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Recent Advances and Emerging Trends in Photo-Electrochemical Solar Energy Conversion

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Title: Recent Advances and Emerging Trends in Photoelectrochemical Solar Energy Conversion

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Photoelectrochemical solar energy conversion offers the promise of low cost renewable fuel generation from abundant sunlight and water. In this Progress Report, recent developments in photoelectrochemical water splitting are discussed with respect to this promise. State-of-the-art photoelectrochemical device performance is put in context with the current understanding of the necessary requirements for cost effective solar hydrogen generation (in terms of solar-to-hydrogen conversion efficiency and system durability, in particular). Several important studies of photoelectrochemical hydrogen generation at p-type photocathodes are highlighted, mostly with protection layers (for enhanced durability), but also a few recent examples where protective layers are not needed. Recent work with the widely studied n-type BiVO₄ photoanode is detailed, which highlights the needs and necessities for the next big photoanode material yet to be discovered. The emerging new research direction of photoelectrocatalytic upgrading of biomass substrates towards value-added chemicals is then discussed, before closing with a commentary on how research on PEC materials remains a worthwhile endeavour.

1. Introduction

The field of solar energy conversion is motivated by the desire to free ourselves from a reliance on fossil fuels for our energy needs. Although the harnessing of fossil fuels has been invaluable for making huge progress in our standard of living over the past two centuries, it has now become clear to nearly everyone that there are perhaps serious consequences to the business-as-usual approach of burning fossil fuels and emitting CO₂ to the air. The decarbonization of our energy systems has been recognized as an important milestone towards stabilizing the global mean temperature,^[1] and it has been estimated that in order to avoid more than 2 °C of warming, net-zero or net-negative emissions should be achieved in the second half of this century.^[2] Although there are many possible technologies to achieve that goal,^[1] they all remain too costly to compete with the burning of fossil fuels coupled with emission to the air, at least while the costs of those emissions remain externalized.

Solar energy is a renewable and carbon-free energy source, and it is by far the most abundant, comprising greater than 99% of the total amount of all renewable energies available on Earth.^[3] However, in order to displace fossil fuels, large scale energy storage solutions will be required to address the intermittency of solar irradiation (and other renewable energies). Although new battery technologies will likely meet the need for cost effective shorter time scale energy storage (1-3 days), fuels are the only effective option for longer term and seasonal storage.^[4]

The field of solar water splitting takes inspiration from Nature in photosynthesis by using light energy to extract electrons from water, and to store those electrons in high energy chemical bonds (i.e. fuels). For the simple water splitting reaction, this generates hydrogen fuel and oxygen as a by-product. The energy of the solar light is stored in the hydrogen molecule, which can then participate directly in a hydrogen-based economy,^[5] or be reacted with CO₂ in Fischer–Tropsch-type processes to generate carbon-based fuels, which are compatible with our current energy infrastructure. If the CO₂ used in the reaction with solar

hydrogen is derived from CO₂ in the air, then the carbon-based fuels would be overall carbon-neutral. However, using the CO₂ stream from a coal-fired power plant does not make sense as a strategy for carbon abatement, as it would be much more efficient from a life cycle perspective to use the solar energy directly and leave the coal unburned.^[6,7]

In any case, renewable hydrogen will play an important role in future energy systems and the chemical industry. In addition to being a carbon-free energy carrier (suitable for use in fuel cells, for example), renewable hydrogen will be needed to supply all of the current processes that rely on fossil-fuel derived hydrogen, such as the large scale synthesis of ammonia through the Haber-Bosch process, which is used as fertilizer for feeding the world population. The question then is, what is the most cost-effective method to generate solar hydrogen?

Presently, the most effective solar energy conversion devices are based on photovoltaics. For semiconductor-based water splitting to generate solar hydrogen, there are two conceptual options: a system that uses separated devices to harvest the light and to electrolyze water (PV-coupled electrolysis), and an integrated system that combines the light capture and catalytic water splitting interface in the same material (photoelectrochemistry) (**Figure 1a**). There are also varying degrees of integration between these two extremes.^[8] PV-coupled electrolysis has the higher technological readiness level at this point, although the solar hydrogen generated by this method is still too expensive to compete with hydrogen derived from fossil fuels, which is the main source of hydrogen today.^[9]

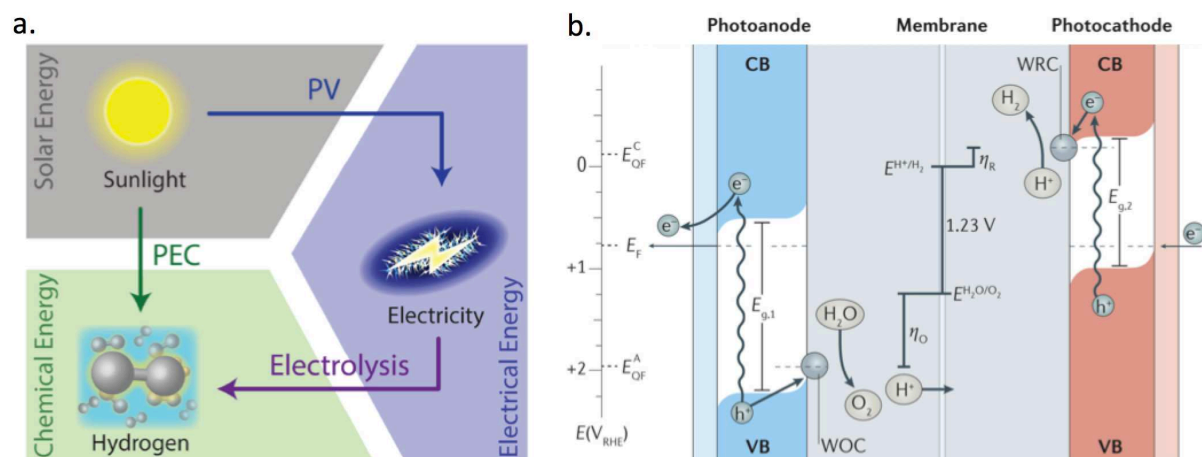


Figure 1. a) Two conceptual options for the generation of solar hydrogen: PV-coupled electrolysis, and direct photoelectrochemical (PEC) water splitting. b) Working principle of a tandem PEC cell for water splitting using a photoanode with bandgap energy $E_{g,1}$, and a photocathode with $E_{g,2}$ (where $E_{g,1} > E_{g,2}$). Briefly, on absorption of a solar photon, an electron (e^-) from the valence band (VB) is promoted to the conduction band (CB) leaving the corresponding electron hole (h^+). The electric field in the depletion layer physically separates these charges and, in the photocathode, the electrons in the CB drift to the semiconductor-liquid junction, increasing the quasi-Fermi energy of the cathode, E_{QF}^C , to drive the reduction of H^+ to H_2 at a water reduction catalysis (WRC) site. Analogously, in the photoanode, electron holes in the VB drift to the semiconductor-liquid junction, increasing the photoanode's quasi-Fermi energy, E_{QF}^A , sufficiently to surmount the overpotential for oxidation (η_o) and oxidize water to O_2 at a water oxidation catalysis (WOC) site. Photogenerated electrons in the CB of the photoanode travel through the external circuit to recombine with the holes in the VB of the photocathode. E_F , Fermi energy; $E(V_{RHE})$, electronic potential with respect to the reversible hydrogen electrode; η_R , overpotential for reduction. Figure 1b and caption reprinted by permission from Springer Nature.^[10]

For many years, photoelectrochemical (PEC) water splitting has offered the promise of low cost hydrogen production via cheap, scalable, easily-produced materials. Since the “electrolyzer” surface area is the same as the light harvesting surface (as they are one in the same), far lower current densities are required compared to standard electrolyzers, and Earth-abundant catalysts can then be used (as the losses are much lower at low current densities).^[6] Importantly, integrated approaches allow for *thermal management* to improve the overall efficiency of the device, by cooling down the light absorber (keeping the photovoltage high) and heating up the catalysts (lowering the required overpotential for the water splitting reactions).^[11,12]

