

# Solar-to-Chemical Energy Conversion with Photoelectrochemical Tandem Cells

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**Abstract:** Efficiently and inexpensively converting solar energy into chemical fuels is an important goal towards a sustainable energy economy. An integrated tandem cell approach could reasonably convert over 20% of the sun's energy directly into chemical fuels like H<sub>2</sub> via water splitting. Many different systems have been investigated using various combinations of photovoltaic cells and photoelectrodes, but in order to be economically competitive with the production of H<sub>2</sub> from fossil fuels, a practical water splitting tandem cell must optimize cost, longevity and performance. In this short review, the practical aspects of solar fuel production are considered from the perspective of a semiconductor-based tandem cell and the latest advances with a very promising technology – metal oxide photoelectrochemical tandem cells – are presented.

**Keywords:** Hydrogen · Oxide semiconductors · Photoelectrochemical water splitting · Solar fuels

## Introduction

The realization of a sustainable energy economy is contingent on developing an energy vector that can be efficiently (re) generated from renewable sources, easily stored, and straightforwardly transported to the point of use. Chemical fuels, which store energy in covalent bonds, are especially attractive for this purpose, as the infrastructure for the widespread use of fossil fuels is already in place. Photoelectrochemical cells can directly convert energy from our largest energy source – the sun – into renewable chemical fuels like H<sub>2</sub> (from the reduction of water) or MeOH (from the reduction of CO<sub>2</sub>).<sup>[1]</sup> Indeed, efficiently producing molecular hydrogen using photoelectrochemical means has been an ultimate goal of electrochemists and material engineers for decades given the abundance of the required raw materials – water and sunlight. Indeed, solar hydrogen is considered the central element in a multifaceted and interconnected chemical network – a 'solar refinery' – which will ultimately convert photons from the sun into raw materials for industrial synthesis and carbon-based chemical fuels.<sup>[2]</sup>

However, any system for converting solar energy on a scale commensurate with the global energy demand must find a balance between minimizing system complexity (*i.e.* device cost) and maximizing device performance (*i.e.* energy conversion efficiency and device longevity). Moreover, any economically feasible system for solar hydrogen production must also compete with the price of H<sub>2</sub> generated from conventional sources (US\$ 2–3 kg<sup>-1</sup> for the steam reforming of natural gas). Attaining this goal remains a major challenge for photoelectrochemists and material engineers, but the severity of the global energy situation has stimulated the development of many promising routes. In this article, an analysis and comparison of promising routes is presented. To begin, an obvious route to solar-generated hydrogen is considered.

## Is PV+ Electrolysis a Viable Solution?

Based on the reduction and oxidation potentials of water, a difference in bias of only 1.23 V should be sufficient to split water into H<sub>2</sub> and O<sub>2</sub>. However, due to the entropic increase needed for this process to be spontaneous as well as the overpotential required to overcome kinetics of the oxygen and hydrogen evolution reactions, modern electrolyzers usually operate at voltages above 1.8 V. The most obvious approach to generate sufficient voltage for water splitting with solar energy is to connect multiple standard photovoltaic (PV) cells in series. For example, a traditional pn-junction silicon PV produces a potential of 0.5–0.6 V at its maximum power point under standard conditions. Thus

three or four of these connected electrical-ly in series would create sufficient potential to split water (depending on the type of electrolyzer employed). The effectiveness of this 'brute force' PV + electrolysis approach is limited by the price and availability of PV devices and electrolyzers, and currently makes the price of the H<sub>2</sub> produced around US\$ 10 kg<sup>-1</sup>.<sup>[3]</sup> Nevertheless, a fair amount of research interest has followed this path and devices with overall solar-to-hydrogen conversion efficiency ( $\eta_{STH}$ ), up to 9.3% have been demonstrated using single crystal silicon PV modules and high-pressure electrolysis.<sup>[4]</sup> It has also been suggested that a comprehensive optimization of these systems could produce H<sub>2</sub> at a price as low as US\$ 4 kg<sup>-1</sup>.<sup>[5]</sup> This price may decline further by employing novel thin-film PV technologies. For example, Dhere and Jahagirdar have reported the use of two high voltage CuIn<sub>1-x</sub>Ga<sub>x</sub>S<sub>2</sub> (GIGS) PV cells side-by-side to generate a  $\eta_{STH}$  up to 8.8%.<sup>[6,7]</sup>

Despite the seemingly straightforward nature of the PV + electrolysis approach, a major and general drawback comes from the voltage output of a tradition pn-junction solar cell, which is strongly dependent on the illumination intensity. This necessitates complicated switching mechanisms to ensure the optimum number of cells are connected in series during variations in light intensity caused by haze, cloud cover, or time of day. This critical drawback can result in as much as a 50% energy loss, and calls into question the viability of the PV+ electrolysis approach. However, this has also inspired researchers to develop systems specifically designed to generate sufficient voltage for water splitting by using tandem cells.

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## The Tandem Cell Concept

One way to overcome the need to use multiple PV devices to generate enough potential for the water splitting reaction would be to develop a single PV device that could produce sufficient voltage by using a material with a sufficiently large semiconductor band-gap energy ( $E_g$ ). However, when  $E_g$  increases, the amount of solar light that the semiconductor can absorb decreases because a semiconductor can only absorb photons with an energy  $h\nu > E_g$ . This drastically lowers the maximum achievable solar conversion efficiency. However, both sufficient voltage and adequate light harvesting can be realized in a water splitting device by stacking multiple cells that can individually harvest different portions of the solar spectrum on-top of one another, in tandem (Fig. 1). If the cells are connected electrically in series the total photocurrent density will be limited by the cell producing the least current, but the total voltage will be the sum of all the cells used.

Fig. 1 also shows the distribution of the standard solar spectrum (AM1.5G 100  $\text{mW cm}^{-2}$ ) and how the tandem concept can allow more complete harnessing of the solar spectra than a single absorber case. If reasonable losses are assumed for the water splitting process (average loss per photon of 0.8 eV), and the requirement for the device to produce sufficient voltage to split water and overcome the overpotentials is accounted for, a semiconductor with  $E_g > 2.1$  eV is required using a single semiconductor absorber. This would leave a valuable part of the solar spectra from 600–1200 nm unused, and limit the maximum possible solar-to-hydrogen conversion efficiency to 17.4%. However, by employing a dual absorber tandem system with the same assumptions, the optimized band gaps of the two absorbers are found to be  $E_{g1} = 1.72$  eV and  $E_{g2} = 1.11$  eV.<sup>[8]</sup> Thus in this case, the top absorber can harvest photons up to 720 nm, while the bottom cell would use the photons from 720–1120 nm giving a maximum possible solar-to-hydrogen conversion efficiency of 27.1%. Even more of the solar spectrum can be harvested with a 3-level tandem configuration.<sup>[9]</sup> Of course in practice, the addition of each cell brings technical difficulties that greatly increase the complexity and cost of these devices. Indeed, the tandem devices used for high efficiency solar-to-electricity conversion are very costly and relegated to specific niches (e.g. extraterrestrial application).

