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Journal

Energy & Environmental Science, 8(10)

ISSN

1754-5692

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Publication Date

2015

DOI

10.1039/c5ee01434d

Peer reviewed

Particle Suspension Reactors and Materials for Solar-Driven Water Splitting

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Abstract

Reactors based on particle suspensions for the capture, conversion, storage, and use of solar energy as H₂ are projected to be cost-competitive with fossil fuels. In light of this, this review paper summarizes state-of-the-art particle light absorbers and cocatalysts as suspensions (photocatalysts) that demonstrate visible-light-driven water splitting on the laboratory scale. Also presented are reactor descriptions, theoretical considerations particular to particle suspension reactors, and efficiency and performance characterization metrics. Opportunities for targeted research, analysis, and development of reactor designs are highlighted.

I. Introduction

Practical solar water splitting, i.e. $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$, using Earth-abundant materials was branded a Holy Grail of chemistry.¹ Specifically, the charge was to demonstrate > 10% efficiency, > 10 year stability, and a cost of hydrogen that is competitive with the cost of fossil fuels, on an energy equivalent basis. Toward this, numerous laboratory demonstrations of photoelectrochemical (PEC) water splitting have been reported. The most efficient ones use a fixed-electrode design where the light-absorber materials resemble that of a solar-cell light absorber immersed into, or in the vicinity of, an aqueous electrolyte. PEC reactors for centralized H₂ production using this design have been termed Type 3 or Type 4 reactors,^{2,3} where the latter is operated under conditions of concentrated solar illumination. The techno-economics of these two designs have been analyzed, and both were projected to produce hydrogen with the energy content of a gallon of gasoline for less than the price of a gallon of gasoline in the United States of America (U.S.). However, this required that the reactors operate at approximately the maximum practical energy-conversion efficiency for solar-to-hydrogen evolution through water splitting (STH), i.e. ~25%.²⁻⁸ Alternative reactor designs for centralized H₂ production utilize particle suspensions where the particles are free to move in their mixture with the electrolyte and are not incorporated as part of a membrane to separate sites of anodic and cathodic redox chemistry. These designs have been termed Type 1 and Type 2 reactors based on the number of different reactor vessels and were projected to be cost-competitive with gasoline sold in the U.S. when operated at an STH efficiency of 5 – 10%, and even lower under certain circumstances. This is particularly notable in light of the laboratory-scale demonstrations that have achieved > 18% STH efficiency for designs

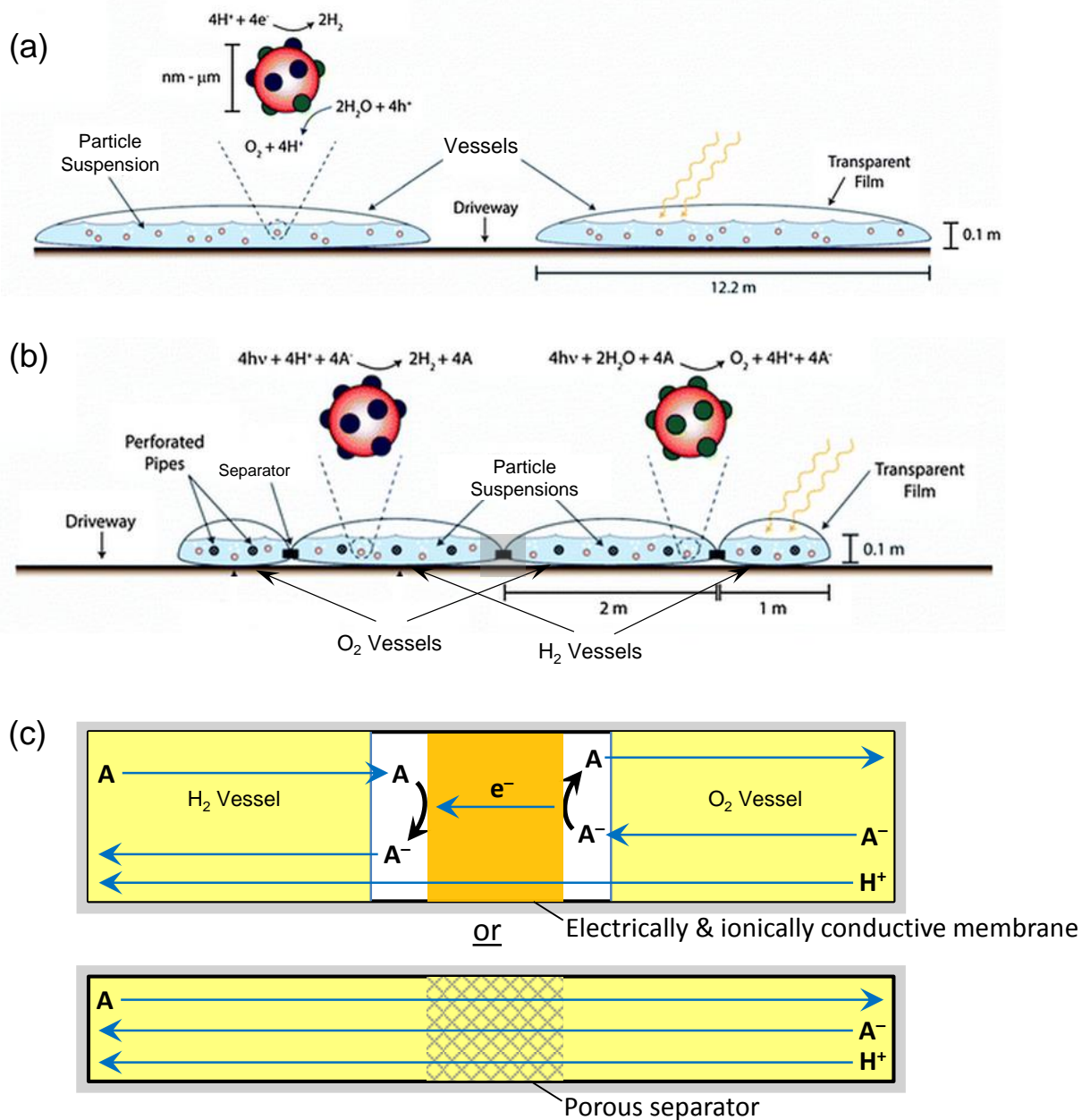


Figure 1. Two general designs for (a) a Type 1 reactor and (b) a Type 2 reactor, where in the Type 2 reactor the separator consists of (c) a nanoporous material or an electrically and ionically conductive material(s). Yellow areas in panel (c) indicate regions where diffusion and/or convection of the redox shuttle, A/A^- , are the dominant transport mechanisms, while the white areas depict regions of redox reactivity and the orange area depicts a region of electron conduction and ion migration.^{2,3} Images in panels (a) and (b) adapted from Ref 3 with permission from the Royal Society of Chemistry.

that are amenable to Type 3 reactors.^{9,10} Although the techno-economic analyses required many technological and cost assumptions, the low projected cost of particle suspension reactors serves as an impetus for continued and expanded research into Type 1 and Type 2 reactor designs, and motivates this review paper. The central focus of this review paper is on particle suspension reactors for solar PEC water splitting, such as slurries of nanoparticles or micron-sized materials.

Reported laboratory-scale demonstrations of solar (visible-light-driven) water splitting using particle suspensions are summarized below. There are two general designs for these reactors: Type 1, which evolves H₂ and O₂ in the same vessel; and Type 2, which evolves H₂ and O₂ in separate vessels and also generates intermediate chemical species that serve as a redox shuttle between the vessels via a Z-scheme mechanism (Figure 1).^{2,3} This and other terminology relevant to this review paper are summarized in Table 1. Reactor-level engineering considerations and particle characterization methods are also presented as well as various opportunities for continued research, analysis, and development that would further the understanding of these complex designs and identify potential routes for advancement of particle suspension technologies for solar PEC water splitting.

Table 1. Device terminology.

photoelectrochemical (PEC) water splitting	Light-driven water electrolysis into only H ₂ and O ₂
suspension	A mixture or slurry solution of non-fixed solid electrode particles, which when completely dispersed and suspended in another substance on the sub-micron scale are termed colloidal
tandem particles	Two light-absorber particles that are connected electrically in series via a solid-state contact or via a redox shuttle
redox shuttle	An electrolyte additive that is redox active and mediates charge transport between two locations
Type 1 reactor	A single-vessel reactor that evolves H ₂ and O ₂ in the same space
Type 2 reactor	A reactor that evolves H ₂ and O ₂ in separate vessels and thus requires a solution redox shuttle to facilitate the transfer of electrons and ions between the vessels.
Z-scheme	A PEC mechanism that utilizes two light-absorber particles either in solid-state contact or requiring a redox shuttle to mediate charge between them, and which is suitable for use in a Type 1 or Type 2 reactor
HER	Hydrogen-evolution reaction, which electrochemically converts H ₂ O or H ⁺ into H ₂ via electron-transfer
OER	Oxygen-evolution reaction, which electrochemically converts H ₂ O or OH ⁻ into O ₂ via electron-transfer
cocatalyst	An electrocatalyst that is incorporated with another material to improve the rate of a faradaic reaction
STH efficiency	Solar-to-hydrogen energy-conversion efficiency for converting the energy in incident solar irradiation to chemical bonds as H ₂ through oxidation of water to O ₂
QY	Quantum yield, which is the ratio of the number of output events that occur per number of input stimuli, which is typically the number of absorbed photons ¹¹
EQY	External quantum yield, which for suspensions is often termed the apparent QY and should be defined as the ratio of two times the rate of collection of H ₂ (mol H ₂ cm ⁻² s ⁻¹) to the incident photon flux (mol photon cm ⁻² s ⁻¹)
overpotential	Potential difference between the equilibrium potential for a half reaction and the experimentally applied bias potential in order to obtain a specific current density
AM1.5G	Air Mass 1.5 Global tilt, which is the standard spectral composition of sunlight

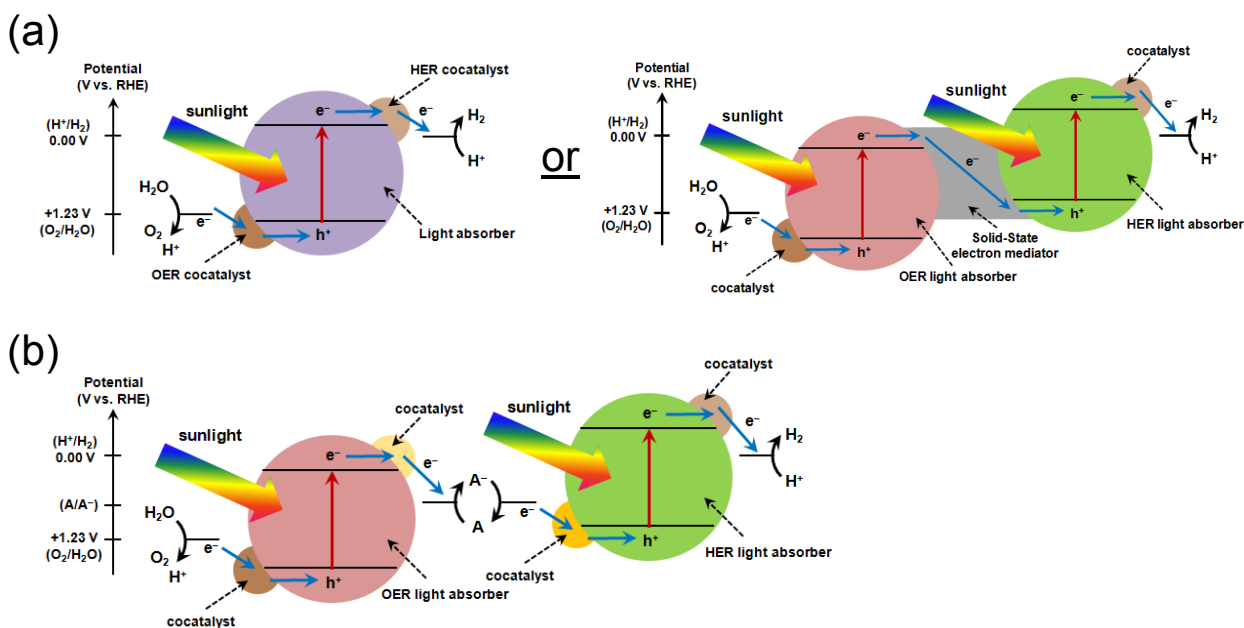


Figure 2. Schematic of materials components, arrangements, and energetics for particles that are suitable for (a) a Type 1 reactor and (b) a Type 2 or Type 1 reactor. Adapted with permission from Maeda, K.; Domen, K. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.¹² Copyright 2010 American Chemical Society.

II. Reactors

By definition, particle suspensions allow complete intermixing of at least two of the oxidation and reduction chemical products in a single electrolyte, which together contain stored electrochemical potential. This is because both oxidation and reduction half-reactions occur on each light-absorber particle (or particles, if multiple particles are in solid-state contact). In the Type 1 reactor design the only required products of the chemical reactions are H_2 and O_2 , and H^+ or OH^- which are assumed to rapidly equilibrate via mass transport around each particle. Each particle (or particles, if multiple are in solid-state contact) drives both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) (Figure 2a).¹² A drawback of this design is that an explosive mixture of H_2 and O_2 are co-evolved in one vessel.

The Type 2 reactor design does not present an explosive hazard but does introduce additional redox-active molecules. The desired products of the chemical reactions are H_2 , O_2 , H^+ or OH^- , and at least two redox states of a reversible (molecular) redox shuttle. H_2 , the redox shuttle in a higher oxidation state, and OH^- (or water via deprotonation of H_3O^+) are generated by particles in one vessel, while O_2 , the redox shuttle in a lower oxidation state, and H^+ (or water via protonation of OH^-) are generated by particles in a second vessel (Figure 2b). In order to neutralize pH differences, protons or hydroxide ions that are generated and consumed by the HER and the OER must be transported large distances between the vessels, by convection and diffusion. If the redox shuttle undergoes proton-coupled electron transfer reactions, then pH differences are not problematic because they are neutralized at each particle. Electronic charge can be transferred between the two vessels by several means. The redox shuttle can carry electrons by mass transport (convection and diffusion), while dragging along counterions due to local electric fields (Figure 1c). Alternatively, electrically conductive materials (e.g. a wire) with low overpotential for redox shuttle electrocatalysis can transport electrons at a much faster rate that is limited only by the

resistance of counterion drift in the liquid electrolyte and through the ion-exchange membrane separator (Figure 1c).¹³ An additional advantage of this design is that redox shuttles in different vessels do not mix and thus each vessel can use a redox shuttle that is best suited for the PEC reactions in that vessel.

A) Vessel Material

A prior sensitivity analysis of both reactor designs suggested that the gravimetric levelized cost of H₂ at the plant gate would be most influenced by the cost of the vessel material, i.e. the plastic.¹⁴ The aforementioned techno-economic analysis proposed that the predominant vessel material be high-density polyethylene (HDPE) in part because it is an inexpensive, mass-produced plastic.¹⁵ HDPE has been used in similar baggie-type reactors, such as those for photo-biological H₂ production from algae, and has exhibited long-term stability under solar irradiation.^{2,3,16} HDPE is chemically stable over the entire pH range (0 – 14) and is thermally stable to at least 60 °C,¹⁷ the approximate maximum temperature that a solar PEC water splitting reactor will likely reach. Also, H₂ permeability in HDPE is low,¹⁸ and a reasonable thickness can be chosen (~0.5 cm) that results in transmission of ~90% of the incident solar illumination with only a < 1% loss of evolved H₂.¹⁹ Thus, HDPE and similar optically transparent, robust, and inexpensive plastics are likely good candidate materials for the reactor vessels.

