell, C.; Hwang, H. Y. Tuning Band Alignment Using Interface Dipoles at the Pt/Anatase TiO₂ Interface. *Adv. Mater.* **2015**, *27* (45), 7458–7461.
- (50) Jovic, V.; Chen, W.-T.; Sun-Waterhouse, D.; Blackford, M. G.; Idriss, H.; Waterhouse, G. I. N. Effect of Gold Loading and TiO₂ Support Composition on the Activity of Au/TiO₂ Photocatalysts for H₂ Production from Ethanol-Water Mixtures. *J. Catal.* **2013**, *305*, 307–317.
- (51) Stevanovic, A.; Ma, S.; Yates, J. T., Jr Effect of Gold Nanoparticles on Photoexcited Charge Carriers in Powdered TiO₂-Long Range Quenching of Photoluminescence. *J. Phys. Chem. C* **2014**, *118* (36), 21275–21280.
- (52) Hirakawa, T.; Kamat, P. V. Charge Separation and Catalytic Activity of Ag@TiO₂ Core-Shell Composite Clusters under UV-Irradiation. *J. Am. Chem. Soc.* **2005**, *127* (11), 3928–3934.
- (53) Novo, C.; Mulvaney, P. Charge-Induced Rayleigh Instabilities In Small Gold Rods. *Nano Lett.* **2007**, *7* (2), 520–524.

- (54) Jakob, M.; Levanon, H.; Kamat, P. V. Charge Distribution between UV-Irradiated TiO₂ and Gold Nanoparticles: Determination of Shift in the Fermi Level. *Nano Lett.* **2003**, *3* (3), 353–358.
- (55) Subramanian, V.; Wolf, E. E.; Kamat, P. V. Catalysis with TiO₂/Gold Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration. *J. Am. Chem. Soc.* **2004**, *126* (15), 4943–4950.
- (56) Kiyonaga, T.; Fujii, M.; Akita, T.; Kobayashi, H.; Tada, H. Size-Dependence of Fermi Energy of Gold Nanoparticles Loaded on Titanium(IV) Dioxide at Photostationary State. *Phys. Chem. Chem. Phys.* **2008**, *10* (43), 6553–6561.
- (57) Anpo, M.; Takeuchi, M. The Design and Development of Highly Reactive Titanium Oxide Photocatalysts Operating under Visible Light Irradiation. *J. Catal.* **2003**, *216* (1–2), 505–516.
- (58) Alsalik, Y. M.; Katsiev, K.; Idriss, H. Electron Transfer from a Semiconductor to a Metal and Its Implication on Photocatalysis for Hydrogen Production. *J. Phys. Chem. C* **2022**, *126* (36), 15184–15190.
- (59) Kamat, P. V. Photophysical, Photochemical and Photocatalytic Aspects of Metal Nanoparticles. *J. Phys. Chem. B* **2002**, *106* (32), 7729–7744.
- (60) Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Anpo, M. Direct Observation of a Picosecond Charge Separation Process in Photoexcited Platinum-Loaded TiO₂ Particles by Femtosecond Diffuse Reflectance Spectroscopy. *Chem. Phys. Lett.* **2001**, *336* (5–6), 424–430.
- (61) Tahiri Alaoui, O.; Herissan, A.; Le Quoc, C.; Zekri, M. e. M.; Sorgues, S.; Remita, H.; Colbeau-Justin, C. Elaboration, Charge-Carrier Lifetimes and Activity of Pd-TiO₂ Photocatalysts Obtained by Gamma Radiolysis. *J. Photochem. Photobiol., A* **2012**, *242*, 34–43.
- (62) Luna, A. L.; Novoseltceva, E.; Louarn, E.; Beaunier, P.; Kowalska, E.; Ohtani, B.; Valenzuela, M. A.; Remita, H.; Colbeau-Justin, C. Synergetic Effect of Ni and Au Nanoparticles Synthesized on Titania Particles for Efficient Photocatalytic Hydrogen Production. *Appl. Catal., B* **2016**, *191*, 18–28.
- (63) Joo, J. B.; Dillon, R.; Lee, I.; Yin, Y.; Bardeen, C. J.; Zaera, F. Promotion of Atomic Hydrogen Recombination as an Alternative to Electron Trapping for the Role of Metals in the Photocatalytic Production of H₂. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (22), 7942–7947.
- (64) Zaera, F. Gold-Titania Catalysts for Low-Temperature Oxidation and Water Splitting. *Top. Catal.* **2018**, *61* (5), 336–347.