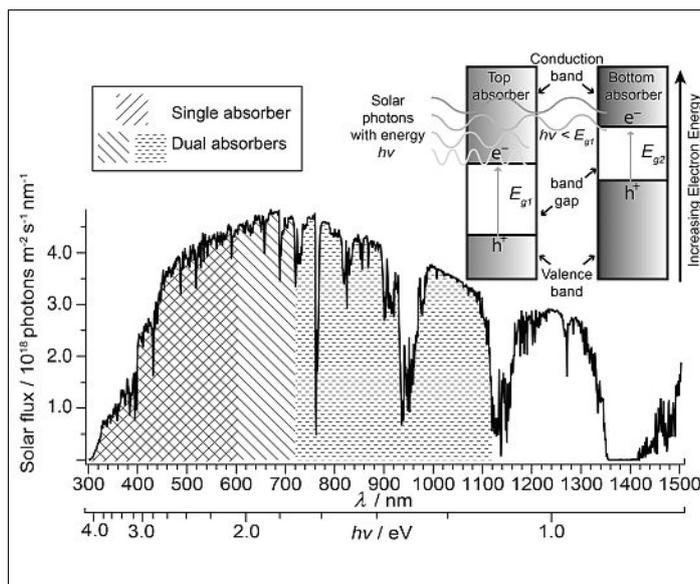


Fig. 1. The benefits of the tandem cell approach are shown through the AM 1.5 G solar photon flux as a function of wavelength and photon energy. The patterned areas of the spectrum represent the photons that could be harvested using a single semiconductor absorber and a dual absorber tandem approach. The inset shows a scheme of the dual absorber tandem device layout and the relative semiconductor energy levels.

## PV/PV Tandems for Solar Water Splitting

Neglecting the practical aspects of device cost and complexity, it is interesting to understand how efficiently solar energy can be converted to chemical energy using 'PV/PV' tandem cells for water splitting. One common strategy is to couple a PV/PV tandem directly to electrolysis electrodes (including the appropriate catalysts) resulting in a device that can be simply placed into an aqueous electrolyte and eliminating the need for a separate electrolyzer. Champion devices of this type use the well-known band-gap engineering of III-V semiconductor systems to optimize light harvesting and voltage generated, and have demonstrated record-breaking solar-to-chemical conversion efficiencies. In particular, Licht *et al.* have employed an AlGaAs/Si (pn-pn) structure using Pt-black and RuO<sub>2</sub> as reduction and oxidation catalysts, respectively, and obtained solar-to-hydrogen conversion efficiencies as high as 18.3% under simulated AM0 sunlight (135  $\text{mW cm}^{-2}$ ).<sup>[10,11]</sup> Turner and co-workers have investigated monolithic GaAs/GaInP<sub>2</sub> (pn-p, pn-pn, or pn-pn-p) systems and attained  $\eta_{STH}$  values up to 12.5%.<sup>[12–14]</sup> While the conversion efficiencies reported with these systems are quite impressive, major concerns exist about the price (due to the requirements of high material purity and costly fabrication methods) and stability of these devices when they are used in contact with aqueous electrolyte.<sup>[15]</sup>

Of course it is not necessary to construct an all-PV tandem system from III-V semiconductors; many other systems have also been reported. One system of particular interest is based on amorphous silicon (a-Si). Bockris and co-workers first showed that a triple stack of n-type/intrinsic/p-type (nip) a-Si on a Ti substrate could give up

to  $\eta_{STH} = 7.5\%$  under AM1 (100  $\text{mW cm}^{-2}$ ) illumination when islands of Pt and RuO<sub>2</sub> were used as a reduction and oxidation catalysts, and the device was directly submerged into aqueous electrolyte.<sup>[16]</sup> Since the band-gap of the a-Si was the same for each nip-junction, the layer thicknesses were optimized so each layer produced the same photocurrent (i.e. the top two layers were thin enough to transmit some photons with energy  $h\nu > E_g$ ). This concept was later developed to increase the efficiency for electricity production by mixing some Ge in with the Si to modify the  $E_g$  of the bottom two layers.<sup>[17]</sup> Using these devices for water splitting, an  $\eta_{STH}$  of 7.8% under AM1.5 (100  $\text{mW cm}^{-2}$ ) illumination was achieved in 1 M KOH electrolyte with reduction and oxidation catalysts of CoMo and NiFe<sub>2</sub>O<sub>4</sub>, respectively.<sup>[18]</sup> The stability of these devices was improved to greater than 31 days while maintaining a  $\eta_{STH}$  value of 5–6% using a fluorine-doped SnO<sub>2</sub> protection layer on the cathode.<sup>[19]</sup> More recent efforts with these devices have also shown that operation at near neutral pH is possible using an optimized cobalt-based oxygen evolution catalyst to give  $\eta_{STH} = 4.7\%$  when using a 'wired' geometry that placed two water splitting electrodes in close proximity to facilitate ion transport between the electrodes.<sup>[20]</sup> In addition, the use of a transparent conducting oxide (ITO) on the surface enhanced stability and stable water splitting was observed for over 10 hours. However, in the 'wireless' geometry (Fig. 2) these devices suffer a limitation from the transport of ions through the electrolyte from one face of the device to the other, and the overall solar to hydrogen efficiency drops to around 3%. Fig. 2 also shows the oxygen produced by this wireless cell, as measured by mass spectrometry (MS) for two different electrolytes with varying ionic strength, and the effect on the

conversion efficiency can be clearly seen. The limitation of ion transport in these types of devices remains an important practical point to address. Moreover, while these a-Si based devices are presumably less expensive than III-V semiconductor based tandem cells, their fabrication still requires relatively expensive vacuum processing. Despite this, the mass production of triple junction a-Si device modules for photovoltaic energy conversion is already underway by several companies. It is yet unclear what the price per kg H<sub>2</sub> would be if these cells would be used for water splitting. Furthermore, the open-circuit voltages produced by such triple junction a-Si cells are around 2.4 V – much higher than is needed for water electrolysis.