B) Challenges for Type 1 Reactors

A major practical technical challenge with the Type 1 reactor is the need to separate the explosive mixture of H₂ and O₂ gases in the headspace of the single vessel. Preventing a flammable mixture by separating 98% of the H₂ from the evolved H₂ and O₂ mixture so that it is below the flammability limit of 4 at % H₂ and 96 at % O₂,²⁰ requires an estimated energy expense equal to 8.7% of the energy stored in the fuel mixture (see Appendix). In practice, the energy expense will be higher, due to the need to power the compressor and to probably include pressure-swing-adsorption components. Gas separation is projected to constitute the largest fraction of the reactor capital costs.^{2,3} Another means to separate the H₂/O₂ product gases is through the use of a carrier gas that dilutes the H₂ and O₂ to beyond their flammability limits.¹⁴ The carrier gas can be an inert gas, such as N₂ or Ar, or the reactor product gases, i.e. H₂ or O₂. Dilution with H₂ makes sense if a small concentration of O₂ (and water) in H₂ is easier to remove than a small concentration of H₂ in O₂. Moreover, this latter composition will form a combustible mixture during the concentration process if O₂ is removed from the mixture. For H₂ dilution, the original 2:1 v/v stoichiometric H₂/O₂ reaction product mixture (66.7 at %, 33.3 at %) would be concentrated to beyond the flammability limit of ~95 at % H₂ and ~5 at % O₂ with at least 17 parts of pure H₂ per 2 parts product H₂ and 1 part product O₂, which results in a 20/3 (6.67) volume dilution factor.¹⁴ The energy required for the repeated H₂ separation and subsequent use as diluent followed by re-separation is projected to use > 60% of the energy stored as H₂, resulting in a > 60% increase in the capital costs of the gas processing subassembly, assuming a \$0.10/kW-hr cost of electricity.¹⁴ These monetary and energy costs were projected to increase the levelized cost of H₂ for a Type 1 reactor by > 90%.¹⁴ This suggests that there is a strong need to design alternative gas separation and management schemes.

C) Challenges for Type 2 Reactors

A major practical technical challenge with the Type 2 reactor is that without proper electrolyte flow, the redox shuttle will not move between the vessels rapidly enough to keep concentration

gradients to a minimum. This macroscopic mass transport is governed by the Nernst–Planck equation which states that mass transfer occurs due to a combination of diffusive flux due to Brownian motion, convective flux due to mixing, and migration flux due to the effect of electric fields on charged particles.^{21,22} Mass transport of redox shuttles in particle suspension reactors will occur across and between vessels mostly by mixing and diffusion. Ionic migration of counterions will occur over a short distance between the sites for each half-reaction on individual particles and alongside charged redox shuttles as they transport across and between vessels. Because these mass-transport processes are decoupled from the light-driven reactions, their rates can differ from the absorbed photon flux but must result in a steady-state concentration profile over day–night cycles and the timescale of days. Per the Nernst equation, every order-of-magnitude change in redox shuttle concentration from the initial conditions results in an additional thermodynamic potential requirement of $(2.303RT/nF) = (59.2 \text{ mV}/n)$ beyond that required for water splitting. Thus, slow redox-shuttle mass transport over large distances can result in significant additional thermodynamic potential requirements and concentration overpotentials. Passive diffusion between vessels modeled in the techno-economic analysis will not reach a stable redox shuttle concentration gradient, because the vessels were modeled to be on the meters length-scale. Thus, in the absence of convection the original redox state of the redox shuttle will become fully depleted during solar illumination and the device will eventually cease to operate. For this reason, flow in Type 2 reactors is very important; however, the largest fraction of the reactor capital costs in a Type 2 reactor are projected to be the piping and control system subassemblies to mix the electrolytes, notably the pipes and pumps.^{2,3}

The separator is also a key component. It must be highly impermeable and electrically insulating with respect to recombination of the reaction products, H₂ and O₂. Many state-of-the-art separators have been developed for other electrochemical technologies and have decades of proven industrial success. However, some are not practical for use in particle suspensions for solar PEC water splitting. In particular, porous materials cannot sustain pressure differentials and thus even small pressure differentials between the vessels will result in forced convection of the electrolyte across the separator.²³ Because crossover currents are approximately independent of the rate of product formation, a $\sim 10 \text{ mA cm}^{-2}$ crossover current is insignificant for major industrial technologies that operate at current densities on the order of A cm^{-2} . However, most solar PEC water splitting devices are projected to operate at rates comparable to this crossover current density, and thus a majority of the reaction products will mix between the vessels before they can be collected.²⁴ Nafion, a polytetrafluoroethylene copolymer containing perfluorinated vinyl ethers and terminal sulfonate ionic functional groups, overcomes this issue because it can withstand large pressure differentials, exhibits a low rate of crossover for H₂ and O₂, and is extremely chemically robust. For these reasons, Nafion is the state-of-the-art ion-exchange membrane used in most fuel cells, electrolyzers, chloralkali plants, and redox-flow batteries, but represents a large fraction of the cost of these electrochemical cells.²⁵ In particle suspension reactors, highly reactive hydroxyl radicals and hydrogen peroxide generated at the particles as undesired side-products of water splitting may be quenched before they can interact with the separator. This is because most of the particles are located far from the separator and although hydrogen peroxide is rather stable in aqueous solution, it rapidly disproportionates at many metal surfaces such as those often used as cocatalysts.²⁶ Thus, a membrane with the outstanding properties and high cost of Nafion may not be required in most particle suspension reactors for solar PEC water splitting.

D) Commercial Interest

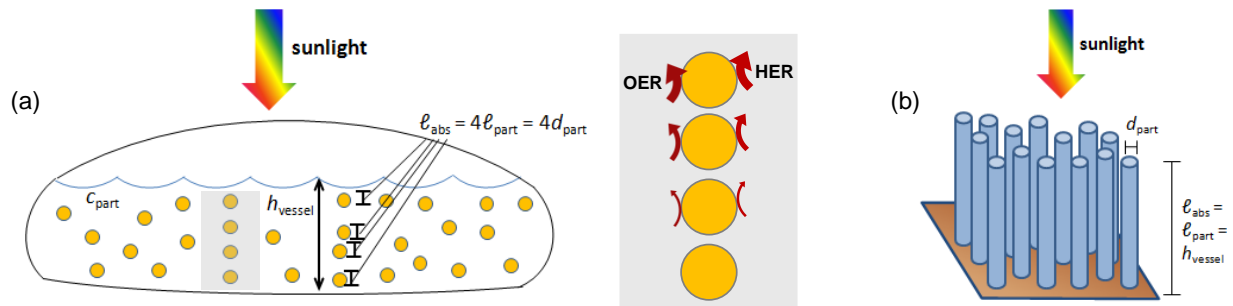


Figure 3. Comparison between (a) a particle-suspension reactor design and (b) a fixed-electrode reactor design. (a) For particle suspension reactors, vessel height (h_{vessel}) and particle concentration (c_{part}) are the main important parameters to determine an optical path length that results in significant above-bandgap sunlight absorption (l_{abs}). Inset: Particles near the bottom of the vessel absorb less light and thus drive HER and OER at slower rates than particles near the top of the vessel, depicted by the sizes of the curved arrows. (b) This fixed-electrode design affords rapid charge collection along the short dimension of the rods/wires (d_{part}) and maximum absorption of sunlight along the long dimension (l_{part}).

Two companies have actively pursued research and development of laboratory-scale particle suspension reactors. HyperSolar, involving Prof. Eric McFarland (University of California, Santa Barbara), fabricates and evaluates rod-shaped particles affixed in insulating alumina pores for light-driven water splitting and HBr splitting into H_2 and Br_2 . Sun Catalytix, founded by Prof. Dan Nocera (Harvard University), previously investigated the techno-economics of particle suspension reactors and fabricated small-scale models.

III. Theoretical Considerations

Theoretically, there are many fundamental considerations for particle suspension reactors for solar PEC water splitting that have not been thoroughly evaluated. Many of these are described below and organized by general theme. There is a great need for not only experimental analyses of the following hypotheses, but also numerical modeling and simulations ranging from the nano-scale to the device and reactor scale. As materials are developed that may be promising for application in particle suspension reactors for solar PEC water splitting, logical particle-scale and reactor-scale designs will become increasingly important and can be most effectively assessed once the considerations outlined below are clarified.

A) Particle Concentration

Without varying the size of the particles, the optical absorption of particle suspensions can be adjusted by changing the particle concentration (c_{part}) and/or vessel height (h_{vessel}) (Figure 3a). Absorption of nearly all incident above-bandgap sunlight is possible with appropriate choice of h_{vessel} and c_{part} . Thus, the volume of the electrolyte used in a particle suspension reactor dictates the amount of light-absorber material, while in fixed-electrode designs this is not the case for the electrolyte dimension orthogonal to the face of the electrode, i.e. the thickness of the electrolyte toward the Sun. Engineering considerations for forced convection (e.g. electrolyte flow and mixing) will depend on the size of the reactor. This will dictate an optimal concentration of particles for sufficient sunlight absorption and maximum STH efficiency, which may in turn redefine the necessary amount of forced convection. The complex interdependence of particle

concentration, light absorption, solvent volume, and mass transfer of reagents may require iterative reactor design engineering, which would benefit from initial assessment *in silico*.

B) Particle Size: Nano-scale vs. Micron-scale

Particle size affects the mechanisms by which light interacts with the particles and photo-excited charge carriers are separated and collected, and thus the STH efficiency of the reactor. Nano-scale particles present a shorter distance in order to collect minority charge carriers, but require p-i-n doping distributions in order to support a space-charge region and assist in charge separation.^{27–30} Another review paper published in this journal issue titled “Experimental Demonstrations of Spontaneous, Solar-Driven Photoelectrochemical Water Splitting” describes the effects of semiconductor–liquid junctions versus buried junctions so this will not be discussed further here, except that fabrication of buried junctions is inherently a more complex and costly process but often results in increased device efficiencies and stabilities.¹⁰ Moreover, in comparison to smooth micron-sized particles, smooth nanoparticles present more surface area per particle volume which lessens cocatalyst requirements. However, micron-sized particles absorb more light, because the optical path length depends on particle size and micron-sized particles also more effectively scatter light likely increasing the number of times light passes through each particle. Larger particles are also more likely to more fully support space-charge regions (Figure 4), which often results in more efficient charge separation and larger open-circuit photovoltages, assuming there are two locations for charge collection, one ohmic and the other rectifying.^{31–33} For example, micron-sized particles of optimally doped silicon are required to support a near-maximum-sized space-charge region;³⁴ however, for optimally doped GaAs particles sub-micron diameters suffice.³⁵ In summary, key challenges for nano-scale and micron-scale particle for solar PEC water splitting are to develop optimally doped light-absorber materials with large thicknesses, to absorb a significant amount of incident above-bandgap irradiation (e.g. > 90%), and large cocatalyst surface areas, to minimize electrocatalytic losses. Moreover, a balance in the size of the minimum dimension must be attained so that it is large enough to support a space-charge region, and assist in excited-state charge separation, while also small enough to afford rapid charge collection.

C) Particle Shape: Symmetric vs. Asymmetric

Particles with highly anisotropic size and shape are desired for fixed-electrode designs. Maximum absorption of sunlight occurs when the long dimension of the particle is nearly collinear with the direction of propagation of solar photons.³⁶ The short dimension of the particle affords

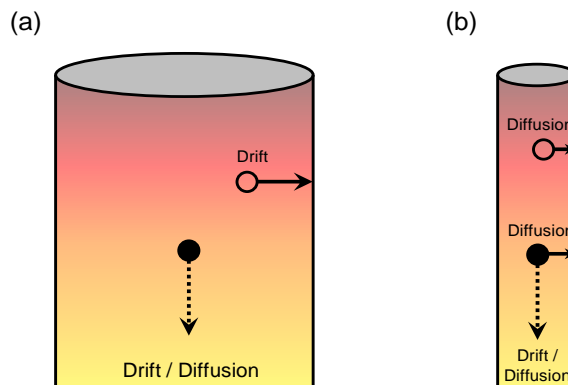


Figure 4. Comparison of the mechanisms by which minority (open circles) and majority (filled circles) charge carriers separate in (a) thick and (b) thin high-aspect-ratio semiconductors containing the same dopant density and in contact with a redox couple that upon equilibration drives the semiconductor into inversion. The structure in (a) can support most of the space-charge region and so the concentration of majority carriers in the bulk does not change upon equilibration. Adapted with permission from Fitch, A.; Strandwitz, N. C.; Brunshwig, B. S.; Lewis, N. S. *J. Phys. Chem. C* **2013**, *117*, 2008–2015.³³ Copyright 2013 American Chemical Society.

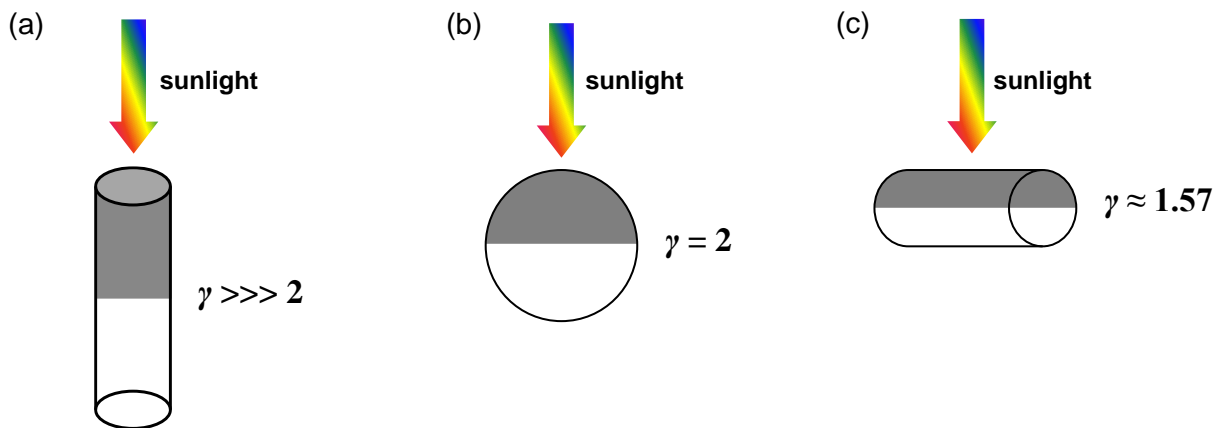


Figure 5. Comparison of effective roughness factor (γ) among (a) high-aspect-ratio rods or wires illuminated collinear with the long dimension, (b) spherical particles, and (c) high-aspect-ratio rods or wires illuminated orthogonal to the long dimension.

rapid charge collection (Figure 3b). However, this design is not entirely favorable, because the dark (recombination) current of high-surface-area materials with many surface recombination sites scales with the junction area.^{31,37} This can be quite large for high-aspect-ratio structures in comparison to planar devices, and increased dark current decreases both the open-circuit photovoltage and STH efficiency. This is an unresolved complication for fixed-electrode reactors that benefit from orthogonalization of light absorption and charge collection. For particle suspension reactors, this orthogonalization approach is not feasible because the particles are dispersed freely.

Reducing surface recombination and interfacial recombination is a significant challenge for development of particle suspension reactors.³⁸ Spherical particles are favored because they have the smallest ratio of surface area to volume compared to other particle shapes. The junction area of spherical particles is increased by only a factor of two over planar materials with the same projected area, irrespective of particle diameter. This effective roughness factor, γ , is calculated as the ratio of the surface area of the particle hemisphere, assuming that is the size over which one half-reaction occurs, to the area of the projected footprint of the particles, i.e. $\gamma = \frac{\frac{1}{2}A_{\text{surface}}}{A_{\text{projected}}} = \frac{\frac{1}{2}\left(4\pi\left(\frac{d_{\text{part}}}{2}\right)^2\right)}{\pi\left(\frac{d_{\text{part}}}{2}\right)^2} = 2$ (Figure 5b). Smaller effective roughness factors can be attained using high-aspect-ratio particles whose long dimension is *orthogonal* to the direction of incident illumination,³⁹ $\gamma = \frac{\frac{1}{2}A_{\text{surface}}}{A_{\text{projected}}} = \frac{\frac{1}{2}(\pi d_{\text{part}})\ell_{\text{part}}}{d_{\text{part}} \cdot \ell_{\text{part}}} = \frac{\pi}{2} \approx 1.57$ (Figure 5c). However, this arrangement has been shown to result in increased optical reflection,⁴⁰ and maintaining this orientation in a particle suspension reactor is a considerable design challenge. In summary, unlike for the fixed-electrode design spherical particles have advantages over anisotropic structures in terms of light absorption and charge separation.

