

UC Berkeley

UC Berkeley Previously Published Works

Title

New Materials for Photoelectrochemical Energy Conversion

Permalink

<https://escholarship.org/uc/item/5fm9d2fc>

Journal

Annual Review of Physical Chemistry, 77(1)

ISSN

0066-426X

Author

Ager, Joel W

Publication Date

2026-04-20

DOI

10.1146/annurev-physchem-082324-020516

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

New Materials for Photoelectrochemical Energy Conversion

Joel W. Ager^{1,2}

¹Materials and Chemical Sciences Divisions, Lawrence Berkeley National Laboratory, Berkeley, California, USA; email: jwager@lbl.gov

²Department of Materials Science and Engineering, University of California, Berkeley, California, USA

ANNUAL
REVIEWS **CONNECT**

www.annualreviews.org

- Download figures
- Navigate cited references
- Keyword search
- Explore related articles
- Share via email or social media

Annu. Rev. Phys. Chem. 2026. 77:177–99

First published as a Review in Advance on
December 23, 2025

The *Annual Review of Physical Chemistry* is online at
physchem.annualreviews.org

<https://doi.org/10.1146/annurev-physchem-082324-020516>

Copyright © 2026 by the author(s). This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (CC BY-NC-ND 4.0), which permits any noncommercial use, sharing, distribution, and reproduction in any medium or format, provided the original author(s) and source are credited; this license does not permit sharing adapted material derived from this article or parts of it. Images or other third-party material in this article are included in the article's Creative Commons license unless indicated otherwise; see credit lines for license information.



Keywords

photoelectrocatalysis, energy conversion, photocatalysis, photosynthesis

Abstract

This review concerns light-to-chemical energy conversion, focusing on approaches that could be driven by terrestrial sunlight to produce hydrogen and/or reduce carbon dioxide. Recent advances in photocatalytic (PC) and photoelectrocatalytic (PEC) materials are covered. In both approaches, the electron-hole pairs that are created by photon absorption must travel in specific directions to the sites that mediate multielectron bond making/breaking redox reactions. Thermodynamic requirements for materials stability are described, although some recently discovered materials appear to be exceptions. For PC materials, the importance of rate matching between reduction and oxidation processes and the mass transfer of intermediates and products is emphasized. Surprisingly, metal sulfides appear to be promising for PC carbon dioxide reduction. For PEC materials, recent work elucidating the elementary step mechanism for oxygen evolution on metal oxides and the discovery of chalcogen-based photocathode materials capable of sustained light-driven CO₂ reduction are discussed.

CO₂R: CO₂ reduction

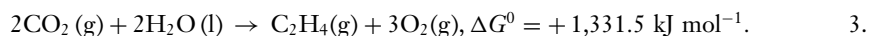
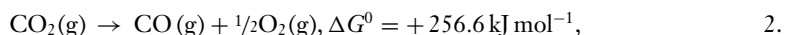
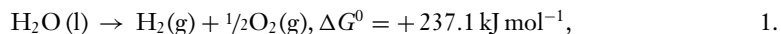
ETL: electron
transport layer

1. INTRODUCTION

For a chemical reaction to be spontaneous, it must have a negative change in Gibbs energy ΔG . However, life on Earth would not be possible if all its chemical processes were proceeding to equilibrium in this way (1). Instead, solar radiation drives uphill ($\Delta G > 0$) processes via photosynthesis. Understandably, it has been of interest since the nineteenth century to learn how photosynthesis works and, more recently, to make systems that have its light-to-chemical energy conversion function (2, 3).

This review focuses on single materials and simple arrangements of materials that can, when illuminated, drive uphill chemical reactions. For semiconductor photocatalysts, all the required steps of light absorption, electron and hole transport, and redox chemistry happen in a single system, which is often a nanoparticle. In photoelectrocatalysis, one of the charges created by photon absorption (i.e., an electron or a hole) participates in redox chemistry at the surface of the photoelectrodes, whereas the other is collected via a conductive contact in an external circuit. For this reason, there are two different types of photoelectrodes. In a photoanode, light-generated holes drive oxidation reactions, whereas in photocathodes, light-generated electrons drive reduction reactions. In this arrangement, it is possible to apply an external bias.

Three examples of relevant, uphill, reactions are



Water splitting is the reaction in Equation 1. The reactions in Equations 2 and 3 use the same substrates as photosynthesis, i.e., CO₂ and water, and make potential chemical building blocks (e.g., the use of CO in Fischer-Tropsch synthesis) or platform chemicals in the case of ethylene. Clearly, practical systems that could use light to drive these types of reactions would have important consequences for fuel production and chemical manufacturing (4–6).

Experimental reports of water splitting and CO₂ reduction (CO₂R) facilitated by semiconductor electrodes and particles date back to the 1970s (7, 8), and interest in artificial photosynthesis and solar fuels continues to this day (3, 9–15). This review concentrates on research, primarily experimental, that addresses the fundamental physical chemistry questions in solar-to-chemical energy conversion. As discussed below, as a first step in driving uphill chemical reactions with light, the carrier populations in an absorbing material or molecule must be driven out of equilibrium. Here, we focus on systems in which nonequilibrium (minority) carriers directly (or close to directly) participate in the reaction. Thus, the well-developed fields of CO₂R performed with metal electrocatalysts (16, 17) and of photoelectrodes integrated with protection layers [i.e., hole transport layers (HTLs) and electron transport layers (ETLs)] and metal cocatalysts are not in scope (18). Additionally, systems invoking plasmonic effects are not in scope (19–22). What is in scope are semiconductor photocatalysts that have been reported to drive, when illuminated, uphill chemical reactions (e.g., Equations 1–3). The focus is on CO₂R with water as the proton source; in this case, stoichiometric amounts of O₂ should be produced. Additionally, semiconductor photoelectrodes in which nonequilibrium carriers drive oxidation or reduction reactions (i.e., photoanodes and photocathodes) associated with uphill chemical reactions are covered.

The review begins with an overview of the essential requirements for light-to-chemical energy conversion via redox reactions. Next, recent work in semiconductor photocatalysis is reviewed. Here, it is important to distinguish systems that catalyze downhill processes, such as

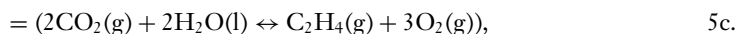
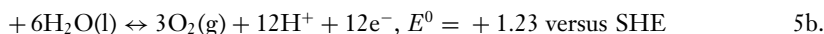
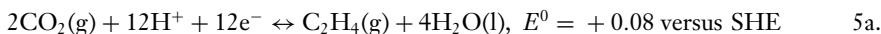
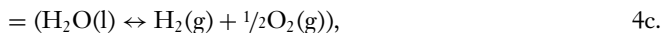
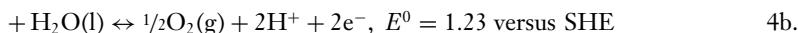
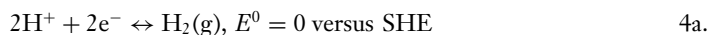
dye degradation or H₂ production aided by a sacrificial reagent, from photosynthetic systems capable of driving uphill processes (23, 24). The limitations of the classic band edge diagrams used to depict the process and search for new materials are emphasized. Also, recent work is showing that, surprisingly, mass-transfer effects play a role in the reaction kinetics in spite of the low turnover frequencies and apparent quantum efficiencies that are typical of these systems (25).

We also consider a subset of photoelectrocatalytic (PEC) approaches (see 26 for a full taxonomy) in which the photogenerated carriers are involved directly in the catalysis. Metal oxide photoanodes composed of n-type materials that perform the oxygen evolution reaction (OER) fall into this category. In n-type materials, electrons are the majority carrier, and in the dark, the hole concentration is very small. However, under illumination, the hole concentration can increase by orders of magnitude, and if holes can be transported to the electrode surface, oxidative chemistry is possible. Recently, there has been considerable experimental and theoretical progress in understanding the elementary step mechanisms of OER performed by holes in semiconductor photoanodes and in identifying the specific surface states that are involved in the catalysis (27).

Comparatively, there has been far less progress with photocathode materials that can perform CO₂R, particularly in aqueous conditions. Materials' stability has been the main roadblock, and in this context, we examine some very recent experiments on PEC CO₂R and critically examine the origin of their stability.

2. ESSENTIAL LIGHT-TO-CHEMICAL ENERGY CONVERSION

It is important to realize that the reactions of interest, e.g., water splitting, cannot be driven thermally. Following the analysis of Fletcher (28), even though the reaction in Equation 1 has a positive entropy change, and could conceivably have a negative Gibbs energy of reaction at high temperatures, the temperatures required to do this (>3,000 K) far exceed those available from heat sources and nuclear reactors. What makes it possible to drive these reactions (actually in both directions) under ambient conditions is the introduction of an additional reactant, namely electrons. Using the reactions in Equations 1 and 3 as examples, they can be written as sums of reduction and oxidation reactions (16):



where SHE designates the standard hydrogen electrode and E^0 is the standard electrode potential at the reference conditions (298.15 K, 1-atm pressure for gas phase species, and unit activity for aqueous species).

Controlling the concentration, and hence the chemical potential, of chemical species will drive a reaction in a given direction: For example, increasing the H₂ pressure in the reaction in Equation 4a with all other reactants at their reference conditions would drive the reaction to the left. Importantly, electrons appear on the left- and right-hand sides of the reactions in

PEC:
photoelectrocatalytic

OER: oxygen
evolution reaction

HER: hydrogen evolution reaction

PC: photocatalytic

HOR: hydrogen oxidation reaction

ORR: oxygen reduction reaction

Equations 4a and 4b, respectively (similar to the reactions in Equations 5a and 5b), and control of their electrochemical (EC) potential is possible. Thus, the essence of electrical to chemical energy is to control, separately, the EC potential of the electrons in the reduction and oxidation reactions (29). For example, a more negative EC potential in Equation 4a and a more positive potential in Equation 4b will drive the reaction in Equation 4c in the water-splitting direction, to the right. And, of course, the reaction in Equation 4c can be run in the opposite direction, as in hydrogen fuel cells, performing chemical-to-electrical energy conversion (30).

Following Würfel (31) and Osterloh (24) [see also Schleuning et al. (32)], we now discuss how light can be used to create the desired EC potential differences, focusing on solid materials as the photoabsorbers. The first requirement is that the material must absorb light. Second, crucially, the light absorption must create carriers (strictly, quasiparticles) of the opposite sign (i.e., electrons and holes) capable of transport in the material. That is, they must not immediately recombine after their creation. A third requirement is an asymmetry in the system that leads to charge separation. These three requirements must be fulfilled for light-to-electrical power conversion as in photovoltaic solar cells (33, 34), noting that band bending, p–n junctions, and built-in electric fields, while often invoked, are not essential. For the next step of light-to-chemical energy conversion, the charge separation must lead to selective redox reactions. Taking the reaction in Equation 4c as an example, nonequilibrium electrons must drive the reaction in Equation 4a to the right, producing H_2 , while nonequilibrium holes drive the reaction in Equation 4b to the right, producing O_2 .

Semiconductor photocatalysts provide the simplest conceptual picture. Here, metal oxides are the most-investigated class of materials. In the conventional picture, which is shown schematically in **Figure 1a** for water splitting, holes in the valence band are thought to go to surface sites or cocatalysts capable of oxidation reactions, whereas electrons in the conduction band go to reduction sites. But how do the carriers know where to go? As discussed in more detail in Section 4, in semiconductor photocatalysis, it is thought that surfaces can provide the needed asymmetry. This can be achieved with cocatalysts, e.g., by situating hydrogen evolution reaction (HER)/ CO_2 R catalysts such as Pt or Cu on one part of the surface and OER catalysts (e.g., Rh) on another (35). This emphasizes the point that photocatalytic (PC) (and PEC) activity is not a property of the bulk material. Some sort of surface modification, intentional or unintentional, is needed to enforce charge separation and the subsequent redox chemistry.