### Direct Solar-to-Chemical Conversion with PEC

The strategies discussed up to this point have employed multiple photovoltaic junctions to generate sufficient voltage to convert solar energy into chemical energy *via* water splitting. Since the employed semiconductor materials are not generally stable in the aqueous environment required for water electrolysis, devices have included encapsulating layers or separate electrolyzing electrodes to accomplish the water oxidation and reduction reactions with reasonable stability. These solutions increase both the complexity of the final device architecture and electrical losses by the introduction of additional interfaces. A more straightforward route to light-driven chemical transformations in general is to directly contact a semiconductor and the electrolyte as in a photoelectrochemical device.

When a semiconductor is placed in direct contact with an electrolyte the equilibration of the semiconductor chemical potential (also called the Fermi level) with the oxidation/reduction potential of the electrolyte creates an electric (space-charge) field in the semiconductor at the semiconductor-liquid junction (SCLJ). The space-charge field can separate photo-generated electrons in the semiconductor's conduction band from their corresponding holes in the valence band. Unlike a traditional photovoltaic cell where the photo-excited carriers are extracted by electrical contacts into an electric circuit, excited carriers in a photoelectrochemical (PEC) electrode travel to the SCLJ to perform redox chemistry directly. For example, with an n-type photoanode under illumination, photogenerated holes directly oxidize water into O<sub>2</sub>, while for a p-type photocathode, photogenerated electrons can directly reduce water into H<sub>2</sub>. In this way a PEC cell can reduce the number of

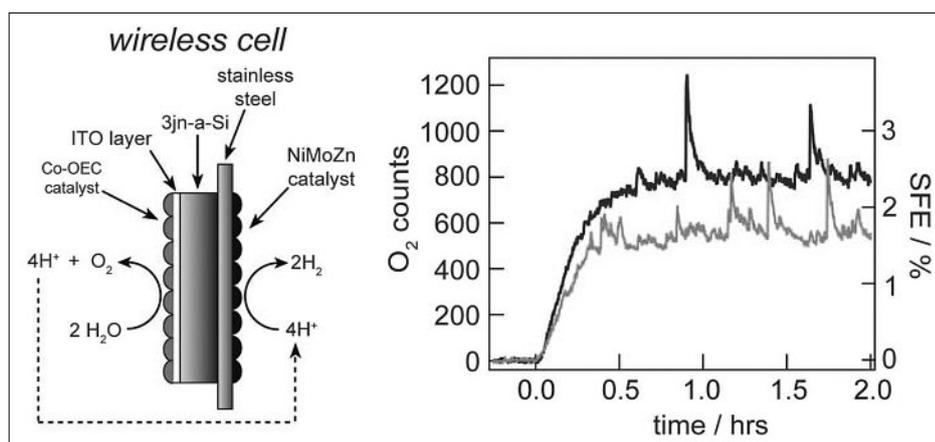


Fig. 2. Demonstration of a triple junction amorphous silicon (3jn-a-Si) tandem cell for solar water splitting is shown with the wireless device scheme (left) and the oxygen evolution data (right) taken by mass spectrometry (MS). The cell was illuminated over the 2 h of the experiment under AM 1.5 illumination in 1 M KBI (light trace) and in 0.5 M KBI and 1.5 M KNO<sub>3</sub> (dark trace) electrolyte. MS signal corresponds to the concentration of O<sub>2</sub> in the carrier gas of the cell. The spikes in the data originate from sudden release of gas bubbles that were adhered to the cells, resulting in a temporary increase of the O<sub>2</sub> concentration in the headspace. The solar-to-fuel efficiency (SFE, or  $\eta_{SFE}$ ) is also shown. Reprinted with permission from S. Y. Reese, *et al.*, *Science* **2011**, 334, 645-648. Copyright 2011 American Association for the Advancement of Science.

materials and interfaces needed to perform an electrochemical reaction driven by solar energy, and potentially reduce the cost of device fabrication.

Indeed interest in performing inexpensive solar water splitting using a PEC device goes back decades, and was first demonstrated using TiO<sub>2</sub> as a single semiconductor absorber over 40 years ago.<sup>[21]</sup> As an oxide semiconductor TiO<sub>2</sub> offers excellent stability in the relatively harsh aqueous conditions of water splitting. However, this material has a semiconductor band-gap around 3.2 eV. Thus it cannot harvest a significant portion of the solar spectrum and therefore its potential solar-to-hydrogen conversion efficiency is very low (less than 2%). Because of this, following the seminal demonstration with TiO<sub>2</sub> chemists and material scientists have invested considerable effort towards identifying ideal PEC materials. However, a single material has not yet been identified that can offer substantial solar light harvesting, adequate stability in the harsh aqueous electrolytes required, and appropriate conduction and valence band energy levels straddling the water reduction and oxidation potentials, respectively. However, the tandem concept can also be applied to a PEC device. In fact, since the water splitting reaction necessarily entails two separate half-reactions, it seems natural to use two light absorbers for PEC water splitting.

Indeed, a simple way to construct a PEC tandem water splitting cell is to use an n-type semiconductor photoanode together with a p-type semiconductor photocathode. The electrochemical scheme for this type of 'D4' device (dual absorber, four photons for one molecule of H<sub>2</sub> produced)

is shown in Fig. 3. Here the bending of the conduction and valence band edge energies induced by the space-charge field is shown schematically for both photoanode and photocathode. The photo-induced splitting of the Fermi level (broken lines) is also shown indicating the amount of externally available free energy,  $\Delta\mu_{ex}$ , developed in each semiconductor. The energetic requirements for water splitting are satisfied when the total  $\Delta\mu_{ex}$  is greater than 1.23 eV plus the overpotential losses at each electrode.

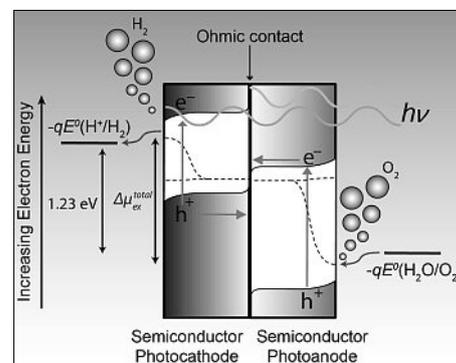


Fig. 3. Electron energy scheme of a dual-absorber PEC tandem cell with direct semiconductor liquid junctions (SCLJ) is shown. Here an n-type photoanode connected to p-type photocathode. Charge separation due to the space-charge field at the SCLJ (as indicated by the bending of the energy bands) allows generation of sufficient free energy ( $\Delta\mu_{ex}$ ) to split water under illumination.