D) Particle Reactivity: Electrocatalysis vs. Dark recombination current

Particles located deeper in the reaction vessels will be illuminated significantly less than those located near the top of the vessels. This is likely true under any illumination conditions and any physics that describes photon propagation, absorption, and scattering. There are pros and cons to absorbing less light. It could be problematic because the open-circuit photovoltage of a particle

must exceed $(E_{\text{fuel}} - E_{\text{bias}})$ in order to drive net water splitting chemistry,⁴¹ and the open-circuit photovoltage decreases by $(a \times (2.303RT/F) = a \times 59.2 \text{ mV})$ per order-of-magnitude decrease in absorbed photon flux (at room temperature), based on the diode equation, and where a is the dimensionless diode quality factor (dqf) and has a value of one for an ideal diode. Thus, to a first approximation particles located deeper in the vessels may not be capable of splitting water, and instead will act as shunts for recombination of H₂ and O₂ to form water (Figure 3a, inset). However, absorbing less light may not be entirely negative assuming even lightly illuminated particles drive net water splitting chemistry. This is because decreased illumination results in a concurrent decrease in the open-circuit photovoltage as well as a decrease in the electrocatalytic overpotential, which are effects that oppose each other. The overpotential can be approximated using the Tafel equation, which is only accurate at intermediate overpotentials, and predicts that when the current through a particle decreases by one order-of-magnitude, the overpotential decreases by the Tafel slope (units: V per order-of-magnitude change in current).²¹ Because the current through a particle is directly related to the absorbed photon flux, particles deeper in the vessel are projected to exhibit both lower open-circuit photovoltages and lower overpotentials. Therefore, the efficiency of particle suspensions as a function of illumination intensity depends on the combination of the diode quality factor(s) of the light absorber(s), \sum_{dqf} , and the combination of the Tafel slope(s) of the electrocatalyst(s), \sum_{TS} . If $(2.303RT/F)\sum_{\text{dqf}}$ is larger than \sum_{TS} then the STH efficiency of weakly illuminated particles (i.e. those deeper in the vessels) decreases, because the photovoltage decreases faster than the required overpotential for electrocatalysis. If \sum_{TS} is larger than $(2.303RT/F)\sum_{\text{dqf}}$ then the efficiency of weakly illuminated particles (i.e. those deeper in the vessels) increases, because the required overpotential for electrocatalysis decreases faster than the photovoltage. Based on state-of-the-art values for OER and HER electrocatalysts and photovoltaic light absorbers,^{42,43} particles deeper in the vessels will likely operate at decreased efficiencies.⁴¹ Again, this assumes that Tafel analysis is valid at small overpotentials and that the photovoltage is large enough to drive net water splitting chemistry. Moreover, this assumes that the rate-limiting recombination steps are independent of light intensity, which may not be the case under strong illumination conditions where high-level injection and equal-concentration second-order recombination become dominant.⁴⁴

E) Colloidal Particle Dispersion

Particles suspensions for solar PEC water splitting can consist of fully dispersed colloids or particulate suspensions assuming convection is sufficient to prevent sedimentation. For particles that fully dispersed as colloids, their stability toward flocculation and sedimentation is affected by several primary factors. Particles are driven together by Brownian motion (quiescent) or shear forces (dynamic) while local forces can be attractive (dispersion) or repulsive (electrostatic).⁴⁵ Any characteristic that affects particle–particle interactions will affect colloidal stability, irrespective of particle size. Moreover, colloids can form from any phase of matter. The most relevant for solar PEC water-splitting reactors are the solid light-absorber particles and gas bubbles.⁴⁶ The following discussion on stability applies to both types, with the main distinction being the result of destabilization: solid particles coalesce into a solid that settles to the bottom of a vessel through gravity, while bubbles flocculate into larger bubbles that escape into the gas phase. In the absence of electrostatic repulsion, Brownian motion results in interparticle condensation and eventual loss of colloidal stability on a timescale determined by the diffusion rate. The primary factors affecting the diffusion rate are the particle dimensions and solution viscosity, related through the Stokes–Einstein equation.

The basic forces between charged colloidal particles in a liquid are described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.^{47,48} According to this theory the stable distance between two particles surrounded by an electrical double layer is determined by the balance between van der Waals attraction and electrostatic repulsion. In the case of solar PEC water splitting systems there are several dominant factors that influence this balance. The ionic strength of the aqueous electrolyte plays a direct role, where the higher the ionic strength the greater the tendency to flocculate due to electrostatic shielding of repulsive forces that would normally maintain a separation between charged particle surfaces. Stability also depends on surface composition and charge which are affected by illumination, temperature, electrolyte composition, impurities, defects, and adsorbed molecules (e.g. reactants, products, ligands). A colloid will be more stable due to repulsion when the particles are highly charged and present more sterically hindered surfaces. However, the characteristics of each particle are not static and are affected by optical intensity, spectral distribution, and temperature which each vary during the day and with seasons, and may also be affected by chemical reactions. The stability of colloidal solutions over wide concentration ranges are also influenced by components in the solution that adsorb to the particle surfaces as well as interparticle repulsions, resulting in varying stabilities with particle and molecular loadings. This is particularly relevant to the Type 2 reactors that require a solution redox shuttle to mediate charge, which in several cases described below has been shown to adsorb to particle and cocatalyst surfaces.

When the concentration of particles is high, stability can be observed due to high charge density and/or molecular surface area density that is very repulsive, stabilizing the colloidal solution due to electrostatic and entropic effects. For a dilute solution with a low concentration of particles, the colloidal solution can also be stable due to kinetic limitations on nucleating a floc. For intermediate concentrations, aggregation is more likely to be favored due to the more complex balance of relevant factors that affect stability and often lead to eventual coagulation. A particle concentration that is optimized for optical absorption and scattering may be completely incompatible with the particle concentration and electrolyte composition required to maintain colloidal stability, leading to limitations on achievable performance. However, colloidal solutions are not quiescent under operating conditions even if there is no imposed flow, so bubbles and solid particles can affect each other. Bubble coalescence and migration into the gas phase imparts flow and shearing activity to the electrolyte and this kinetic energy can increase the tendency of solid particles to flocculate by driving them closer together. In summary, there is a complex interplay of various phenomena that determine whether a colloidal solution of particles is stable and appropriate for a solar PEC water-splitting device.

F) Cocatalyst Materials and Selective Catalysis

Electrocatalysts are necessary components of PEC water splitting devices, because it is unlikely that a given light-absorber material also facilitates rapid redox chemistry. Electrocatalysts chosen specifically to catalyze the desired redox chemistry and used in conjunction with a light-absorber material are termed cocatalysts. Light-absorber materials generate power through sunlight absorption while cocatalysts decrease the activation energy for the desired fuel-forming reactions, which is manifest by an increased exchange current density and decreased electrocatalytic overpotential. Because cocatalysts are in physical contact with light-absorber materials, sunlight-transmitting cocatalysts are desired.

Many electrocatalyst materials and molecules have been examined as cocatalysts for application in solar PEC water splitting. An extensive list is beyond the scope of this review paper, and various reviews already exist.^{12,42,43,49–57} Instead, this section focuses on unique cocatalysts

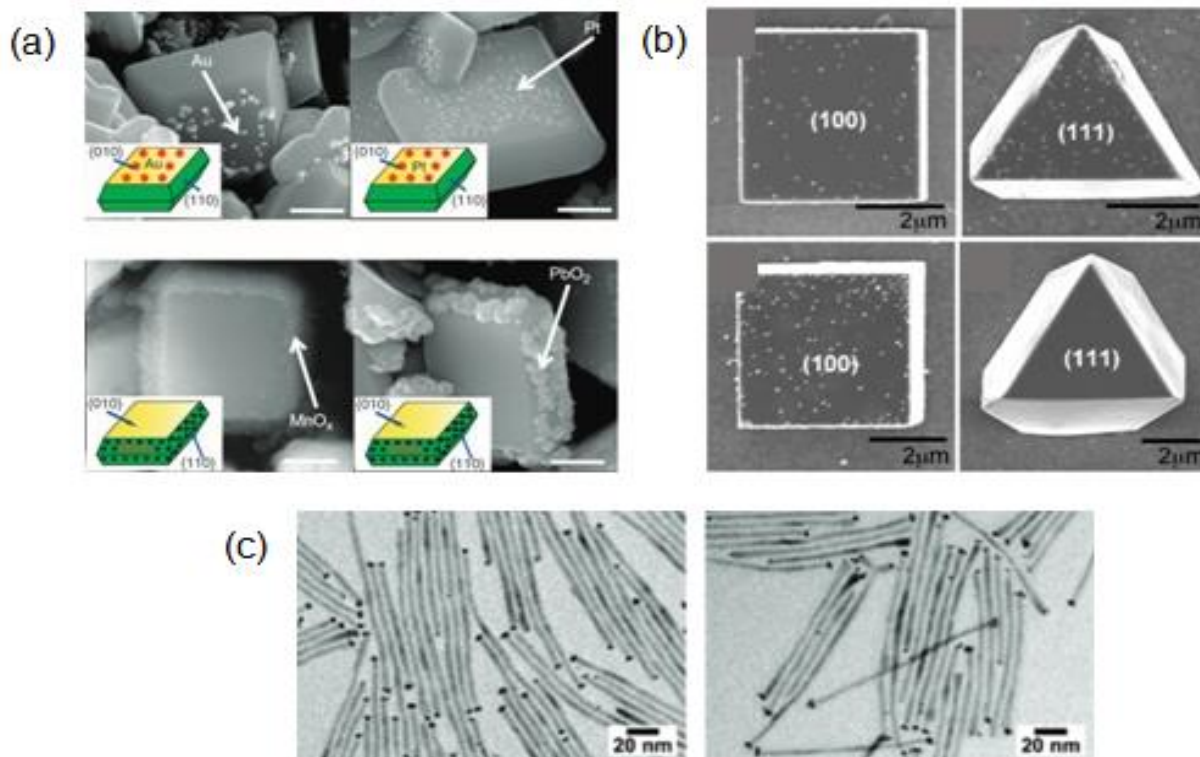


Figure 6. (a) Scanning-electron micrographs of micron-sized BiVO₄ crystallites after facet-selective PEC deposition of the indicated materials (scale bars are 500 nm). Reprinted by permission from Macmillan Publishers Ltd: Nature Communications (59), copyright 2013. (b) Scanning-electron micrographs of micron-sized Cu₂O crystallites with Au deposited in the absence (top) or in the presence (bottom) of sodium dodecylsulfate. Adapted with permission from Read, C. G.; Steinmiller, E. M. P.; Choi, K. S. *J. Am. Chem. Soc.* **2009**, *131*, 12040–12041.⁶¹ Copyright 2009 American Chemical Society. (c) Transmission-electron micrographs of PtNi and PtCo chemically deposited on the tips of CdSe nanorods. Reprinted with permission from Habas, S. E.; Yang, P.; Mokari, T. *J. Am. Chem. Soc.* **2008**, *130*, 3294–3295.⁶² Copyright 2008 American Chemical Society.

and materials architectures that are specific and/or beneficial to the particle suspension reactors described herein. In addition, this section explains the role of the cocatalyst in a particle suspension reactor where at least four redox-active chemical species exist near any region of a particle, at any time. Thus, the cocatalyst must be selective for one half-reaction in the presence of reaction products from other half-reaction(s). This requirement is unique to particle suspension reactors, because in fixed-electrode designs the reaction products are physically separated and by design crossover of reaction products is small.

Traditionally the surfaces of light-absorber semiconductor particles do not contain active sites for efficient electrocatalytic generation of H₂ or O₂. Cocatalysts are desired, but fabricating anisotropic distributions of cocatalysts for the HER, the OER, and/or redox shuttle electrochemistry on nanometer-to-micron-sized particles is challenging. One option is to use PEC deposition where cocatalysts are photoelectrochemically deposited at the sites of preferential collection of photogenerated electrons or holes. Cathodic deposition of HER catalysts and anodic deposition of OER catalysts on surfaces aligns the intrinsic carrier-selective sites to the electrocatalytic sites, which may be beneficial to charge collection and electrocatalysis, and distinguishes the locations for the electron-selective and hole-selective surface sites to attenuate intraparticle shunts. Ag⁺, AuCl₄⁻, and PtCl₆²⁻ are often used as precursors for cocatalyst deposition on electron-transfer sites, while Pb²⁺, Mn²⁺, and Ni²⁺ are used for hole-transfer sites.^{58–60} Selective

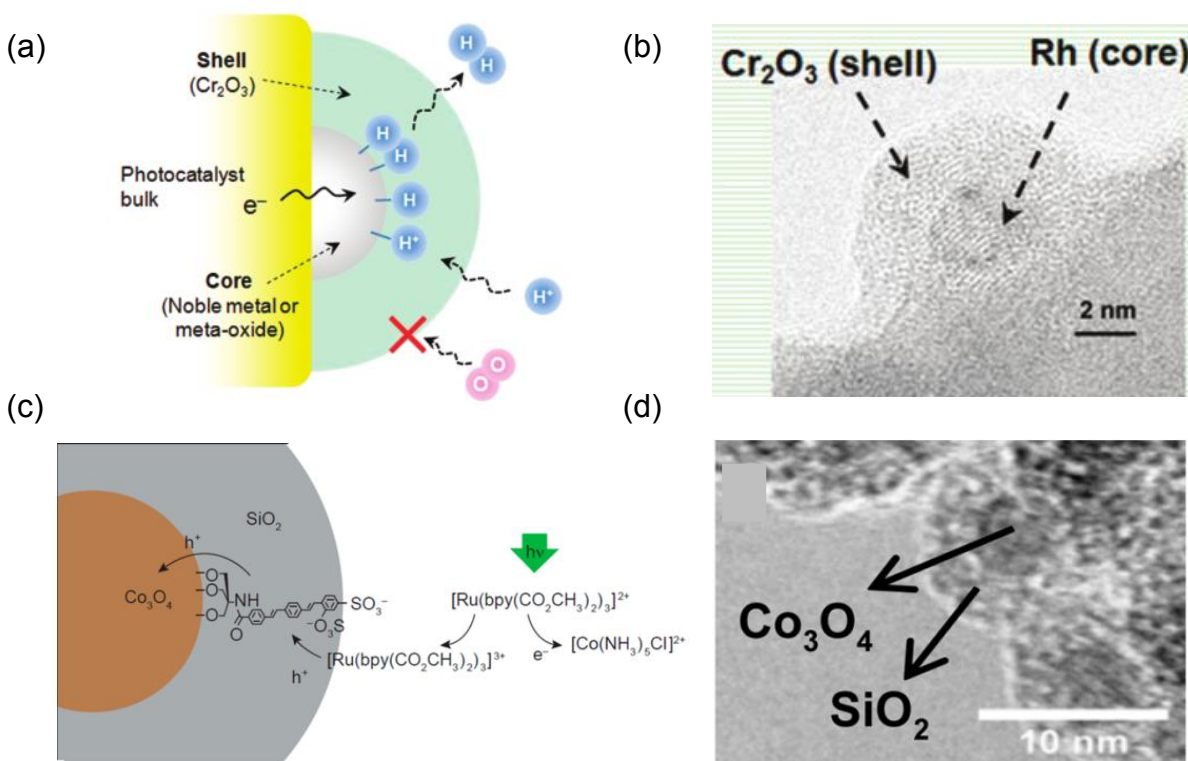


Figure 7. (a) Schematic of materials catalyst architecture used to size exclude molecules from electrocatalysts and (b) accompanying transmission-electron micrograph. Reprinted with permission from Maeda, K.; Domen, K. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.¹² Copyright 2010 American Chemical Society. (c) Schematic of material–molecule hybrid catalyst architecture used to size exclude molecules from electrocatalysts and (d) accompanying transmission-electron micrograph of materials. Reprinted/adapted with permission from Agiral, A.; Soo, H. Sen; Frei, H. *Chem. Mater.* **2013**, *25*, 2264–2273.¹³ Copyright 2013 American Chemical Society.

PEC deposition on BiVO_4 was attained on the $\{010\}$ facets using solution-phase cathode catalyst precursors and on the $\{110\}$ facets using anode catalyst precursors (Figure 6a).⁵⁹ Moreover, through use of surfactants that preferentially adsorbed onto certain crystal facets of Cu_2O and ZnO , deposition of Au particles was inhibited on these facets and thus was selective to the remaining other facets (Figure 6b).⁶¹ Pt nanoparticles have been selectively deposited on the tips of CdS nanorods, which presents a different crystal facet than along their sidewalls (Figure 6c).⁶² As a demonstration, this method was used to promote H_2 evolution from the as-deposited Pt tips of CdSe/CdS core–shell nanorods.⁶³

While selective *deposition* of cocatalysts may be useful for driving reactions at preferred locations on the light-absorber materials surfaces, selective *catalysis* is also extremely important in order to prevent recombination shunts due to unwanted reactions with reaction products.³⁸ Size exclusion has been remarkably successful in realizing selective catalysis for demonstrations of solar PEC water splitting using particle suspensions. Domen and colleagues reported that thin shells of amorphous, porous oxides, e.g. Cr_2O_3 , selectively facilitate proton transport to the HER cocatalysts while allowing H_2 to exit the structure and size-excluding larger species like O_2 (Figure 7a and Figure 7b).^{12,49,64} In addition, Frei and colleagues showed that solid silica shells (2 nm thick) with embedded electrically conductive organic molecules afforded protonic conduction through the silica matrix and electronic conduction through the organic groups (Figure 7c and Figure 7d).¹³ Larger species like O_2 were size excluded from entering into and through the silica.