Several technoeconomic analyses indicate that the PEC approach to generate hydrogen can compete with PV-coupled electrolysis (and even with steam reforming of methane) if certain efficiency and stability metrics are met.^[13–15] Sathre et al. carried out a prospective life cycle analysis on a large scale thin film-based PEC plant in order to identify those aspects that have the greatest impact on the energy payback time.^[16] Similarly as to what had been found before,^[17,18] the solar-to-hydrogen (STH) efficiency and the device lifetime were found to have the largest influence on the cost of the resulting hydrogen. The authors state that the STH efficiency should be “well above 5%” with a cell lifetime of at least 5 years in order to have a positive net energy balance. Notably, they also found that the fabrication of the active materials played an important role, where low cost fabrication techniques of the thin films had a significant effect. These analyses contain many assumptions, and it can be argued how accurate they are for estimating costs for technologies with a low technological readiness level. However, the relative importance of the contributing factors to the cost (i.e. STH efficiency, cell lifetime, active material fabrication costs) is likely correct. An important point, also, is that these analyses do not consider the effect of thermal management in the integrated systems, and so likely overestimate the cost of hydrogen from PEC systems.^[11,12]

A key challenge of PEC systems is that the efficiency and stability requirements^[16] are far from being met, even at the laboratory scale.^[19] These challenges represent an opportunity for research to determine the kinds of materials that are necessary and the best architecture of the water splitting device for high efficiency and durable fuel generation on a time scale of years. It is clear that if we are to produce solar hydrogen in the short term (some few years), PV-coupled electrolysis is the only option that is sufficiently advanced enough at this time. In the medium-to-long term, however, PEC systems may indeed become advantageous.^[9]

It is well understood that a so-called “tandem” approach, using two light absorbers in series to capture different parts of the solar spectrum, is far more efficient than a single bandgap system.^[20] Thus, the great majority of works have focused on improving the efficiency and the stability of photocathodes to generate hydrogen, photoanodes to generate oxygen (which supplies the electrons to make hydrogen at the cathode), and combinations of photocathodes and photoanodes to make overall water splitting cells (see Figure 1b). In this Progress Report, I highlight important recent works and emerging trends in PEC that are advancing the field towards cost-effective solar water splitting.

2. Photocathodes for Hydrogen Evolution

Photocathodes are based on p-type materials, and photoelectrons are used to carry out the hydrogen evolution reaction at the photoelectrode surface. It was quickly discovered that most semiconductors undergo photocorrosion in aqueous electrolytes, and so corrosion protection layers were investigated. Hu et al. and Bae et al. have recently written thorough reviews on corrosion protection layers for photoelectrochemical electrodes.^[21,22] Here, I highlight a few notable advances in the use of corrosion protection layers for photocathodes.

2.1. Photocathode Materials With Corrosion Protection Layers

As is evident from the Hu review,^[21] there were only few attempts at stabilizing semiconductors for hydrogen evolution from the 1970's to the 2000's. Then in 2011, a high profile paper appeared from Paracchino et al. that demonstrated stabilized hydrogen generation and high photocurrents for an oxide material, cuprous oxide (Cu_2O), using atomic layer deposited (ALD) TiO_2 as a protection layer.^[23,24] The following year Seger et al. reported a stabilized silicon-based photocathode with earth-abundant MoS_x hydrogen evolution catalyst using a thin Ti metal film as protection layer.^[25] These works ignited a renaissance in research on protection layers for photocathodes, as the benchmarks moved from hours, to days, to weeks of stability in the following years (Table 1).

Emerging materials such as Sb_2Se_3 ,^[26,27] CZTS,^[28–30] CuO ,^[31] CIGS,^[32] and CuBi_2O_4 ^[33,34] have also been investigated with protective overlayers. One major advance was the realization that relatively thick ALD- TiO_2 layers were required to achieve good stabilities on many materials. When considering the mechanism of growth of an ALD film,^[35] a perfectly conformal, protective film should be able to be generated with only 1-2 nm of thickness, even on nanostructured surfaces. However, it was demonstrated that when using the common ALD- TiO_2 precursor tetrakis-dimethylaminotitanium (TDMAT) on slightly rough surfaces (i.e. not perfectly flat silicon wafers), thicknesses greater than ~50 nm were required in order to be reliably pinhole free over larger areas.^[36] As one early example, Tilley et al. demonstrated vastly improved stability of Cu_2O photocathodes by using 100 nm of ALD TiO_2 coupled with a RuO_x hydrogen evolution catalyst (**Figure 2**).^[37] Although RuO_2 is more commonly known as an efficient water oxidation catalyst, it is also a good hydrogen evolution catalyst, and is more resistant to poisoning than platinum.^[38] Spectroelectrochemical studies were carried out by Pastor et al. on this composite material in order to identify the rate law and mechanism of the RuO_x catalyst on both electrochemical and photoelectrochemical water reduction. It was found that the hydrogen evolution reaction was 2nd order with respect to

doubly reduced RuO_x , implying a homolytic mechanism for H_2 evolution.^[39] This work represents a rare example of shedding light on the mechanism of a heterogeneous catalyst using optical absorbance spectroscopy. Interestingly, in a recent study with thermally oxidized Cu_2O photocathodes, Niu et al. uncovered a limitation in the hydrous amorphous RuO_x catalyst used in these PEC studies at higher light intensities (approaching one sun).^[40] It is therefore clear that if the catalytic interface can be improved, the efficiency of these Cu_2O -based systems can be significantly increased.

A stacked tandem device was fabricated that utilized a transparent Cu_2O photocathode with a perovskite PV cell underneath, achieving unbiased water splitting of $\sim 2.5\%$ solar to hydrogen efficiency.^[41] It was found that a thin layer of Au (~ 3 nm) was sufficient to enable an ohmic contact and good nucleation of the electrodeposited Cu_2O film on FTO, with only minimal loss in the transmission to the underlying perovskite photovoltaic.

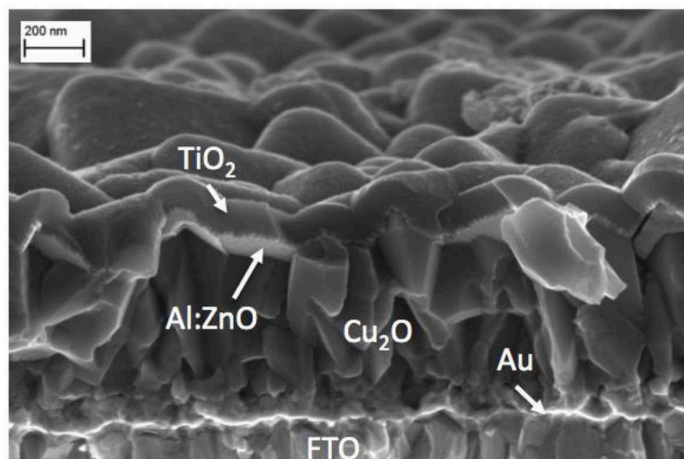


Figure 2. Cross-sectional scanning electron microscope (SEM) image of an ALD- TiO_2 protected $\text{Cu}_2\text{O}/\text{Al}:\text{ZnO}$ buried junction photocathode. Photogenerated electrons from the underlying photoabsorber are injected into the conductive TiO_2 layer and diffuse to the catalyst on the surface, which carries out the hydrogen evolution reaction (catalyst not shown). Reproduced with permission from Wiley.^[37]

Annealing studies have been carried out in an attempt to improve the stability of photocathodes. Azevedo et al. reported a steam treatment of ALD-coated Cu_2O photocathodes that further improved the stability, as standard high temperature annealing treatments severely degraded the performance. This improvement was attributed to a modification of the surface morphology that helped improve charge transfer, preventing photoelectron build-up in the TiO_2 overlayer and subsequent degradation.^[42] High temperature annealing of ALD- TiO_2 films on suitable substrates such as silicon improved the stability to weeks,^[43] and recent studies with TiO_2 overlayers using simulated day/night cycles revealed months of stability.^[44] The cost-effective scalability of the ALD process is uncertain, and so efforts to deposit conformal blocking layers by solution processed methods have also been investigated with success.^[45–47]

One emerging trend in PEC is the use of organic semiconductors as the light harvesting material in photoelectrodes. With regards to hydrogen evolution, standard bulk-heterojunction organic semiconductors have been combined with a TiO_2 protective layer and platinum hydrogen evolution catalyst to generate photocurrents $>5 \text{ mA cm}^{-2}$ at an applied bias of 0 V vs. RHE.^[48] This approach could become quite interesting, as a new efficiency record of 17.3% was recently reported for an organic photovoltaic material,^[49] and such materials could theoretically also be designed with an eye towards corrosion-resistance, even in the absence of protective overlayers.