## Examples of Photoanode/Photocathode Materials and Tandem Cells for Water Splitting

Within the framework of the photoanode/photocathode tandem cell for PEC water splitting many photoelectrode materials have been identified as promising candidates for a device that maximizes stability and minimizes complexity of fabrication and material costs. In general, transition metal oxides have been particularly attractive due to their superior stability in water-based systems. Stable n-type materials for water oxidation are well-developed in the scientific literature.  $\text{TiO}_2$  is probably the most well studied material, and although its band-gap is too large for efficient solar energy conversion, methods to sensitize it,<sup>[22]</sup> or reduce its band gap with carbon or nitrogen impurities<sup>[23]</sup> have been reported to have limited success. More promising photoanode materials are  $\text{WO}_3$  ( $E_g = 2.6$  eV) and  $\text{Fe}_2\text{O}_3$  (hematite,  $E_g = 2.0$  eV), which could respectively convert a maximum of about 6% and 16% of incident solar energy into chemical fuels based on their band-gaps. These materials have gained significant interest due to their observed stability in aqueous systems, light harvesting ability, and composition from abundant and inexpensive elements. However, these materials are not noted for their exceptional semiconducting properties. As such, much effort has been invested in improving the performance of these materials as water oxidizing photoanodes through doping and nanostructuring efforts.<sup>[24,25]</sup> In addition, methods have been developed to obtain high performance electrodes using inexpensive and scalable solution-based techniques for both of these materials.<sup>[26,27]</sup> Similar efforts have also been employed to increase the performance scalability of other promising photoanode materials such as  $\text{BiVO}_4$ ,<sup>[28]</sup> and  $\text{TaON}$ .<sup>[29]</sup>

Despite the large amount of effort invested in developing high performance photoanodes for the tandem cell approach, only a few demonstrations of actual photoanode/photocathode devices can be found in the literature. The reason for this is clearly due to a lack of suitable photocathode materials for water reduction. Many materials, for example  $\text{GaInP}_2$ ,<sup>[30]</sup>  $\text{Si}$ ,<sup>[31,32]</sup>  $\text{SiC}$ ,<sup>[33]</sup>  $\text{WS}_2$ ,<sup>[34]</sup>  $\text{Cu(In,Ga)Se}_2$ ,<sup>[35]</sup>  $\text{Cu}_2\text{O}$ ,<sup>[36]</sup>  $\text{CuYO}_2$ ,<sup>[37]</sup>  $\text{CaFe}_2\text{O}_4$ ,<sup>[38]</sup> and even p-type ( $\text{Mg}^{2+}$  doped)  $\text{Fe}_2\text{O}_3$ <sup>[39]</sup> have been investigated as water reducing p-type electrodes, but the magnitude of the photocurrent or the stability in aqueous solutions have remained limiting factors. Despite this, a few efforts have been made to demonstrate photoanode/photocathode tandem cells.

Early work by Nozik<sup>[40]</sup> established the general theory for combining photoanodes

and photocathodes into tandem cells and introduced the  $\text{TiO}_2/\text{GaP}$  system. Ohmic contacts between single crystals of n-type  $\text{TiO}_2$  and p-type GaP ( $E_g = 2.26$  eV) gave a tandem cell that was found to evolve both hydrogen and oxygen without an externally applied potential. A high internal resistance limited the conversion efficiency of the cell for  $\text{H}_2$  evolution, which was calculated to be 0.25% at zero bias (based on a total electrode area of  $1.9$   $\text{cm}^2$  and  $85$   $\text{mW cm}^{-2}$  of net incident simulated sunlight). An oxide layer forming on the surface of the p-GaP was the likely cause of the device instability.<sup>[41]</sup>

Very little research attention was given to constructing photoanode/photocathode tandem devices for many years after this seminal demonstration. More recently, following the advances in oxide photoanode performance, additional demonstrations of photoanode/photocathode tandem devices have appeared. For example, while also known to be unstable in aqueous systems,<sup>[15]</sup>  $\text{GaInP}_2$  ( $E_g = 1.83$  eV) photocathodes have been combined with either  $\text{WO}_3$ <sup>[30]</sup> or  $\text{Fe}_2\text{O}_3$ <sup>[42]</sup> photoanodes by Wang and Turner. Under intense white light illumination ( $>200$   $\text{mW cm}^{-2}$ ) the  $\text{WO}_3/\text{GaInP}_2$  combination produced a detectable photocurrent that rose linearly with light intensity to reach operating photocurrents of about  $20$   $\mu\text{A cm}^{-2}$  at  $1000$   $\text{mW cm}^{-2}$  (solar-to-hydrogen efficiency  $\eta_{\text{STH}} < 0.01\%$ ). Due to the insufficient potential difference the system did not function at illumination intensities below  $200$   $\text{mW cm}^{-2}$  (recall that the minority carrier quasi Fermi level and thus the  $\Delta\mu_{\text{ex}}$  of each electrode should change proportional to the logarithm of the illumination intensity). For the case of  $\text{Fe}_2\text{O}_3/\text{GaInP}_2$ , negligible photocurrent was observed even at 10 sun illumination due to the mismatch of the conduction band minimum of the  $\text{Fe}_2\text{O}_3$  thin film and the valence band maximum in the  $\text{GaInP}_2$ . Employing surface dipoles to raise the conduction band<sup>[43]</sup> of  $\text{Fe}_2\text{O}_3$  may be useful for this combination of materials, which is clearly not ideal. Moreover the limited availability of indium in the Earth's crust prevents the application of this material on a global scale.

A more novel p-type material made from abundant elements,  $\text{CaFe}_2\text{O}_4$  ( $E_g = 1.9$  eV), has been paired with n- $\text{TiO}_2$  (in a side-by-side configuration) to give a device operating photocurrent,  $J_{\text{op}}$ , of  $110$   $\mu\text{A cm}^{-2}$  in  $0.1$  M NaOH electrolyte with the light from a  $500$  W Xe lamp.<sup>[44]</sup> However, the Faradaic efficiency for water splitting was found to be only 12% and Fe and Ca were detected in the electrolyte after the device test, suggesting the photocurrent was mostly due to corrosive side reactions as opposed to water splitting.