A materials fabrication-independent scenario has also been proposed by Abe, Kudo, Matsumura, and colleagues, where molecular redox shuttles in solution, e.g. IO_3^- and Fe^{3+} , bind to the surface of the light-absorber material thereby attenuating reduction of these chemical species by H_2 or photogenerated electrons in the material.^{65–68}

It may also be possible to achieve selective catalysis via engineering the kinetics at the particles. Selective redox-shuttle catalysis will occur due to the small solubility (Henry’s law) constants for the water-splitting reaction products, i.e. H_2 and O_2 , in water and large activation overpotentials for the HER and the OER at redox-shuttle cocatalysts, which will likely be carbon materials or the light-absorber surfaces. To prevent mass-transport-limited reactivity of the redox shuttle at these cocatalysts the tradeoff between cocatalyst area and the rate of forced convection needs to be determined. Selective catalysis at the fuel-forming electrocatalysts will occur due to mass-transport limitations of the redox shuttle, because the area of the efficient HER and OER cocatalysts will be small and the diffusion coefficient of many redox shuttles is at least an order-of-magnitude smaller than that of protons, hydroxide ions, and water. These engineering approaches to selective catalysis will be successful only through careful choice of cocatalyst material, electrochemically active cocatalyst area, redox-shuttle concentration, and rate of forced convection, but will benefit in that advanced nanoscale materials design and synthesis required to size exclude reaction products is not required.

IV. Efficiency Metrics

A) System STH Efficiency

The most important performance metric for a practical solar PEC water-splitting technology is the STH efficiency, which is a ratio of the power output to the solar power input. Two versions of this that contain variables that can be measured experimentally and are most relevant to particle suspension reactors follow:

$$\eta_{STH} = \frac{2F \cdot v_{\text{coll}}(E_{\text{fuel}} - E_{\text{bias}})}{P_{\text{in}} \cdot A_{\text{reactor}}} \quad (1)$$

$$\eta_{STH} = \frac{N_A \cdot c_p \cdot \ell \cdot \phi_{\text{coll}} \cdot I_{\text{particle}}(E_{\text{fuel}} - E_{\text{bias}})}{P_{\text{in}}} \quad (2)$$

where in the first equation, the factor of two is the stoichiometry of electrons required to generate H_2 from H^+ , F is Faraday’s constant ($96,485 \text{ C mol}^{-1}$), and v_{coll} is the rate of collection of H_2 (mmol product s^{-1}), E_{fuel} is the potential available from the reaction products when utilized in an electrochemical cell (V; e.g. 1.229 V for aqueous water splitting at 25 °C and under standard-state conditions), E_{bias} is the bias applied to the system (V), P_{in} is the input solar irradiance (mW cm^{-2} ; e.g. 100 mW cm^{-2} , or 1 Sun intensity, of AM1.5G sunlight), and A_{reactor} is the projected geometric area of the reactor perpendicular to the direction of illumination (cm^2).⁶⁹ Because this metric is a measure of the power output based on the *solar* power input, the E_{bias} term is subtracted from E_{fuel} and not added to P_{in} . Another review paper published in this journal issue titled “Methods for Comparing the Performance of Energy-Conversion Systems for Use in Solar Fuels and Solar Electricity Generation” describes this and other efficiency definitions. These efficiency equations are only applicable when $E_{\text{bias}} < E_{\text{fuel}}$, because otherwise no sunlight energy is stored in the chemical bonds of H_2 and O_2 . By analogy to fixed-electrode STH efficiency measurements, if the average net current through an illuminated particle is known, the second equation may be useful,

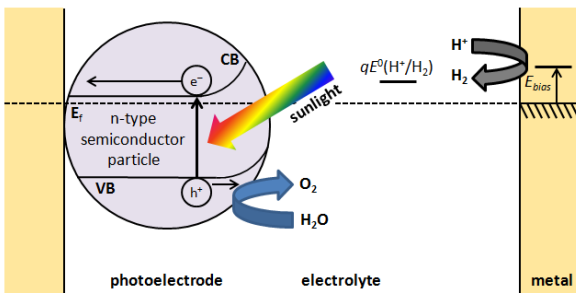
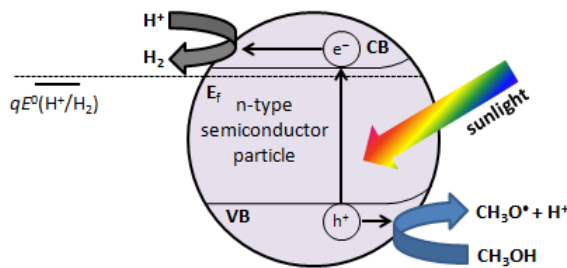
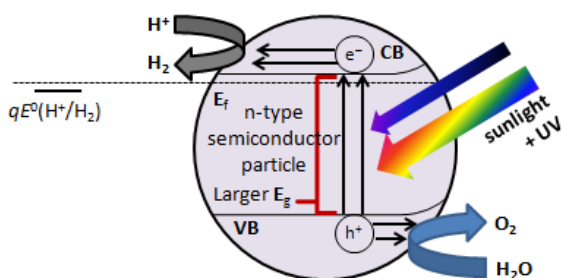
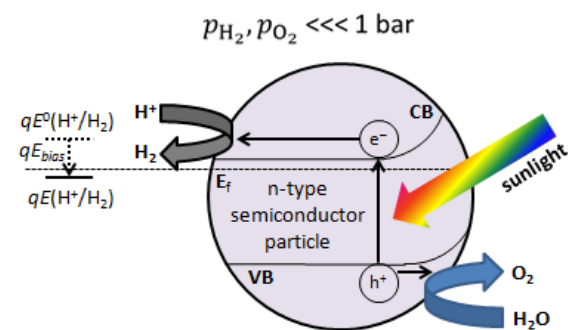
(a) Potential-bias assisted**(b) Chemical-bias assisted****(c) Optical-bias assisted****(d) Pressure-bias assisted**

Figure 8. Schematic representations of bias-assisted mechanisms for solar PEC water splitting using an n-type semiconductor. (a) Potential bias: Electrical bias for fixed electrodes modulates the Fermi level (E_f) of the illuminated photoanode so that it is sufficient to drive net H_2 evolution; this bias (E_{bias}) compensates for the difference in electrochemical potential between E_f and $qE^0(H^+/H_2)$. (b) Chemical bias: Sacrificial reagents like methanol are introduced into the electrolyte and reductively quench photo-excited particles, promoting H_2 evolution. (c) Optical bias: Ultraviolet light adds additional energy to the system allowing larger band-gap ultraviolet-light-absorbing particles to be used. (d) Pressure bias: A positive E_{bias} is introduced by decreasing the partial pressure of H_2 and/or O_2 gas in the headspace which removes dissolved H_2 and O_2 and makes $E(H^+/H_2)$ and/or $E(O_2/H_2O)$ more thermodynamically favorable.

where N_A is Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), c_p is the concentration of particles in solution (mol cm^{-3}), ℓ is the reactor thickness (cm), $\phi_{\text{collection}}$ is the quantum yield (QY) for external collection of a stream of H_2 , and I_{particle} is the average net current through a single particle (A).

Traditionally, gases from the headspace(s) of reactor vessels are collected using flow systems. The quantity of collected gas is often used to approximate the amount of products produced, and more thorough analyses identify the product distributions using a gas chromatograph and/or mass spectrometer. Many fixed-electrode measurements do not identify the products of their reactions and instead rely on current through the electrodes, assuming the yield for electron-transfer reactions forming H_2 or O_2 is unity and the yield for collection of pure products is unity; an analogous measurement for particle suspensions has also been used for a Type 2 reactor design. The two vessels were connected ionically using a Nafion membrane and electrically using electrodes inserted into each vessel.⁶⁵ Using a two-electrode potentiostatic measurement poised at the initial, dark open-circuit potential, the current through the circuit due to equilibration of the redox shuttles was used to approximate the H_2/O_2 generation rate.

The maximum theoretical efficiency for both reactor designs is the single-junction solar-cell detailed-balance limit of $\sim 31\%$, which can be attained with a 1.1 – 1.4 eV bandgap material.⁷⁰

This theoretical single-junction efficiency limit holds for the Type 2 (tandem-junction) reactor, in the absence of spectral splitting, because the vessels are arranged side-by-side, as in Figure 1b, and not stacked optically in series which would result in a substantially larger theoretical efficiency limit. In reality these efficiency limits will be much smaller due to required activation overpotentials, which are present in any device for PEC water splitting irrespective of the reactor type.^{4-7,71,72} Solar water-splitting reactors do not necessarily require that the evolved O₂ is collected. However, ideally H₂ and O₂ should be evolved in the 2:1 mol/mol or v/v stoichiometry expected for water splitting. If the amount of O₂ generated is quantified, any discrepancy from the ideal 2:1 stoichiometry implies leaks in the reactor or imperfect water splitting chemistry and undesired additional side reactions, which may not be sustainable over the long-term if the “missing” charges performed irreversible redox chemistry with the particles.

B) Bias Assistance

In addition to the requisite input of sunlight (e.g. simulated 1 Sun AM1.5G illumination), several other energy inputs can be introduced to bias the system. These biases can be separated into five categories: chemical, electrical, optical, vacuum, or thermal (Figure 8). Electrical potential bias is not described in detail below because it is only pertinent to fixed-electrode designs. The purpose of any of these biases is to slow charge recombination, increase the yield of charge generation or charge collection, and/or increase rates of electrocatalysis.

Chemical bias. When particle suspensions are evaluated, a chemical bias is particularly useful because it obviates rapid and undesired recombination reactions (Figure 8b). These chemical biases are attained through corrosion or passivation of the particle itself or via redox chemistry with redox-active sacrificial molecules or materials in the electrolyte or at the material surface, e.g. alcohols, sulfite, Ag⁺, amines, [Co(NH₃)₆]^{3+/2+}, ethylenediaminetetraacetate (EDTA²⁻). Sacrificial reagents quench photo-excited particles via electron-transfer reactions so that the particle subsequently resembles a ground-state particle with one additional or one fewer electron. This state is essentially identical to that formed through electrical bias (e.g. from an electrode), and so a chemical bias is analogous to an electrical bias, which must be taken into consideration when calculating the STH efficiency. The biasing species are often termed sacrificial because their electrochemical reactivity is irreversible or they have extremely slow reverse reaction rates. They react with the illuminated particle and remove one of the electronic charge carriers, i.e. an electron or a hole. The remaining electronic charge carrier can then perform the desired fuel-forming redox half-reaction, i.e. the HER or the OER. These chemical biases constitute a non-regenerative, non-solar-energy input, because additional energy is required to synthesize and introduce the sub-stoichiometric sacrificial reagents. As a consequence, a potential that is less than E_{fuel} , and often times less than zero, is stored in the chemical bonds of the reaction products, i.e. H₂ and O₂.

Sacrificial reagents are, however, useful for investigating charge-transfer processes across particle/electrolyte interfaces and subsequent electrocatalysis in bulk electrolytes. Sacrificial reagents perform rapid electron-transfer for one half-reaction so that the behavior of the other fuel-forming half-reaction can be isolated and investigated without complications from recombination of electrons and holes.⁷³⁻⁷⁷ These photogalvanic-type methods are useful for characterizing interfacial charge-transfer processes but do not store net photon energy in chemical bonds. Thus, sacrificial reagents should only be used to learn more about the fundamental charge-transfer

reaction mechanisms and electrocatalysis, and any chemistry that results from their use should not be considered useful solar-energy conversion chemistry.

Optical bias. An optical bias is present when a non-solar optical input is supplied, typically ultraviolet light, in addition to solar illumination in order to assist the water-splitting reaction or drive it entirely (Figure 8c). Unlike a chemical or electrical bias, the energy in an optical bias is lost irrespective of whether it is used by the particle, e.g. regardless of whether the photon is absorbed. Thus, the total optical bias must be amortized over every charge that results in net H₂ and O₂ evolution. This non-solar optical input is typically supplied by high-energy photons and differs from the incident (simulated) solar illumination, which is the only relevant source of power input for a *solar* PEC water-splitting reactor.

Pressure bias. A pressure bias is another type of chemical bias. It relies on partial evacuation of H₂ and/or O₂ from the headspace and out of solution, or dilution of the headspace with another (carrier) gas, which makes the thermodynamics for net water-splitting redox chemistry more favorable (Figure 8d). Although E_{fuel} for aqueous water splitting at 25 °C and under standard-state conditions is 1.229 V, the photo-potential required to split water by solar illumination depends on the partial pressure of H₂ and O₂. This is important because in many reports of solar PEC water splitting, H₂ and O₂ were evolved under reduced pressure, which constitutes a non-zero E_{bias} . According to the Nernst equation, the bias potential can be estimated as 29.6 mV per order-of-magnitude reduction in H₂ pressure from 1 bar, and 14.8 mV per order-of-magnitude reduction in O₂ pressure from 1 bar. As an example, a report by Domen and colleagues using Rh_{2-γ}Cr_γO₃-modified GaN:ZnO particles was specifically not operated under a reduced pressure, but instead in a static air atmosphere.⁷⁸ Under this condition the initial potential required to impart water splitting was also not 1.229 V but rather approached $-\infty$ V because no H₂ was present and therefore $E_{\text{bias}} \rightarrow \infty$ V. It is often assumed that during rapid water splitting under ambient atmosphere, enough H₂ and O₂ exists near the surface of the electrodes (or particles) so that generally the standard potential, E_{fuel}^0 , is an accurate approximation of E_{fuel} .⁷⁹ It is unclear if this approximation holds when H₂ and/or O₂ are present at reduced partial pressures. To assess whether particle suspensions are suitable for use in an actual solar PEC water-splitting reactor, they should be evaluated in the presence of H₂ above the HER reactor at 1 bar pressure and O₂ above the OER reactor at 1 bar pressure. Formation of products can then be measured by a change in gas volume or a change in pressure, along with quantification of the purity of the product gas streams.

Thermal bias. No standard temperature has been set for solar PEC water-splitting applications. However, because most solar installations will operate at temperatures greater than room temperature, it is best to define the standard potential, E_{fuel}^0 , using this elevated temperature. Then, use of other temperatures will constitute a bias. This is particularly important, because apparent activation energies for solar PEC water splitting using certain particles were reported to be 8 – 15 kJ mol⁻¹, implying that thermal bias can potentially increase the rate of electrocatalysis and the STH efficiency for solar PEC water splitting.⁴⁴ For the purpose of this review, 25 °C is the standard temperature, because that is approximately the temperature utilized for the laboratory-scale demonstrations reported below of solar PEC water splitting using particle suspension.

C) Spectral Response (Quantum Yield)

Although ultimate STH efficiency is the parameter that dictates effectiveness of solar PEC water splitting, research demonstrations using particle suspensions do not often report the STH efficiency and instead report the (monochromatic) spectral response. The spectral response is often performed as a function of optical excitation wavelength with values ranging from 0 to 1 at each wavelength. This fraction quantifies the amount of product collected based on the number of photons incident or absorbed.⁸⁰ This information can be used along with the spectrum of the simulated solar illumination source to calculate the STH efficiency by weighting the simulated solar spectrum by the absorbed (internal) spectral response and integrating. If the yields are reported at only several excitation wavelengths, integration over only those selected wavelengths results in a lower bound to the STH efficiency. Most demonstrations of solar PEC water splitting using particle suspensions (reported below) only indicate the spectral response at one wavelength or one small range of wavelengths. In either case, the calculated value for the lower bound of the STH efficiency is not a meaningful approximation of the actual STH efficiency. Instead, for most solar PEC water splitting demonstrations, the monochromatic, or near-monochromatic, spectral response is reported, often as an external (incident) quantum yield (EQY) based on the incident photon flux (Table 1). This is not often converted into an internal (absorbed) quantum yield (IQY) but could if absorption by the particle suspensions was determined using a spectrophotometer that contains an integrating sphere. Instead, most demonstrations utilize highly concentrated suspensions that are assumed to absorb nearly all incident above-bandgap light and in which case $IQY \approx EQY$.

D) Alternative Characterization Strategies

Unlike for fixed electrodes, few means to characterize the performance of particle suspensions for solar PEC water splitting exist.^{69,80} For example, although STH efficiency can be determined through quantification of the amount of reaction products, the current–potential behavior of individual particles or particle suspensions has not been reported.