- (65) Dillon, R. J.; Joo, J.-B.; Zaera, F.; Yin, Y.; Bardeen, C. J. Correlating the Excited State Relaxation Dynamics as Measured by Photoluminescence and Transient Absorption with the Photocatalytic Activity of Au@TiO₂ Core-Shell Nanostructures. *Phys. Chem. Chem. Phys.* **2013**, *15* (5), 1488–1496.
- (66) Colón, G. Towards the Hydrogen Production by Photocatalysis. *Appl. Catal., A* **2016**, *518*, 48–59.
- (67) Christoforidis, K. C.; Fornasiero, P. Photocatalytic Hydrogen Production: A Rift into the Future Energy Supply. *ChemCatChem* **2017**, *9* (9), 1523–1544.
- (68) Murdoch, M.; Waterhouse, G. I. N.; Nadeem, M. A.; Metson, J. B.; Keane, M. A.; Howe, R. F.; Llorca, J.; Idriss, H. The Effect of Gold Loading and Particle Size on Photocatalytic Hydrogen Production from Ethanol over Au/TiO₂ Nanoparticles. *Nat. Chem.* **2011**, *3* (6), 489–492.
- (69) Serpone, N.; Emeline, A. V.; Horikoshi, S.; Kuznetsov, V. N.; Ryabchuk, V. K. On the Genesis of Heterogeneous Photocatalysis: A Brief Historical Perspective in the Period 1910 to the Mid-1980s. *Photochem. Photobiol. Sci.* **2012**, *11* (7), 1121–1150.
- (70) Méndez-Medrano, M. G.; Kowalska, E.; Lehou, A.; Herissan, A.; Ohtani, B.; Rau, S.; Colbeau-Justin, C.; Rodríguez-López, J. L.; Remita, H. Surface Modification of TiO₂ with Au Nanoclusters for Efficient Water Treatment and Hydrogen Generation under Visible Light. *J. Phys. Chem. C* **2016**, *120* (43), 25010–25022.
- (71) Kiwi, J.; Graetzel, M. Projection, Size Factors, and Reaction Dynamics of Colloidal Redox Catalysts Mediating Light Induced Hydrogen Evolution from Water. *J. Am. Chem. Soc.* **1979**, *101* (24), 7214–7217.
- (72) Matheson, M. S.; Lee, P. C.; Meisel, D.; Pelizzetti, E. Kinetics of Hydrogen Production from Methyl Viologen Radicals on Colloidal Platinum. *J. Phys. Chem.* **1983**, *87* (3), 394–399.
- (73) Sato, H.; Sugimoto, T. Direct Operando Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides. *J. Am. Chem. Soc.* **2024**, *146* (36), 24800–24807.
- (74) Bond, G. C. Chemisorption and Catalytic Reactions of Hydrogen at Metal Surfaces. *Surf. Sci.* **1969**, *18* (1), 11–27.
- (75) Nguyen-Phan, T.-D.; Baber, A. E.; Rodriguez, J. A.; Senanayake, S. D. Au and Pt Nanoparticle Supported Catalysts Tailored for H₂ Production: From Models to Powder Catalysts. *Appl. Catal., A* **2016**, *518*, 18–47.
- (76) Walenta, C. A.; Kollmannsberger, S. L.; Courtois, C.; Pereira, R. N.; Stutzmann, M.; Tschurl, M.; Heiz, U. Why Co-Catalyst-Loaded Rutile Facilitates Photocatalytic Hydrogen Evolution. *Phys. Chem. Chem. Phys.* **2019**, *21* (3), 1491–1496.
- (77) AlSalka, Y.; Al-Madanat, O.; Curti, M.; Hakki, A.; Bahnemann, D. W. Photocatalytic H₂ Evolution from Oxalic Acid: Effect of Cocatalysts and Carbon Dioxide Radical Anion on the Surface Charge Transfer Mechanisms. *ACS Applied Energy Materials* **2020**, *3* (7), 6678–6691.
- (78) Majeed, I.; Ali, H.; Idrees, A.; Arif, A.; Ashraf, W.; Rasul, S.; Khan, M. A.; Nadeem, M. A.; Nadeem, M. A. Understanding the Role of Metal Supported on TiO₂ in Photoreforming of Oxygenates. *Energy Adv.* **2022**, *1* (11), 842–867.