In addition to the thick protective overlayers discussed above, ultrathin protective layers have been utilized in the so-called metal-insulator-semiconductor (MIS) approach, whereby a thin insulating layer on a semiconductor serves the purpose of corrosion protection, yet is thin enough to allow photo-excited minority carriers to tunnel through to the metallic catalyst. This configuration is essentially a Schottky junction where the photovoltage is generated by the difference in the Fermi levels of the semiconductor and the metallic catalyst under illumination.^[50] Esposito et al. investigated this approach with a p-type silicon

semiconductor, a 2 nm thermally grown SiO₂ insulating layer, and a micro-patterned bilayer metallic catalyst.^[51] Although Pt is an excellent catalyst for the hydrogen evolution reaction, the work function is similar to p-Si, and thus does not offer a built-in voltage to help separate photogenerated charges, giving a low photovoltage. Thus, the authors first deposited a thin titanium layer, which has a lower work function, and can therefore generate a larger photovoltage across the MIS junction. The titanium also serves as a good adhesion layer for the Pt. With this approach, the authors were able to generate significantly improved photovoltage, and good performance for hydrogen evolution. Several more examples of the MIS approach are discussed in the context of water oxidation in Section 3.1.

Table 1. Selected examples of stability measurements of photocathodes. The light source is AM1.5G 100 mW cm⁻² unless otherwise stated.

Photocathode Material	Protective Film Composition	Co-catalyst	pH	Onset Potential [V _{RHE}]	Photo-current [mA cm ⁻²] ^{a)}	Stability (J/J ₀); time; applied bias	Ref. (year)
With Protective Layers							
InP	"thin surface oxide"	Ru, Rh, Pt	0	0.8	60 ^{b)}	70%; 24 h ; +0.5 V _{RHE}	Heller ^[52] (1982)
Cu ₂ O	AZO/TiO ₂	Pt	5	0.4	4	25%; 10 h ; 0 V _{RHE}	Paracchino ^[53] (2012)
Cu ₂ O	AZO/TiO ₂	RuO _x	5	0.48	7.5	65%; 57 h ; 0 V _{RHE}	Luo ^[54] (2016)
Cu ₂ O	Ga ₂ O ₃ /TiO ₂	RuO _x	5	0.9	4	100%; 120 h ; +0.5 V _{RHE}	Pan ^[55] (2018)
n ⁺ p-Si	Mo/MoS ₂	MoS _x	0	0.33	10 ^{c)}	100%; 120 h ; 0 V _{RHE}	Laursen ^[56] (2013)
n ⁺ p-Si	Ti/TiO ₂	Pt	0	0.51	20 ^{c)}	100%; 72 h ; +0.3 V _{RHE}	Seeger ^[57] (2013)
Si	TiO ₂ :H	Pt	0	0.55	22 ^{c)}	60%; 82 days ; +0.4 V _{RHE}	Bae ^[44] (2018)
GaInP	AlInP/TiO ₂	Rh	7	— ^{d)}	15	85%; 20 h ; -0.4 V vs. counter	Cheng ^[58] (2018)
Sb ₂ Se ₃	TiO ₂	RuO _x	0	0.2	10	100%; 2 h ; 0 V _{RHE}	Yang ^[59] (2018)
Without Protective Layers							
Si	none	Pt	0	0.3	4.5 ^{e)}	87%; 60 days ; +0.2 V _{RHE}	Maier ^[60] (1996)
GaInP ₂	none	Pt	0	— ^{f)}	8.5 ^{d)}	96%; 9 h ; 0 V vs. counter	Khasalev ^[61] (1999)
GaInP ₂	none	Pt-Ru	0	— ^{d)}	15	80%; 1.3 h ; 0 V vs. counter	Young ^[62] (2017)

Sb ₂ Se ₃	none	MoS _x	0	0.2	14	71%; 2 h ; 0 V _{RHE}	Prabhakar ^[63] (2017)
CuGa ₃ Se ₅	none	none	0	0.1	12	100%; 10 days ; −1.0 V _{RHE}	Muzzillo ^[64] (2018)
WSe ₂	none	Pt-Cu	0	0.4	1.5	100%; 2 h ; 0 V _{RHE}	Yu ^[65] (2018)
AgRhO ₂	none	none	7	0.6	1 ^{h)}	100%; 4h ; 0 V _{RHE}	Park ^[66] (2018)

^{a)}Photocurrent at beginning of stability measurement; ^{b)}100 W QTH, 2–3 suns; ^{c)}AM1.5 >635 nm; ^{d)}unbiased 2-electrode measurement, water oxidation at counter electrode; ^{e)}W halogen, 33 mW cm^{−2}; ^{f)}unbiased 2-electrode measurement, iodide oxidation at counter electrode (electrolyte 2 M HI / 2 M NaClO₄); ^{g)}W halogen, 106 mW cm^{−2}; ^{h)}465 nm LED, 15 mW cm^{−2}.

2.2. Photocathode Materials Without Corrosion Protection Layers

The use of corrosion protection layers is an intermediate configuration between PV-coupled electrolysis and PEC, as the photovoltage is generated at a position other than the semiconductor-electrolyte junction (so called “buried junctions”).^[67] The use of these layers also adds complexity and cost to the device, which is then reflected in the final price of the generated hydrogen. Thus, the identification of materials that are intrinsically stable towards corrosion and generate (high) photovoltage at the semiconductor-electrolyte interface towards their respective water splitting reactions (true PEC systems, as in Figure 1b) is highly desirable.

It has long been recognized that oxides are good candidates for materials that are stable in aqueous media.^[68] However, there are few oxides that are p-type (and therefore suitable for use as a photocathode), and the most famous p-type oxide Cu₂O is unstable without corrosion protection layers (*vide supra*). However, a few examples of p-type photocathodes that do not require a protective overlayer have emerged.