Nanostructuring techniques have also

been employed to enhance the performance of inexpensive electrode materials for photoanode/photocathode tandem cells. Grimes and co-workers used an anodization technique to oxidize Cu-Ti films and obtain p-type nanotubular (1000 nm length, 65 nm pore diameter, 35 nm wall thickness) Cu-Ti-O films.<sup>[45]</sup> The films were primarily CuO ( $E_g = 1.4$  eV) with a  $\text{Cu}_4\text{Ti}_3$  impurity phase detected. These films (on transparent F:SnO<sub>2</sub> substrates) were placed in tandem with nanotubular  $\text{TiO}_2$  to give a working tandem device (Fig. 4). A  $J_{\text{op}} = 0.25$   $\text{mA cm}^{-2}$  ( $\eta_{\text{STH}}$  around 0.30%) under standard illumination conditions and a reasonable stability for a duration of minutes were observed (photocurrent was negligible after 5 h). It should be noted that the  $\text{TiO}_2$  was exposed to 1 M KOH while the Cu-Ti-O was exposed to 0.1 M  $\text{Na}_2\text{HPO}_4$  and the electrolyte compartments were connected by a salt bridge. The dissimilar pH values lead to a favorable chemical bias of about 0.4 V in this case. Exposing the Cu-Ti-O to the KOH caused the rapid decay of photocurrent as the CuO was reduced to copper. Recent efforts to stabilize p-type photocathodes using overlayers deposited *via* atomic layer deposition may improve the performance of this and many other photocathode ma-

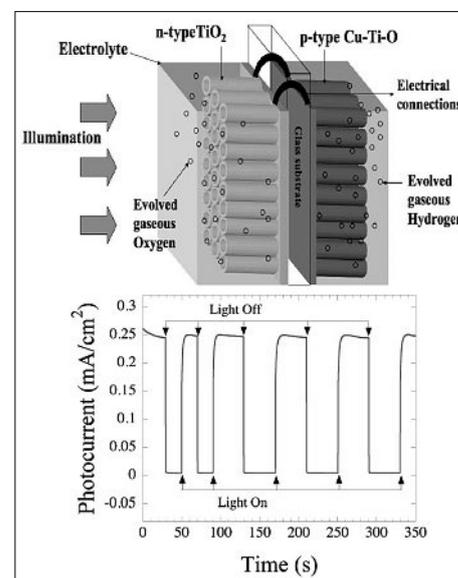


Fig. 4. (Top) Illustration of a D4 tandem cell comprised of n-type  $\text{TiO}_2$  and p-type Cu-Ti-O nanotube array films, with their substrates connected through an ohmic contact. (Bottom) Photocurrent from the D4 tandem cell under global AM 1.5 illumination. Light is incident upon the oxygen evolving  $\text{TiO}_2$  side of the diode, with the visible portion of the spectrum passing to the Cu-Ti-O side. The n- $\text{TiO}_2$  side of the device is kept immersed in a 1 M KOH aqueous solution, the p-Cu-Ti-O side is kept in 0.1 M  $\text{Na}_2\text{HPO}_4$  with a salt bridge linking the two sides solution. Reprinted with permission from G. K. Mor, *et al.*, *Nano Lett.* **2008**, *8*, 1906–1911. Copyright 2008 American Chemical Society.

materials.<sup>[46]</sup> However, the addition of these layers increases the device complexity and cost (especially using atomic layer deposition, which is not a scalable technique). Thus the identification of stable p-type photocathodes for water reduction remains the limiting factor for these photoanode/photocathode devices.

### A Hybrid Approach Using Dye-sensitized Regenerative Cells

Overall, identifying semiconductor materials that form stable junctions with water under illumination has been a major challenge in the field of PEC water splitting. The particular difficulty identifying stable p-type cathodes, together with the availability of stable photoanode materials like  $\text{WO}_3$  and  $\text{Fe}_2\text{O}_3$ , makes a photoanode/PV tandem device a good compromise for device complexity and stability. Indeed, the possibility of a photoanode/PV tandem device to employ a stable transition metal oxide photoanode and a complimentary PV device has attracted many research groups to investigate various promising systems. For example, a  $\text{TiO}_2$  photoanode in tandem with a thin film PV device based on  $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{CdS}$  produced hydrogen at a rate of  $0.052 \mu\text{L s}^{-1} \text{cm}^{-2}$  during unassisted solar water splitting (corresponding to an external quantum efficiency of 1.02%).<sup>[47]</sup> While less interest has been paid towards using the prototypical  $\text{TiO}_2$  as a photoanode due to its large band-gap this work demonstrated the importance of using optimized protective layers ( $\text{Nb}_{0.03}\text{Ti}_{0.97}\text{O}_{1.84}$  in this case) to eliminate corrosion of the PV cell in the aqueous conditions.

Further research efforts have focused on using more promising transition metal oxides. Miller and co-workers have investigated combining  $\text{WO}_3$ <sup>[48]</sup> or  $\text{Fe}_2\text{O}_3$ <sup>[49]</sup> photoanodes in tandem with a-Si:Ge PV. As a drawback, the large overpotential for water oxidation and the relatively low voltage output of an a-Si device requires a double junction PV in tandem to provide sufficient potential to drive the overall water splitting reaction (similar to the PV-only case where 3 pn-junctions were needed with a-Si). Despite this, 3%  $\eta_{\text{STH}}$  was obtained with the  $\text{WO}_3/\text{a-Si:Ge}/\text{a-Si:Ge}$  device.<sup>[48]</sup> A similar device for iron oxide with only one PV ( $\text{Fe}_2\text{O}_3/\text{a-Si:Ge}$ ) did not split water without an external bias, but it was shown that a 0.65 V bias ‘savings’ was earned under AM1.5G illumination.<sup>[49]</sup> This result could reasonably be improved with the recent advances in  $\alpha\text{-Fe}_2\text{O}_3$  photoanode performance.<sup>[25]</sup>

### The Photoanode/DSC Tandem Cell

From a practical perspective, the attractive aspects of using a widely available, highly stable and inexpensively produced photoanode are diminished when using a tandem component that requires relatively expensive processing techniques (e.g. the plasma-enhanced chemical vapor deposition of a-Si). Thus more recently, investigations have focused on using next-generation photovoltaics that can also be fabricated with inexpensive, solution-based processing methods. The dye sensitized solar cell (DSC) is the prototype example<sup>[50]</sup> of this class of photovoltaic device and thus has attracted significant attention for use in solar water splitting tandem cells with a stable photoanode.<sup>[51]</sup>