Additionally, the possibility of the reverse reaction needs to be included (23, 24). At an oxidation site, the reverse of the reduction reaction [e.g., hydrogen oxidation reaction (HOR) or organic oxidation] needs to be suppressed. A similar requirement exists at the reduction site where the oxygen reduction reaction (ORR), the reverse of Equation 4b, is always thermodynamically favorable compared to any CO_2 R reaction and to water/proton reduction. For semiconductor PC materials, we see that this is a challenge to increasing efficiency.

In the PEC approach, as discussed above and as shown schematically in **Figure 1b**, the half reactions are separated, e.g., OER for photoanodes and HER/ CO_2 R for photocathodes (36). The same requirements apply: The photoelectrodes must absorb light, have sufficiently long-lived carriers, and have charge-selective contacts/catalysts. However, in this idealized case, only one carrier is involved in the surface chemistry for each photoelectrode, as the other one goes to another photoelectrode or to a counterelectrode in another part of the circuit. As stated above, there is considerable work on modifying semiconductor surfaces to achieve this charge separation function through protective layers that facilitate the transport of a specific carrier: ETLs for electrons and HTLs for holes (18). Here I focus on the very basic case where the semiconductor surface, with minimal modification, is capable of selective catalysis, thus enforcing the asymmetry needed in charge transport.

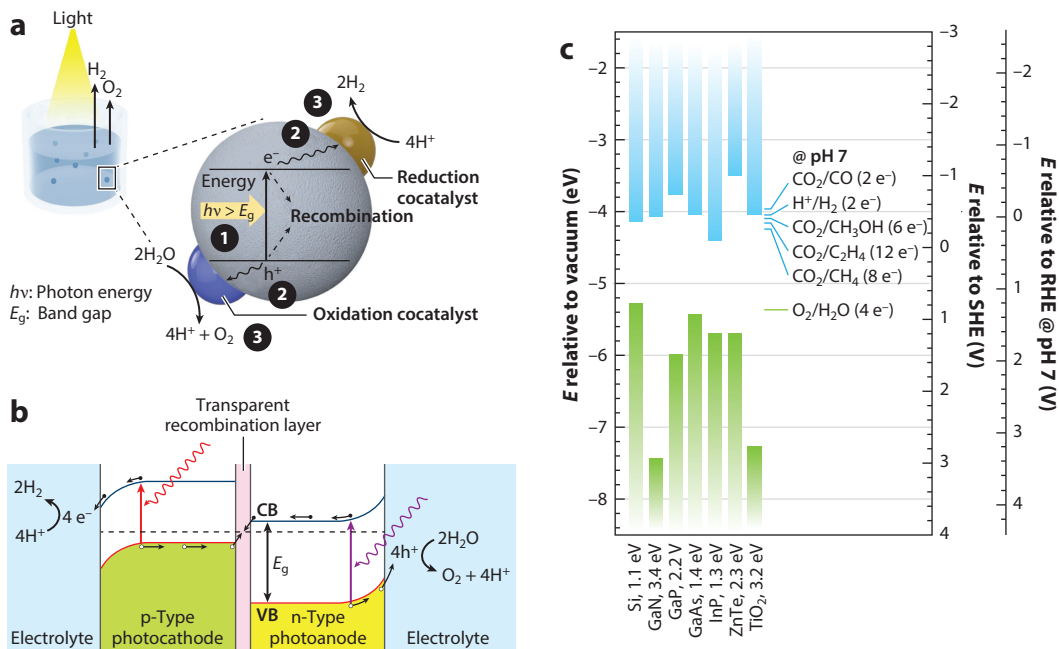


Figure 1

Energetic requirements for light-to-chemical energy conversion using semiconductor absorbers. (a) PC solar water splitting using a semiconductor absorber combined with HER and OER catalysts; the concept for PC CO_2 R is similar. ① Electrons and holes are generated by the absorption of light. ② Photon-excited electrons and holes diffuse to the HER (CO_2 R) and OER catalysts, respectively, with recombination being an undesirable loss process. ③ Electrons reduce H^+ to H_2 (Equation 4a), and holes oxidize water to O_2 (Equation 4b). Panel adapted from Reference 88. (b) Photoelectrocatalytic water splitting with an idealized tandem-junction photoanode and photocathode device. Proton conduction in the electrolyte from the anode to the cathode is required for continuous operation. Panel adapted from Reference 36. (c) Schematic band alignment for selected group IV, III-V, II-VI, and oxide semiconductors with the valence band shaded in green and the conduction band in blue. The equilibrium potentials for CO_2 reduction, the hydrogen evolution, and water oxidation reactions are also shown for pH 7, a typical experimental condition. Panel adapted from Reference 15 (CC BY 4.0). Abbreviations: CB, conduction band; CO_2 R, CO_2 reduction; HER, hydrogen evolution reaction; OER, oxygen evolution reaction; PC, photocatalytic; RHE, reversible hydrogen electrode; SHE, standard hydrogen electrode; VB, valence band.

At this point, the explanation resembles standard descriptions in the literature that lead to the band diagram shown in **Figure 1c**. For photocatalysis, it is thought that the conduction band minimum (CBM) and valence band maximum (VBM) must straddle the standard redox potentials of the reactions of interest. More specifically, it is thought that the CBM must be more negative than the standard redox potential (E^0) of, e.g., HER or CO_2 R, and the VBM must be more positive. The idea here is that the nonequilibrium concentrations of the carriers resulting from light illumination separately change the EC potential of electrons and holes (this phenomenon is also called quasi-Fermi level splitting). Under sufficiently strong illumination, the EC potential of electrons can approach the CBM, and the EC potential of holes can approach the VBM. Under these nonequilibrium conditions, redox reactions such as those in Equations 4a and 4b can be driven separately by electrons and holes, and light-to-chemical energy conversion (that is, driving an uphill chemical reaction) is possible.

There is a similar picture for PEC, except that band bending that results from the equilibrium of carriers in the semiconductor with the redox couples in the electrolyte is considered (37). For simplicity, a paired semiconductor photocathode (p-type) and photoanode (n-type) are depicted in **Figure 1b**. At equilibrium, the band bending depletes holes at the surface of the photocathode

CBM: conduction band minimum

VBM: valence band maximum

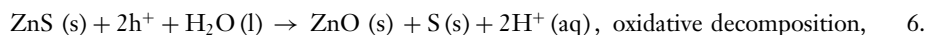
and depletes electrons at the surface of the photoanode. Under illumination, electrons in the photocathode are available for reduction reactions, and holes in the photoanode are available for oxidation reactions. The idea that this type of tandem, similar to the tandem function of chlorophyll in natural photosynthesis (38, 39), could drive water splitting and similar reactions without any external power source goes back to the 1970s (40).

At this point, the reader might think that it would be straightforward to search computationally for materials with the requisite band edge positions, leading to promising materials for solar-to-chemical energy conversion. Indeed, a combination of computation and high-throughput experimentation has been used to screen for both PC (41–43) and PEC (44, 45) materials. But, objectively, these efforts have not yielded materials that are substantially superior, in terms of either activity or stability, compared to those known for years, e.g., TiO_2 and SrTiO_3 for solar-driven PC water splitting (46–49), C_3N_4 for PC CO_2R (50), or to any photocathode capable of stable CO_2R operation without isolation via ETLs (51). It is thus reasonable to question whether there are aspects not shown in **Figure 1** that need to be considered.

This review takes the point of view that **Figure 1** is inadequate for the multielectron redox reactions that are required for chemical bond making/breaking. Two main points are emphasized. Firstly, the lines showing the alignment of standard redox potentials E^0 are drawn for the hypothetical case of concerted transfer, e.g., in the case of the OER (Equation 4b) of four holes and four protons. In fact, the reaction happens step-by-step, and each of the elementary steps should have its own standard potential. Moreover, as argued recently by Peper & Mayer (52), the charge transfer events themselves will shift the band edges, particularly in the limit of small particles where charging will modify the band structure. Secondly, electrons and holes in the extended states that form the CBM and VBM cannot engage in chemical reactions; they need to be localized to participate in electrochemistry. We see that this essential point is left out of most analyses.

3. MATERIALS STABILITY

Here, I briefly discuss the standard picture of EC stability, as it is common to both the photocatalysts and PEC materials in this review. A useful thermodynamic model was introduced by Gerischer (53). The photoexcited electrons and holes should perform the desired redox chemistry as opposed to engaging in reactions that will decompose the material, as illustrated for ZnS:



Using this criterion and taking water splitting as an example (half reactions for CO_2R have very similar energetics), we see that for photoanodes, the potential at which the material decomposes by oxidation should lie below the VBM (**Figure 2a**). Similarly, for photocathodes, the reduction potential for material decomposition should lie above the CBM.

Chen & Wang (54) performed a computational screen on this basis (**Figure 2b**). Some known experimental trends are consistent with this analysis. For example, while no materials in the study were found to be oxidatively stable by the criterion in **Figure 2a**, metal oxides known to be stable for PEC water oxidation (e.g., TiO_2 , Fe_2O_3) have their decomposition potentials below $E^0(\text{O}_2/\text{H}_2\text{O})$, suggesting that they should be kinetically stable. In principle, a photocatalyst should be stable against both oxidation and reduction. We see that sulfides (e.g., ZnS, CdS) and nitrides (e.g., Ta_3N_4) are predicted to be stable against reduction but not oxidation. This would seem to preclude these classes of materials as photocatalysts and photocathodes for CO_2R , but we

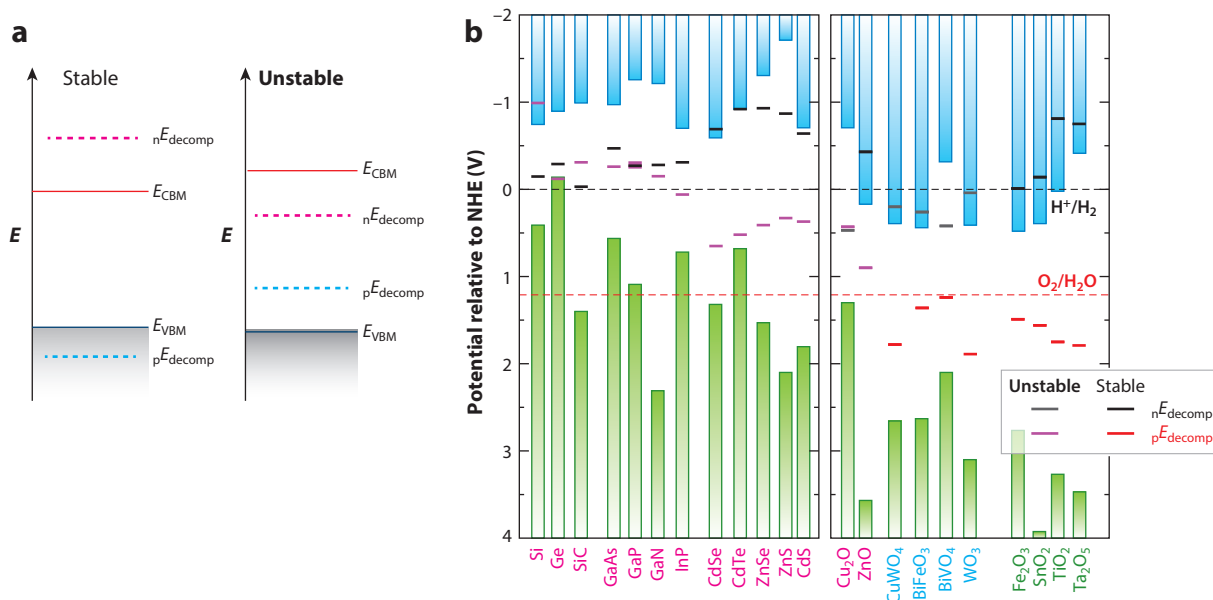


Figure 2

Stability of photocatalytic and photoelectrocatalytic materials. (a) If the potential of oxidative (reductive) decomposition (dashed lines), lies below (above) the VBM (CBM), material is thermodynamically stable. If the decomposition potentials lie in the bandgap, material decomposition would be favorable under electrocatalytic or photoelectrocatalytic conditions. (b) Thermodynamic stability analysis of selected semiconductors is shown (pH = 0). Most metal oxides are kinetically stable for PEC OER, with the decomposition potential lying below $E^0(\text{O}_2/\text{H}_2\text{O})$. Sulfides and tellurides are predicted to be unstable for PEC OER because the decomposition potential is above $E^0(\text{O}_2/\text{H}_2\text{O})$. Panel b adapted with permission from Reference 54; copyright 2012 American Chemical Society. Abbreviations: CBM, conduction band minimum; NHE, normal hydrogen electrode; OER, oxygen evolution reaction; PEC, photoelectrocatalytic; VBM, valence band maximum.

see below that they are, surprisingly, quite promising for this application. This knowledge gap is emphasized in this review.

