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Preview

Toward Practical Solar Hydrogen Production

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Two articles recently published in *Joule* represent efforts in material discovery and new engineering for practical solar hydrogen production. Wong and colleagues improved the solar hydrogen production performance of Cu_2ZnSnS_4 by Cd substitution, and Domen and co-workers presented a panel design to take advantage of particulate Al-doped $SrTiO_3$ photocatalysts for overall water splitting.

Decades of research have led the scientific community to reach several consensuses concerning a future powered by renewable energy. They include that solar energy will most likely play a critical role when we break our dependence on fossil fuels. Being able to store solar energy on a terawatt scale will be critical. How to do so, nevertheless, remains unclear. For instance, it is generally agreed upon that purely relying on a combination of solar panels (such as photovoltaics [PV]) and advanced batteries is unlikely to be cost effective. Instead, we need a new scheme involving commodity chemicals—such as hydrogen (H_2) or hydrocarbons—that are easy to store, transport, and utilize. Whether these chemicals, commonly referred to as solar fuels in the context of solar energy storage, should be produced directly or through the connection of solar panels with electrolyzers is a main point of contention. Settling this debate is no easy task. It requires high-level technoeconomical analysis (TEA), such as the one conducted by Pinaud et al., who concluded that solar hydrogen production by photocatalysis and/or photoelectrochemistry could reach the price target of $2.00-$4.00 per kg H_2.[1] More recently, Rothschild and Dotan argued that new configurations combining PV and photoelectrochemical (PEC) cells might be more efficient than a simple combination of PV and electrolyzers.[2] It is important to note, however, that most existing TEAs rely on assumptions of performance metrics that have not been, or are not easily, realized in terms of cost and efficiency. This is because direct solar fuel production is still in its infancy. Many scientific and engineering issues remain open questions. Two recent papers published in *Joule* take important steps to answer these open questions.[3,4]

On a most fundamental level, we need significant advances in at least three areas to make strides toward practical, cost-competitive solar fuel production (Figure 1). First, discoveries of stable and low-cost materials that are highly efficient are necessary. Second, we need highly selective chemical catalysis to utilize the photogenerated charges for the synthesis of solar fuels. The second point is especially critical when we move away from simple reactions (such as the hydrogen evolution reaction) to more complex, value-added hydrocarbon synthesis based on CO_2 reduction. Third, once these scientific challenges are solved, we will need new engineering designs to take full advantage of solar fuels. These two recent publications in *Joule* hit two of the three points: Wong and colleagues focus on the discovery of high-performance photoelectrode materials, and Domen and co-workers address engineering needs for solar hydrogen production.

With regard to the goal of material discovery, it would be ideal to find all desired features—including high performance, low cost, and long durability—in a single composition. However, this goal has proven elusive. Increasingly, the community is realizing that working from two opposite ends toward a common goal could be more practical. In one scheme, the focus is to identify a high-performance material and address its shortcomings, such as poor stability and high cost. To this end, compound semiconductors, such as GaAs and $GaInP_2$, are important platforms that have received a great deal of attention. The reasons are obvious: they feature nearly ideal optoelectronic properties for photo-to-electrical energy conversion. Indeed, >15% solar-to-hydrogen (STH) conversion efficiencies have been demonstrated with these materials,[5] but the high cost and poor stability remain challenging. New strategies are being developed to address these issues. For example, Gu et al. recently reported that a p-$GaInP_2$ photocathode could be protected by atomic-layer-deposited (ALD) TiO_2 to enable stable solar water reduction for over 20 hr.[6] Kang et al. proposed and proved an effective approach to addressing the cost issue by an epitaxial lift-off and printing-assembly technique that also decouples the illumination and electrocatalysis interfaces for high efficiencies.[7] At the other end of the spectrum sits the strategy for improving the performance of low-cost and stable materials. To this end, hematite might be