- (79) Eder, M.; Tschurl, M.; Heiz, U. Toward a Comprehensive Understanding of Photocatalysis: What Systematic Studies and Alcohol Surface Chemistry on TiO₂(110) Have to Offer for Future Developments. *J. Phys. Chem. Lett.* **2023**, *14* (26), 6193–6201.
- (80) Mills, A.; Valenzuela, M. A. Photo-Oxidation of Water Sensitized by TiO₂ and WO₃ in Presence of Different Electron Acceptors. *Rev. Mex. Fis.* **2004**, *50* (3), 287–296.
- (81) Litter, M. I.; Quici, N.; Meichtry, J. M.; Senn, A. M. Photocatalytic Removal of Metallic and Other Inorganic Pollutants. In *Photocatalysis: Applications*; Dionysiou, D. D., Li Puma, G., Ye, J., Schneider, J., Bahnemann, D., Schneider, J., Bahnemann, D., Ye, J., Li Puma, G., Dionysiou, D. D., Eds.; The Royal Society of Chemistry: 2016; p 0.
- (82) Litter, M. I. Last Advances on TiO₂-Photocatalytic Removal of Chromium, Uranium and Arsenic. *Curr. Opin. Green Sustainable Chem.* **2017**, *6*, 150–158.
- (83) Vera, M. L.; Traid, H. D.; Henrikson, E. R.; Ares, A. E.; Litter, M. I. Heterogeneous Photocatalytic Cr(VI) Reduction with Short and Long Nanotubular TiO₂ Coatings Prepared by Anodic Oxidation. *Mater. Res. Bull.* **2018**, *97*, 150–157.
- (84) de la Fournière, E. M.; Meichtry, J. M.; Gautier, E. A.; Leyva, A. G.; Litter, M. I. Treatment of Ethylmercury Chloride by Heterogeneous Photocatalysis with TiO₂. *J. Photochem. Photobiol., A* **2021**, *411*, 113205.
- (85) Gopinath, K. P.; Madhav, N. V.; Krishnan, A.; Malolan, R.; Rangarajan, G. Present Applications of Titanium Dioxide for the Photocatalytic Removal of Pollutants from Water: A Review. *J. Environ. Manage.* **2020**, *270*, 110906.
- (86) Gao, X.; Meng, X. Photocatalysis for Heavy Metal Treatment: A Review. *Processes* **2021**, *9*, 1729.
- (87) Luna, A. L.; Dragoe, D.; Wang, K.; Beaunier, P.; Kowalska, E.; Ohtani, B.; Bahena Uribe, D.; Valenzuela, M. A.; Remita, H.; Colbeau-Justin, C. Photocatalytic Hydrogen Evolution Using Ni-Pd/TiO₂: Correlation of Light Absorption, Charge-Carrier Dynamics, and Quantum Efficiency. *J. Phys. Chem. C* **2017**, *121* (26), 14302–14311.
- (88) Peper, J. L.; Gentry, N. E.; Boudy, B.; Mayer, J. M. Aqueous TiO₂ Nanoparticles React by Proton-Coupled Electron Transfer. *Inorg. Chem.* **2022**, *61* (2), 767–777.
- (89) Nedzbal, H. S.; Westbroek, D.; Margavio, H. R. M.; Yang, H.; Noh, H.; Magpantay, S. V.; Donley, C. L.; Kumbhar, A. S.; Parsons, G. N.; Mayer, J. M. Photoelectrochemical Proton-Coupled Electron Transfer of TiO₂ Thin Films on Silicon. *J. Am. Chem. Soc.* **2024**, *146* (15), 10559–10572.

- (90) Zou, K.; Yamamoto, A.; Yoshida, H. Coupling of Hydrogen Radicals Catalyzed by Pt Nanoparticles after Traveling Several Millimeters from TiO₂ Photocatalyst. *Int. J. Hydrogen Energy* **2024**, *91*, 989–996.
- (91) Mahdavi-Shakib, A.; Rich, L. C.; Whittaker, T. N.; Chandler, B. D. Hydrogen Adsorption at the Au/TiO₂ Interface: Quantitative Determination and Spectroscopic Signature of the Reactive Interface Hydroxyl Groups at the Active Site. *ACS Catal.* **2021**, *11* (24), 15194–15202.
- (92) Islam, M. M.; Calatayud, M.; Pacchioni, G. Hydrogen Adsorption and Diffusion on the Anatase TiO₂(101) Surface: A First-Principles Investigation. *J. Phys. Chem. C* **2011**, *115* (14), 6809–6814.