The photoanode/DSC combination was first suggested by Augustynski and Grätzel<sup>[52]</sup> with  $\text{WO}_3$  as the photoanode – suggesting that the device would be capable of 4.5%  $\eta_{\text{STH}}$  given the performance of the two devices.<sup>[52]</sup> In practice, tandem devices with  $\text{WO}_3$  were constructed by Park and Bard<sup>[54]</sup> and Arakawa *et al.*<sup>[55]</sup> to give  $\eta_{\text{STH}}$ 's up to 2.8% at AM1.5G ( $100 \text{ mW cm}^{-2}$ ) using Pt as the cathode. However, similar to the a-Si based devices, two DSCs connected in series to the photoanode were necessary to afford overall water splitting. This was accomplished by positioning these two DSCs side-by-side behind the  $\text{WO}_3$  photoanode.

This photoanode/2×DSC architecture does not fundamentally provide a limitation to the possible solar-to-hydrogen conversion efficiency for  $\text{WO}_3$  or even the more promising  $\text{Fe}_2\text{O}_3$ , as less than one third of the available solar photons have a wavelength shorter than 600 nm and

pan-chromatic dyes with high quantum efficiency extending past 900 nm are being developed.<sup>[56]</sup> However, it does present a challenge to device assembly as the two DSCs need to be constructed each with half of the active area of the photoanode in order to normalize the total area of the device. Brillet *et al.* have addressed this problem by employing a narrow bandwidth squaraine dye together with a pan-chromatic ruthenium dye to study the efficacy of a true three-level photoanodes/DSC/DSC tandem. A  $\eta_{\text{STH}}$  of slightly greater than 1% was found with this construction, based on the performance of the individual components.<sup>[57]</sup> However, it is not clear that the complexity of this device, even though slightly reduced from the 2×DSC side-by-side approach, could be offset by the performance to make a commercially viable device. DSCs with slightly higher voltage and photoanodes with slightly lower overpotential losses would enable a true D4 photoanode/DSC water splitting tandem cell, and offer a big advance in device simplicity.

Indeed, in 2012 a specifically designed cobalt redox couple combined with an all-organic dye (coded Y123) gave DSCs with open circuit voltages of over 1.0 V at 1 sun conditions.<sup>[58]</sup> This breakthrough, together with advances on reducing photoanode overpotential using passivating overlayers and catalysts<sup>[59]</sup> allowed the first demonstration of a D4 photoanode/DSC water splitting tandem cell.<sup>[60]</sup> Devices were assembled with both nanostructured  $\text{WO}_3$  and (silicon doped)  $\text{Fe}_2\text{O}_3$  photoanodes, and the actual operating photocurrents were measured to give a  $\eta_{\text{STH}}$  of 3.10% and 1.17% with the  $\text{WO}_3/\text{DSC}$  and  $\text{Fe}_2\text{O}_3/\text{DSC}$  combinations, respectively. In this work,

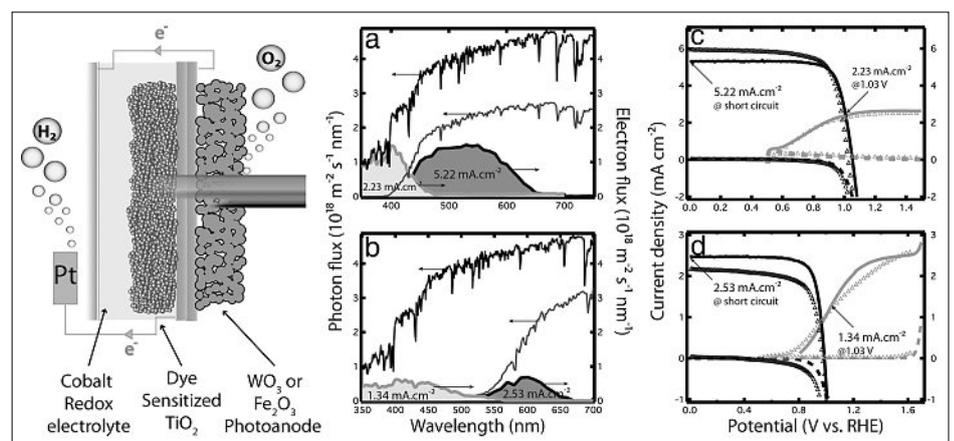


Fig. 5. General scheme (left) of a photoanode/dye-sensitized solar cell D4 tandem cell. Spectral response and J-V characteristics of the  $\text{WO}_3$  (light)/DSC (dark) (a, c) and  $\text{Fe}_2\text{O}_3$  (light)/DSC (dark) (b, d) tandem cells. The transmittance of the photoanode (not shown) convoluted to the AM 1.5 G photon flux on the photoanode (a, b black lines) allows the calculation of the photon flux incident to the DSC (a, b grey lines). IPCE data (not shown) and the photon flux incident to each element is used to estimate the photocurrent density (shaded areas under the curves in a and b). J-V curves (c and d) of the cells are shown under AM 1.5 G irradiation. The filled lines represent the J-V curves predicted from calculation (see ref) and the triangles represent data from *in situ* device measurements. Adapted with permission from Brillet *et al.*, *Nat. Photonics* **2012**, 6, 824–828.

an optical analysis also compared the predicted photocurrent from the integration of IPCE measurements and the actual current–voltage behavior measured *in situ* in the device. This optical analysis and the current voltage curves for each device are shown in Fig. 5. In the case of the Fe<sub>2</sub>O<sub>3</sub>/DSC tandem cell, the operating photocurrent,  $J_{op}$  (shown by the intersection of the DSC photocurrent and the DSC photocurrent curves) is far from the plateau region of the hematite electrode photocurrent. This results in a performance far from the maximum obtainable. The limitation of this system is clearly the late onset of the photocurrent in the photoelectrode caused by a high overpotential, despite the use of state-of-the-art strategies to cathodically shift the onset of the photocurrent by means of surface catalysis and passivation. Regardless of this, the Fe<sub>2</sub>O<sub>3</sub>/DSC device still exhibited a near unity faradaic efficiency and a good stability over an eight hour testing period.