4. PHOTOCATALYSTS

There are many reviews on PC water splitting and CO₂R with semiconductor nanoparticles (55–57), including the comprehensive and still-relevant work of Habisreutinger et al. (35). Here, we review recent results in sulfide-based materials and discuss what is known about the elementary step mechanism. We raise some fundamental and unanswered questions regarding matching the oxidation and reduction reactions. We discuss two water-splitting reports that emphasize the importance of selective catalysts. Finally, we discuss a very recent report of PC CO₂R performed in a gas diffusion electrode (GDE) geometry, which could point the way to both improved activity and a deeper fundamental understanding of the mechanism.

4.1. Recent Photocatalytic CO₂ Reduction Reports

This review focuses on PC CO₂R experiments that follow recommended best practices (35, 58). First, ¹³C labeling must be performed to confirm that carbon-containing reaction products are from the CO₂ reactant as opposed to from some other source. Second, referring to the reactions in Equations 2 and 3, stoichiometric oxygen production must be reported. For this reason, we do not emphasize experimental reports that are performed with a sacrificial donor (hole scavenger) like

GDE: gas diffusion electrode

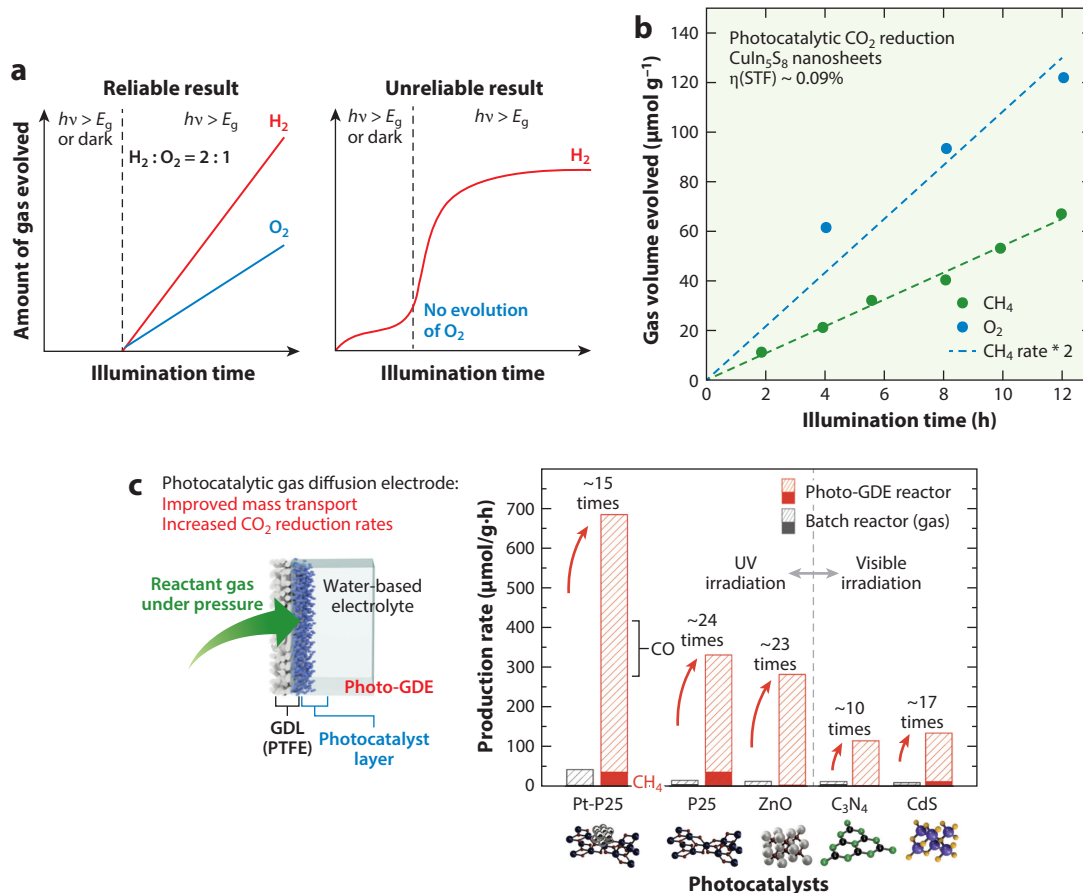
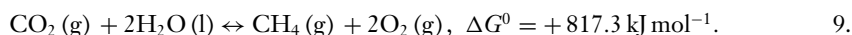
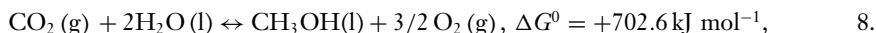


Figure 3

PC water splitting and CO_2 reduction. (a) For overall light-to-chemical energy conversion in PC water splitting, H_2 and O_2 must be observed in a 2:1 stoichiometric ratio. Panel a adapted with permission from Reference 61; copyright 2019 Royal Society of Chemistry. (b) PC CO_2 reduction on thin $CuIn_5S_8$ layers; stoichiometric production of methane and O_2 (2:1) was reported. Panel b based on data from Reference 72. (c) PC CO_2 reduction using a semiconductor nanoparticle integrated with a GDE. Improved mass transfer of reactants (e.g., CO_2 , water) and intermediates/products leads to a more than 10 times improvement in activity for TiO_2 , ZnO, C_3N_4 , and CdS photocatalysts. Panel c adapted from Reference 25. Abbreviations: GDE, gas diffusion electrode; GDL, gas diffusion layer; PC, photocatalytic; PTFE, polytetrafluoroethylene; STF, solar to fuel; UV, ultraviolet.

triethanolamine (TEOA) (59, 60). As emphasized in **Figure 3a**, reliable photocatalysis efficiency claims are supported by data showing linear growth of both the reduction and oxidation products in time and in the expected stoichiometric ratios (61), e.g., 2:1 for $H_2:O_2$ in water splitting in Equation 1, 2:1 for $CO:O_2$ for Equation 2, 2:3 for methanol: O_2 for Equation 8, and 1:2 for $CH_4:O_2$ for Equation 9:



Still, we mention, for completeness, some intriguing recent PC CO_2R studies that did not report a steady-state stoichiometric formation of O_2 . Kang et al. (62) reported that $CuO/CuFeO_2/Pt$

heterostructures produced aliphatic acids up to C₆ (citric acid) in a thin geometry under PC (no-bias) conditions. The authors invoked a Z-scheme mechanism in which CuO drove the CO₂R reactions and CuFeO₂ drove water oxidation. Oxygen was detected, but in substoichiometric amounts. Solar-to-chemical conversion efficiencies, relative to simulated 1 sun (AM1.5G) illumination, of nearly 3% were reported. Interestingly, when operated in PEC mode, formate was the major product and O₂, formed at the counterelectrode, was detected at the expected 2:1 ratio. Wu et al. (63) reported that the PC CO₂R activity of Cu₂O is facet dependent: The (100) facet is unreactive, while the (110) facet can produce methanol with an initial quantum efficiency of 72%. In this study, the methanol concentration in a closed reactor was monitored as a function of time. It reached a maximum after a few minutes and then declined, indicating that methanol was being consumed, eventually reaching a steady state that the authors attributed to equal rates of production and consumption. Oxygen was also observed, but in substoichiometric amounts and with a different time signature. A possible rationalization for decoupled reduction and oxidation processes is discussed below in Section 4.3.

For most metal oxides, the band edge straddling picture shown in **Figure 1c** is thought to be satisfied due to the very positive position of the O(2p) level that usually forms the valence band. Also, metal oxides seem to satisfy the stability criteria discussed in Section 3. For these reasons, hundreds of metal oxide photocatalysts have been investigated, as can be seen in the comprehensive reviews by Habisreutinger et al. (35) and Osterloh (49). Comparatively, metal sulfides seem to be less promising as photocatalysts for CO₂R. Metal sulfides tend to have higher VBMs. Also, they are thermodynamically unstable against oxidation as can be seen in **Figure 2b** for selected sulfides [and can be checked for many more by using the Pourbaix Explorer feature of the Materials Project (64)]. On this basis, reports of overall PC CO₂R on metal sulfides are surprising (65, 66).

Shown et al. (67) reported that C-doped SnS₂ nanostructures produced acetaldehyde, an eight-electron reduction product, with a visible light quantum efficiency of close to 1%. Here, it was thought that S²⁻ oxidation to elemental sulfur was occurring to provide charge conservation. Lai et al. (68) reported that In₂S₃/In₂O₃ heterojunctions produced methane with selectivity close to 100%, whereas In₂S₃ and In₂O₃ by themselves produced a mixture of methane and CO. Oxygen production was not reported in this study. Referring to the mechanism discussion in Section 4.2, it was thought that the S vacancies stabilized *CO and *CHO intermediates. Chai et al. (69) also reported the ability to influence the relative selectivities to CO and CH₄ with sulfide photocatalysts. In their case, they reported that exposed (111) planes of CuInSnS₄ octahedral nanocrystals led to methane production, while the individual metal sulfides In₂S₃, SnS₂, and Cu₂S produced CO. Similarly, Li et al. (70) found that Sn/Cd₃(C₃N₃S₃)₂ composites were selective for CO. Oxygen production was not reported in this study.

An example of a report that used both ¹³C labeling and measured stoichiometric O₂ is that of Kudo and coworkers (71). A wide-bandgap metal oxide, BaLa₄Ti₄O₁₅, was loaded with Ag, dispersed in CO₂-saturated water, and illuminated with an Xe lamp (as discussed below, this is a typical batch measurement method). CO (Equation 2) and formate were the products and O₂ was detected in the expected 2:1 ratio (both CO and formate are two-electron reduction products).

In this context, Li et al. (72) published a notable PC CO₂R study using a metal sulfide. They employed atomically thin layers of sulfur-deficient CuIn₅S₈ and reported stoichiometric production of methane and O₂ (**Figure 3b**). Notably, H₂¹⁸O labeling was used to ensure that the observed O₂ came from water oxidation. In their analysis, they attribute the selectivity for CH₄ to dual-metal Cu-In sites that stabilize a *CO intermediate and facilitate its subsequent protonation. Interestingly, and similar to most PC CO₂R studies, they do not provide an elementary step mechanism for water oxidation.

Finally, the study of Li & Sun (73) is highlighted. Here, a very simple photocatalyst preparation was used: ball milling of SiC powders. When milled to nanoparticle size and illuminated, CH₄ was the main PC CO₂R product along with a small amount (5% of the total) of methanol. Time-resolved photoluminescence experiments suggested that surface states located near the conduction band edge trapped electrons and aided with charge separation. We discuss in Section 5.1 the possible significance of these types of surface states in the CO₂ mechanism.