- (93) Calegari Andrade, M. F.; Ko, H.-Y.; Zhang, L.; Car, R.; Selloni, A. Free Energy of Proton Transfer at the Water-TiO₂ Interface from Ab Initio Deep Potential Molecular Dynamics. *Chem. Sci.* **2020**, *11* (9), 2335–2341.
- (94) Panayotov, D. A.; Yates, J. T. Spectroscopic Detection of Hydrogen Atom Spillover from Au Nanoparticles Supported on TiO₂: Use of Conduction Band Electrons. *J. Phys. Chem. C* **2007**, *111* (7), 2959–2964.
- (95) Szczepankiewicz, S. H.; Colussi, A. J.; Hoffmann, M. R. Infrared Spectra of Photoinduced Species on Hydroxylated Titania Surfaces. *J. Phys. Chem. B* **2000**, *104* (42), 9842–9850.
- (96) Sravan Kumar, K. B.; Whittaker, T. N.; Peterson, C.; Grabow, L. C.; Chandler, B. D. Water Poisons H₂ Activation at the Au-TiO₂ Interface by Slowing Proton and Electron Transfer between Au and Titania. *J. Am. Chem. Soc.* **2020**, *142* (12), 5760–5772.
- (97) Mahdavi-Shakib, A.; Whittaker, T. N.; Yun, T. Y.; Sravan Kumar, K. B.; Rich, L. C.; Wang, S.; Rioux, R. M.; Grabow, L. C.; Chandler, B. D. The Role of Surface Hydroxyls in the Entropy-Driven Adsorption and Spillover of H₂ on Au/TiO₂ Catalysts. *Nat. Catal.* **2023**, *6* (8), 710–719.
- (98) Panayotov, D. A.; Yates, J. T. Depletion of Conduction Band Electrons in TiO₂ by Water Chemisorption - IR Spectroscopic Studies of the Independence of Ti-OH Frequencies on Electron Concentration. *Chem. Phys. Lett.* **2005**, *410* (1), 11–17.
- (99) Li, B.; Wu, S.; Gao, X. Theoretical Calculation of a TiO₂-Based Photocatalyst in the Field of Water Splitting: A Review. *Nanotechnol. Rev.* **2020**, *9* (1), 1080–1103.
- (100) Aschauer, U.; Selloni, A. Hydrogen Interaction with the Anatase TiO₂(101) Surface. *Phys. Chem. Chem. Phys.* **2012**, *14* (48), 16595–16602.
- (101) Litke, A.; Su, Y.; Tranca, I.; Weber, T.; Hensen, E. J. M.; Hoffmann, J. P. Role of Adsorbed Water on Charge Carrier Dynamics in Photoexcited TiO₂. *J. Phys. Chem. C* **2017**, *121* (13), 7514–7524.
- (102) Shirai, K.; Fazio, G.; Sugimoto, T.; Selli, D.; Ferraro, L.; Watanabe, K.; Haruta, M.; Ohtani, B.; Kurata, H.; Di Valentin, C.; et al. Water-Assisted Hole Trapping at the Highly Curved Surface of Nano-TiO₂ Photocatalyst. *J. Am. Chem. Soc.* **2018**, *140* (4), 1415–1422.
- (103) Parrino, F.; De Pasquale, C.; Palmisano, L. Influence of Surface-Related Phenomena on Mechanism, Selectivity, and Conversion of TiO₂-Induced Photocatalytic Reactions. *ChemSusChem* **2019**, *12* (3), 589–602.
- (104) Chen, H.-Y. T.; Tosoni, S.; Pacchioni, G. Hydrogen Adsorption, Dissociation, and Spillover on Ru₁₀ Clusters Supported on Anatase TiO₂ and Tetragonal ZrO₂ (101) Surfaces. *ACS Catal.* **2015**, *5* (9), 5486–5495.
- (105) Wu, X.; Li, W.; Sheng, S.; Zhu, L.; Yuan, L.; Liu, J.; Jin, S.; Zhang, Z. Enhanced H₂ Evolution Reaction Due to H Spillover During Electrolytic Reduction of Water on a Au/TiO₂ Electrode. *Electrochem. Commun.* **2021**, *129*, 107085.
- (106) Karim, W.; Spreafico, C.; Kleibert, A.; Gobrecht, J.; VandeVondele, J.; Ekinci, Y.; van Bokhoven, J. A. Catalyst Support Effects on Hydrogen Spillover. *Nature* **2017**, *541* (7635), 68–71.