In the case of the WO<sub>3</sub>/DSC tandem cell, the photocurrent onset was not a limitation and the  $J_{op}$  is very close to the plateau region of the photoanode. The limiting factor in this case is the low photocurrent obtainable by the photoanode due to less-than-ideal absorption capability of tungsten trioxide in the visible region of the solar spectrum. Overall this work suggests that the low  $\eta_{STH}$  of the D4 hematite/DSC tandem cell offers the larger potential for improvement, in particular, further reduction of the overpotential for water oxidation. The recent advances in this field suggest that a hematite/DSC tandem device may soon advance significantly further towards its maximum solar-to-hydrogen conversion efficiency of over 16%. While the cost of hydrogen produced with the hematite/DSC tandem cell is still unknown given the immaturity of the technology, the anticipated improvements together with the inexpensive and scalable processing techniques used to fabricate both the hematite photoanode and the DSC are expected to be able to produce a water-splitting device that balances complexity and performance to an economically feasible level.

## Conclusions and Outlook

In this short review the practical aspects of solar fuel production have been considered from a tandem cell perspective. While a single perfect material could reasonably convert more than 10% of the incident solar irradiation to chemical energy stored in hydrogen, that single perfect material has not been found. An integrated tandem approach (D4 scheme) could reasonably convert over 20% of the sun's energy (even with large assumed losses)

and is more flexible regarding material choice. Many different systems have been investigated using various combinations of photovoltaic cells and photoelectrodes. In order to be economically competitive with simple 'brute force' strategies or the production of H<sub>2</sub> from fossil fuels, a practical water-splitting tandem cell must optimize cost, longevity and performance. The most straightforward approach is to use one photoanode and one photocathode, both constructed from stable and readily available materials. However, due to the lack of stable photocathode materials, a promising approach to meet the cost and performance targets is to use a stable photoanode material in tandem with an inexpensive PV cell like the dye sensitized solar cell. Promising photoanode materials are stable transition metal oxides exemplified by hematite, which has vast potential given its band-gap energy levels, abundance, and stability. The successful demonstration of a D4 Fe<sub>2</sub>O<sub>3</sub>/DSC tandem cell with an solar-to-hydrogen efficiency,  $\eta_{STH}$  of 1.17%, gives convincing promise to this device, but much more research is needed to realize a D4 tandem device from hematite with an  $\eta_{STH} > 10\%$ . Further reducing the overpotential for the oxygen evolution reaction (by passivating surface traps and adding catalysts)<sup>[59,61]</sup> and increasing the photocurrent (by nanostructuring)<sup>[27,62,63]</sup> are ongoing research topics for hematite and other encouraging photoanode materials. Device complexity and cost would also drop dramatically if stable photocathode materials with suitable band-gap energies for operation with hematite could be identified. Recent review articles describing approaches to improving the performance of materials like hematite using new approaches in nanotechnology,<sup>[64]</sup> plasmonics,<sup>[65]</sup> catalysis,<sup>[66]</sup> and to finding new materials<sup>[67]</sup> that will someday be employed in an efficient, inexpensive and stable tandem device may be of interest to the reader who is concerned about finding a viable route for the overall conversion and storage of the sun's energy into chemical species like molecular hydrogen.

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- [1] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446.
- [2] R. Schlögl, *ChemSusChem* **2010**, *3*, 209.
- [3] N. R. C. Committee on Alternatives and Strategies for Future Hydrogen Production and Use, National Academy of Engineering, 'The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs', National Academies Press, Washington, **2004**.
- [4] N. Kelly, T. Gibson, D. Ouwkerk, *Int. J. Hydrogen Energy* **2008**, *33*, 2747.
- [5] T. L. Gibson, N. A. Kelly, *Int. J. Hydrogen Energy* **2008**, *33*, 5931.
- [6] N. G. Dhere, A. H. Jahagirdar, *Thin Solid Films* **2005**, *480*, 462.
- [7] A. H. Jahagirdar, N. G. Dhere, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1488.
- [8] J. R. Bolton, S. J. Strickler, J. S. Connolly, *Nature* **1985**, *316*, 495.
- [9] J. R. Bolton, *Solar Energy* **1996**, *57*, 37.
- [10] S. Licht, B. Wang, S. Mukerji, T. Soga, M. Umeno, H. Tributsch, *J. Phys. Chem. B* **2000**, *104*, 8920.
- [11] S. Licht, B. Wang, S. Mukerji, T. Soga, M. Umeno, H. Tributsch, *Int. J. Hydrogen Energy* **2001**, *26*, 653.
- [12] X. Gao, S. Kocha, A. J. Frank, J. A. Turner, *Int. J. Hydrogen Energy* **1999**, *24*, 319.
- [13] S. S. Kocha, D. Montgomery, M. W. Peterson, J. A. Turner, *Sol. Energy Mater. Sol. Cells* **1998**, *52*, 389.
- [14] O. Khaselev, J. A. Turner, *Science* **1998**, *280*, 425.
- [15] O. Khaselev, J. A. Turner, *J. Electrochem. Soc.* **1998**, *145*, 3335.
- [16] G. H. Lin, M. Kapur, R. C. Kainthla, J. O. M. Bockris, *Appl. Phys. Lett.* **1989**, *55*, 386.
- [17] X. Deng, X. Liao, S. Han, H. Povolny, P. Agarwal, *Sol. Energy Mater. Sol. Cells* **2000**, *62*, 89.
- [18] R. E. Rocheleau, E. L. Miller, A. Misra, *Energy and Fuels* **1998**, *12*, 3.
- [19] N. A. Kelly, T. L. Gibson, *Int. J. Hydrogen Energy* **2006**, *31*, 1658.
- [20] S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* **2011**, *334*, 563.
- [21] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.
- [22] W. J. Younblood, S. H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust, T. E. Mallouk, *J. Am. Chem. Soc.* **2009**, *131*, 926.
- [23] X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891.
- [24] B. D. Alexander, P. J. Kulesza, L. Rutkowska, R. Solarzka, J. Augustynski, *J. Mater. Chem.* **2008**, *18*, 2298.
- [25] K. Sivula, F. Le Formal, M. Grätzel, *ChemSusChem* **2011**, *4*, 432.
- [26] C. Santato, M. Ulmann, J. Augustynski, *J. Phys. Chem. B* **2001**, *105*, 936.
- [27] J. Brillet, M. Grätzel, K. Sivula, *Nano Lett.* **2010**, *10*, 4155.
- [28] Y. Liang, T. Tsubota, L. P. A. Mooij, R. van de Krol, *J. of Phys. Chem. C* **2011**, *115*, 17594.
- [29] M. Higashi, K. Domen, R. Abe, *J. Am. Chem. Soc.* **2012**, *134*, 6968.
- [30] H. Wang, T. Deutsch, J. A. Turner, *J. Electrochem. Soc.* **2008**, *155*, F91.
- [31] R. N. Dominey, N. S. Lewis, J. A. Bruce, D. C. Bookbinder, M. S. Wrighton, *J. Am. Chem. Soc.* **1982**, *104*, 467.
- [32] Y. Hou, B. L. Abrams, P. C. K. Vesborg, M. E. Björketun, K. Herbst, L. Bech, A. M. Setti, C. D. Damsgaard, T. Pedersen, O. Hansen, J. Rossmeisl, S. Dahl, J. K. Nørskov, I. Chorkendorff, *Nat. Mater.* **2011**, *10*, 434.
- [33] D. H. van Dorp, N. Hijnen, M. Di Vece, J. J. Kelly, *Angew. Chem. Int. Ed.* **2009**, *48*, 6085.
- [34] J. A. Baglio, G. S. Calabrese, D. J. Harrison, E. Kamieniecki, A. J. Ricco, M. S. Wrighton, G. D. Zoski, *J. Am. Chem. Soc.* **1983**, *105*, 2246.
- [35] D. Yokoyama, T. Minegishi, K. Maeda, M. Katayama, J. Kubota, A. Yamada, M. Konagai, K. Domen, *Electrochem. Commun.* **2010**, *12*, 851.
- [36] W. Siripala, A. Ivanovskaya, T. F. Jaramillo, S.-H. Baeck, E. W. McFarland, *Sol. Energy Mater. Sol. Cells* **2003**, *77*, 229.
- [37] M. Trari, A. Bouguelia, Y. Bessekhouad, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 190.
- [38] Y. Matsumoto, M. Omae, K. Sugiyama, E. Sato, *J. Phys. Chem.* **1987**, *91*, 577.
- [39] C. Leygraf, M. Hendewerk, G. Somorjai, *J. Solid State Chem.* **1983**, *48*, 357.