The overall quantum yield for product detection (i.e. spectral response for a given range of illumination wavelengths) can be written as the product of the quantum yields of several individual steps: optical absorption, charge separation, charge transport, fuel-forming catalysis, and product collection. To glean more information into the causes of the observed STH conversion efficiencies and overall quantum yields for these particle suspensions, quantitative values for the quantum yields for each sub-step are beneficial. This, however, is not straightforward because each of these steps occurs in/on individual isolated particles. Measuring the performance of each process requires new characterization methods specific to particle suspensions.

For example, surface photovoltage (SPV) measurements have been used to investigate the interplay of charge separation and charge recombination to cocatalyst materials. An advantage of this technique is that it can be used to measure processes in/on individual particles, but is not effective in the presence of electrolyte. The changes in surface photovoltage as a function of incident photon energy reveal locations with altered yields for charge separation, charge collection, or charge recombination.^{81–84} Another paper in this issue titled “Methods of Photoelectrode Characterization with High Spatial and Temporal Resolution” describes additional characterization techniques relevant to these types of designs. Alternatively, particles are often cast onto conductive electrodes like fluorine-doped tin oxide (FTO) or gold films to evaluate their ensemble photoelectrochemical and transient spectroscopic behavior in a fixed-electrode form factor.⁸⁵ However, it is unclear if the behavior observed using fixed electrodes is indicative of the behavior of particle suspensions.

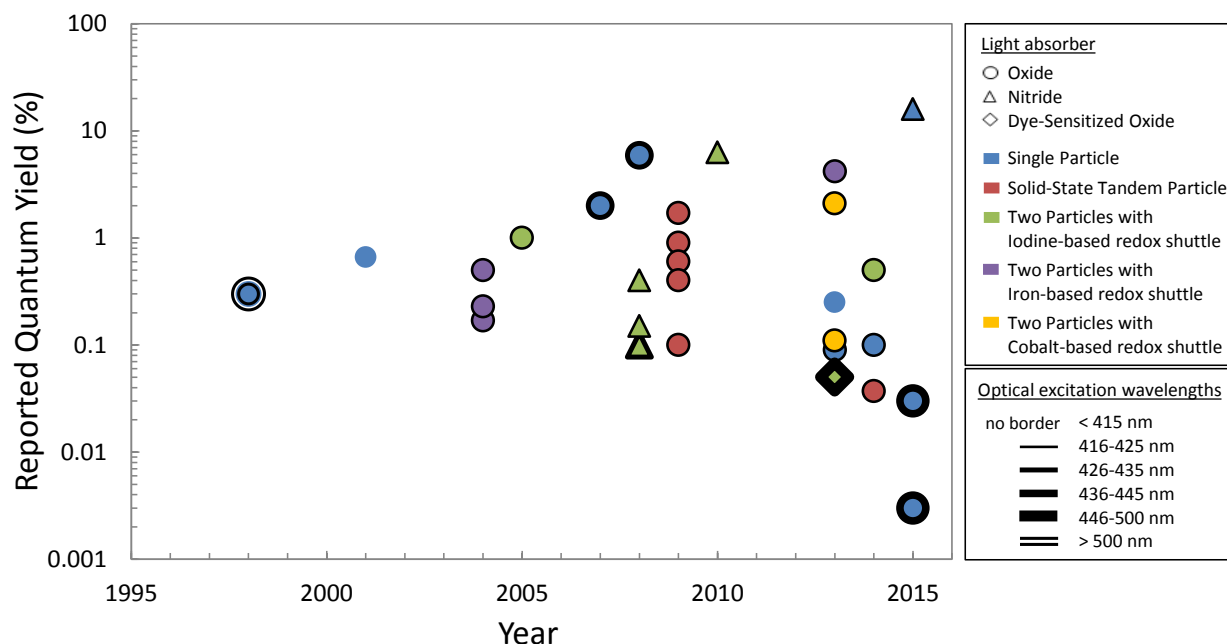


Figure 9. Maximum reported quantum yields for literature demonstrations of visible-light-driven PEC water splitting categorized by type of system (color), type of light-absorber material (shape), and wavelength of light used to excite the particles (size).

V. Experimental Demonstrations

Concerted research efforts in PEC date back to the seminal work by Brattain, Garrett, Gerischer, Boddy, et al. in the 1950s – 1960s using materials from the photovoltaics community and metal-oxide materials in fixed-electrode arrangements.^{51,86–88} Several decades later, research into PEC water splitting using particle suspensions was reported.^{89–91} Although initial reports were promising,^{92,93} it quickly became apparent that the fixed-electrode demonstrations were far more efficient.^{50,61,62,86} Thus, although particle suspension designs remained an active area of research, many more research advances were realized using fixed-electrode demonstrations. Notwithstanding, there have been many demonstrations of PEC water splitting using particle suspensions illuminated with only ultraviolet light. Recently this topic has been extensively reviewed,^{12,44,50–52,97–101} and it is beyond the scope of this review paper.

Suspensions for solar PEC water splitting typically contain particles with diameters on the nanometer to micron size ranges. The first demonstrations of PEC water splitting using particle suspensions utilized TiO₂, where upon ultraviolet-light illumination redox chemistries occurred that are amenable to a Type 1 reactor.^{89–91} Most metal-oxides have bandgap energies that are too large to absorb visible light, yet many of them are the most stable PEC materials.¹⁰² To extend the absorption of metal-oxides into the visible spectral region, many metal oxides have been doped with other transition metals or had some or all of the oxygen atoms replaced with pnictogens, other chalcogenides, or halides.^{52,103}

The first demonstration that required redox shuttle chemistries amenable to a Type 2 reactor and that demonstrated PEC water splitting at the expected 2:1 stoichiometric ratio of H₂ and O₂ were reported in 2001, over twenty years later, by Arakawa and colleagues.²³ It also required

ultraviolet light excitation ($\lambda > 300$ nm) and consisted of a suspension of Pt-loaded anatase TiO₂ ($E_{\text{bg}} = 3.2$ eV) HER particles, rutile TiO₂ ($E_{\text{bg}} = 3.0$ eV) OER particles, and an IO₃⁻/I⁻ redox shuttle in pH 11 NaI aqueous electrolyte.

The first non-oxide particle for PEC water splitting via a process amenable to a Type 1 reactor was reported in 2005 by Domen and colleagues.¹⁰⁴ The authors described β -Ge₃N₄ particles (bandgap energy (E_{bg}) = 3.8 – 3.9 eV) loaded with a RuO₂ HER cocatalyst (1 wt %) in pH 0 H₂SO₄ aqueous electrolyte which were reported to evolve H₂ and O₂ in a 2:1 mol/mol stoichiometry when illuminated by ultraviolet light, with an external quantum yield of ~9 % at an excitation wavelength of 300 nm (EQY_{300 nm}). Little N₂ was produced (< 0.3 mol % of the H₂ produced), which is a common degradation product of nitride materials, and > 6 turnovers were reported per particle.

Some additional unique examples of PEC water splitting using particle suspensions, a redox shuttle(s), and ultraviolet light excitation include the following. A partially solid-state redox shuttle, MnO₄²⁻(aq)/MnO₂(s), was used with TiO₂ particles in pH 13 NaOH aqueous electrolyte to impart PEC water splitting under ultraviolet light excitation.¹⁰⁵ Another demonstration required photoexcitation of the redox shuttle in order to evolve H₂. A suspension of RuO₂-loaded (3 wt %) WO₃ ($E_{\text{bg}} \approx 2.7$ eV) OER particles in an aqueous electrolyte consisting of 1.4 mM Fe^{III}(SO₄)₃, 5.7 mM Fe^{II}(SO₄), and 29 mM H₂SO₄ was reported to evolve stoichiometric H₂ and O₂ under concomitant photoexcitation of WO₃ (> 400 nm) and Fe²⁺ (< 280 nm).¹⁰⁶ Lastly, a Type 2 reactor design was reported that connected the two vessels ionically using a Nafion membrane and electrically using a wire that shorted out two Pt electrodes with one immersed in each vessel. Pt-loaded (0.9 wt %) rutile TiO₂ HER particles and 2 M KBr in pH 2.4 aqueous electrolyte were confined to one electrochemical cell and rutile TiO₂ OER particles and 6.5 mM FeCl₂ (with some Fe^{III} generated photoelectrochemically) in pH 2.4 aqueous electrolyte were confined to a second electrochemical cell.⁶⁵ This design afforded use of two different redox shuttles, i.e. Br₃⁻/Br₂/Br⁻ and Fe³⁺/Fe²⁺.

Demonstrations of visible-light-driven PEC water splitting are plotted in Figure 9 as a function of the year of the report. Each of these demonstrations is described in greater detail below in the text. For each of the unique light-absorber particle(s) (and redox shuttle) combinations, data relevant to the demonstration with the highest reported quantum yield are tabulated in chronological order in Tables 2 – 5 based on each type of system: single particles, solid-state tandem particles, two particles with an iodine-based redox shuttle, and two particles with a non-iodine-based redox shuttle.

A) Single particles

This section compiles and describes demonstrations of solar PEC water splitting using particle suspensions where *each* particle was reported to drive overall water splitting. These particles can only be used in a Type 1 reactor, where advanced product gas separation schemes are required to prevent the existence of large volumes of explosive mixtures, and to generate pure H₂ product streams as required for ultimate use. Each of the following eleven light-absorber materials has been reported to split water when in the form of a suspension and excited by visible light with at most an applied pressure bias (i.e. decreased pressure): Cu₂O, In_{0.9}Ni_{0.1}TaO₄, (Ga_{1-x}Zn_x)(N_{1-x}O_x), (Zn_{1+x}Ge)(N₂O_x), Au/TiO₂, ZrO₂-modified TaON, doped SrTiO₃, CoO, C₃N₄ composite, LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}, and CaTaO₂N. Parameters for the best-performing systems within each materials class are displayed in chronological order in Table 2. Several recent reports of high-efficiency materials seem promising but have yet to be reproduced in the peer-reviewed literature

and are either unstable on the timescale of hours or require specific protocols for continued solar PEC water splitting activity.

Cu₂O. In 1998, the first single-particle suspension to achieve visible-light-driven PEC water splitting was reported by Domen and colleagues. The authors described Cu₂O ($E_{bg} = 2.0 - 2.2$ eV) particles in pure water that evolved stoichiometric H₂ and O₂ (by 175 hours into the experiment) when illuminated with visible light (460 nm – 600 nm) and with an EQY_{550–600 nm} $\approx 0.3\%$.¹⁰⁷ The system was stable over 1900 hours of continuous illumination, and isotopic labeling studies with mass spectroscopic detection suggested that O₂ evolution occurred from water, and not from decomposition of the material itself. However, follow-up studies reported that a significant fraction of the observed water splitting activity was due to mechanochemistry introduced by the interaction of the stir bar with the Cu₂O particles and the bottom of the glass reaction vessel, termed mechanocatalytic.¹⁰⁸ NiO, Co₃O₄, and Fe₃O₄ were also reported to be mechanocatalytic. Later reports demonstrated that the HER took place only when no O₂ was co-evolved, and that it was accompanied by self-oxidation of the light absorber to CuO.¹⁰⁹ Co-evolution of H₂ and O₂ from Cu₂O are also incompatible with the limited redox stability of Cu₂O.¹¹⁰

In_{0.9}Ni_{0.1}TaO₄. In 2001, a suspension of monoclinic wolframite In_{1-x}Ni_xTaO₄ ($x = 0 - 0.2$; $E_{bg} = 2.3$ eV) particles loaded with a NiO_x cocatalyst (1.0 wt %) in pure water was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (420 nm – 540 nm) and with a QY_{402 nm} $\approx 0.66\%$.^{111,112} The system was reported to be stable for 400 hours of continuous illumination and with > 5 turnovers per particle. RuO₂ was also used as a cocatalyst in place of NiO_x, but the performance was inferior. Recently, there is renewed interest in the basic materials parameters of this system.^{113,114}

(Ga_{1-x}Zn_x)(N_{1-x}O_x). In 2005, a suspension of wurtzite (Ga_{1-x}Zn_x)(N_{1-x}O_x) ($x \approx 0.14$ and $E_{bg} \approx 2.7$ eV) solid-solution particles loaded with RuO₂ HER cocatalyst (5.0 wt %) in pH 3 H₂SO₄ aqueous solution was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (≤ 460 nm), with a QY_{300–480 nm} $\approx 0.14\%$.¹¹⁵ The solid solution forms because of the similar hexagonal wurtzite lattice parameters of the individual alloyed ZnO and GaN materials. Isotopic labeling studies with mass spectroscopic detection suggested that O₂ evolution occurred from water, and not from decomposition of the material itself, and by ICP-MS, Zn was not detected in solution. In 2006, the RuO₂ HER cocatalyst was replaced by a Rh_{2-y}Cr_yO₃ cocatalyst and the EQY_{420–440 nm} increased to $\sim 2.5\%$, with nearly 3 turnovers per (Ga_{1-x}Zn_x)(N_{1-x}O_x) particle.⁶⁴ The amorphous Cr₂O₃ shell on the HER cocatalyst was reported to attenuate the back reaction between H₂ and O₂, due to size exclusion of O₂,¹¹⁶ and allowed solar PEC water splitting to proceed with little loss in activity even under atmospheric pressure of O₂.¹¹⁷ In 2008, using (Ga_{0.82}Zn_{0.18})(N_{0.82}O_{0.18}) particles, 2.5 wt % Rh and 2 wt % Cr, and a post-calcination step at 823 K, Domen and colleagues reported an EQY_{420–440 nm} $\approx 5.9\%$, and stability was markedly enhanced as evidenced by little production of N₂ (< 0.12 mol % of the H₂ produced), a common degradation product of nitride materials.¹¹⁸ In 2010, for the first time two cocatalysts were utilized on a single light-absorber particle to drive solar PEC water splitting, where both Rh/Cr₂O₃ core-shell HER cocatalysts and Mn₃O₄ OER cocatalysts were deposited on (Ga_{1-x}Zn_x)(N_{1-x}O_x) particles, which resulted in a QY_{> 420 nm} $\approx 1\%$.¹¹⁹ In 2012, the stability of Rh_{2-y}Cr_yO₃/GaN:ZnO particles under continuous illumination was reported to be over 3 months when operated at a reduced EQY_{400–500 nm} $\approx 0.16\%$, and the suspension retained 50% of its initial activity for over half a year of continuous

illumination.⁷⁸ Deactivation was ascribed to a decrease in the Cr and N contents over time, the latter of which in part could be slowed via initial co-loading with RuO₂ OER cocatalyst.

(Zn_{1+x}Ge)(N₂O_x). In 2007, a suspension of wurtzite (Zn_{1+x}Ge)(N₂O_x) ($x = 0.44$, $E_{bg} \approx 2.7$ eV) solid-solution particles loaded with a RuO₂ HER cocatalyst (5 wt %) in pure water was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (≤ 460 nm).¹²⁰ The lattice parameters of the pure materials, i.e. ZnO and ZnGeN₂, were very similar and afforded a solid solution. N₂ was detected by gas chromatography during the first five hours of illumination, but none was detected during the second five hours of illumination. Replacement of RuO₂ with a Rh_{2-y}Cr_yO₃ cocatalyst (3.0 wt % Rh and 0.2 wt % Cr) resulted in approximately an 8-fold increase in activity and an EQY_{420 nm} $\approx 0.20\%$, and stable water splitting activity for > 50 hours of continuous illumination with no detection of N₂, a common degradation product of nitride materials.¹²¹ In 2008, a post-calcination step at 673 K under an atmosphere of N₂ was utilized, similar to that used with (Ga_{1-x}Zn_x)(N_{1-x}O_x), which resulted in a ten-fold increase in the EQY_{420–440 nm} $\approx 2.0\%$.¹²² The enhanced activity was attributed to a decrease in the density of surface defect states and an increase in the illumination intensity, because it was determined that the EQY did not scale linearly with the illumination intensity.

Au/TiO₂/Al₂O₃. In 2013, gold nanorods electrodeposited into a porous alumina template on an ITO/TiO₂ substrate, capped with electron-beam-deposited TiO₂, and loaded with both Pt HER cocatalysts (2 nm planar equivalent) and Co-based OER cocatalysts in pH 9.6 potassium borate aqueous solution were reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light from simulated solar irradiation (> 410 nm; AM1.5G, 3 Suns intensity).¹²³ The visible-light absorption was due to excitation of surface plasmons which resulted in EQY_{600 nm} ≈ 0.25 and stable water splitting activity for > 60 hours of continuous illumination. The stoichiometry of H₂ and O₂ measured by gas chromatography was not strictly 2:1 and this imperfection was posited to be due to contamination by atmospheric O₂ during sample extraction. Although not strictly free-floating particles in solution, the demonstration of solar PEC water splitting from these Al₂O₃-confined free-floating units of approximately ten billion gold nanorods is relevant to particle suspension reactors, because each particle operates autonomously.