4.2. Rate Matching in Semiconductor Photocatalysis

Whether it is performing CO₂R coupled to water oxidation (e.g., Equations 2, 3, 8, and 9) or performing a different oxidation reaction (e.g., oxidation of a sacrificial donor), there is no reason to assume that the reduction and oxidation rates for a given semiconductor photocatalyst will be the same. Evidently, this would lead to a situation in which a given semiconductor nanoparticle would have a time-averaged net charge. For example, if the reduction reaction(s) were faster than oxidation, particles would have a positive charge. To my knowledge, this essential aspect of PC CO₂R has been almost entirely neglected. Particularly for small-sized semiconductor nanoparticles, positive or negative charging would be expected to change the band structure (in the same way that the electron structure of molecular ions is different than their neutral counterparts). This, in turn, would add a stochastic component to the band alignments depicted in **Figure 1**, and it might also be expected that the time-dependent availability of electrons and holes will influence the selectivity of competing reduction/oxidation processes.

One study from PC water splitting sheds light on this subject. Ohtani and coworkers (74) examined the reaction order of PC OER on titania particles as a function of size, employing sacrificial electron acceptors (Fe³⁺ or IO₃[−]) to react rapidly with electrons and thus maximize the kinetic asymmetry between reactions involving electrons and holes. Under conditions in which the hole-transfer reactions were rate limiting, the reaction order increased with light intensity, and for the smallest particles in the study, there was evidence of fourth-order kinetics at the highest illumination intensity (**Figure 4a**). Results were consistent, overall, with a microkinetic model that assumed that the OER rate depended on the integer number of trapped holes (**Figure 4b**). Intriguingly, this work suggests the possibility of selectivity control: Two accumulated holes should lead to H₂O₂ production with an overall second-order rate with respect to illumination, while four accumulated holes should lead directly to O₂.

Two comments are in order here. First, it may be possible to observe the charge state experimentally. Although the study was not performed under PC conditions, Aso et al. (75) used electron holography to determine the distribution of charge states for Pt nanoparticles on TiO₂. Net charge on Pt ranged from approximately $-6q_e$ to $+2q_e$, indicating that while charge transfer from TiO₂ to Pt is more prevalent (negative charging values), charge transfer in the opposite direction, from Pt to TiO₂, can also occur. Although challenging, it would be valuable to leverage recent advances in in situ electron microscopy to perform similar studies under PC conditions (76). Second, Peper & Mayer (52) have emphasized that the band structure of nanoscale particles will be significantly renormalized by changes in charge state and have called into question the ubiquitous use of band diagrams (such as the ones in **Figure 1c**). Electron transfer to/from a small photocatalyst particle will lead to a rearrangement of the solvent shell and the surrounding ions. As a result, the initial and final states of the nanoparticle will be quite different following an electron transfer event. This may explain why the band alignments shown in **Figure 1c** are not generally predictive of either catalyst selectivity or activity to a certain product. More generally, the accumulation of multiple charges on the semiconductor, leading to either a net positive or negative charge, would add a time-varying component to the energetic alignment of electrons and holes and to the redox reductions.

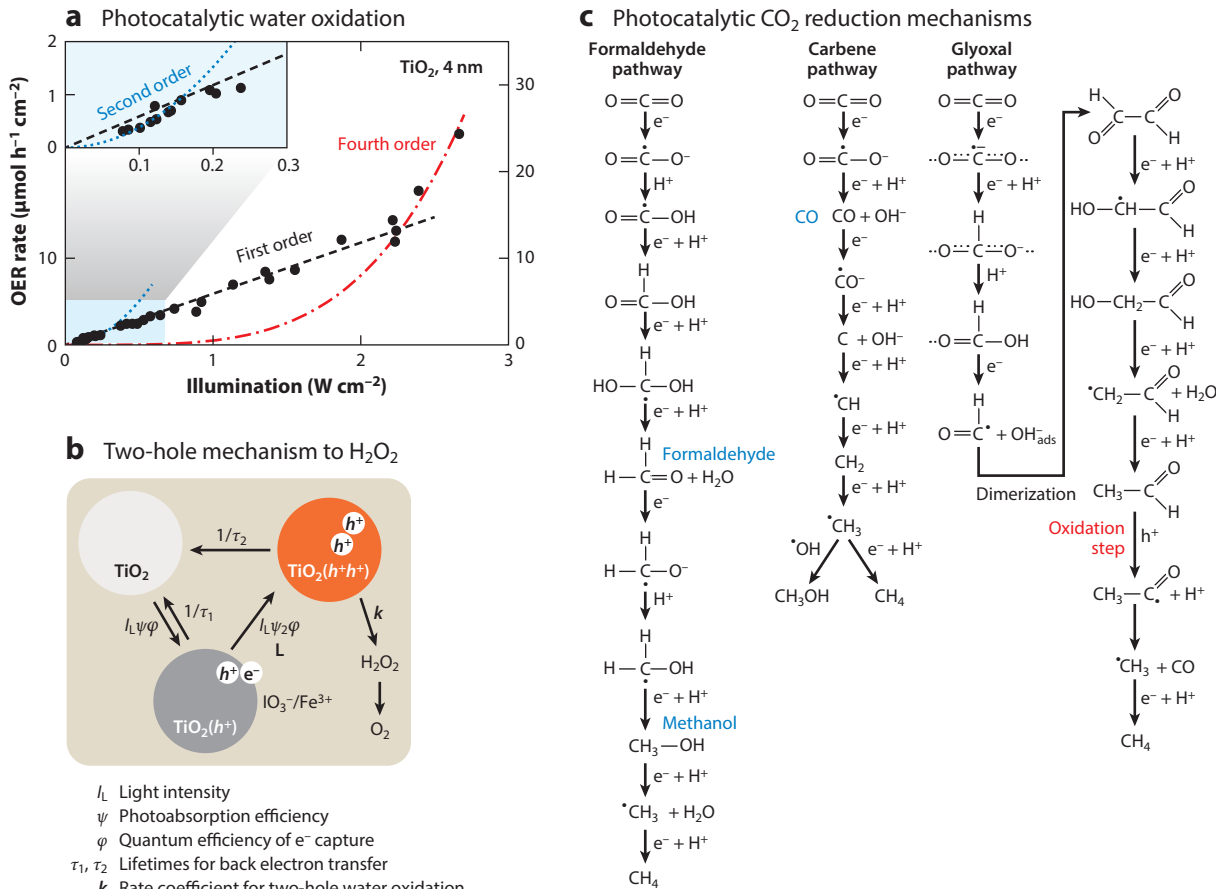


Figure 4

PC water splitting and CO_2R mechanism. (a) Observation of change in PC OER reaction order (second to first to fourth) with increasing light intensity on 4-nm-diameter TiO_2 nanoparticles. Panel a based on data from Reference 74. (b) Proposed mechanism for second-order process: Two holes accumulate on TiO_2 , leading to the selective production of hydrogen peroxides. Panel b adapted with permission from Reference 74; copyright 2018 Chemical Society of Japan. (c) Proposed elementary step mechanisms for PC CO_2R : formaldehyde, carbene, and glyoxal pathways. Panel c adapted with permission from Reference 35; copyright 2013 Wiley. Abbreviations: CO_2R , CO_2 reduction; OER, oxygen evolution reaction; PC, photocatalytic.

4.3. Photocatalytic CO_2 Reduction Mechanism

Formally, CO_2R and the coupled water oxidation reaction should occur via a series of proton-coupled electron transfers, along with possible chemical steps. In the related field of EC CO_2R , first-principles theory has led to a good understanding of the elementary step mechanism, initially by calculating the adsorption free energy of key intermediates (77) and, more recently, by calculating transition states and barriers and treating solvation with increasing rigor (78–80). However, direct application of this approach to PC CO_2R faces challenges associated with the unknown surface potential and the possibility of oxidation and reduction reactions occurring in the mechanism.

Focusing on the formation of CH_4 , which formally requires eight electrons and eight protons, the comprehensive review by Habisreutinger et al. (35) is still an excellent resource. The

three most-invoked mechanisms are depicted in **Figure 4c**: formaldehyde, carbene, and glyoxal pathways. As pointed out in the review by Fresno et al. (81), a key plausibility challenge for these mechanisms is that many of the proposed intermediates have been shown to be oxidized rather than undergo further reduction. On this basis, the complicated glyoxal pathway is based on observations that putative intermediates (formate, formaldehyde, and methanol) are more likely to be oxidized than to be further reduced when fed to systems that do not have a sacrificial donor such as TEOA to scavenge the holes. This pathway avoids these intermediates and, interestingly, has an oxidation step. It also could be consistent with studies that report C_2 products.

Thompson et al. (82) have reviewed the application of kinetic models for PC CO_2 R, focusing on a Langmuir-Hinshelwood mechanism with adsorption of CO_2 and H_2O , reaction with electrons, surface diffusion of intermediates, and desorption. The possibility of blocking surface catalytic sites (poisoning), for example, by bicarbonate species, is considered; we return to this point in Section 4.5. Wang et al. (83) provide an informative review regarding the choice of cocatalysts to favor certain products such as CO or methanol. While the perspective of Eder et al. (84) is written from the point of view of alcohol oxidation on TiO_2 , it makes the important point that insights from the analogous EC reaction are not applicable due to the differences in surface chemistry and the possibility (in the PC case) of thermal steps.

4.4. Importance of Selective Catalysts

In the related field of PC water splitting there have been two main experimental drivers: (a) the development of selective HER and OER catalysts that can be deposited on different sites on the semiconductor nanoparticles and (b) reducing the bandgap of oxide- and nitride-based absorbers into the visible region of the light spectrum to increase solar-to-hydrogen efficiency (61). An excellent example of approach (b) is the work of Domen and coworkers (85) in which a solar-to-hydrogen (STH) conversion efficiency of $\sim 1\%$ was achieved in spite of the rather large bandgap (3.2 eV) of the $SrTiO_3$ absorber. Here, charge directionality was achieved with selective cocatalysts. For HER, Ru with a semiporous Cr_2O_3 shell was used; the metal oxide sheet is thought to suppress the competing OER while maintaining HER function. RuO_x was the OER catalyst. This approach is scalable and durable, as evidenced by a 100-m^2 demonstration with a multi-month lifetime (86).

Recently, Mi and coworkers (87) used a similar cocatalyst scheme with a lower bandgap absorber to demonstrate, at the lab scale, nearly 10% STH conversion. Their absorber, which is composed of alloys of InN and GaN (InGaN) grown in a nanowire form on silicon, has a range of bandgaps, the lowest being about 1.9 eV, allowing the wires to capture a significant fraction of the solar spectrum. The InGaN quality is exceptionally high, which reduces carrier recombination, and the charge transfer to the HER (Cr_2O_3/Rh) and OER (Co_3O_4) cocatalysts appears to be effective. Using Fresnel lenses for concentration, 9% STH conversion efficiency was achieved in the laboratory and 6% outside using natural sunlight.

This work emphasizes the importance of suppressing the reverses of the reactions in Equations 4a and 4b, i.e., hydrogen oxidation and oxygen reduction, which are strongly downhill at the Co_3O_4 and Cr_2O_3/Rh sites (88). Exemplifying Le Chatelier's principle, this is done by reducing the activity of O_2 and H_2 by operating the reactor at reduced pressure, with the headspace of the reactor being, initially, water vapor only. When the reactor is operated in this way, the initial efficiency is high but declines and drops to zero after 40–50 min when the forward rates of the reactions in Equations 4a and 4b, which are driven by light, are balanced by the reverse reactions, HOR and ORR. Reapplying the vacuum, which has the effect of degassing the water, resets the system, and high efficiencies can be observed again. Over 70 cycles of operation

were demonstrated in this way. More generally, the suppression of back reactions has been underappreciated in PC CO₂R, which leads to the discussion in the next section.