- [40] A. J. Nozik, 'p-n photoelectrolysis cells', vol. 29, AIP, **1976**.
- [41] D. S. Ginley, M. B. Chamberlain, *J. Electrochem. Soc.* **1982**, *129*, 2141.
- [42] H. Wang, J. A. Turner, *J. Electrochem. Soc.* **2010**, *157*, F173.
- [43] Y. S. Hu, A. Kleiman-Shwarscstein, G. D. Stucky, E. W. McFarland, *Chem. Commun.* **2009**, 2652.
- [44] S. Ida, K. Yamada, T. Matsunaga, H. Hagiwara, Y. Matsumoto, T. Ishihara, *J. Am. Chem. Soc.* **2010**, *132*, 17343.
- [45] G. K. Mor, O. K. Varghese, R. H. T. Wilke, S. Sharma, K. Shankar, T. J. Latempa, K.-S. Choi, C. A. Grimes, *Nano Lett.* **2008**, *8*, 1906.
- [46] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen, *Nat. Mater.* **2011**, *10*, 456.
- [47] B. Neumann, P. Bogdanoff, H. Tributsch, *J. Phys. Chem. C* **2009**, *113*, 20980.
- [48] A. Stavrides, *Proc. SPIE* **2006**, *6340*, 63400K.
- [49] E. Miller, R. E. Rocheleau, S. U. M. Khan, *Int. J. Hydrogen Energy* **2004**, *29*, 907.
- [50] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
- [51] M. Grätzel, *Nature* **2001**, *414*, 338.
- [52] J. Augustynski, G. Calzaferri, J. C. Courvoisier, M. Grätzel, in 'Hydrogen energy progress XI: Proceedings of the 11th World Hydrogen Energy Conference', vol. 3, Stuttgart, Germany, **1996**, pp. 2379-2387.
- [53] M. Grätzel, *Cattech* **1999**, *3*, 3.
- [54] J. H. Park, A. J. Bard, *Electrochem. Solid-State Lett.* **2006**, *9*, E5.
- [55] H. Arakawa, C. Shiraishi, M. Tatamoto, H. Kishida, D. Usui, A. Suma, A. Takamisawa, T. Yamaguchi, *Sol. Hydrogen and Nanotechnol. II* **2007**, *6650*, 65003.
- [56] M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Cointe, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* **2001**, *123*, 1613.
- [57] J. Brillet, M. Cornuz, F. Le Formal, J. H. Yum, M. Grätzel, K. Sivula, *J. Mater. Res.* **2010**, *25*, 17.
- [58] J.-H. Yum, E. Baranoff, F. Kessler, T. Moehl, S. Ahmad, T. Bessho, A. Marchioro, E. Ghadiri, J.-E. Moser, C. Yi, M. K. Nazeeruddin, M. Grätzel, *Nat. Commun.* **2012**, *3*, 631.
- [59] F. Le Formal, N. Tetreault, M. Cornuz, T. Moehl, M. Grätzel, K. Sivula, *Chemical Science* **2011**, *2*, 737.
- [60] J. Brillet, J. H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, M. Grätzel, K. Sivula, *Nat. Photonics* **2012**, *6*, 824.
- [61] D. K. Zhong, M. Cornuz, K. Sivula, M. Grätzel, D. R. Gamelin, *Energy Environ. Sci.* **2011**, *4*, 1759.
- [62] K. Sivula, F. Le Formal, M. Grätzel, *Chem. Mater.* **2009**, *21*, 2862.
- [63] K. Sivula, R. Zboril, F. Le Formal, R. Robert, A. Weidenkaff, J. Tucek, J. Frydrych, M. Grätzel, *J. Am. Chem. Soc.* **2010**, *132*, 7436.
- [64] F. E. Osterloh, *Chem. Soc. Rev.* **2013**, doi: 10.1039/C2CS35266D.
- [65] S. C. Warren, E. Thimsen, *Energy Environ. Sci.* **2012**, *5*, 5133.
- [66] K. J. Young, L. A. Martini, R. L. Milot, R. C. Snoeberger Iii, V. S. Batista, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, *Coord. Chem. Rev.* **2012**, *256*, 2503.
- [67] F. E. Osterloh, *Chem. Mater.* **2007**, *20*, 35.