TaON. Also in 2013, a suspension of ZrO₂-modified TaON ($E_{bg} = 2.5$ eV) particles co-loaded with both RuO_x/Cr₂O₃ core-shell HER cocatalysts and IrO₂ OER cocatalysts in pure water was reported to evolve stoichiometric H₂ and O₂, and no N₂, when illuminated with visible light (> 400 nm) and exhibited EQY_{420 nm} $< 0.1\%$.¹²⁴ The ZrO₂ modifier helped decrease the number of anionic vacancies in TaON generated during nitridation and, again, the core-shell structure of RuO_x/Cr₂O₃ attenuated reduction of O₂ due to impermeability of O₂ in the Cr₂O₃ shell.

SrTiO₃. In 2014, a suspension of Rh (0.5%) and Sb (1.0%) codoped SrTiO₃ ($E_{bg} = 2.5$ eV) particles loaded with IrO₂ (3.0 wt %) HER/OER cocatalysts in pH 3 H₂SO₄ aqueous solution was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (≤ 500 nm), and with an EQY_{420 nm} $\approx 0.1\%$.¹²⁵ The system was reported to be stable for 21 hours of continuous illumination from a concentrated light source and with > 14 turnovers per IrO₂ cocatalyst. Other cocatalysts (i.e. RuO₂ or Ru) were also reported to successfully evolve stoichiometric H₂ and O₂, but with a lesser efficiency.

CoO. Also in 2014, Bao and colleagues reported that a suspension of cubic CoO ($E_{bg} = 2.6$ eV) particles in pure water evolved H₂ and O₂ with a 5% STH efficiency when illuminated with 1 Sun AM1.5G simulated sunlight, but the particles were unstable on the hours timescale.¹²⁶ The nanocrystals of CoO were generated using laser ablation. Isotopic labeling studies with mass spectroscopic detection suggested that O₂ evolution occurred from water, and not from decomposition of the material itself.

C₃N₄. In 2015, a carbon nitride–carbon nanodot (C₃N₄/CDots) nanocomposite ($E_{bg} \approx 2.76$ eV) in pure water was reported by Kang, Lee, Lifshitz, and colleagues to evolve stoichiometric H₂ and O₂ via an H₂O₂ intermediate that rapidly disproportionated at the CDots, and exhibited an EQY_{420 nm} = 16%, EQY_{600 nm} = 4.42%, and a ~2% STH efficiency when illuminated with 0.7 – 1 Suns of AM1.5G simulated sunlight.¹²⁷ The activity persisted for up to 200 days, with no observation of CO₂ or N₂ as a reaction product, and isotopic labeling studies with mass spectroscopic detection suggested that O₂ evolution occurred from water. Interestingly, this 200 day stability was reported with regular removal and drying of the catalyst every 24 hours. However, the system was also highly stable for 45 days of continuous illumination, with no intermediate catalyst treatment and no intermediate evacuation of the evolved gases.

LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}. Also in 2015, a suspension of perovskite LaMg_xTa_{1-x}O_{1+3x}N_{2-3x} ($x = 1/3$; $E_{bg} \approx 2.1$ eV) solid-solution particles loaded with Rh/Cr mixed oxide (0.5 wt % Rh, 0.5 wt % Cr) HER cocatalysts in deionized water was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (≥ 420 nm) and with an EQY_{440 ± 30 nm} = 0.03% and activity to 600 nm.¹²⁸ The lattice parameters of the pure materials, i.e. LaTaON₂ and LaMg_{2/3}Ta_{1/3}O₃, were very similar and afforded a solid solution. Notably, a thin, amorphous hydrous TiO_{2-m}(OH)_{2m} layer coated the particle–cocatalyst composites as a protective layer to prevent self-oxidation of the oxynitride to N₂. Only when coated by TiO_{2-m}(OH)_{2m} was the system reported to be stable for 22 hours of continuous illumination with no N₂ detected.

CaTaO₂N. Also in 2015, a suspension of perovskite CaTaO₂N ($E_{bg} \approx 2.43$ eV) particles loaded with RhCrO_y HER cocatalysts was reported to evolve stoichiometric H₂ and O₂ when illuminated with ≥ 420 nm, and with an EQY_{440 ± 30 nm} $\approx 0.003\%$.¹²⁹ The same thin-layer of amorphous hydrous TiO_{2-m}(OH)_{2m} was used to coat the particle–cocatalyst composites, which resulted in complete stability during 30 hours of continuous illumination with no N₂ detected.

Table 2. Reports of visible-light-driven water splitting using suspensions consisting of one type of particle (**bold typeface** indicates the designs with the largest reported quantum yield and largest reported STH efficiency; underline typeface indicates the design that absorbs at the longest wavelength)[#]

Light-Absorber	HER Cocatalyst (wt %)	OER Cocatalyst (wt %)	Aqueous Electrolyte (pH)	Illumination ^a (Irradiance (mW cm ⁻²), Wavelength (nm))	Activity Measurement		Quantum Yield, % (Wavelength (nm))	Year ^{Ref}
					H ₂ , μmol h ⁻¹	O ₂ , μmol h ⁻¹		
Cu ₂ O	<i>none</i>	<i>none</i>	pure water	Xe (n.r., 460 – 600) ^b	2	1	0.3 (550 – 600)	1998 ¹⁰⁷
In _{1-x} Ni _x TaO ₄	NiO _x (1.0)	<i>none</i>	pure water	Xe (n.r., > 420)	16.6	8.3	0.66 (402)	2001 ¹¹¹

(Zn _{1-x} Ge)(N ₂ O _x)	Rh _{2-y} Cr _y O ₃	<i>none</i>	pure water	Hg (~50, > 400) ^{c,d}	316	158	2.0 (420 – 440) ^e	2008 ¹²²
(Ga _{1-x} Zn _x)(N _{1-x} O _x)	Rh _{2-y} Cr _y O ₃	<i>none</i>	H ₂ SO ₄ (3)	Hg (n.r., > 400)	927	460	5.9 (420 – 440) ^e	2008 ¹¹⁸
Au/TiO ₂ /Al ₂ O ₃	Pt	Co-OEC ^f	K ₃ BO ₃ (9.6)	Xe (300, AM1.5G)	~0.45	~0.2	~0.25 (> 410)	2013 ¹²³
ZrO ₂ -TaON	RuO _x /Cr ₂ O ₃	IrO ₂	pure water	Hg (n.r., > 400)	~3	~1.5	~0.1 (420)	2013 ¹²⁴
SrTiO ₃ :Rh,Sb	IrO ₂ (3.0)	IrO ₂ (3.0)	H ₂ SO ₄ (3)	Xe (100, > 440)	3.4	1.5	0.1 (420) 0.1% STH	2014 ¹²⁵
CoO	<i>none</i>	<i>none</i>	pure water	Xe (100, AM1.5G)	n.r.	n.r.	n.r. 5% STH	2014¹²⁶
C₃N₄/CDots	<i>none</i>	<i>none</i>	pure water	Xe (70 – 100, > 420)	45.3	22.7	16 (420) ~2% STH	2015¹²⁷
<u>LaMg₃Ta_{1-x}O_{1+3x}N_{2-3x}</u>	RhCrO _y	<i>none</i>	pure water	Xe (~29, ≥ 420) ^c	~1	~0.5	0.03 (440 ± 30)	2015 ¹²⁸
CaTaO ₂ N	RhCrO _y	<i>none</i>	pure water	Xe (~24, ≥ 420) ^c	~0.12 5	~0.06	~0.003 (440 ± 30)	2015 ¹²⁹

[#] For each light-absorber material only the highest reported quantum yield is included.

^a Xe = 300 W xenon lamp with a Pyrex cell; Hg = 450 W high-pressure mercury lamp with a Pyrex cell

^b n.r. = not reported

^c Calculation performed from reported rate of incident photons, and assuming the median excitation wavelength in the range

^d No active area specified, so assumed to be 1 cm²

^e Xe setup used for quantum yield measurement

^f Co-OEC = Cobalt-based oxygen-evolution catalyst

B) Solid-state tandem particles

This section compiles and describes reports of solar PEC water splitting using solid-state tandem-junction particles that together drive overall water splitting, akin to tandem-junction solar cells. This mechanism is often referred to as a Z-scheme due to similarities with the mechanism of natural photosynthesis. One challenge with this design is its ability to capitalize on the STH efficiency advantages of a tandem architecture which requires that sunlight be incident on the large bandgap material first. This optical condition cannot be enforced, because the particles are free to rotate in the suspension. In addition, these particles can also only be used in a Type 1 reactor. Parameters for the best-performing systems within each materials pair are displayed in chronological order in Table 3.

SrTiO₃. In 2009, the first solid-state tandem-junction particle suspension to achieve visible-light-driven PEC water splitting was reported by Kudo and colleagues.¹³⁰ The authors described Rh-doped SrTiO₃ ($E_{bg} = 2.4$ eV) HER particles loaded with Ru (1 wt %) and BiVO₄ ($E_{bg} = 2.4$ eV) OER particles which aggregated in pH 3.5 H₂SO₄ aqueous solution to form a solid-state tandem structure that evolved stoichiometric H₂ and O₂ under AM1.5G illumination. The STH efficiency was reported to be 0.12% with an EQY_{420 nm} = 1.7%, and stability over 120 hours of continuous illumination.^{130,131} Photochemical reduction of graphene oxide on the particles resulted in a slightly increased quantum yield, which was thought to arise from more rapid charge conduction between the particles.¹³² Other solid-state tandem structures for solar PEC water splitting using SrTiO₃ were also demonstrated using other visible-light-absorbing OER materials, albeit with smaller quantum yields. These included WO₃, AgNbO₃, Bi₂MoO₆ ($E_{bg} = 2.7$ eV), Cr and Sb

codoped rutile TiO₂, Rh and Sb codoped rutile TiO₂,¹³⁰ and anosovite Ta₃N₅ ($E_{bg} = 2.1$ eV) co-loaded with CoO_x and Ir.¹³³

ZnRh₂O₄//Ag//Ag_{1-x}SbO_{3-y}. In 2014, a suspension of solid-state tandem particles consisting of Ag sandwiched between ZnRh₂O₄ and Ag_{1-x}SbO_{3-y} was also reported to evolve stoichiometric H₂ and O₂ under visible-light irradiation (> 500 nm) and exhibited a QY_{420 nm} = 0.037%.¹³⁴ The system was reported to be stable for 144 hours of continuous illumination with no N₂ detected.

Graphene oxide. Also in 2014, a suspension of nitrogen-doped graphene-oxide quantum dots (8.1 ± 1.8 nm in diameter; $E_{bg} \approx 2.3$ eV) in pH 3 pure water was reported to evolve stoichiometric H₂ and O₂, and no N₂, when illuminated with visible light (> 420 nm).¹³⁵ The metal-free slurries were stable over 3 days of continuous illumination and in comparison to a suspension of Rh_{2-y}Cr_yO₃/GaN:ZnO evolved H₂ and O₂ at about half the rate. It was hypothesized that a tandem pn-type photochemical diode¹³⁶ was generated between p-type and n-type domains.

Table 3. Reports of visible-light-driven water splitting using suspensions consisting of pairs of particles in solid-state contact (**bold typeface** indicates the design with the largest reported quantum yield; underline typeface indicates the design that absorbs at the longest wavelength)[#]

Light Absorbers	HER Cocatalyst (wt %)	OER Cocatalyst (wt %)	Aqueous Electrolyte (pH)	Illumination ^a (Irradiance (mW cm ⁻²), Wavelength (nm))	Activity Measurement			Year ^{Ref}
					H ₂ , μmol h ⁻¹	O ₂ , μmol h ⁻¹	Quantum Yield, % (Wavelength (nm))	
SrTiO₃:Rh//BiVO₄	Ru (1)	<i>none</i>	H₂SO₄ (3.5)	Xe (100, > 420)	40	19	1.7 (420)	2009¹³⁰
SrTiO ₃ :Rh//Bi ₂ MoO ₆	Ru (1)	<i>none</i>	H ₂ SO ₄ (3.5)	Xe (100, > 420)	12	5.2	~0.9 (420)	2009 ¹³⁰
SrTiO ₃ :Rh//TiO ₂ :Cr,Sb	Ru (1)	<i>none</i>	H ₂ SO ₄ (3.5)	Xe (100, > 420)	6.7	3.3	~0.6 (420)	2009 ¹³⁰
SrTiO ₃ :Rh//WO ₃	Ru (1)	<i>none</i>	H ₂ SO ₄ (3.5)	Xe (100, > 420)	5.7	2.4	~0.4 (420)	2009 ¹³⁰
SrTiO ₃ :Rh//AgNbO ₃	Ru (1)	<i>none</i>	H ₂ SO ₄ (3.5)	Xe (100, > 420)	1.9	0.7	~0.1 (420)	2009 ¹³⁰
<u>SrTiO₃:Rh//Ta₃N₅</u>	<u>Ru (1)</u>	<u>Ir/CoO_x</u>	<u>H₂SO₄ (3.9)</u>	<u>Xe (100, > 420)</u>	<u>n.r.^b</u>	<u>n.r.</u>	<u>n.r. 0.013% STH</u>	<u>2013¹³³</u>
ZnRh ₂ O ₄ //Ag//Ag _{1-x} SbO _{3-y} ^c	<i>none</i>	<i>none</i>	pure water	Xe (1.5, > 460)	~0.004	~0.002	0.037 (420)	2014 ¹³⁴
p-GO:N//n-GO:N	<i>none</i>	<i>none</i>	pure water (3)	Xe (n.r., 420 – 800)	~0.6	~0.3	n.r.	2014 ¹³⁵

[#] For each combination of light-absorber materials only the highest reported quantum yield is included

^a Xe = 300 W xenon lamp with a Pyrex cell

^b n.r. = not reported

^c Ag acts as a solid-state mediator for electron transfer

C) Tandem particles requiring a redox shuttle

This section compiles and describes reports of solar PEC water splitting using pairs of particles that are not in solid-state contact and instead require a solution redox shuttle in order to drive

sustained overall water splitting. This alternative tandem design uses a redox-active electrolyte to mediate electrons between the visible-light-absorbing OER particles and visible-light-absorbing HER particles. This is the mechanism that must be utilized in Type 2 reactors and is also often termed a Z-scheme. (Note that Z-scheme mechanisms with or without a redox shuttle can also be used in Type 1 reactors.) In Type 2 reactors, solar PEC water splitting occurs by illumination of two vessels each containing a particle suspension and where one of the electronic charge carriers from each particle reacts with a redox shuttle to mediate charge exchange between the vessels. Implementation of such a design is non-trivial because redox shuttles often exhibit facile redox kinetics and thus undesired recombination reactions are often prevalent. For example, the OER particle can oxidize the redox shuttle instead of water (or hydroxide ions), and/or the HER particle can reduce the redox shuttle instead of water (or protons).

Each of the following six light-absorber materials has been reported for use as HER particles in a system that split water under visible-light irradiation when in the form of a suspension, and with inclusion of OER particles and at most an applied pressure bias (i.e. decreased pressure): doped SrTiO₃, (modified) TaON, CaTaO₂N, BaTaO₂N, doped BaTiO₃, and dye-sensitized H₄Nb₆O₁₇; seven light-absorber materials/proteins have been reported that can serve as the visible-light-absorbing OER particles: WO₃, TaON, modified Ta₃N₅, BiVO₄, Bi₂MoO₆, doped TiO₂, and photosystem II (PSII) (Table 4 and Table 5). Three general types of redox shuttle have been used with these particle combinations, i.e. those based on iodine (IO₃⁻/I⁻ or I₃⁻/I⁻), those based on iron (FeCl₃/FeCl₂ or [Fe(CN)₆]^{3-/4-}), and those based on cobalt ([Co(bpy)₃]SO₄ or [Co(phen)₃]Cl₂). Parameters for the best-performing systems within each materials pair are displayed in chronological order in Table 4 and Table 5.