The delafossite CuFeO₂ is one such materials that is earth-abundant, p-type, and stable under illumination in aqueous media. Prévot et al. reported a sol-gel synthesis of this materials that dramatically reduced the required synthesis temperature of the material, and demonstrated good photocurrents for oxygen reduction, although only small photocurrents for

hydrogen evolution were observed in the bare/uncatalysed state (**Figure 3**).^[69–71] Oh et al. demonstrated that 2D CuFeO₂ could be used for both hydrogen evolution and oxygen reduction.^[72]

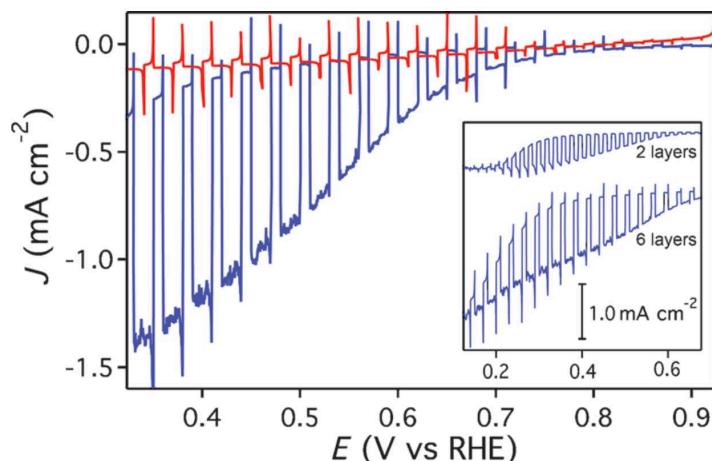


Figure 3. Linear sweep voltammogram of a CuFeO₂ photocathode in 1 M NaOH electrolyte, under intermittent simulated one sun illumination. The blue curve is for oxygen-purged electrolyte, and the red curve is for argon-purged electrolyte. Reproduced with permission from Wiley.^[69]

Although composed of less abundant elements than the above example, AgRhO₂ (also a delafossite) has demonstrated good stability as a photocathode in aqueous solutions.^[66] It possesses a favorable bandgap of 1.7 eV, and suitable band positions for water and CO₂ reduction. Importantly, this material demonstrated ~100% faradaic efficiency for hydrogen evolution across the entire pH range, with measurements carried out at pH 0, 7, and 14. Although the quantum efficiency increases rather steeply once the wavelength exceeds the bandgap energy, it tops out at ~24% in the blue, giving room for improvement with this promising material.

Chalcogenides are another class of materials that have demonstrated stability for water splitting in aqueous media under reductive conditions. For example, MoS₂ is one of the most well known earth-abundant hydrogen evolution catalysts, and is typically employed as a

replacement for platinum.^[73] Tungsten diselenide (WSe_2), has excellent optoelectronic properties as a single crystal,^[74] and Yu et al. have recently investigated this material as 2D exfoliated sheets, with hydrogen evolving photocurrents up to 4 mA cm^{-2} being achieved with this solution-processed material.^[65,75] DeAngelis et al. have reported a $\text{CuGa}(\text{S},\text{Se})_2$ photocathode that gives very high photocurrents in the absence of both protective overlayers and co-catalysts, with an onset of photocurrent of -0.03 V vs. RHE , and 15 mA cm^{-2} photocurrent obtained at -0.35 V vs. RHE .^[76] Prabhakar et al. demonstrated that thin film Sb_2Se_3 , a material previously investigated for water splitting with protective overlayers,^[26,27] is actually stable towards corrosion in harsh acidic conditions under full sun illumination *without* protective layers, and generates high hydrogen-evolving photocurrents when coupled with an amorphous MoS_x layer (**Figure 4**).^[63] If the photovoltage of this material can be improved, it is a strong candidate for a high efficiency, stable, and scalable water splitting photocathode.

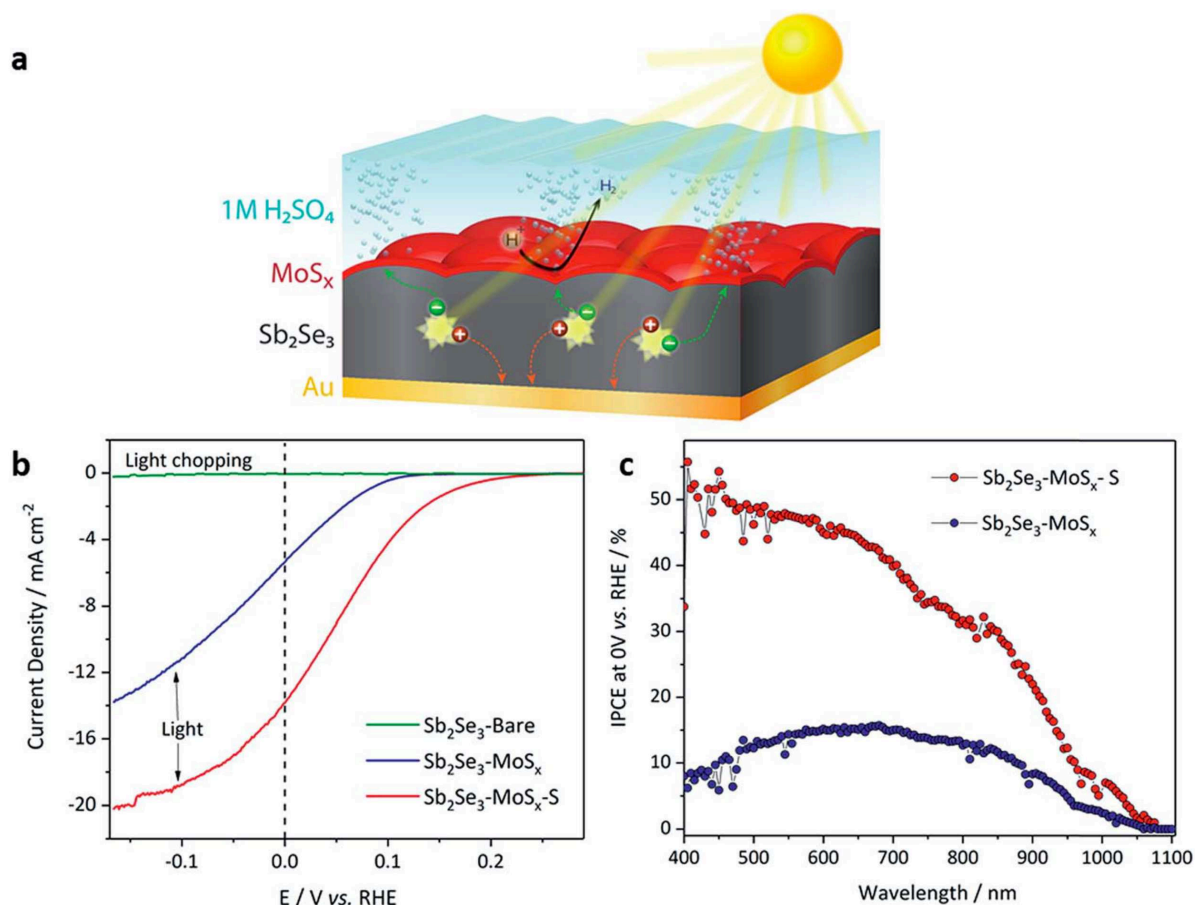


Figure 4. a) Schematic representation of the $\text{Sb}_2\text{Se}_3\text{--MoS}_x$ photocathode. b) Linear sweep voltammograms of the bare Sb_2Se_3 (under light chopping), $\text{Sb}_2\text{Se}_3\text{--MoS}_x$ (non-sulfurized) and $\text{Sb}_2\text{Se}_3\text{--MoS}_x\text{--S}$ (sulfurized) photocathode in 1 M H_2SO_4 under simulated 1 sun illumination (100 mW cm^{-2}). c) IPCE spectra of $\text{Sb}_2\text{Se}_3\text{--MoS}_x$ and $\text{Sb}_2\text{Se}_3\text{--MoS}_x\text{--S}$ photocathodes in 1 M H_2SO_4 at 0 V vs. RHE, indicating improvement of the conversion efficiency over the entire range of absorption. Reproduced by permission of The Royal Society of Chemistry.^[63]

3. Photoanodes

3.1. Oxygen Evolution

To the best of my knowledge, the first example of photocatalytic water oxidation on a semiconductor surface was reported 50 years ago by P. J. Boddy.^[77] Several years later, the famous Fujishima & Honda paper appeared, which demonstrated the utility of this reaction towards generating a solar fuel.^[78] As the bandgap of TiO_2 is too large for solar conversion efficiencies exceeding $\sim 1\%$, more traditional high efficiency semiconductors such as Si, GaP, and GaAs were investigated over the following decades using metal and/or metal oxide protective layers.^[21] In the 2000's, interest was renewed in intrinsically stable oxide materials. Of these, hematite was the only simple monometallic oxide material with a small enough bandgap for efficient solar energy conversion ($E_g \sim 2.0 \text{ eV}$), and a report by Kay et al. with nanostructured hematite photoanodes renewed hope in this material.^[79–82] Several thorough review and perspective articles on hematite have been published recently, and the interested reader is referred to these articles for the history and advancements with iron oxide photoanodes.^[83–86]