- (107) Spreafico, C.; Karim, W.; Ekinci, Y.; van Bokhoven, J. A.; VandeVondele, J. Hydrogen Adsorption on Nanosized Platinum and Dynamics of Spillover onto Alumina and Titania. *J. Phys. Chem. C* **2017**, *121* (33), 17862–17872.
- (108) Gao, Z.; Wang, G.; Lei, T.; Lv, Z.; Xiong, M.; Wang, L.; Xing, S.; Ma, J.; Jiang, Z.; Qin, Y. Enhanced Hydrogen Generation by Reverse Spillover Effects over Bicomponent Catalysts. *Nat. Commun.* **2022**, *13* (1), 118.
- (109) Lee, Y. J.; Joo, J. B.; Yin, Y.; Zaera, F. Evaluation of the Effective Photoexcitation Distances in the Photocatalytic Production of H₂ from Water Using Au@Void@TiO₂ Yolk-Shell Nanostructures. *ACS Energy Lett.* **2016**, *1* (1), 52–56.
- (110) Zhu, Y.; Liu, D.; Meng, M. H₂ Spillover Enhanced Hydrogenation Capability of TiO₂ Used for Photocatalytic Splitting of Water: A Traditional Phenomenon for New Applications. *Chem. Commun.* **2014**, *50* (45), 6049–6051.
- (111) Yamazaki, Y.; Mori, K.; Kuwahara, Y.; Kobayashi, H.; Yamashita, H. Defect Engineering of Pt/TiO_{2-x} Photocatalysts via Reduction Treatment Assisted by Hydrogen Spillover. *ACS Appl. Mater. Interfaces* **2021**, *13* (41), 48669–48678.
- (112) Shao, C.; Gao, D.; Zhang, X.; Long, H.; Yu, H. Optimizing H-Adsorption Affinity on Electron-Enriched Pd^{δ-} Active Sites for Efficient Photocatalytic H₂ Evolution. *Appl. Surf. Sci.* **2025**, *680*, 161438.
- (113) Warren, S. C.; Thimsen, E. Plasmonic Solar Water Splitting. *Energy Environm. Sci.* **2012**, *5* (1), 5133–5146.
- (114) Ban, C.; Li, B.; Ma, J.; Feng, Y.; Lin, C.; Chen, Y.; Wang, Y.; Duan, Y.; Zhou, K.; Gan, L.; et al. Plasmonic Au-TiO₂ Interactions for Augmented Photocatalytic Hydrogen Evolution. *Ceram. Int.* **2024**, *50*, 15444–15451.
- (115) Du, L.; Furube, A.; Hara, K.; Katoh, R.; Tachiya, M. Ultrafast Plasmon Induced Electron Injection Mechanism in Gold-TiO₂ Nanoparticle System. *J. Photochem. Photobiol., C* **2013**, *15*, 21–30.
- (116) Kumar, A.; Choudhary, P.; Kumar, A.; Camargo, P. H. C.; Krishnan, V. Recent Advances in Plasmonic Photocatalysis Based on TiO₂ and Noble Metal Nanoparticles for Energy Conversion, Environmental Remediation, and Organic Synthesis. *Small* **2022**, *18* (1), 2101638.
- (117) Deka, T.; G Nair, R. Recent Advancements in Surface Plasmon Resonance and Schottky Junction Assisted Photocatalytic Water Splitting of Noble Metal Decorated Titania: A Review. *Int. J. Hydrogen Energy* **2024**, *59*, 322–342.
- (118) Kamat, P. V.; Jin, S. Semiconductor Photocatalysis: “Tell Us the Complete Story!” *ACS Energy Lett.* **2018**, *3* (3), 622–623.
- (119) Fang, J.; Cao, S.-W.; Wang, Z.; Shahjamali, M. M.; Loo, S. C. J.; Barber, J.; Xue, C. Mesoporous Plasmonic Au-TiO₂ Nanocomposites for Efficient Visible-Light-Driven Photocatalytic Water Reduction. *Int. J. Hydrogen Energy* **2012**, *37* (23), 17853–17861.
- (120) Nadeem, M. A.; Al-Oufi, M.; Wahab, A. K.; Anjum, D.; Idriss, H. Hydrogen Production on Ag-Pd/TiO₂ Bimetallic Catalysts: Is There a Combined Effect of Surface Plasmon Resonance with Schottky Mechanism on the Photo-Catalytic Activity? *ChemistrySelect* **2017**, *2* (9), 2754–2762.