4.5. Overcoming Mass-Transfer Limitations for Reactants and Products

Semiconductor PC CO₂R experiments are typically performed in one of two batch geometries: (a) an immobile catalyst bed with a headspace (or feed) of humidified CO₂ (72) or (b) an aqueous suspension of nanoparticles (89, 90). Neither case allows for the optimal mass transfer of reactants, intermediates, and products. For example, in (a), the activity of water is limited, while in (b) the activity of CO₂ is limited by its solubility (33 mM at 1 atm in water). In both cases, intermediates and products can accumulate on the surface of the photocatalyst, which prevents reactants from occupying the reaction sites, slowing the reaction rate and accelerating the degradation of the photocatalyst (91).

It might be thought that because the overall turnover rates of PC CO₂R are very slow compared to PEC CO₂R and, especially, to EC CO₂R, mass transfer would not play an important role. Recently, Jung et al. (25) have shown that this is not the case. In this study, semiconductor nanoparticles were loaded onto a GDE. In this arrangement, reactant availability and product removal are easily controlled by the pressure/flow of CO₂ and water on opposite sides of the GDE. In comparison to batch reactor controls, more than 10 times higher production rates of CO₂R products were reported for TiO₂, ZnO, C₃N₄, and CdS photocatalysts (**Figure 3c**). In addition, for TiO₂, CO selectivity (>90%) and long-term stability (>100 h) were significantly enhanced compared to control experiments in batch reactors.

Clearly, the role of mass transport in PC CO₂R has been underestimated, in terms of both reactant supply and product removal such that sites can turn over again. It is also possible that optimal mass transfer may remove poisoning species, explaining the superior lifetimes observed by Jung et al. (25). Importantly, it appears that semiconductor photocatalysts can be much more efficient (more than 10 times) than previously thought because what were thought to be inherent limitations (i.e., a high rate of recombination) are, in fact, due to inefficient mass transfer. Also, it appears that product selectivity can be steered via control of mass transport.

5. PHOTOELECTROCATALYSIS

Dating back to the space-charge-layer recombination model developed by Reichman (92), PEC processes involving one-electron transfers are well-understood. The review by Lewis (93) in this journal and a series of papers by Peter and coworkers (94–96), which detailed the important role of surface states, are excellent resources. Notably, Mills et al. (97) explicitly considered the coupling to catalysts for multielectron reactions and provided a simulation framework based on the drift-diffusion model.

Here, the discussion focuses on recent experimental work in PEC OER and PEC CO₂R. In PEC OER, there has been substantial progress in understanding its elementary step mechanism. Kumar et al. (98) in this journal provided a comprehensive review of PEC CO₂R up to 2012. Here, I focus on materials developments, which may make experimental approaches that have been so illuminating for PEC OER feasible for PEC CO₂R.

5.1. Photoelectrocatalytic Oxygen Evolution Reaction

In Section 2, I mentioned that the band diagram shown in **Figure 1c** in which the extended states of the semiconductor (valence and conduction band edges) are aligned with redox potentials is an oversimplification. The extended states as depicted in band diagrams should not be capable of catalysis: The electron or hole needs to localize first. In the context of PEC OER, this important

point was considered by Sprik and coworkers (99, 100) for TiO_2 . They located states capable of hole capture in the midgap region for a number of configurations and also found a large reorganization energy between their oxidized (after capture) and reduced (prior to capture) states. This is an important, but overlooked, consideration in interpreting PEC OER studies.

The control of the electrode potential and the overall faster reaction rates, which are inherent in PEC, make experiments possible that are currently infeasible for PC studies. Here, we illustrate progress made in understanding the elementary step mechanism in PEC OER. In a series of works, Durrant and coworkers (27, 101, 102) used a spectroscopic signature assigned to trapped holes at the surface of metal oxides to perform kinetic studies. **Figure 5a** is a notable example of this work in which a change in the reaction order from first to third with increasing surface

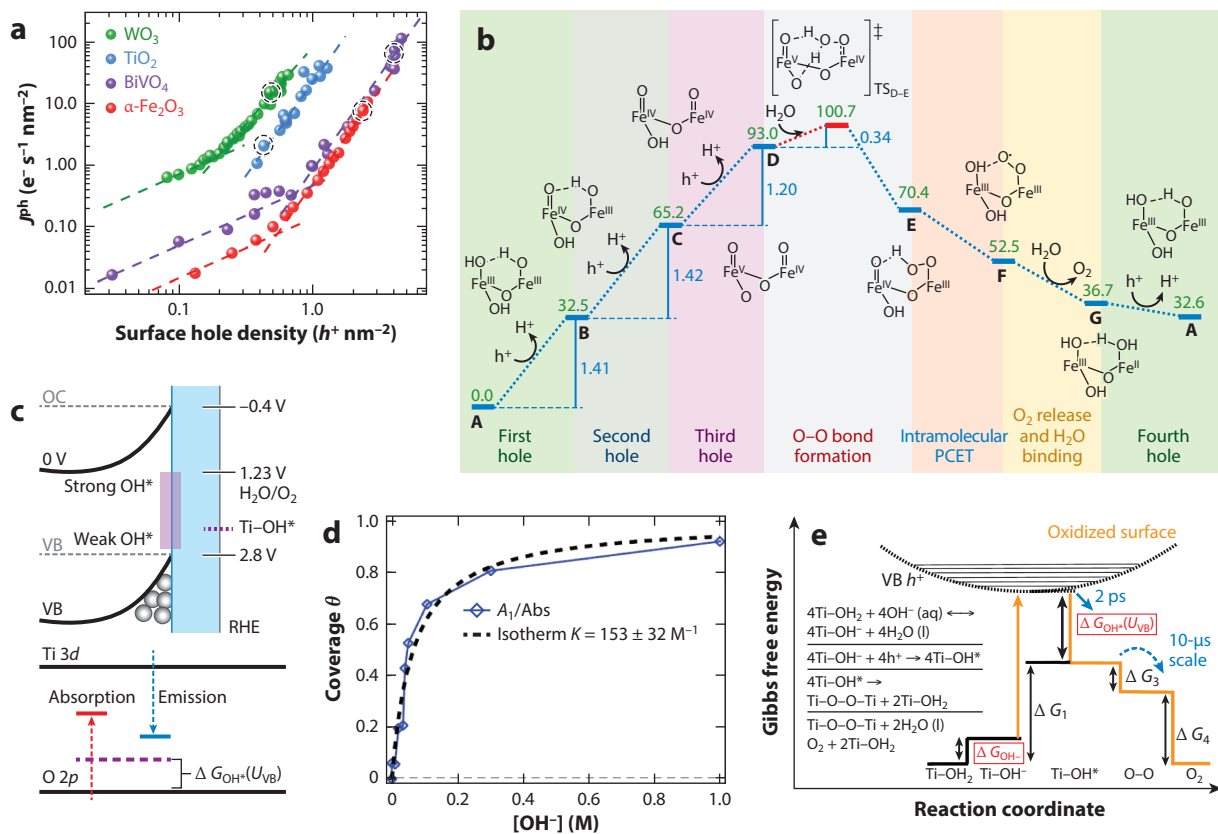


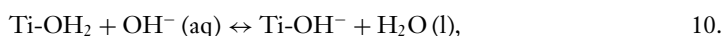
Figure 5

Mechanistic studies of PEC OER on metal oxides. (a) Current density for PEC OER as a function of surface hole density derived from transient absorption spectroscopy for WO_3 , TiO_2 , BiVO_4 , and Fe_2O_3 . A transition to third-order kinetics is seen at high surface hole densities. (b) Proposed elementary step mechanism for Fe_2O_3 consistent with third-order kinetics. Relative free energies are given in green in units of kilocalorie per mole and free energy changes are given in blue in units of electron volts. A photovoltage of 0.80 V is used for all oxidation steps. The rate-determining step, O-O bond formation, is shown in red. (c) Schematic depiction of the pH-dependent redox level of the Ti-OH^* intermediate on SrTiO_3 and its optical absorption and emission transitions. (d) Langmuir isotherm showing increasing coverage of Ti-OH^* with increasing pH. (e) Free energy diagram for the OER mechanism with photoexcited steps shown in orange. Formation of Ti-OH^* is rate determining. Panels a and b adapted with permission from Reference 102; copyright 2020 Nature Springer. Panels c-e adapted with permission from Reference 106; copyright 2022 Nature Springer. Abbreviations: Abs, absorption; OC, open circuit; OER, oxygen evolution reaction; PEC, photoelectrocatalytic; PCET, proton-coupled electron transfers; RHE, reversible hydrogen electrode; VB, valence band.

hole concentration is observed for Fe₂O₃ and BiVO₄ [note the similarity to the work of Ohtani and coworkers (74) in PC OER (**Figure 4a**)]. **Figure 5b** depicts the elementary step mechanism invoked for the third-order process.

This work raises important questions regarding the role of minority carriers (holes) in the surface chemistry. Interestingly, at the highest illumination conditions, the surface hole density greatly exceeds the expected densities of surface defect states. Intriguingly, it might be expected that surface holes under these conditions would have significant lateral mobility. The assignment of third-order kinetics has also been challenged (103, 104), and Wang et al. (105) have emphasized the importance of considering the thermal steps in the reaction, which can be rate limiting at high hole concentrations.

Toward a kinetic understanding of PEC OER, Cuk and coworkers (106, 107) have employed comprehensive transient spectroscopy studies of SrTiO₃ complemented by first-principles calculations. Certain optical absorption/emission spectral features were assigned to the Ti-OH* intermediate (**Figure 5c**). Importantly, this work enabled the chemical deprotonation step of adsorbed water (Equation 8) to be distinguished from the first electron-transfer step, which involves a surface-bound hole (Equation 9):



The authors derived a Langmuir isotherm for the coverage of the Ti-OH* intermediate, normalized to the hole concentration (**Figure 5d**). In the proposed mechanism, the formation of Ti-OH* is the rate-determining step; the subsequent transfers of surface holes are downhill, as shown in **Figure 5f**.

5.2. Photoelectrocatalytic CO₂ Reduction

Given that recent work has yielded considerable insight into the elementary step mechanisms of PEC OER and HER, as discussed in a recent perspective by Peter (108), it is relevant to ask if similar studies could be performed on PEC CO₂R, which could also inform the PC CO₂R mechanism. To this end, materials are required that are, as the metal oxides are for OER, both capable of light absorption and have surfaces that are catalytically competent for the desired reaction. If such studies could be performed, they would complement the extensive literature on EC CO₂R performed on metal electrodes. Moreover, it is possible, as discussed above for photocatalysis, that the PEC CO₂R mechanism might be quite different than on metal electrodes.