Also in the 2000's, interest was gaining in a new multinary oxide material, BiVO_4 , as the bandgap was reasonably small for an oxide ($\sim 2.4 \text{ eV}$) and it was composed of earth abundant elements. A major step forward was made with this material when a spray-pyrolysis synthesis method was reported that reproducibly gave currents in the mA cm^{-2} range,^[87]

kicking off a flurry of investigation by other researchers.^[88–93] Pihosh et al. have demonstrated impressively high photocurrents using a so-called “extremely thin absorber” approach where a thin BiVO_4 layer was coated on WO_3 nanowires, obtaining 6.7 mA cm^{-2} at an applied bias of 1.23 V vs. RHE, which corresponds to about 90% of the theoretical maximum photocurrent value for this material (**Figure 5**).^[94] The authors also paired this photoanode with a GaAs/InGaAsP photovoltaic cell to achieve unassisted overall water splitting, obtaining stable photocurrents of about 6.6 mA cm^{-2} (8.1% solar to hydrogen efficiency).

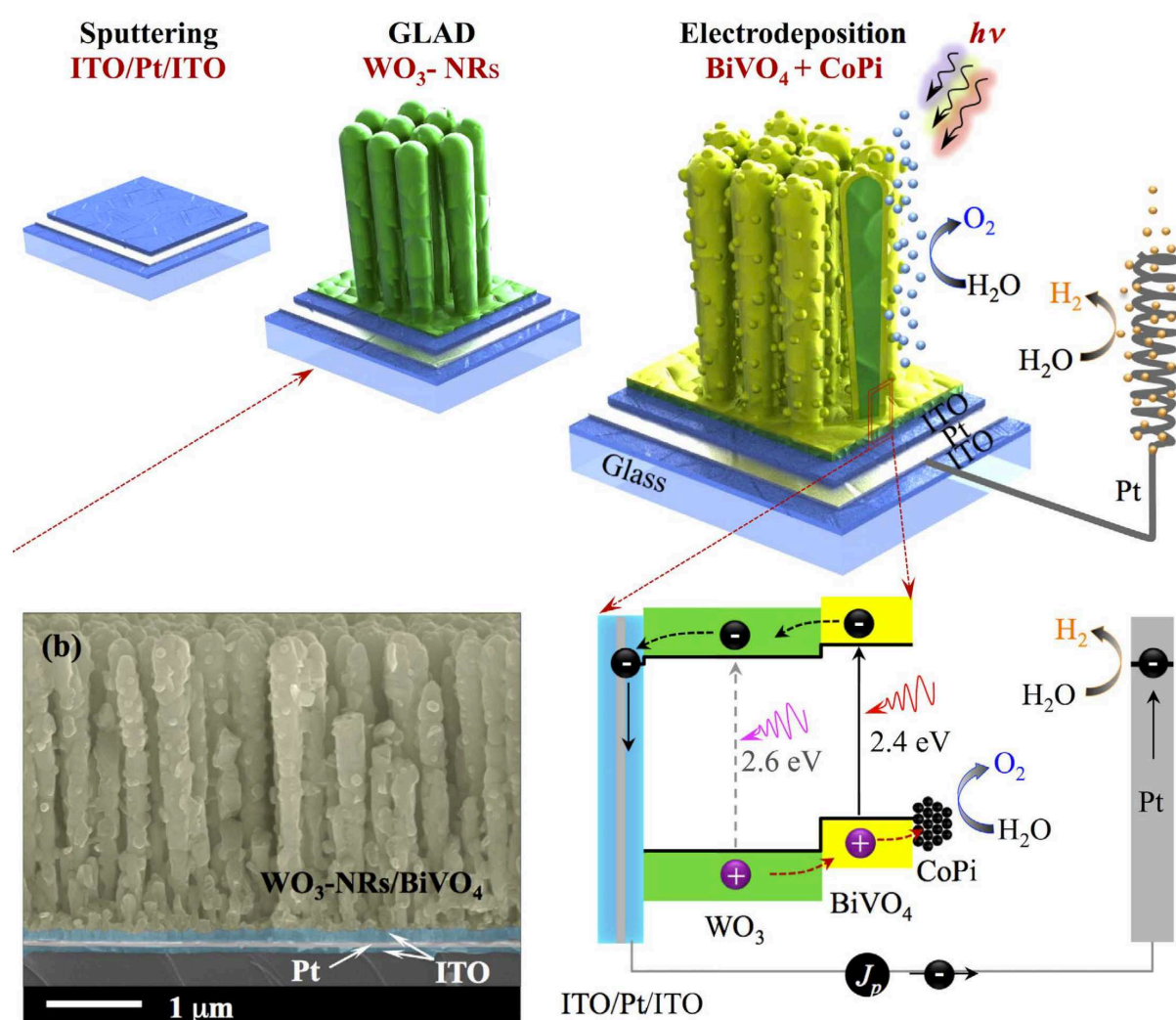


Figure 5. Schematic of the fabrication of the high efficiency extremely thin absorber BiVO_4 photoanode. The SEM image is a cross section of the $\text{ITO/Pt/ITO/WO}_3/\text{BiVO}_4+\text{CoPi}$ photoanode. Reproduced under a Creative Commons Attribution 4.0 International License.^[94]

Photoelectrochemical tandem cells have been prepared using BiVO_4 anodes and Cu_2O photocathodes (**Figure 6**). Although the bandgaps are too large to achieve very high efficiencies, this represents a nice demonstration of an all-oxide overall water splitting cell that does not require any additional electrical bias. Bornoz et al. combined an electrodeposited Cu_2O -based photocathode with a spray-pyrolysis fabricated W-doped BiVO_4 photoanode to achieve unassisted overall water splitting, although the stability was limited due to dissolution of the cobalt-phosphate catalyst on the BiVO_4 surface under insufficient anodic surface potential.^[95] A recent demonstration of this all-oxide tandem couple using a co-axial nanowire $\text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3$ -based photocathode paired with a Mo-doped BiVO_4 photoanode generated stable unassisted overall water splitting of $\sim 3\%$ solar-to-hydrogen.^[55]

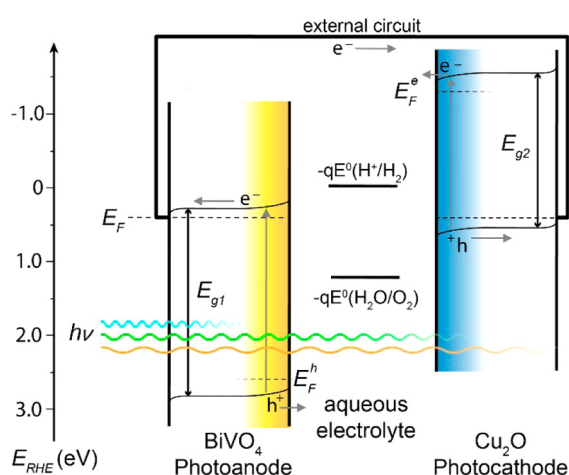


Figure 6. A tandem cell coupling a BiVO_4 photoanode with a Cu_2O photocathode. Reprinted with permission from Reference 95. Copyright 2014 American Chemical Society.