- (121) Yang, X.-F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis. *Acc. Chem. Res.* **2013**, *46* (8), 1740–1748.
- (122) Wang, A.; Li, J.; Zhang, T. Heterogeneous Single-Atom Catalysis. *Nat. Rev. Chem.* **2018**, *2* (6), 65–81.
- (123) Cui, X.; Li, W.; Ryabchuk, P.; Junge, K.; Beller, M. Bridging Homogeneous and Heterogeneous Catalysis by Heterogeneous Single-Metal-Site Catalysts. *Nat. Catal.* **2018**, *1* (6), 385–397.
- (124) Lang, R.; Du, X.; Huang, Y.; Jiang, X.; Zhang, Q.; Guo, Y.; Liu, K.; Qiao, B.; Wang, A.; Zhang, T. Single-Atom Catalysts Based on the Metal-Oxide Interaction. *Chem. Rev.* **2020**, *120* (21), 11986–12043.
- (125) Liang, X.; Fu, N.; Yao, S.; Li, Z.; Li, Y. The Progress and Outlook of Metal Single-Atom-Site Catalysis. *J. Am. Chem. Soc.* **2022**, *144* (40), 18155–18174.
- (126) Gao, C.; Low, J.; Long, R.; Kong, T.; Zhu, J.; Xiong, Y. Heterogeneous Single-Atom Photocatalysts: Fundamentals and Applications. *Chem. Rev.* **2020**, *120* (21), 12175–12216.
- (127) Wang, L.; Wang, D.; Li, Y. Single-Atom Catalysis for Carbon Neutrality. *Carbon Energy* **2022**, *4* (6), 1021–1079.

- (128) Xu, F.; Weng, B. Photocatalytic Hydrogen Production: An Overview of New Advances in Structural Tuning Strategies. *J. Mater. Chem. A* **2023**, *11* (9), 4473–4486.
- (129) Tang, Y.; Wang, Y.-G.; Li, J. Theoretical Investigations of Pt1@CeO₂ Single-Atom Catalyst for CO Oxidation. *J. Phys. Chem. C* **2017**, *121* (21), 11281–11289.
- (130) DeRita, L.; Resasco, J.; Dai, S.; Boubnov, A.; Thang, H. V.; Hoffman, A. S.; Ro, I.; Graham, G. W.; Bare, S. R.; Pacchioni, G.; et al. Structural Evolution of Atomically Dispersed Pt Catalysts Dictates Reactivity. *Nat. Mater.* **2019**, *18* (7), 746–751.
- (131) Ye, X.; Wang, H.; Lin, Y.; Liu, X.; Cao, L.; Gu, J.; Lu, J. Insight of the Stability and Activity of Platinum Single Atoms on Ceria. *Nano Res.* **2019**, *12* (6), 1401–1409.
- (132) Jeong, H.; Shin, D.; Kim, B.-S.; Bae, J.; Shin, S.; Choe, C.; Han, J. W.; Lee, H. Controlling the Oxidation State of Pt Single Atoms for Maximizing Catalytic Activity. *Angew. Chem., Int. Ed.* **2020**, *59* (46), 20691–20696.
- (133) Li, Y.; Frenkel, A. I. Deciphering the Local Environment of Single-Atom Catalysts with X-Ray Absorption Spectroscopy. *Acc. Chem. Res.* **2021**, *54* (11), 2660–2669.
- (134) Hu, X.; Song, J.; Luo, J.; Zhang, H.; Sun, Z.; Li, C.; Zheng, S.; Liu, Q. Single-Atomic Pt Sites Anchored on Defective TiO₂ Nanosheets as a Superior Photocatalyst for Hydrogen Evolution. *J. Energy Chem.* **2021**, *62*, 1–10.
- (135) Xing, J.; Chen, J. F.; Li, Y. H.; Yuan, W. T.; Zhou, Y.; Zheng, L. R.; Wang, H. F.; Hu, P.; Wang, Y.; Zhao, H. J.; et al. Stable Isolated Metal Atoms as Active Sites for Photocatalytic Hydrogen Evolution. *Chem. Eur. J.* **2014**, *20* (8), 2138–2144.
- (136) Xue, Z.; Yan, M.; Zhang, Y.; Xu, J.; Gao, X.; Wu, Y. Understanding the Injection Process of Hydrogen on Pt₁-TiO₂ Surface for Photocatalytic Hydrogen Evolution. *Appl. Catal., B* **2023**, *325*, 122303.