The key issue is that there are few materials that are stable under the required reducing conditions such that detailed PEC CO₂R experiments can be performed (109). Hinogami et al. (110) performed pioneering work with p-Si. While this study focused on p-Si interfaced with small particles of metal cocatalysts (Cu, Ag, or Au), data from bare Si were also reported. At a photocurrent density of 2.4 mA cm⁻² in CO₂-saturated bicarbonate buffer, although H₂ was the primary product, small amounts of CO [10% Faradaic efficiency (FE)] and formate (5% FE) were reported. Gu et al. (111) reported that p-type Mg-doped CuFeO₂ delafossite was active for PEC CO₂R to formate. However, the catalytic activity was attributed to the presence of metallic Cu on the surface rather than to the semiconductor itself. Cu₂O was reported to form ethylene under PEC CO₂R conditions, but in nonaqueous media due to its instability in water (112). Similarly, Cu(In,Ga)S₂ (CIGS) has been reported to yield CO and formate under illumination in 0.1-M tetrabutylammonium bromide in acetonitrile (113). Chalcopyrite Cu(In,Ga)Se₂ (CIGSe) with a CdS ETL has been reported to be active for PEC CO₂R when a molecular coating is used to limit Cd

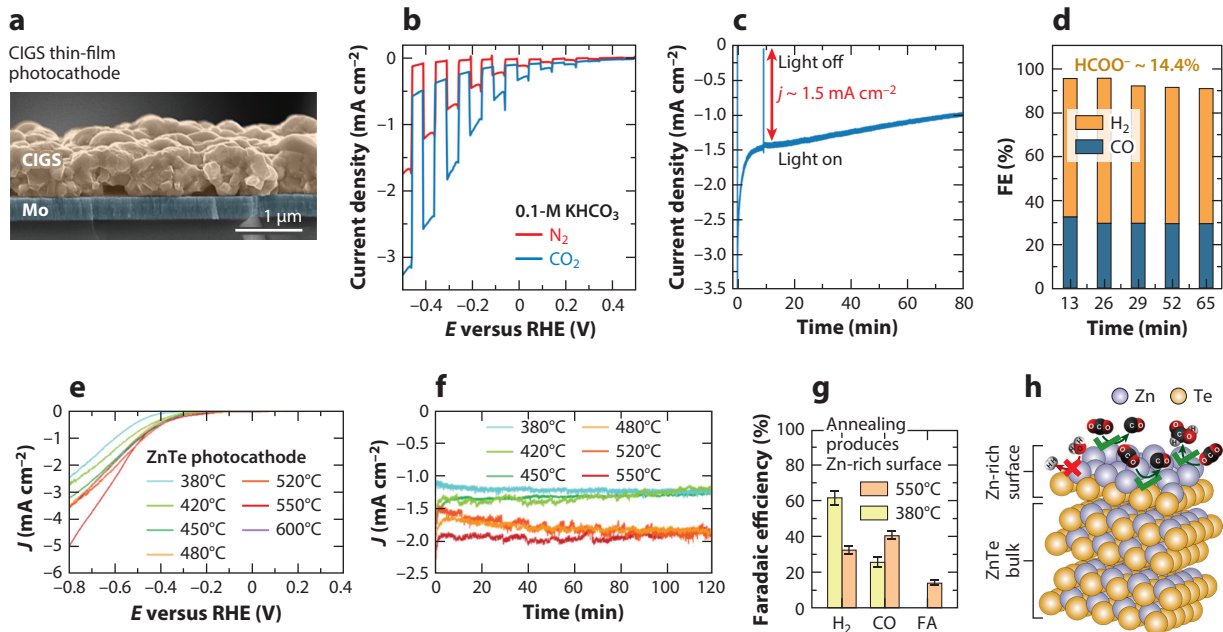


Figure 6

Photoelectrocatalytic CO₂R using semiconductor photocathodes in aqueous media. Thin films of Cu-deficient CIGS (*a*) are active for PEC CO₂R (*b,c*) with ~30% FE for CO and 14% for formic acid (*d*). Less than 1 h of stable operation is observed. ZnTe thin films with postprocessing annealing (380–600°C) show activity for PEC CO₂R (*e,f*). Annealing produces a Zn-rich surface that suppresses H₂ evolution and improves the FE for CO and formic acid (*g,h*). Panels *a–c* adapted from Reference 115. Panels *d–h* adapted from Reference 116 (CC BY 4.0). Abbreviations: CIGS, Cu(In,Ga)S₂; CO₂R, CO₂ reduction; FA, formic acid; FE, Faradaic efficiency; Mo, molybdenum; PEC, photoelectrocatalytic; RHE, reversible hydrogen electrode.

corrosion (114). Still, few studies report direct PEC CO₂R without the intentional use of cocatalysts in aqueous media, analogous to the PEC OER studies discussed in Section 5.1.

Very recently, Prabhakar et al. (115) reported that Cu-deficient CIGS thin films yielded formate (14% FE) and CO (30% FE) when operated in PEC CO₂R conditions in aqueous media (**Figure 6a–d**). Stable operation for >1 h was reported, whereas similarly prepared CIGS films decomposed within 10 min. X-ray photoelectron spectroscopy and X-ray absorption spectroscopy analysis suggested that the CO₂R stability could be related to self-passivation by oxides/hydroxides of Ga and In formed during operation. Density functional theory calculations also reveal that Ga and In are the preferential sites for the adsorption of CO₂R intermediates, whereas Cu sites were predicted to be catalytically less active. Similarly, Zeng et al. (116) reported that certain CdTe thin films were active for PEC CO₂R in aqueous media, forming CO (up to 40% FE) and formate (up to 10% FE) with >2-h stability (**Figure 6e–h**). Here, it was found that annealing conditions that led to a Zn-rich surface were required for activity and stability.

6. OUTLOOK

This review began by emphasizing the requirement of charge separation/directionality in light-to-energy conversion in generality. In this context, semiconductor photocatalysis is conceptually simple. However, for driven uphill reactions like water splitting and CO₂R (with water oxidation as the proton source), it has the daunting requirement of catalyzing two different multielectron redox reactions at separate sites, while at the same time avoiding oxidation of the reduction

products (and reduction of the oxidation products). For PC CO₂R specifically, the very slow overall conversion rates have made it difficult to perform kinetic studies as it typically takes several minutes, and in some cases hours, to build up detectable products (117). The discovery that reaction rates can be sped up at least ten times may enable the real-time detection of products using mass spectrometry methods that are currently employed for EC CO₂R (118–120). Recent reports on PC methane oxidation to methanol, which employed a gas diffusion geometry and used time-resolved mass spectrometry with isotope labeling, are encouraging in this respect (121, 122). It may also be possible to elucidate poisoning mechanisms by postmortem thermal desorption combined with high-sensitivity detection (123). Additionally, the promoting/inhibiting effect of reaction intermediates like CO should be investigated, again using an analogy with EC CO₂R (124, 125).

It should also be possible to clarify the role of particle charging in the rates of the reduction and oxidation reactions, taking into account the role change in electronic structure and the solvent environment (52). The recent study by Moss et al. (126) of La,Rh:SrTiO₃ water-splitting photocatalysts is promising in this respect. Using transient absorption spectroscopy, in concert with first-principles calculations, it was shown that La codoping fixes Rh in the 3+ state, which results in long-lived photogenerated electrons, desirable for HER, even at the very positive potentials at which the sheet photocatalysts are expected to be operating.

Still, there are unanswered questions involving the photocatalyst charge state under operation (127). Are all the photocatalysts in similar charge states or could some be positively charged and some negative, as suggested by Aso et al. (75)? In this case, some particles could be primarily responsible for producing the reduction (CO₂R) products while other are producing O₂, with ORR and intermediate oxidation functioning as effective redox shuttles. Further, the surface sites that are responsible for selective catalysis, and the resultant charge separation, may undergo transformations as a function of time, as would be anticipated by studies of electrocatalyst restructuring in CO₂R (128, 129).

In PEC OER, there has been substantial progress in understanding the catalytic surface sites and the elementary step mechanism. Still, there are unanswered questions regarding the specific role of near-surface holes (105). Is the supply of holes rate limiting? Some oxides used for PEC OER, notably BiVO₄, form polarons and even bipolarons (130, 131). While these are deleterious for charge transport, could it be that charge localization is beneficial for catalysis?

In PEC CO₂R, similar questions remain as to the identity of the surface site trapping and catalysis. Due to the paucity of suitable materials compared to PEC OER, reaction rate selectivities and reaction orders as a function of near-surface electron concentration are not known. Additionally, one might expect that the product distribution would be a function of the surface electron density, similar to the control of H₂O₂ versus O₂ production that has been reported for photoanodes (132, 133). Finally, if there is better understanding of the surface electron concentration and the surface structure, it may be possible to apply first-principles theory, similar to what has been done in EC CO₂R, for the elucidation of the elementary step mechanisms (134, 135).

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

J.W.A. acknowledges support from the Liquid Sunlight Alliance, which is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under award DE-SC0021266.

1. Highly readable account of the importance of enzymatic catalysis, which can drive the uphill reactions responsible for life on Earth.

LITERATURE CITED

- Branscomb E, Biancalani T, Goldenfeld N, Russell M. 2017. Escapement mechanisms and the conversion of disequilibria; the engines of creation. *Phys. Rep.* 677:1–60
- Schrödinger E. 1992. *What Is Life? With Mind and Matter and Autobiographical Sketches*. Cambridge University Press
- Barber J, Tran PD. 2013. From natural to artificial photosynthesis. *J. R. Soc. Interface* 10(81):20120984
- Faunce TA, Lubitz W, Rutherford AW, MacFarlane D, Moore GF, et al. 2013. Energy and environment policy case for a global project on artificial photosynthesis. *Energy Environ. Sci.* 6(3):695–98
- Bushuyev OS, De Luna P, Dinh CT, Tao L, Saur G, et al. 2018. What should we make with CO₂ and how can we make it? *Joule* 2(5):825–32
- De Luna P, Hahn C, Higgins D, Jaffer SA, Jaramillo TF, Sargent EH. 2019. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* 364(6438):eaav3506
- Fujishima A, Honda K. 1972. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37–38
- Inoue T, Fujishima A, Konishi S, Honda K. 1979. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* 277(5698):637–38
- Wasielowski MR. 1992. Photoinduced electron transfer in supramolecular systems for artificial photosynthesis. *Chem. Rev.* 92(3):435–61
- Bard AJ, Fox MA. 1995. Artificial photosynthesis: solar splitting of water to hydrogen and oxygen. *Acc. Chem. Res.* 28(3):141–45
- Gust D, Moore TA, Moore AL. 2009. Solar fuels via artificial photosynthesis. *Acc. Chem. Res.* 42(12):1890–98
- McDaniel ND, Bernhard S. 2010. Solar fuels: thermodynamics, candidates, tactics, and figures of merit. *Dalton Trans.* 39(42):10021–30
- Montoya JH, Seitz LC, Chakthranont P, Vojvodic A, Jaramillo TF, Nørskov JK. 2016. Materials for solar fuels and chemicals. *Nat. Mater.* 16(1):70–81
- Sayre HJ, Tian L, Son M, Hart SM, Liu X, et al. 2021. Solar fuels and feedstocks: the quest for renewable black gold. *Energy Environ. Sci.* 14(3):1402–19
- Segev G, Kibsgaard J, Hahn C, Xu ZJ, Cheng W-H, et al. 2022. The 2022 solar fuels roadmap. *J. Phys. D Appl. Phys.* 55(32):323003
- Nitopi S, Bertheussen E, Scott SB, Liu X, Engstfeld AK, et al. 2019. Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte. *Chem. Rev.* 119(12):7610–72
- He J, Janáky C. 2020. Recent advances in solar-driven carbon dioxide conversion: expectations versus reality. *ACS Energy Lett.* 5(6):1996–2014
- Hu S, Lewis NS, Ager JW, Yang J, McKone JR, Strandwitz NC. 2015. Thin-film materials for the protection of semiconducting photoelectrodes in solar-fuel generators. *J. Phys. Chem. C* 119(43):24201–28
- DuChene JS, Tagliabue G, Welch AJ, Cheng W-H, Atwater HA. 2018. Hot hole collection and photoelectrochemical CO₂ reduction with plasmonic Au/p-GaN photocathodes. *Nano Lett.* 18(4):2545–50
- Creel EB, Corson ER, Eichhorn J, Kostecki R, Urban JJ, McCloskey BD. 2019. Directing selectivity of electrochemical carbon dioxide reduction using plasmonics. *ACS Energy Lett.* 4(5):1098–105
- Kazuma E. 2023. Key factors for controlling plasmon-induced chemical reactions on metal surfaces. *J. Phys. Chem. Lett.* 15:59–67
- Offen AJ, Geng Z, Yu Y, Liu J. 2023. “A lot’s in a name”: insights from debates on thermal and nonthermal effects in plasmonic catalysis. *ACS Appl. Energy Mater.* 6:11762–72
- Ohtani B. 2014. Revisiting the fundamental physical chemistry in heterogeneous photocatalysis: its thermodynamics and kinetics. *Phys. Chem. Chem. Phys.* 16(5):1788–97
- Osterloh FE. 2017. Photocatalysis versus photosynthesis: a sensitivity analysis of devices for solar energy conversion and chemical transformations. *ACS Energy Lett.* 2(2):445–53