Interestingly, despite being an oxide, it was shown that BiVO_4 is not perfectly stable in aqueous solution, even though the Pourbaix diagram suggests that a thermodynamically stable oxide surface layer should form. In a very detailed study, Toma et al. characterized BiVO_4 photoanodes with a variety of techniques, and showed that it is susceptible to both chemical and photochemical corrosion that is accelerated by illumination, higher pH, and anodic

bias.^[89] The authors used computational modeling to show that photoexcited charge carriers that accumulate at the surface destabilize the lattice, and that the formation of a chemically stable passivating layer is kinetically hindered. It was found that BiVO_4 undergoes chemical corrosion that is accelerated by light, and that this degradation initiates from surface and grain boundaries, dissolving the bulk of the film. Although a stable Bi_2O_3 layer was expected to form on the surface, thermodynamically stable phases of this oxide would require substantial rearrangement from the low density V-depleted state, which cannot occur at room temperature. This paper nicely illustrates that it is not enough to only consider the Pourbaix-predicted (thermodynamic) stability windows when assessing the stability of materials on a theoretical basis, as the expected Bi_2O_3 passivation layer was not formed for kinetic reasons. Stabilization strategies have therefore been sought, and McDowell et al. demonstrated that an ultrathin ALD- TiO_2 layer coupled with a thin Ni layer can effectively stabilize BiVO_4 photoanodes.^[96]

Regarding the stabilization of photoanodes, another high profile paper appeared in 2011 by Chen et al. that demonstrated the MIS approach with ultrathin ALD TiO_2 as a tunnel junction protective layer for silicon photoanodes.^[97] Two nanometers of ALD TiO_2 were deposited onto n-type Si, followed by 3 nm of iridium metal by physical vapor deposition, which gave a stable silicon based photoanode with ~550 mV of photovoltage and excellent stability over 24 hours. As mentioned in Section 2.1, the photovoltage of the MIS approach derives from the Schottky junction of the semiconductor and the metallic catalyst (in electronic contact through a thin insulating layer, which serves to protect the underlying semiconductor from corrosion in the electrolyte). Engineering of the interface can be used to tune the band alignments and therefore maximize the photovoltage obtained with these photoelectrodes. Scheuermean et al. showed that forming gas annealing treatments of n-Si/ SiO_2 /ALD- TiO_2 /Ir MIS photoanodes dramatically improved the photovoltage, with a record photovoltage of 623 mV for this Schottky junction photoanode.^[98]

Hill et al. demonstrated that an inhomogeneously deposited Co/CoOOH-based catalyst on an n-Si/SiO_x photoanode resulted in an increased barrier height and therefore increased photovoltage versus the solid-state Schottky barrier produced in vacuum.^[99] Moreover, the Co/CoOOH catalyst was deposited by a low energy intensity electrodeposition technique, an inexpensive method that results in a large increase in efficiency. The anode was reported to be stable at pH 9, but decayed in more strongly basic conditions, perhaps due to dissolution of the CoOOH in strong base.

Digdaya et al. demonstrated that a 1 nm-thick ALD aluminum oxide layer is a high quality tunneling layer on silicon photoanodes, which suppresses Fermi-level pinning and enables Schottky junction formation between the silicon and the metal catalyst on the surface.^[100,101] A thin platinum layer was used as the Schottky contact as it has a suitable work function for generating a large MIS photovoltage with n-type silicon. Next, a thin layer of nickel was added, which serves as a protection layer and simultaneously as a good catalyst for water oxidation (Figure 7). This configuration resulted in a photoanode with an onset potential of -233 mV versus the reversible thermodynamic water oxidation potential (1.23 V vs. RHE), and 200 hours of stable water oxidation at high photocurrents ($\sim 25 \text{ mA cm}^{-2}$) in corrosive electrolyte (1 M KOH). This result indicates that relatively thin protective layers (<10 nm in total) can give highly stable electrodes, and is perhaps suitable for the extreme durability requirements of practical PEC cells.

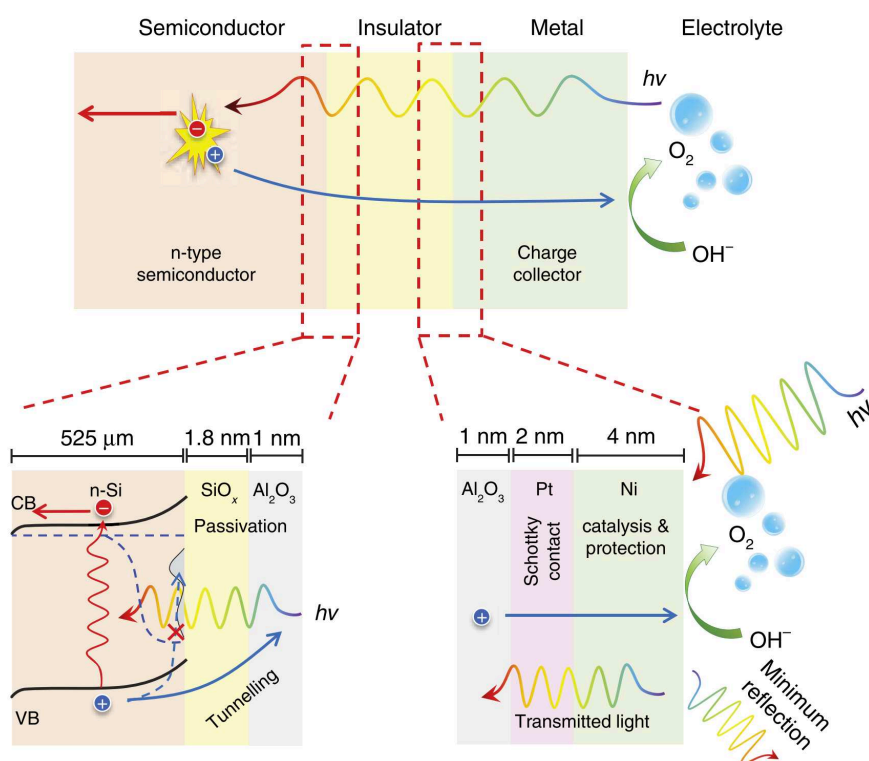


Figure 7. Schematic illustration of a metal-insulator-semiconductor (MIS) photoanode, with magnification of the interfaces indicating the functionality of each layer. Reproduced under a Creative Commons Attribution 4.0 International License.^[100]

Quinn et al. have recently shown that the thickness of the insulating layer of the MIS photoelectrode is a tunable parameter that can dramatically affect the performance, even for MIS junctions with moderate inherent barrier heights.^[102] The authors investigated an n-type silicon-based system with a Ni electrocatalyst and a HfO_2 protective layer, due to the moderate barrier height of the n-Si/Ni system. Interestingly, the obtained photovoltage in the MIS photoanode was found to be a function of insulator thickness. By screening a range of thicknesses of the ALD-deposited HfO_2 layer, a maximum of photovoltage was obtained with 2.1 nm. This interesting and non-intuitive result highlights another method of fine-tuning this promising class of photoelectrodes for water splitting.

An interesting discovery was reported in 2014 when Hu et al. showed efficient and stable water oxidation with high efficiency materials such as Si, GaAs, and GaP after coating

with a rather thick amorphous ALD-TiO₂ layer.^[103] This was a surprising result, as a simple analysis of band alignments of these materials with a TiO₂ overlayer would predict that the overlayer should be blocking. It was proposed that a defect band in the amorphous TiO₂ was responsible for transmitting the photoholes to the surface catalyst, although Mei et al. demonstrated that crystalline TiO₂ could also function as a protective layer for photoanodes when a thin Ti layer was inserted between the photoabsorber and the TiO₂.^[104] Nevertheless, the possibility to stabilize high efficiency p–n junction photoanodes with thick ALD-TiO₂ layers enabled the fabrication of overall water splitting cells with high efficiency. As one example, Verlage et al. showed a standalone water splitting cell featuring a protective hole-conductive TiO₂ layer that gave 10% solar-to-hydrogen, and 8.6% efficiency when coupled with a membrane that separated the hydrogen and oxygen gas streams (**Figure 8**).^[105]