For nearly all demonstrations of solar PEC water splitting only one redox state of the redox shuttle was present initially, and thus the expected 2:1 stoichiometry of H₂ and O₂ was not attained at early times. Several exceptions have been reported, including the first demonstration of visible-light-driven PEC water splitting in 2001 by Arakawa and colleagues.¹³⁷ To support that the I⁻ did not compete with water for photogenerated holes in WO₃, Pt-loaded WO₃ particles photoelectrochemically generated O₂ in the presence IO₃⁻ electron acceptor during 70 hours of continuous illumination, and at which time > 96% of the initial IO₃⁻ had been converted to I⁻. Moreover, in 2013, Kudo and workers evaluated their PEC systems in the presence of both the Co³⁺ and Co²⁺ states of their redox shuttles.¹³⁸ This was also the first report of a tandem solar PEC water splitting demonstration using a two-vessel, Type 2 reactor design which incorporated a porous separator, and it had pore sizes of ~10 μm.¹³⁸

Iodine-Based Redox Shuttles. Table 4 presents, in chronological order, the best performing designs featuring an iodine-based redox shuttle. Clear and general mechanisms that elucidate the reasons for the success of iodine-based redox shuttles do not exist, but it has been suggested that single-electron-transfer recombination reactions with I₃⁻, which requires two electrons to generate I⁻, may play a role.¹³⁹⁻¹⁴¹ This is an active area of research in the dye-sensitized solar cell community and needs more attention for application in particle suspension reactors for solar PEC water splitting, especially for the I⁻/IO₃⁻ redox chemistry which requires that six electrons be transferred.

WO₃ OER Particles. In 2001, the first ever particle suspension to achieve visible-light-driven PEC water splitting was reported by Arakawa and colleagues.¹³⁷ Pt-loaded (0.3 wt %), Cr (1 at %) and Ta (1 at %) codoped SrTiO₃ HER particles and Pt-loaded (1 wt %) WO₃ OER particles ($E_{bg} \approx 2.7$ eV) were placed in a single vessel containing an aqueous IO₃⁻/I⁻ redox shuttle at neutral pH and

were reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (420 – 440 nm), with an QY_{420.7 nm} ≈ 0.1%, and stability for over 10 days of intermittent illumination (with the light on for at least 6 days).^{67,137,142} Moreover, Pt-loaded WO₃ evolved O₂ in the presence of up to 100 mM I⁻, which is much easier to oxidize thermodynamically than water, whereas Pt-loaded BiVO₄ did not evolve O₂ when the concentration of I⁻ was > 10 mM. It was suggested that the success of the Pt-loaded WO₃ was due in part to preferential adsorption of the IO₃⁻ electron acceptor to its surface, thus blocking recombination reactions. I₃⁻ did not serve as a suitable electron acceptor in place of IO₃⁻, reported to be due to poor adsorption of I₃⁻ on the light-absorber material.

In 2005, the doped SrTiO₃ particles were replaced with TaON HER particles ($E_{bg} = 2.5$ eV) with the same Pt loading, and the system was reported to be stable for 100 hours of continuous illumination with no N₂ detected and an EQY_{420 nm} ≈ 0.4%.¹⁴³ In 2008, the wavelength onset for H₂ evolution for PEC water splitting was extended to 510 nm using CaTaO₂N HER particles with the same Pt loading, and to 660 nm using BaTaO₂N HER particles with the same Pt loading, but with a decreased EQY_{420 – 440 nm} ≈ 0.1% (in conjunction with the same Pt-loaded WO₃ OER particles) and some initial N₂ evolution.¹⁴⁴ In 2010, Domen and colleagues reported Pt-loaded (0.5 wt %) ZrO₂-modified TaON (9.1 at % ZrO₂) ($E_{bg} = 2.2$ eV) HER particles that resulted in an EQY_{420.5 nm} which increased by over an order-of-magnitude to 6.3% (in conjunction with the same Pt-loaded WO₃ OER particles).¹⁴⁵ In 2014, a suspension of Pt-loaded (0.25 wt %), Rh-doped (1.0 mol %) perovskite BaTiO₃ HER particles and PtO_x-loaded (0.5 wt % Pt) WO₃ OER particles was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light (> 420 nm) and was stable for 30 hours of continuous illumination.¹⁴⁶

Tantalum–Nitride OER Particles. Particles that perform the OER and absorb more visible light than WO₃ are also actively being investigated. In 2008, a suspension of Pt-loaded (0.3 wt %) TaON HER particles and RuO₂-loaded (0.3 wt %) TaON OER particles was reported to evolve stoichiometric H₂ and O₂ when illuminated with visible light, and with only a small amount of initial N₂ evolution.¹⁴⁷ The initial EQY_{420 nm} ≈ 0.1 – 0.2% was smaller than that observed using WO₃ even though TaON absorbed more visible light. In 2010, a suspension of Pt-loaded (1 wt %) ZrO₂-modified TaON HER particles and Ta₃N₅ ($E_{bg} = 2.1$ eV) OER particles modified with Ir (5 wt %) and rutile TiO₂ was reported to evolve H₂ and O₂ for 60 hours when continuously illuminated with visible light (> 420 nm).¹⁴⁸

Molecular Dyes on Oxide Particles. Molecular dye light absorbers have been used to drive solar PEC water splitting.^{92,149–151} In 1980, Grätzel and colleagues reported the first successful use of dye sensitizers to impart PEC water splitting using visible light (> 450 nm), and Ru–polypyridyl dyes anchored to TiO₂ particles co-loaded with Pt and RuO₂ cocatalysts.¹⁵⁰ The reported stoichiometry of H₂ and O₂ often deviated from the ideal 2:1 v/v ratio, and other studies indicated that reduction of adsorbed O₂ may have been the cause of the reduced O₂ stoichiometry.^{77,152–154} In 2009, an aqueous suspension of Pt-loaded (0.5 wt %) H₄Nb₆O₁₇ HER particles with anchored coumarin organic dyes as sensitizers, WO₃ OER particles co-loaded with IrO₂ (0.5 wt %) and Pt (0.5 wt %), and the I₃⁻/I⁻ redox shuttle was reported to evolve approximately stoichiometric H₂ and O₂ when illuminated with visible light (> 400 nm).¹⁵⁵ The system was stable for 48 hours of illumination, where it exhibited > 200 turnovers per dye; however, the rate of water splitting was limited by the low QY_{500 nm} < 0.1% for dye-sensitized H₂ evolution. Insertion of an oligothiophene moiety between the donor and acceptor part of coumarin or carbazole dyes was reported to

significantly improve the stability of the dye sensitizers in aqueous electrolytes, resulting in stability for 64 hours of continuous illumination and a maximum of > 500 turnovers per dye for a coumarin dye containing two thiophenes rings.¹⁵⁶

Table 4. Reports of visible-light-driven water splitting using two particle suspensions and an iodine-based redox shuttle (**bold typeface** indicates the design with the largest reported quantum yield; underline typeface indicates the design that absorbs at the longest wavelength)[#]

HER Light Absorber	HER Cocatalyst (wt %)	OER Light Absorber	OER Cocatalyst (wt %)	Aqueous Electrolyte (Concentration (mM), pH)	Illumination ^a (Irradiance (mW cm ⁻²), Wavelength (nm))	Activity Measurement			Year ^{Ref}
						H ₂ , μmol h ⁻¹	O ₂ , μmol h ⁻¹	Quantum Yield, % (Wavelength (nm))	
SrTiO ₃ :Cr,Ta	Pt (0.3)	WO ₃	Pt (0.5)	NaI (5, 6.5)	Xe (n.r., > 420)	16	8	1 (420)	2005 ⁶⁷
TaON	Pt (0.3)	WO ₃	Pt (0.5)	NaI (5, 7)	Xe (n.r., > 420)	24	12	0.4 (420)	2005 ¹⁴³
CaTaO ₂ N	Pt	WO ₃	Pt (0.5)	NaI (5)	Xe (n.r., > 420)	~1	n.r. ^b	n.r.	2008 ¹⁴⁴
<u>BaTaO₂N</u>	<u>Pt</u>	<u>WO₃</u>	<u>Pt (0.5)</u>	<u>NaI (5)</u>	<u>Xe (n.r., > 420)</u>	<u>~0.4</u>	<u>n.r.</u>	<u>0.1 (420 – 440)</u>	<u>2008¹⁴⁴</u>
TaON	Pt (0.3)	TaON	RuO ₂ (0.3)	NaI (1, 6)	Xe (n.r., > 420)	~7	~2.5	0.1 – 0.2 (420)	2008 ¹⁴⁷
ZrO₂-TaON	Pt (0.5)	WO₃	Pt (0.5)	NaI (0.5)	Xe (~38, > 350)	52	26.6	6.3 (420.5)	2010¹⁴⁵
ZrO ₂ -TaON	Pt (1)	TiO ₂ -Ta ₃ N ₅	Ir (5)	NaI (0.1)	Xe (~435, 420 – 600) ^c	~3	~1	n.r.	2010 ¹⁴⁸
Coumarin-H ₄ Nb ₆ O ₁₇	Pt (0.5)	WO ₃	IrO ₂ (0.5) and Pt (0.5)	KI (5)	Xe (n.r., > 410)	2.2	0.9	0.05 (480)	2013 ¹⁵⁶
Carbazole-H ₄ Nb ₆ O ₁₇	Pt (0.5)	WO ₃	IrO ₂ (0.5) and Pt (0.5)	KI (5)	Xe (n.r., > 410)	1.7	0.7	n.r.	2013 ¹⁵⁶
BaTiO ₃ :Rh	Pt (0.25)	WO ₃	PtO _x (0.5 (Pt))	NaI (10)	Xe (~150, > 420)	30.8	n.r.	0.5 (420)	2014 ¹⁴⁶

[#] For each combination of light-absorber materials only the highest reported quantum yield (≥ 0.1%) is included

^a Xe = 300 W xenon lamp with a Pyrex cell

^b n.r. = not reported

^c Calculation performed from reported rate of incident photons, and assuming the median excitation wavelength in the range

Iron-Based Redox Shuttles. Iodate/iodide redox chemistry is somewhat irreversible due to the plethora of iodine oxide intermediates that can be formed during oxidation of iodide (I⁻) from the 1- to 5+ oxidation state, as IO₃⁻. Thus, other redox shuttles may be of practical interest. Toward this, in 2004, Kudo and colleagues used a chloride salt of the Fe^{3+/2+} redox shuttle in pH 2.4 aqueous electrolyte containing Pt-loaded (0.5 wt %), Rh-doped (1 at %) SrTiO₃ HER particles and BiVO₄, WO₃, or Bi₂MoO₆ OER particles to impart H₂ and O₂ evolution when illuminated with visible light (> 420 nm).^{66,68} EQY_{440 nm} = 0.3%, 0.2%, and 0.2% was reported for each system, respectively, as well as stability for 120 hours, 158 hours, and 22 hours of continuous illumination, and multiple turnovers per Fe³⁺ ion in each case. Only systems with either WO₃ or BiVO₄ were

reported to produce stoichiometric H₂ and O₂ with EQY_{420 nm} = 0.5% and 0.4%, respectively. The pH was adjusted with H₂SO₄ and the experimental pH value was chosen to prevent formation of iron oxide colloids. Although reduction of Fe³⁺ at Pt is a recombination mechanism, as the concentration of Fe³⁺ increased, the rate of H₂ evolution also increased. It was suggested that, akin to IO₃⁻, the proposed Fe³⁺ species ([Fe^{III}(SO₄)(H₂O)₅]⁺ and [Fe^{III}(OH)(H₂O)₅]²⁺) adsorbed onto Pt and suppressed the undesired H₂ + Fe³⁺ recombination reaction that is typically catalyzed at Pt.

In 2008, the Pt HER cocatalysts were replaced with Ru (0.7 wt %) and when mixed with BiVO₄ OER particles an EQY_{420 nm} = 0.3% was reported for stoichiometric H₂ and O₂ evolution when illuminated with visible light (> 420 nm).¹⁵⁷ Moreover, the reported activity did not depend on the amount of evolved H₂ and O₂ in the headspace during 70 hours of continuous evolution of gases, whereas when Pt HER cocatalysts were used decreased activity was apparent by 20 hours. Fe^{3+/2+}-mediated recombination reactions under pressurized H₂ or O₂ were reported to be slower at the oxidized Ru cocatalysts than at previously reported metallic Pt cocatalysts. Pt activity was returned upon releasing the built-up H₂ and O₂ pressure. In 2013, an EQY_{420 nm} = 4.2% and a 0.1% STH efficiency for stoichiometric H₂ and O₂ evolution were reported for these materials when the HER particles were synthesized by a new procedure and illuminated with 1 Sun AM1.5G simulated sunlight. The optimal procedure included excess Sr, 2 at % Rh dopant, and 1 wt % Ru HER cocatalysts.¹⁵⁸ In 2014, these SrTiO₃ HER particles were combined with Rh (1.0%) and Sb (1.0%) codoped SrTiO₃ particles loaded with IrO_x (3.0 wt %) OER cocatalysts to demonstrate stable H₂ and O₂ evolution for 90 hours of continuous illumination.¹⁵⁹

Also in 2014, Li, Chen, and colleagues reported a hybrid suspension consisting of PSII, an [Fe(CN)₆]^{3-/4-} redox shuttle, and Ru-loaded (0.5 wt %) SrTiO₃:Rh or Ru₂S₃-loaded (0.2 wt %) hexagonal CdS dispersed in a sodium phosphate buffer solution (pH 6.0 or pH 7.0) that evolved near stoichiometric H₂ and O₂ when illuminated with visible light (> 420 nm).¹⁶⁰ The SrTiO₃ system at pH 7.0 was reported to be most efficient with approximately stoichiometric gas evolution, > 3700 turnovers per PSII, and an activity of ~2500 mol H₂ (mol PSII)⁻¹ hr⁻¹, which corresponds to ~80 μmol H₂ h⁻¹, when assuming 35 chlorophyll per PSII.¹⁶¹

Cobalt-Based Redox Shuttles. Historically, efficient dye-sensitized solar cells use iodine-based redox electrolytes in nitrile solvents to mediate charge transport from metal-oxide nanoparticles, because recombination is much slower than with most other redox shuttles.¹⁴⁰ Alternative redox shuttles consisting of inorganic coordination compounds based on cobalt tris(bipyridine), which absorb much less visible light than I₃⁻, have also been used in efficient dye-sensitized solar cells,¹⁶² including the state-of-the-art demonstration.¹⁶³ In 2013, Kudo and colleagues used Co^{3+/2+} coordination compounds as the redox shuttle in particle suspensions for solar PEC water splitting.¹³⁸ Ru-loaded (0.7 wt %), Rh-doped (1 at %) SrTiO₃ HER particles and OER particles consisting of BiVO₄, WO₃, or Cr (2.3%) and Sb (3.45%) codoped TiO₂ were reported to evolve H₂ and O₂ when illuminated with visible light (> 420 nm). The WO₃ OER particles were reported to exhibit QY_{≥420 nm} = 0.1%, while the BiVO₄ OER particles reached a maximum QY_{420 nm} = 2.1% (0.06% STH efficiency), and evolved the gases in an approximately 2:1 stoichiometry for > 100 hours of continuous illumination, when the particles were prepared using 3% excess Sr (to Ti + Rh) and were evaluated at pH 3.8 with 0.5 mM redox shuttle (0.2 mM for STH measurement). Each particle was evaluated in the presence of redox shuttle molecules in just one redox state or equimolar concentrations of molecules in both redox states. Comparing the case with only one redox state present versus both, the Rh-doped SrTiO₃ HER particles lost only 6% (bpy, pH 6.8), 14% (bpy, pH 3.8), and 23% (phen, pH 6.8) of initial activity, while the BiVO₄ OER particles lost

23% (bpy, pH 6.8), 87% (bpy, pH 3.8), and 71% (phen, pH 6.8) of initial activity (bpy is 2,2'-bipyridine and phen is 1,10-phenanthroline). In addition, this was the first report where an electrochemical cell with two vessels separated by a membrane was used, which strongly resembled a Type 2 reactor design and exhibited an initial $QY_{\geq 420 \text{ nm}} \approx 0.05\%$ under sunlight illumination in autumn in Tokyo.¹³⁸

Table 5. Reports of visible-light-driven water splitting using two particle suspensions and a non-iodine-based redox shuttle (**bold typeface** indicates the design with the largest reported quantum yield and STH efficiency; underline typeface indicates the design that absorbs at the longest wavelength)[#]