- (137) Resasco, J.; Yang, F.; Mou, T.; Wang, B.; Christopher, P.; Resasco, D. E. Relationship between Atomic Scale Structure and Reactivity of Pt Catalysts: Hydrodeoxygenation of m-Cresol over Isolated Pt Cations and Clusters. *ACS Catal.* **2020**, *10* (1), 595–603.
- (138) Li, Q.; Yan, G.; Vlachos, D. G. Theoretical Insights into H₂ Activation over Anatase TiO₂ Supported Metal Adatoms. *ACS Catal.* **2024**, *14* (2), 886–896.
- (139) Kuo, C.-T.; Lu, Y.; Kovarik, L.; Engelhard, M.; Karim, A. M. Structure Sensitivity of Acetylene Semi-Hydrogenation on Pt Single Atoms and Subnanometer Clusters. *ACS Catal.* **2019**, *9* (12), 11030–11041.
- (140) Di Liberto, G.; Cipriano, L. A.; Pacchioni, G. Role of Dihydride and Dihydrogen Complexes in Hydrogen Evolution Reaction on Single-Atom Catalysts. *J. Am. Chem. Soc.* **2021**, *143* (48), 20431–20441.
- (141) Zhang, Q.; Lee, I.; Joo, J. B.; Zaera, F.; Yin, Y. Core-Shell Nanostructured Catalysts. *Acc. Chem. Res.* **2013**, *46* (8), 1816–1824.
- (142) Fu, Y.-s.; Li, J.; Li, J. Metal/Semiconductor Nanocomposites for Photocatalysis: Fundamentals, Structures, Applications and Properties. *Nanomaterials* **2019**, *9*, 359.
- (143) Zaera, F. Designing Sites in Heterogeneous Catalysis: Are We Reaching Selectivities Competitive with Those of Homogeneous Catalysts? *Chem. Rev.* **2022**, *122* (9), 8594–8757.
- (144) Shafiee, A.; Rabiee, N.; Ahmadi, S.; Baneshi, M.; Khatami, M.; Irvani, S.; Varma, R. S. Core-Shell Nanophotocatalysts: Review of Materials and Applications. *ACS Applied Nano Materials* **2022**, *5* (1), 55–86.
- (145) Lee, I.; Albitzer, M. A.; Zhang, Q.; Ge, J.; Yin, Y.; Zaera, F. New Nanostructured Heterogeneous Catalysts with Increased Selectivity and Stability. *Phys. Chem. Chem. Phys.* **2011**, *13* (7), 2449–2456.
- (146) Zhang, Q.; Lima, D. Q.; Lee, I.; Zaera, F.; Chi, M.; Yin, Y. A Highly Active Titanium Dioxide Based Visible-Light Photocatalyst with Nonmetal Doping and Plasmonic Metal Decoration. *Angew. Chem., Int. Ed.* **2011**, *50* (31), 7088–7092.
- (147) Joo, J. B.; Zhang, Q.; Dahl, M.; Lee, I.; Goebel, J.; Zaera, F.; Yin, Y. Control of the Nanoscale Crystallinity in Mesoporous TiO₂ Shells for Enhanced Photocatalytic Activity. *Energy Environm. Sci.* **2012**, *5* (4), 6321–6327.
- (148) Joo, J. B.; Zhang, Q.; Lee, I.; Dahl, M.; Zaera, F.; Yin, Y. Mesoporous Anatase Titania Hollow Nanostructures Through Silica-Protected Calcination. *Adv. Funct. Mater.* **2012**, *22* (1), 166–174.
- (149) Joo, J. B.; Zhang, Q.; Dahl, M.; Zaera, F.; Yin, Y. Synthesis, Crystallinity Control, and Photocatalysis of Nanostructured Titanium Dioxide Shells. *J. Mater. Res.* **2013**, *28* (03), 362–368.
- (150) Joo, J. B.; Lee, I.; Dahl, M.; Moon, G. D.; Zaera, F.; Yin, Y. Controllable Synthesis of Mesoporous TiO₂ Hollow Shells: Toward an Efficient Photocatalyst. *Adv. Funct. Mater.* **2013**, *23* (34), 4246–4254.
- (151) Joo, J. B.; Dahl, M.; Li, N.; Zaera, F.; Yin, Y. Tailored Synthesis of Mesoporous TiO₂ Hollow Nanostructures for Catalytic Applications. *Energy Environm. Sci.* **2013**, *6* (7), 2082–2092.