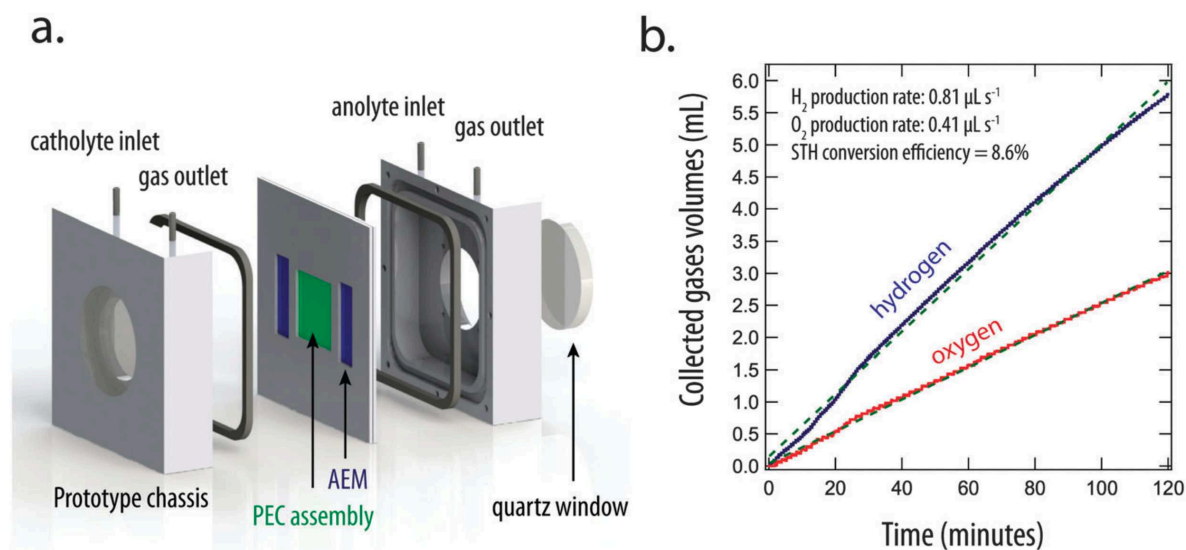


Figure 8. a) Schematic illustration of a monolithic solar hydrogen generation system prototype. b) Measured H₂ and O₂ for a device of surface area 1.0 cm² for both the photoanode and cathode, under one sun illumination in 1 M KOH electrolyte. Reproduced with permission from the Royal Society of Chemistry.^[105]

High levels of stability has been achieved with protected photoanodes. A silicon-based system featuring a 2.5 nm ALD TiO₂ layer covered by a 12 nm Ni layer demonstrated >500 hours of stability at a current density of $\sim 30 \text{ mA cm}^{-2}$.^[106] This result appears to be in contrast to the finding discussed in Section 2.1 that relatively thick ALD TiO₂ layers are required to be pin-hole free.^[36] However, it should be noted that reports that use such thin ALD protection layers that show some reasonable degree of stability also use metal layers on top, which offers additional protection.^[96,97] A NiO_x layer on a CdTe photoanode demonstrated 1000 hours of stability at $\sim 22 \text{ mA cm}^{-2}$ photocurrent.^[107]

Interestingly, organic semiconductors have also appeared in the photoanode literature.^[10] Borno et al. reported a stable poly[benzimidazobenzophenanthroline] conjugated polymer that effectively carries out water oxidation (**Figure 9**).^[108] Long term stability measurements and other physical characterization techniques indicated that the organic polymer is stable under these harsh oxidizing conditions.

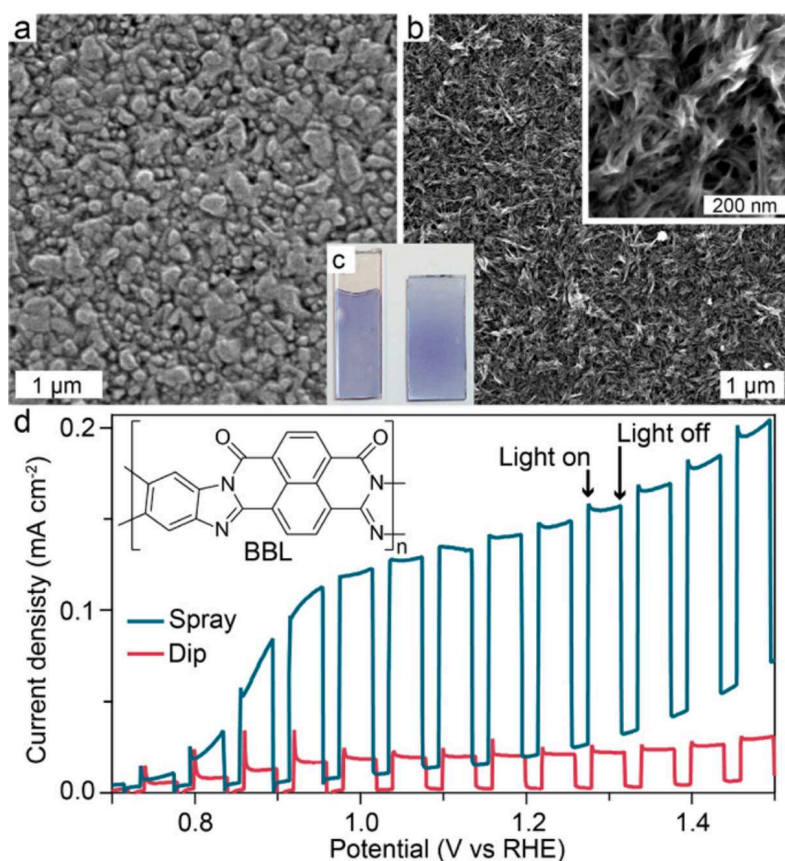


Figure 9. Scanning electron microscope (SEM) images of a) dip-coated and b) sprayed films. c) Optical image of both electrodes. d) Linear sweep voltammograms of the films under intermittent illumination in sacrificial electrolyte (0.5 M Na₂SO₃, pH 7). Reproduced under an ACS AuthorChoice License.^[108]

3.2. Photoelectrosynthesis of Value-Added Chemicals

As several recent technoeconomic analyses have found that thin film-based PEC water splitting is still too costly to compete with fossil-fuel derived hydrogen,^[14,15] researchers have sought a way to improve the value of the output stream from the PEC cell. It must be stated that if solar hydrogen is to be used as a primary energy source for humanity, water is the only source of electrons that is sufficiently abundant to reach such a large scale. However, for smaller, more niche markets, the oxidation reaction could be replaced in order to generate a product with much higher value than oxygen, and this may be a first medium-term step

towards larger scale water splitting PEC systems in the long term.^[9] The advantages of an integrated system versus a PV-coupled electrolysis system would be the same as those for typical water splitting, capitalizing on the improvements brought about by thermal management strategies, as detailed in the introduction.^[11,12] Several reviews have appeared on this topic recently, which hints at a growing interest of a new and important direction within the field (**Figure 10**).^[109–113]