HER Light Absorber	HER Cocatalyst (wt %)	OER Light Absorber	OER Cocatalyst (wt %)	Aqueous Electrolyte (Concentration (mM), pH)	Illumination ^a (Irradiance (mW cm ⁻²), Wavelength (nm))	Activity Measurement			Year ^{Ref}
						H ₂ , $\mu\text{mol h}^{-1}$	O ₂ , $\mu\text{mol h}^{-1}$	Quantum Yield, % (Wavelength (nm))	
SrTiO ₃ :Rh	Pt (0.5)	Bi ₂ MoO ₆	<i>none</i>	FeCl ₃ (2, 2.4 w/ H ₂ SO ₄)	Xe (n.r., > 420)	16.9 ^b	6.9 ^c	0.2 (440)	2004 ⁶⁶
SrTiO ₃ :Rh	Pt (0.5)	WO ₃	<i>none</i>	FeCl ₃ (2, 2.4 w/ H ₂ SO ₄)	Xe (n.r., > 420)	–	23.7 ^c	0.5 (420)	2004 ⁶⁶
SrTiO₃:Rh	Ru (1)	BiVO₄	<i>none</i>	FeCl₃ (2, 2.4 w/ H₂SO₄)	Xe (100, > 420)	128	64	4.2 (420) 0.1% STH	2013¹⁵⁸
SrTiO ₃ :Rh	Ru (0.7)	BiVO ₄	<i>none</i>	[Co(phen) ₃]Cl ₂ (1, 7)	Xe (100, > 420)	7.9	3.5	0.1 (≥ 420)	2013 ¹³⁸
SrTiO ₃ :Rh	Ru (0.7)	TiO ₂ :Cr,Sb	<i>none</i>	[Co(phen) ₃]SO ₄ (1, 7)	Xe (100, > 420)	3.0	0.8	n.r. ^d	2013 ¹³⁸
SrTiO ₃ :Rh (3% excess Sr)	Ru (0.7)	BiVO ₄	<i>none</i>	[Co(bpy) ₃]SO ₄ (0.5, 3.8)	Xe (100, > 420)	~100	~40	2.1 (420) 0.06% STH	2013 ¹³⁸
<u>SrTiO₃:Rh</u>	<u>Ru (0.5)</u>	<u>PSII</u>	<i>none</i>	<u>Fe(CN)₆^{3-/4-} (5, 6)</u>	<u>Xe (250, > 420)</u>	<u>~80^d</u>	<u>~43^d</u>	n.r.	<u>2014¹⁶⁰</u>

[#] For each combination of light-absorber materials and redox shuttle only the highest reported quantum yield ($\geq 0.1\%$) is included

^a Xe = 300 W xenon lamp with a Pyrex cell

^b For HER, aqueous electrolyte solution is 2 mM FeCl₂ at pH 2.4

^c OER materials evolved O₂ on separate runs from HER materials evolving H₂

^d n.r. = not reported

^e Converted from mol H₂ (mol PSII)⁻¹ hr⁻¹ to $\mu\text{mol H}_2 \text{ hr}^{-1}$ by assuming 35 chlorophyll per PSII

VI. Conclusions

Solar water splitting could supply clean, renewable fuel for our civilization, assuming an inexpensive, efficient, and stable reactor is realized. PEC reactors based on particle suspensions, i.e. Type 1 and Type 2 reactors, have low projected levelized costs of H₂ and are projected to be cost-competitive with gasoline sold in the U.S. even at only single-digit STH conversion efficiencies. However, many challenges remain before these reactors become commercial realities. At least twenty different light-absorber materials have demonstrated solar PEC water splitting using either a single particle or solid-state tandem particle in a Type 1 reactor design, as well as particles and redox shuttles that would be suitable for a Type 2 reactor design. Two *STH efficiencies* were reported that exceeded 1%: a CoO suspension that exhibited a 5% STH efficiency but was only stable on the timescale of hours, and a carbon nanodot–carbon nitride composite that

demonstrated a ~2% STH efficiency and 200 days of operation, with daily particle removal and drying. In lieu of these unsustainable demonstrations, all other reported *quantum yields* were < 7%, which is over an order-of-magnitude smaller than the values reported for state-of-the-art fixed electrodes.¹⁶⁴ In other words, efficient, stable, inexpensive, and proven particles for solar PEC water splitting that can be used as suspensions in these reactors *do not yet exist*. Only through continued funding and research into particle materials and reactors for solar PEC water splitting will these technologies one day constitute an affordable and practical option for centralized renewable H₂ generation from water. Thus, in conclusion, big-picture target research goals for those interested in particle suspension reactors for solar PEC water splitting are presented below:

- Fabricate particle suspensions that are able to split water under 1 Sun of AM1.5G illumination against pressures of 1 bar H₂ and 1 bar O₂. For Z-scheme mechanisms involving a redox shuttle, also include both halves of the redox shuttle.
- Engineer and evaluate separation processes (Type 1 reactors) and separator materials (Type 2 reactors).
- Through numerical modeling and simulation, determine which reactor design, vessel arrangement, vessel dimensions, etc. and which particle size, shape, concentration, etc. satisfy chemical engineering demands.
- Perform techno-economic cost analyses for plausible alternative piping designs, flow schemes, and product separation technologies, and assess their applicability computationally.
- Computationally model and perform techno-economic cost analyses on the active materials (e.g. particles, cocatalysts, redox shuttles, separators), in order to optimize the selection and fabrication of future improved materials.
- Fabricate particles and cocatalysts that are most amenable to the reactor design constraints and result in the most efficient, robust, inexpensive, and scalable reactors, and evaluate entire prototype reactors under solar illumination conditions.

VII. Appendix

For a sustainable and safe Type 1 reactor, the H₂ and O₂ reaction products from the water-splitting reactions must be separated to at least beyond the flammable limits, where the lower limit is 4% H₂ in O₂.²⁰ The energy loss due to isothermally separating H₂ from an ideal 2:1 v/v stoichiometric H₂/O₂ reaction product mixture can be estimated to be 8.7% of the energy stored in H₂, per the following calculation: the H₂/O₂ gas mixture inside (in) the water splitting reactor vessel has initial mole fractions of H₂ and O₂ of $X(\text{H}_2, \text{in}) = 2/3$ (0.667) and $X(\text{O}_2, \text{in}) = 1/3$ (0.333). Then, it is assumed that an H₂-selective membrane puts this mixture into diffusional equilibrium with pure H₂ outside (out) the reactor vessel, in a storage tank at a pressure of 1 bar. For equilibrium to hold between the reactor vessel and the storage tank, the partial pressures of H₂ inside and outside the reactor vessel must be equal, i.e. $p(\text{H}_2, \text{in}) = p(\text{H}_2, \text{out}) = 1$ bar. After pressurization and equilibration due to H₂ diffusion, this requires that the total pressure inside the reactor vessel be 25 bar (i.e. 1 bar H₂ (4%) and 24 bar O₂ (96%)), according to Equations 3,

$$X(\text{H}_2, \text{in}) \times p(\text{tot}, \text{in}) = X(\text{H}_2, \text{out}) \times p(\text{tot}, \text{out}) \quad (3a)$$

$$p(\text{tot}, \text{in})_{\text{final}} = X(\text{H}_2, \text{out}) \times p(\text{tot}, \text{out}) / X(\text{H}_2, \text{in})_{\text{final}} \quad (3b)$$

$$p(\text{tot}, \text{in})_{\text{final}} = (1.0 \times 1 \text{ bar}) / 0.04 = 25 \text{ bar}$$

Because the partial pressure of O₂ in the pressurized gas mixture does not change during H₂ diffusion, the initial 2:1 v/v stoichiometric H₂/O₂ mixture at 1 bar must be pressurized to 72 bar prior to H₂ diffusion out of the reactor vessel. This assumes a one-step reversible and isothermal pressurization process (in a closed system) and is calculated using Equation 4,

$$p(\text{tot,in})_{\text{initial}} = (v_{\text{H}_2} + v_{\text{O}_2}) \times p(\text{O}_2,\text{in}) \quad (4)$$

$$p(\text{tot,in})_{\text{initial}} = (2 + 1) \times 24 \text{ bar} = 72 \text{ bar}$$

The pV work required to pressurize the initial H₂/O₂ mixture from 1 bar to 72 bar is 10.6 kJ mol⁻¹. Again, this assumes a one-step reversible and isothermal pressurization process (in a closed system) and is calculated using the equation for the differential Gibbs free energy and the ideal gas law at 25 °C, according to Equation 5,

$$\Delta G = nRT \ln (p_2/p_1) \quad (5)$$

$$\Delta G = 2479 \ln (72 \text{ bar}/1 \text{ bar}) = 10.6 \text{ kJ per mole of initial products}$$

This equals 6.7% of the free energy content in the initial 1 mole of gas mixture (i.e. 0.667 x 237 kJ mol⁻¹ = 158 kJ mol⁻¹). This brief estimate shows that overall the STH efficiency is reduced by ~8.7% for this type of gas separation (6.7% pressurization energy loss plus 2% H₂ energy loss due to the residual 4% H₂ remaining in the vessel).

VIII. Acknowledgements

The authors thank Dr. Eric Miller for the inspiration to compile this review, and the members of the Photoelectrochemical Working Group for helpful comments, suggestions, and discussions, specifically Prof. Ryu Abe (Kyoto University), Prof. Jason Baxter (Drexel University), Prof. Jiming Bao (University of Houston), Prof. Dan Esposito (Columbia University), Dr. Arnold Forman (Bio-Logic), Prof. Sophia Haussener (École polytechnique fédérale de Lausanne), Prof. Akihiko Kudo (Tokyo University of Science), Dr. Kazuhiko Maeda (Tokyo Institute of Technology), Dr. Sixto Malato (Plataforma Solar de Almería), Dr. Steve Reece (Sun Catalytix), and Prof. Wilson Smith (Delft University of Technology). D.M.F. acknowledges support by the National Science Foundation Graduate Research Fellowship under Grant No. DGE-1321846. This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, as follows: work by S.H. and F.A.H. was supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993. N.S. is supported by the University of California Santa Barbara Air Products Fellowship and by the National Science Foundation (EFRI-1038234). T.H. and K.D. acknowledge financial support via a Grant-in-Aids for Specially Promoted Research (no. 23000009) of the Japan Society for the Promotion of Science (JSPS). F.E.O. thanks Research Corporation for Science Advancement for a Scialog award and the National Science Foundation under CHE – 1152250 and CBET 1133099. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the National Science Foundation. S.A. acknowledges support from the Department of Chemistry and the School of Physical Sciences at the University of California Irvine and the U.S. Department of Energy under Award No. DE-EE0006963. A summary version of this review paper (DOI: *TBD*) can be found on the working group website

(<http://energy.gov/eere/fuelcells/photoelectrochemical-working-group>), and associated summary tables that will be updated as the field progresses.

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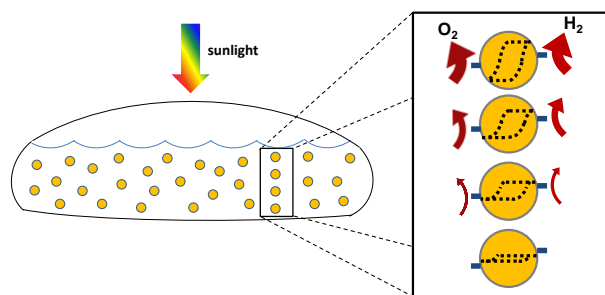
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Graphical Abstract



Reactor and particle design considerations of particle suspension reactors for solar photoelectrochemical water splitting

Broader Context

Global climate disruption fueled by anthropogenic greenhouse gas emissions is a major concern for humanity and life on Earth. The only way to significantly attenuate the rate of carbon dioxide emitted into the atmosphere is to reduce fossil fuel use for energy and industrial applications. Hydrogen produced by water splitting using renewable solar energy is a clean replacement for fossil fuels. Solar photoelectrochemical water splitting represents a “Holy Grail” technology, but faces challenges before solar hydrogen can compete with fossil fuels on a cost-per-energy basis. To make solar hydrogen feasible, particle suspension reactors projected to cost less than fixed-electrode designs must be coupled with low-cost, stable, and efficient materials. Should these proposed technologies become a reality, society will have an economic impetus to use clean hydrogen as a fuel source for important industrial processes such as transportation and production of chemicals including ethylene and ammonia.

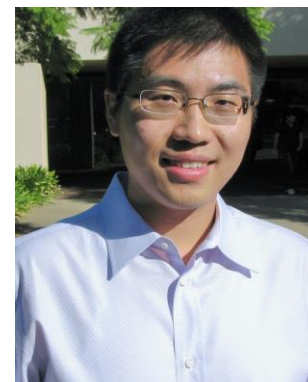
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David Fabian is a second-year graduate student in the Department of Chemistry at the University of California, Irvine under the supervision of Prof. Shane Ardo. He received his bachelor's degree in chemistry from The College of William & Mary in 2013 and is a 2014 NSF Graduate Research Fellow. His major research interest covers synthesis and characterization of hybrid organic-inorganic materials for applications in solution-



processed thin-film photovoltaics. Shane Ardo obtained a BS in mathematics from Towson University in 1999, an MS in nutrition and food science from UM-College Park in 2005, and a PhD in photo-physical inorganic chemistry from Johns Hopkins University under Prof. Gerald Meyer in 2010. After a post-doctoral appointment at the California Institute of Technology under Prof. Nathan Lewis, he joined the faculty at the University of California, Irvine in 2013 where he is now an Assistant Professor in the Department of Chemistry with a joint appointment in the Department of Chemical Engineering and Materials Science. Prof. Ardo's research interests are driven by the pursuit of understanding and controlling energy conversion mechanisms for applications in solar fuels devices, photovoltaics, seawater desalination, and redox flow batteries.

Shu Hu is a senior postdoctoral scholar at Joint Center for Artificial Photosynthesis. He received his B.Eng. (Honors) from Tsinghua University in 2006 and completed a Ph.D. in Materials Science at Stanford University in 2011. Shu then joined the group of Prof. Nathan S. Lewis in Division of Chemistry and Chemical Engineering at California Institute of Technology, where his work spans experimental and modeling areas in Si and III-V nanocrystal synthesis, nanophotonic phenomena, and solid-electrolyte interfaces for photoelectrochemical solar-fuel production. His main thrust includes the stabilization of technologically important, efficient yet unstable semiconductors under photoanodic conditions relevant to water oxidation.



Nirala Singh received his PhD in 2015 from the University of California at Santa Barbara. At UCSB he researched catalysts for the efficient production of hydrogen from sources such as hydrogen bromide, techno-economics of renewable energy production, and photoelectrochemical absorbers for fuel and chemical production. His previous works include developing a Solar Energy Course and Lab Equipment at the University of Michigan, electrolysis of water for hydrogen production and bacteria decomposition for water purification, and testing and characterization of high-power semiconductor devices. His interests include the use of catalysis for energy production and storage.



Frances Houle is Department Head for the Science of Large Scale Systems in the Joint Center for Artificial Photosynthesis, and Senior Scientist in the Chemical Sciences Division at Lawrence Berkeley National Laboratory. Her scientific interests are in the areas of nanoscale mechanisms of surfaces and thin-film chemical transformations. She received a BA from University of California Irvine and PhD from California Institute of Technology, both in chemistry. Prior to joining LBNL she was Research Staff Member in the IBM Research Division in San Jose, California, and Manager of Materials Development at InVisage Technologies, a startup company making nanoparticle-based image sensors.



Takashi Hisatomi received his PhD in Engineering from the University of Tokyo under Prof. Dr. Domen's supervision in March 2010. He joined Laboratory of Photonics and Interfaces in École Polytechnique Fédérale de Lausanne led by Prof. Dr. Grätzel in April 2010 as a postdoctoral fellow. He has been studying in Prof. Dr. Domen's laboratory in the University of Tokyo since April 2012 and works as an assistant professor currently. His



major research interest covers material development and device design for photocatalytic and photoelectrochemical solar water splitting as well as kinetic assessments of photocatalysis and photoelectrochemistry. Prof. Kazunari Domen received BSc (1976), MSc (1979), and PhD (1982) honors in chemistry from the University of Tokyo. Dr. Domen joined Chemical Resources Laboratory, Tokyo Institute of Technology, in 1982 as Assistant Professor and was promoted to Associate Professor in 1990 and Professor in 1996, having moved to the University of Tokyo as Professor in 2004. Prof. Domen has been working on the overall water splitting reaction on heterogeneous photocatalysts to generate clean and recyclable hydrogen. His research interest now includes heterogeneous catalysis and materials chemistry, with particular focus on surface chemical reaction dynamics, photocatalysis, solid-acid catalysis, and mesoporous materials.

Frank Osterloh is an inorganic chemist working on nanoparticle devices for artificial photosynthesis. He received M.A. and Ph.D. degrees in chemistry in 1994 and 1997 from the Carl von Ossietzky University in Oldenburg, Germany, while working with late Prof. Siegfried Pohl. After completing postdoctoral training with Prof. Richard H. Holm at Harvard University, he joined the faculty at the Chemistry Department at the University of California, Davis in 2000. Since then, Frank has authored four review articles and over 75 experimental papers. In 2010, his contributions to the chemistry of nanoparticles were recognized with the ACS Inorganic Nanoscience award.