25. Jung H, Kim C, Yoo H-W, You J, Kim JS, et al. 2023. Continuous-flow reactor with superior production rate and stability for CO₂ reduction using semiconductor photocatalysts. *Energy Environ. Sci.* 16(7):2869–78
26. Nielander AC, Shaner MR, Papadantonakis KM, Francis SA, Lewis NS. 2015. A taxonomy for solar fuels generators. *Energy Environ. Sci.* 8(1):16–25
27. Corby S, Rao RR, Steier L, Durrant JR. 2021. The kinetics of metal oxide photoanodes from charge generation to catalysis. *Nat. Rev. Mater.* 6(12):1136–55
28. Fletcher EA. 2001. Solarthermal processing: a review. *J. Sol. Energy Eng.* 123(2):63–74
29. Chu S, Majumdar A. 2012. Opportunities and challenges for a sustainable energy future. *Nature* 488(7411):294–303
30. Barbir F. 2005. *PEM Fuel Cells: Theory and Practice*. Academic
31. Würfel P. 2005. *Physics of Solar Cells: From Principles to New Concepts*. Wiley
32. Schleuning M, Ahmet IY, van de Krol R, May MM. 2022. The role of selective contacts and built-in field for charge separation and transport in photoelectrochemical devices. *Sustain. Energy Fuels* 6(16):3701–16
33. Cuevas A, Yan D. 2013. Misconceptions and misnomers in solar cells. *IEEE J. Photovolt.* 3(2):916–23
34. Würfel U, Cuevas A, Würfel P. 2015. Charge carrier separation in solar cells. *IEEE J. Photovolt.* 5(1):461–69
35. Habisreutinger SN, Schmidt-Mende L, Stolarczyk JK. 2013. Photocatalytic reduction of CO₂ on TiO₂ and other semiconductors. *Angew. Chem. Int. Ed.* 52(29):7372–408
36. Ager JW. 2018. Approaches for stable and efficient photoelectrodes. In *Integrated Solar Fuel Generators*, ed. ID Sharp, HA Atwater, H-JL Lewerenz. Royal Society of Chemistry
37. Grätzel M. 2001. Photoelectrochemical cells. *Nature* 414(6861):338–44
38. Wydrzynski TJ, Satoh K, eds. 2005. *Photosystem II: The Light-Driven Water: Plastoquinone Oxidoreductase*. Springer
39. Golbeck JH, ed. 2006. *Photosystem I: The Light-Driven Plastocyanin: Ferredoxin Oxidoreductase*. Springer
40. Nozik AJ. 1976. *p-n* photoelectrolysis cells. *Appl. Phys. Lett.* 29(3):150–53
41. Wu Y, Lazic P, Hautier G, Persson K, Ceder G. 2013. First principles high throughput screening of oxynitrides for water-splitting photocatalysts. *Energy Environ. Sci.* 6(1):157–68
42. Nursam NM, Wang X, Caruso RA. 2015. High-throughput synthesis and screening of titania-based photocatalysts. *ACS Comb. Sci.* 17(10):548–69
43. Takanabe K. 2017. Photocatalytic water splitting: quantitative approaches toward photocatalyst by design. *ACS Catal.* 7(11):8006–22
44. Arai T, Konishi Y, Iwasaki Y, Sugihara H, Sayama K. 2007. High-throughput screening using porous photoelectrode for the development of visible-light-responsive semiconductors. *J. Comb. Chem.* 9(4):574–81
45. Yan Q, Yu J, Suram SK, Zhou L, Shinde A, et al. 2017. Solar fuels photoanode materials discovery by integrating high-throughput theory and experiment. *PNAS* 114(12):3040–43
46. Osterloh FE. 2008. Inorganic materials as catalysts for photochemical splitting of water. *Chem. Mater.* 20(1):35–54
47. Kudo A, Miseki Y. 2009. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* 38(1):253–78
48. Maeda K, Domen K. 2010. Photocatalytic water splitting: recent progress and future challenges. *J. Phys. Chem. Lett.* 1(18):2655–61
49. Osterloh FE. 2013. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.* 42(6):2294–320
50. Cao S-W, Liu X-F, Yuan Y-P, Zhang Z-Y, Fang J, et al. 2013. Artificial photosynthetic hydrogen evolution over g-C₃N₄ nanosheets coupled with cobaloxime. *Phys. Chem. Chem. Phys.* 15(42):18363–66
51. Gurudayal, Beeman JW, Bullock J, Wang H, Eichhorn J, et al. 2019. Si photocathode with Ag-supported dendritic Cu catalyst for CO₂ reduction. *Energy Environ. Sci.* 12(3):1068–77
52. Peper JL, Mayer JM. 2019. Manifesto on the thermochemistry of nanoscale redox reactions for energy conversion. *ACS Energy Lett.* 4(4):866–72
53. Gerischer H. 1991. Electron-transfer kinetics of redox reactions at the semiconductor/electrolyte contact. A new approach. *J. Phys. Chem.* 95(3):1356–59

25. In spite of the low overall rate, there are mass-transfer limitations in PC CO₂R.

52. Typically used Fermi-level description of charge transfer is inadequate for semiconductor nanoparticles.

72. Remarkable observation of CO₂ reduction and water oxidation on a metal sulfide photocatalyst.

74. Intriguing observation of digital hole occupancy dependence on kinetics of photoelectrochemical water oxidation on TiO₂ nanoparticles.

54. Chen S, Wang L-W. 2012. Thermodynamic oxidation and reduction potentials of photocatalytic semiconductors in aqueous solution. *Chem. Mater.* 24(18):3659–66
55. Alberio J, Peng Y, García H. 2020. Photocatalytic CO₂ reduction to C₂₊ products. *ACS Catal.* 10(10):5734–49
56. Fang S, Rahaman M, Bharti J, Reisner E, Robert M, et al. 2023. Photocatalytic CO₂ reduction. *Nat. Rev. Methods Primers* 3(1):61
57. Bonchio M, Bonin J, Ishitani O, Lu T-B, Morikawa T, et al. 2023. Best practices for experiments and reporting in photocatalytic CO₂ reduction. *Nat. Catal.* 6(8):657–65
58. Kamat PV, Jin S. 2018. Semiconductor photocatalysis: “Tell us the complete story!” *ACS Energy Lett.* 3(3):622–23
59. Schneider J, Bahnemann DW. 2013. Undesired role of sacrificial reagents in photocatalysis. *J. Phys. Chem. Lett.* 4(20):3479–83
60. Sampaio RN, Grills DC, Polyansky DE, Szalda DJ, Fujita E. 2020. Unexpected roles of triethanolamine in the photochemical reduction of CO₂ to formate by ruthenium complexes. *J. Am. Chem. Soc.* 142(5):2413–28
61. Wang Z, Li C, Domen K. 2019. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem. Soc. Rev.* 48(7):2109–25
62. Kang U, Yoon SH, Han DS, Park H. 2019. Synthesis of aliphatic acids from CO₂ and water at efficiencies close to the photosynthesis limit using mixed copper and iron oxide films. *ACS Energy Lett.* 4(9):2075–80
63. Wu YA, McNulty I, Liu C, Lau KC, Liu Q, et al. 2019. Facet-dependent active sites of a single Cu₂O particle photocatalyst for CO₂ reduction to methanol. *Nat. Energy* 4(11):957–68
64. Patel AN, Nørskov JK, Persson KA, Montoya JH. 2019. Efficient Pourbaix diagrams of many-element compounds. *Phys. Chem. Chem. Phys.* 21(45):25323–27
65. Wang J, Lin S, Tian N, Ma T, Zhang Y, Huang H. 2021. Nanostructured metal sulfides: classification, modification strategy, and solar-driven CO₂ reduction application. *Adv. Funct. Mater.* 31(9):2008008
66. Zhu Q, Xu Q, Du M, Zeng X, Zhong G, et al. 2022. Recent progress of metal sulfide photocatalysts for solar energy conversion. *Adv. Mater.* 34(45):2202929
67. Shown I, Samireddi S, Chang Y-C, Putikam R, Chang P-H, et al. 2018. Carbon-doped SnS₂ nanostructure as a high-efficiency solar fuel catalyst under visible light. *Nat. Commun.* 9(1):169
68. Lai K, Sun Y, Li N, Gao Y, Li H, et al. 2024. Photocatalytic CO₂-to-CH₄ conversion with ultrahigh selectivity of 95.93% on S-vacancy modulated spatial In₂S₃/In₂O₃ heterojunction. *Adv. Funct. Mater.* 34(49):2409031
69. Chai Y, Kong Y, Lin M, Lin W, Shen J, et al. 2023. Metal to non-metal sites of metallic sulfides switching products from CO to CH₄ for photocatalytic CO₂ reduction. *Nat. Commun.* 14(1):6168
70. Li X, Zhang J, Dai K, Fan K, Liang C. 2021. Cd₃(C₃N₃S₃)₂ polymer/Sn Schottky heterojunction for broadband-solar highly selective photocatalytic CO₂ reduction. *Sol. RRL* 5(12):2100788
71. Iizuka K, Wato T, Miseki Y, Saito K, Kudo A. 2011. Photocatalytic reduction of carbon dioxide over Ag cocatalyst-loaded ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba) using water as a reducing reagent. *J. Am. Chem. Soc.* 133(51):20863–68
72. Li X, Sun Y, Xu J, Shao Y, Wu J, et al. 2019. Selective visible-light-driven photocatalytic CO₂ reduction to CH₄ mediated by atomically thin CuInS₈ layers. *Nat. Energy* 4(8):690–99
73. Li H, Sun J. 2021. Highly selective photocatalytic CO₂ reduction to CH₄ by ball-milled cubic silicon carbide nanoparticles under visible-light irradiation. *ACS Appl. Mater. Interfaces* 13(4):5073–78
74. Takeuchi S, Takashima M, Takase M, Ohtani B. 2018. Digitally controlled kinetics of titania-photocatalyzed oxygen evolution. *Chem. Lett.* 47(3):373–76
75. Aso R, Hojo H, Takahashi Y, Akashi T, Midoh Y, et al. 2022. Direct identification of the charge state in a single platinum nanoparticle on titanium oxide. *Science* 378(6616):202–6
76. Zhang Q, Song Z, Sun X, Liu Y, Wan J, et al. 2024. Atomic dynamics of electrified solid-liquid interfaces in liquid-cell TEM. *Nature* 630(8017):643–47
77. Peterson AA, Abild-Pedersen F, Studt F, Rossmeisl J, Nørskov JK. 2010. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy Environ. Sci.* 3(9):1311–15
78. Rendón-Calle A, Builes S, Calle-Vallejo F. 2018. A brief review of the computational modeling of CO₂ electroreduction on Cu electrodes. *Curr. Opin. Electrochem.* 9:158–65