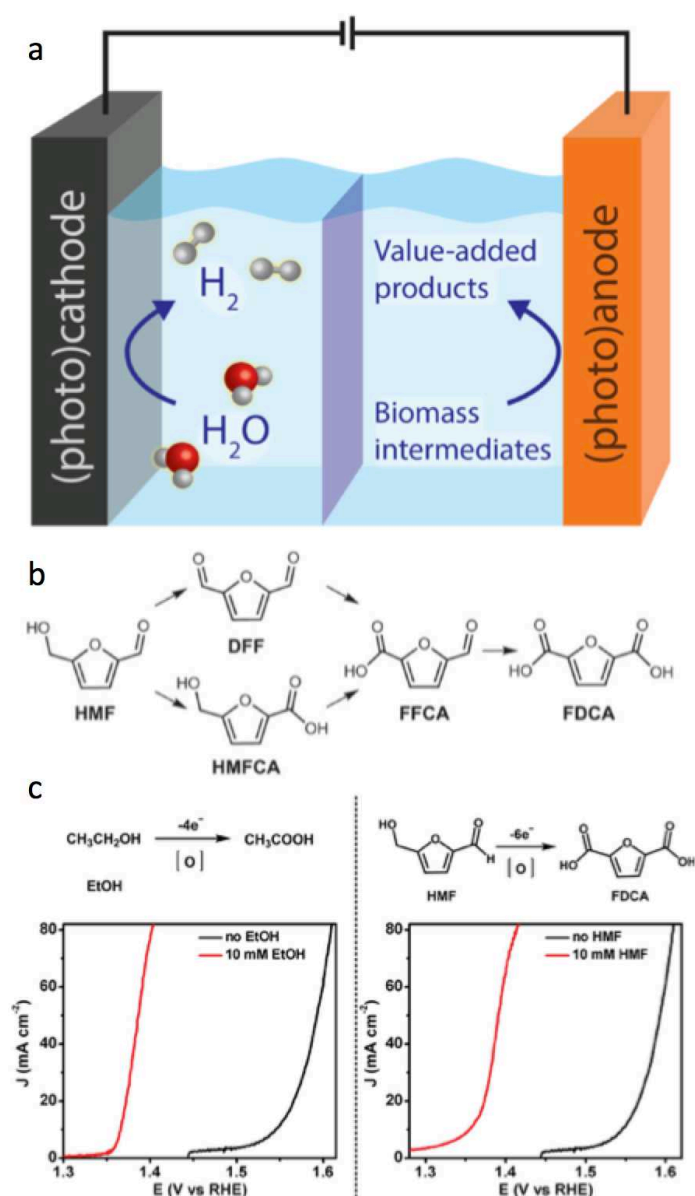


Figure 10. a) Schematic illustration of a PEC cell coupling hydrogen evolution to oxidation of biomass substrates to value-added products. b) Possible routes for HMF oxidation to FDCA. c) J-V curves for ethanol and HMF oxidation (red curves) versus water oxidation

(black curves). Figure 10b reprinted by permission from Springer Nature.^[114] Figure 10c reprinted with permission from Ref. ^[115]. Copyright 2017 American Chemical Society.

Alternatives to the demanding water oxidation reaction have been investigated beginning in the early 1980's by carrying out halide oxidation coupled with hydrogen evolution.^[21] Recently, attention has turned to more complex small molecules, and in particular substrates from biomass. One attractive target is 2,5-furandicarboxylic acid (FDCA), which can be synthesized by oxidation of 5-hydroxymethylfurfural (HMF), a platform molecule available from biomass (Figure 10b). FDCA is considered as a bio-based alternative to fossil-based terephthalic acid used in polyethylene terephthalate (PET) plastics. Polyethylene furanoate (PEF), which is produced from FDCA, is a so-called “drop-in” material, which can be used in current polymer manufacturing processes without the need for infrastructure modifications. Moreover, PEF has superior barrier, thermal and mechanical properties compared to PET.^[116] Cha and Choi were able to carry out photooxidation of HMF to FDCA using BiVO₄ photoanodes, using the redox mediator molecule 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO).^[114] Li et al. used the non-aqueous electrolyte MeCN to circumvent the problem of BiVO₄ corrosion when trying to use this photoanode directly without a redox mediator.^[117]

As a large portion of solar energy has already been stored in the HMF molecule through natural photosynthesis, only a relatively small amount of additional energy input is required to carry out the HMF → FDCA reaction coupled with water reduction (co-generating H₂ fuel). However, the six electron oxidation process of HMF to FDCA is complex (Figure 10b), even more so than oxygen evolution. Although the oxidation of C-H bonds is much more facile than water oxidation in a thermodynamic sense, the experimental overpotentials for HMF oxidation remain relatively high, and the onset potentials for (photo)electrocatalytic oxidation of HMF are similar to those found for oxygen evolution (Figure 10c). If one

considers the thermodynamic data for methanol oxidation to formaldehyde, and from formaldehyde to formic acid,^[118] it is observed that these oxidation events are ~100-150 mV uphill in energy when coupled with proton reduction to hydrogen. Thus, one would expect a theoretical onset potential for alcohol oxidations to aldehydes and carboxylic acids at around +0.15 V vs. RHE (with hydrogen evolution at the counter electrode). Further research in this direction will continue to lower the overpotential required, and important insights will likely come from the field of CO₂ reduction, which studies the reverse reaction: the formation of C-H bonds from C-O bonds. If good catalysts or photocatalytic materials are found with low overpotential, then near infrared (NIR) materials could be utilized to carry out the reaction, harvesting a complementary portion of the solar spectrum than traditional water splitting materials. NIR materials would provide a relatively small voltage, but large photocurrents, generating large amounts of H₂ in addition to the FDCA product.

4. Summary and Outlook

In this progress report, I have highlighted some recent examples of state-of-the-art performance and emerging trends with respect to integrated PEC systems for solar water splitting and the generation of value-added chemicals. High PEC water splitting efficiencies have been reported, although these demonstrations use very costly semiconductors that are highly efficient. For example, Young et al. demonstrated >16% solar-to-hydrogen efficiency using a dual bandgap GaInP/GaInAs tandem cell,^[62] and Cheng et al. reported a monolithic water splitting device using the same photoabsorber materials that gave >19% solar-to-hydrogen efficiency.^[119] These are important benchmarks, although the cost of the fabrication of the photoabsorber is much too high to generate hydrogen at a competitive cost.

New materials are needed that achieve high efficiency and stability, and that can also be fabricated at low cost. Antimony selenide (Sb₂Se₃) is a promising photocathode candidate, as it can be easily fabricated by an electrodeposition/selenization process, it gives high

photocurrents, and is stable in 1 M H_2SO_4 under illumination.^[63] However, the efficiency (in particular the photovoltage) must be improved if it is to become truly practical.

So far, there is no good photoanode material that approaches the requirements for low cost and practical PEC (high efficiency, intrinsic stability, low-cost fabrication). BiVO_4 is probably the best material so far, and has been thoroughly investigated, but is now mostly seen as a model material, as the band gap is too large for high efficiency water splitting. The field is waiting for the discovery of a new material, and the unexplored material space is vast considering most studies until now have utilized materials containing only 1-2 metal cations.

Skepticism has arisen in recent years as to whether the PEC field has a future, in light of the strikingly rapid decline in the price of silicon photovoltaics.^[120] It is certainly a good thing to be critical and to try to be realistic about the potential impact of one's own research. Indeed, a case can be made that it is simply a matter of public policy whether or not we move to solar hydrogen in the near future, which would happen by increasing the economic incentives with a carbon tax. In the absence of such a political move, we can simply try to make solar hydrogen as cheaply as possible through fundamental, use-inspired research. Although thin film-based PEC may never be cheaper than fossil H_2 without a carbon tax (at least not in the near future), research in this area enables us to find new materials, composites, and strategies for efficient and stable water splitting in aqueous electrolytes. These insights can then guide research into particulate-based PEC systems, which would be a potentially very cheap technology, even cheaper than fossil H_2 .^[14] Studying thin films enables access to characterization of the internal electronic structure of materials that is much harder in particulate systems,^[121–123] and the construction of tandem systems can inform the material choices in particulate Janus-type systems or photocatalyst sheets.^[124] Although there are also significant challenges to overcome in particulate systems (e.g. explosive gas mixtures, finding a suitable redox mediator for separated particulate systems), advances in both fields in the coming years may bring about a new and practical energy conversion system that need not

rely on a carbon tax. With these aspects in mind, there is still plenty to explore in the PEC field, with a potential for the discovery of a materials system leading to a disruptive new technology, independent of current photovoltaic market forces and circumstances.

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Photoelectrochemical water splitting is a promising route to low cost solar fuels generation. Recent advances for photocathodes and photoanodes are reviewed, with a particular focus on the durability of materials for water splitting. New emerging research directions within the field such as upgrading of biomass substrates and the use of organic photoabsorber materials are highlighted.

Keyword photoelectrochemical, water splitting, hydrogen, value added chemicals

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