- (152) Plascencia-Hernández, F.; Valverde-Aguilar, G.; Singh, N.; Derk, A. R.; McFarland, E. W.; Zaera, F.; Cayetano-Castro, N.; Vázquez-Arreguín, R.; Valenzuela, M. A. Photocatalytic Hydrogen Production from Aqueous Methanol Solution Using Pt Nanocatalysts Supported on Mesoporous TiO₂ Hollow Shells. *J. Sol-Gel Sci. Technol.* **2016**, *77* (1), 39–47.
- (153) Joo, J. B.; Liu, H.; Lee, Y. J.; Dahl, M.; Yu, H.; Zaera, F.; Yin, Y. Tailored Synthesis of C@TiO₂ Yolk-Shell Nanostructures for Highly Efficient Photocatalysis. *Catal. Today* **2016**, *264*, 261–269.
- (154) Chiu, Y.-H.; Naghadeh, S. B.; Lindley, S. A.; Lai, T.-H.; Kuo, M.-Y.; Chang, K.-D.; Zhang, J. Z.; Hsu, Y.-J. Yolk-Shell Nanostructures as an Emerging Photocatalyst Paradigm for Solar Hydrogen Generation. *Nano Energy* **2019**, *62*, 289–298.
- (155) He, Q.; Sun, H.; Shang, Y.; Tang, Y.; She, P.; Zeng, S.; Xu, K.; Lu, G.; Liang, S.; Yin, S.; et al. Au@TiO₂ Yolk-Shell Nanostructures for Enhanced Performance in Both Photoelectric and Photocatalytic Solar Conversion. *Appl. Surf. Sci.* **2018**, *441*, 458–465.
- (156) Yang, J.; Wang, D.; Han, H.; Li, C. Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis. *Acc. Chem. Res.* **2013**, *46* (8), 1900–1909.
- (157) Bai, S.; Yin, W.; Wang, L.; Li, Z.; Xiong, Y. Surface and Interface Design in Cocatalysts for Photocatalytic Water Splitting and CO₂ Reduction. *RSC Adv.* **2016**, *6* (62), 57446–57463.
- (158) Meng, A.; Zhang, L.; Cheng, B.; Yu, J. Dual Cocatalysts in TiO₂ Photocatalysis. *Adv. Mater.* **2019**, *31* (30), 1807660.
- (159) Nakamura, R.; Imanishi, A.; Murakoshi, K.; Nakato, Y. In Situ FTIR Studies of Primary Intermediates of Photocatalytic Reactions on Nanocrystalline TiO₂ Films in Contact with Aqueous Solutions. *J. Am. Chem. Soc.* **2003**, *125* (24), 7443–7450.
- (160) Li, K.; Peng, B.; Peng, T. Recent Advances in Heterogeneous Photocatalytic CO₂ Conversion to Solar Fuels. *ACS Catal.* **2016**, *6* (11), 7485–7527.
- (161) Zheng, Y.; Zhang, W.; Li, Y.; Chen, J.; Yu, B.; Wang, J.; Zhang, L.; Zhang, J. Energy Related CO₂ Conversion and Utilization: Advanced Materials/Nanomaterials, Reaction Mechanisms and Technologies. *Nano Energy* **2017**, *40*, 512–539.
- (162) Li, X.; Yu, J.; Jaroniec, M.; Chen, X. Cocatalysts for Selective Photoreduction of CO₂ into Solar Fuels. *Chem. Rev.* **2019**, *119* (6), 3962–4179.
- (163) Gao, J.; Ren, D.; Guo, X.; Zakeeruddin, S. M.; Grätzel, M. Sequential Catalysis Enables Enhanced C-C Coupling Towards Multi-Carbon Alkenes and Alcohols in Carbon Dioxide Reduction: A Study on Bifunctional Cu/Au Electrocatalysts. *Faraday Discuss.* **2019**, *215* (0), 282–296.
- (164) Choukroun, D.; Daems, N.; Kenis, T.; Van Everbroeck, T.; Hereijgers, J.; Altantzis, T.; Bals, S.; Cool, P.; Breugelmanns, T. Bifunctional Nickel-Nitrogen-Doped-Carbon-Supported Copper Electrocatalyst for CO₂ Reduction. *J. Phys. Chem. C* **2020**, *124* (2), 1369–1381.
- (165) Shang, X.; Tang, J.-H.; Sun, Y. Recent Advances in Electrocatalytic Organic Transformations Coupled with H Evolution. *Water Photo- and Electro-Catalysis* **2024**, 303–320.