79. Chan K. 2020. A few basic concepts in electrochemical carbon dioxide reduction. *Nat. Commun.* 11(1):5954
80. Li H, Luan D, Long J, Guo P, Xiao J. 2024. Electrochemical reaction kinetics at constant interfacial potential. *ACS Catal.* 14(17):12814–23
81. Fresno F, Villar-García JJ, Collado L, Alfonso-González E, Reñones P, et al. 2018. Mechanistic view of the main current issues in photocatalytic CO₂ reduction. *J. Phys. Chem. Lett.* 9(24):7192–204
82. Thompson WA, Sanchez Fernandez E, Maroto-Valer MM. 2020. Review and analysis of CO₂ photoreduction kinetics. *ACS Sustain. Chem. Eng.* 8(12):4677–92
83. Wang S, Wang J, Wang Y, Sui X, Wu S, et al. 2024. Insight into the selectivity-determining step of various photocatalytic CO₂ reduction products by inorganic semiconductors. *ACS Catal.* 14(14):10760–88
84. Eder M, Tschurl M, Heiz U. 2023. 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.* 14(26):6193–201
85. Wang Q, Hisatomi T, Jia Q, Tokudome H, Zhong M, et al. 2016. Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nat. Mater.* 15(6):611–15
86. Nishiyama H, Yamada T, Nakabayashi M, Maehara Y, Yamaguchi M, et al. 2021. Photocatalytic solar hydrogen production from water on a 100-m² scale. *Nature* 598(7880):304–7
87. **Zhou P, Navid IA, Ma Y, Xiao Y, Wang P, et al. 2023. Solar-to-hydrogen efficiency of more than 9% in photocatalytic water splitting. *Nature* 613(7942):66–70**
88. Jung H, Ager JW. 2023. A tipping point for solar production of hydrogen? *Joule* 7(3):459–61
89. Niu K, Xu Y, Wang H, Ye R, Xin HL, et al. 2017. A spongy nickel-organic CO₂ reduction photocatalyst for nearly 100% selective CO production. *Sci. Adv.* 3(7):e1700921
90. Fabian DM, Hu S, Singh N, Houle FA, Hisatomi T, et al. 2015. Particle suspension reactors and materials for solar-driven water splitting. *Energy Environ. Sci.* 8(10):2825–50
91. Navalón S, Dhakshinamoorthy A, Álvaro M, Garcia H. 2013. Photocatalytic CO₂ reduction using non-titanium metal oxides and sulfides. *ChemSusChem* 6(4):562–77
92. Reichman J. 1980. The current-voltage characteristics of semiconductor-electrolyte junction photo-voltaic cells. *Appl. Phys. Lett.* 36(7):574–77
93. Lewis NS. 1991. An analysis of charge transfer rate constants for semiconductor/liquid interfaces. *Annu. Rev. Phys. Chem.* 42:543–80
94. Peter LM, Li J, Peat R. 1984. Surface recombination at semiconductor electrodes: part I. Transient and steady-state photocurrents. *J. Electroanal. Chem. Interfacial Electrochem.* 165(1–2):29–40
95. Li J, Peat R, Peter LM. 1984. Surface recombination at semiconductor electrodes: part II. Photoinduced “near-surface” recombination centres in *p*-GaP. *J. Electroanal. Chem. Interfacial Electrochem.* 165(1–2):41–59
96. Li J, Peter LM. 1985. Surface recombination at semiconductor electrodes: part III. Steady-state and intensity modulated photocurrent response. *J. Electroanal. Chem. Interfacial Electrochem.* 193(1–2):27–47
97. Mills TJ, Lin F, Boettcher SW. 2014. Theory and simulations of electrocatalyst-coated semiconductor electrodes for solar water splitting. *Phys. Rev. Lett.* 112(14):148304
98. Kumar B, Llorente M, Froehlich J, Dang T, Sathrum A, Kubiak CP. 2012. Photochemical and photoelectrochemical reduction of CO₂. *Annu. Rev. Phys. Chem.* 63:541–69
99. **Cheng J, VandeVondele J, Sprik M. 2014. Identifying trapped electronic holes at the aqueous TiO₂ interface. *J. Phys. Chem. C* 118(10):5437–44**
100. Cheng J, Liu X, Kattirtzi JA, VandeVondele J, Sprik M. 2014. Aligning electronic and protonic energy levels of proton-coupled electron transfer in water oxidation on aqueous TiO₂. *Angew. Chem. Int. Ed.* 53(45):12046–50
101. Le Formal F, Pendlebury SR, Cornuz M, Tilley SD, Grätzel M, Durrant JR. 2014. Back electron-hole recombination in hematite photoanodes for water splitting. *J. Am. Chem. Soc.* 136(6):2564–74
102. Mesa CA, Francàs L, Yang KR, Garrido-Barros P, Pastor E, et al. 2020. Multihole water oxidation catalysis on hematite photoanodes revealed by operando spectroelectrochemistry and DFT. *Nature Chem.* 12(1):82–89

87. Remarkable demonstration of nearly 10% solar-to-hydrogen conversion efficiency using a semiconductor photocatalyst.

99. First theory prediction of catalytically active surface states within the bandgap of TiO₂.

103. Zhang S, Leng W. 2020. Questioning the rate law in the analysis of water oxidation catalysis on haematite photoanodes. *Nat. Chem.* 12(12):1097–98
104. Mesa CA, Rao RR, Francàs L, Corby S, Durrant JR. 2020. Reply to: Questioning the rate law in the analysis of water oxidation catalysis on haematite photoanodes. *Nat. Chem.* 12(12):1099–101
105. Wang P, Benitez G, Houle FA. 2025. Influence of hole transport and thermal reactions in photo-driven water oxidation kinetics on crystalline TiO₂. *ACS Catal.* 15(9):7653–65
106. Vinogradov I, Singh S, Lyle H, Paolino M, Mandal A, et al. 2022. Free energy difference to create the M-OH* intermediate of the oxygen evolution reaction by time-resolved optical spectroscopy. *Nat. Mater.* 21(1):88–94
107. Cuk T. 2024. Phenomenology of intermediate molecular dynamics at metal-oxide interfaces. *Annu. Rev. Phys. Chem.* 75:457–81
108. Peter L. 2021. Fundamental aspects of photoelectrochemical water splitting at semiconductor electrodes. *Curr. Opin. Green Sustain. Chem.* 31:100505
109. Wang K, Ma Y, Liu Y, Qiu W, Wang Q, et al. 2021. Insights into the development of Cu-based photocathodes for carbon dioxide (CO₂) conversion. *Green Chem.* 23(9):3207–40
110. Hinogami R, Mori T, Yae S, Nakato Y. 1994. Efficient photoelectrochemical reduction of carbon dioxide on a p-type silicon (p-Si) electrode modified with very small copper particles. *Chem. Lett.* 23(9):1725–28
111. Gu J, Wuttig A, Krizan JW, Hu Y, Detweiler ZM, et al. 2013. Mg-doped CuFeO₂ photocathodes for photoelectrochemical reduction of carbon dioxide. *J. Phys. Chem. C* 117(24):12415–22
112. Liu G, Zheng F, Li J, Zeng G, Ye Y, et al. 2021. Investigation and mitigation of degradation mechanisms in Cu₂O photoelectrodes for CO₂ reduction to ethylene. *Nat. Energy* 6(12):1124–32
113. Sun J, Guijarro N, Li P, Thumu U, Yum J-H, et al. 2023. Ink-based CuIn_{0.3}Ga_{0.7}S₂ nanocrystal thin films as photocathodes for photoelectrochemical CO₂ reduction reaction. *ACS Appl. Nano Mater.* 6(12):10106–14
114. Lai Y, Watkins NB, Muzzillo C, Richter M, Kan K, et al. 2022. Molecular coatings improve the selectivity and durability of CO₂ reduction chalcogenide photocathodes. *ACS Energy Lett.* 7(3):1195–201
115. Prabhakar RR, Shukla S, Li H, Kim RS, Chen W, et al. 2025. Origin of photoelectrochemical CO₂ reduction on bare Cu(In,Ga)S₂ (CIGS) thin films in aqueous media without co-catalysts. *EES Catal.* 3(2):327–36
116. Zeng G, Liu G, Panzeri G, Kim C, Song C, et al. 2025. Surface composition impacts selectivity of ZnTe photocathodes in photoelectrochemical CO₂ reduction reaction. *ACS Energy Lett.* 10(1):34–39
117. Hong J, Zhang W, Ren J, Xu R. 2013. Photocatalytic reduction of CO₂: a brief review on product analysis and systematic methods. *Anal. Methods* 5(5):1086–97
118. Khanipour P, Löffler M, Reichert AM, Haase FT, Mayrhofer KJJ, Katsounaros I. 2019. Electrochemical real-time mass spectrometry (EC-RTMS): monitoring electrochemical reaction products in real time. *Angew. Chem.* 131(22):7351–55
119. Wang X, de Araújo JF, Ju W, Bagger A, Schmies H, et al. 2019. Mechanistic reaction pathways of enhanced ethylene yields during electroreduction of CO₂-CO co-feeds on Cu and Cu-tandem electrocatalysts. *Nat. Nanotechnol.* 14(11):1063–70
120. Ren H, Kovalev M, Weng Z, Muhamad MZ, Ma H, et al. 2022. Operando proton-transfer-reaction time-of-flight mass spectrometry of carbon dioxide reduction electrocatalysis. *Nat. Catal.* 5(12):1169–79
121. Zhang Q, Yang C, Chen Y, Yan Y, Kan M, et al. 2025. Efficient photocatalytic CH₄-to-ethanol conversion by limiting interfacial hydroxyl radicals using gold nanoparticles. *Angew. Chem. Int. Ed.* 64(7):e202419282
122. Xie J, Fu C, Quesne MG, Guo J, Wang C, et al. 2025. Methane oxidation to ethanol by a molecular junction photocatalyst. *Nature* 639(8054):368–74
123. Kovalev MK, Ren H, Zakir Muhamad M, Ager JW, Lapkin AA. 2022. Minor product polymerization causes failure of high-current CO₂-to-ethylene electrolyzers. *ACS Energy Lett.* 7(2):599–601
124. Osiewacz J, Löffelholz M, Weseler L, Turek T. 2023. CO poisoning of silver gas diffusion electrodes in electrochemical CO₂ reduction. *Electrochim. Acta* 445:142046
125. Cui Z, Wong AJ-W, Janik MJ, Co AC. 2024. Negative reaction order for CO during CO₂ electroreduction on Au. *J. Am. Chem. Soc.* 146(34):23872–80

126. Moss B, Wang Q, Butler KT, Grau-Crespo R, Selim S, et al. 2021. Linking in situ charge accumulation to electronic structure in doped SrTiO₃ reveals design principles for hydrogen-evolving photocatalysts. *Nat. Mater.* 20(4):511–17
127. Hori H, Takashima M, Takase M, Ohtani B. 2018. Kinetic analysis supporting multielectron reduction of oxygen in bismuth tungstate-photocatalyzed oxidation of organic compounds. *Catal. Today* 313:218–23
128. Kim Y-G, Javier A, Baricuatro JH, Torelli D, Cummins KD, et al. 2016. Surface reconstruction of pure-Cu single-crystal electrodes under CO-reduction potentials in alkaline solutions: a study by serial-tim ECSTM-DEMS. *J. Electroanal. Chem.* 780:290–95
129. Vavra J, Ramona GPL, Dattila F, Kormányos A, Priamushko T, et al. 2024. Solution-based Cu⁺ transient species mediate the reconstruction of copper electrocatalysts for CO₂ reduction. *Nat. Catal.* 7(1):89–97
130. Shibuya T, Yasuoka K, Mirbt S, Sanyal B. 2014. Bipolaron formation induced by oxygen vacancy at rutile TiO₂(110) surfaces. *J. Phys. Chem. C* 118(18):9429–35
131. Ambrosio F, Wiktor J. 2019. Strong hole trapping due to oxygen dimers in BiVO₄: effect on the water oxidation reaction. *J. Phys. Chem. Lett.* 10(22):7113–18
132. Liu J, Zou Y, Jin B, Zhang K, Park JH. 2019. Hydrogen peroxide production from solar water oxidation. *ACS Energy Lett.* 4(12):3018–27
133. Xue Y, Wang Y, Pan Z, Sayama K. 2021. Electrochemical and photoelectrochemical water oxidation for hydrogen peroxide production. *Angew. Chem. Int. Ed.* 60(19):10469–80
134. Liu J-Y, Gong X-Q, Alexandrova AN. 2019. Mechanism of CO₂ photocatalytic reduction to methane and methanol on defected anatase TiO₂(101): a density functional theory study. *J. Phys. Chem. C* 123(6):3505–11
135. Zhang W, Jin Z, Chen Z. 2022. Rational-designed principles for electrochemical and photoelectrochemical upgrading of CO₂ to value-added chemicals. *Adv. Sci.* 9(9):2105204