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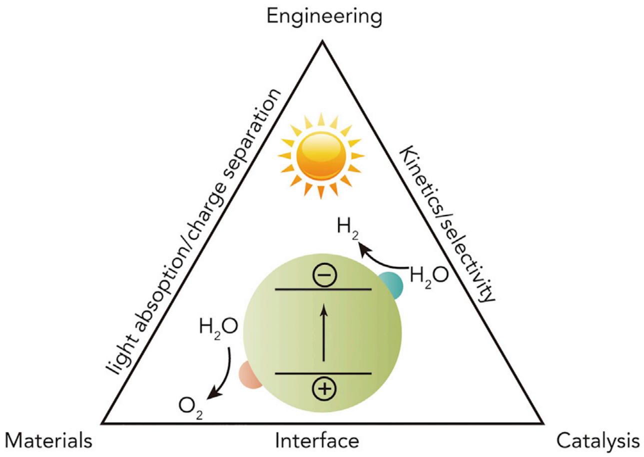

Figure 1. Significant Advances in at Least Three Directions Are Necessary for Realizing the Goal of Practical, Cost-Effective Solar Fuel Synthesis: Discovery of Materials, Advanced Catalysis, and New Engineering

one of the most studied material platforms. Its appeals as a photoelectrode material for solar fuel production include low cost, high stability, and a suitable band gap. Unfortunately, despite decades of research, the highest efficiency that has been measured on hematite remains far below its theoretical limit.[8–10]

The recent *Joule* article by Wong and colleagues represents efforts toward improving potentially low-cost materials for high-efficiency demonstrations.[3] The chosen material platform, Cu_2ZnSnS_4 (CZTS), has the potential to compete with high-performance copper-based chalcogenide photocathode materials, such as $Cu(InGa)Se_2$ (CIGSe), because of its good optoelectronic properties. The authors aim to reduce the cost associated with material fabrication by advancing solution deposition instead of vacuum techniques. However, the performance of the solution-processed CZTS photocathode is generally low, mainly because of its poor bulk properties. In this work, the authors greatly improved the performance of sol-gel CZTS by Cd substitution. The results open up new doors to future large-scale fabrication of high-efficiency photocathodes by solution processing.

Experimentally, Wong and colleagues present evidence showing that Cd-substituted CZTS (CCZTS) enabled a much higher photocurrent density than unsubstituted CZTS. When both photocathodes were coated with CdS/TiMo/Pt, the photocurrent density at 0 V_{RHE} increased from 4 to 17 mA/cm^2 with Cd substitution, and the V_{on} was shifted negatively by 0.15 V. The role of Cd substitution was examined by several techniques. The newly formed "spike-like" interface between CCZTS and CdS, detected by X-ray photoelectron spectroscopy, is thought to reduce charge recombination at the interface and increase the photocurrent. Nevertheless, the interface also introduced a barrier of 0.13 eV for electron transfer from CCZTS to CdS, consistent with the observed V_{on} change. Further experimental results indicated an increase in carrier lifetime and a decrease in bulk defects as a result of Cd substitution. As a whole, the enhanced performance with Cd substitution was attributed to improved bulk properties of CCZTS.

Going back to the considerations of the three directions shown in Figure 1, let us now examine the importance of catalysis. As far as efficient charge transfer (measured by low overpotentials) and product selectivity (important for reactions such as CO_2 reduction) are concerned, research on catalysts for direct solar fuel production is not different from that on electrocatalysis. Consider catalysts for water splitting as an example. A large number of metals, metal oxides and chalcogenides, and metal (oxy)hydroxides have been investigated, and significant progress has been made.[11] For water oxidation reactions, metal (oxy)hydroxides such as $NiFeO_x$ have been shown to compare favorably (especially in alkaline solutions) with highly effective but expensive catalysts such as IrO_x and RuO_x in terms of performance, as measured by overpotentials. For water reduction, MoS_2 and Ni_2P (as well as FeP) have been identified as promising candidates to replace Pt.

What distinguishes research on catalysis for direct solar fuel production lies in the unique interactions between the catalysts and the light-absorbing, charge-separating materials. This is because, by and large, the performance of a direct solar fuel synthesis system is defined by the behaviors of the interface between the light absorber and the liquid. To characterize this interface, photoelectrochemistry, which reports on how the application of co-catalysts might influence the light absorption and charge-separation capabilities of the photoelectrode, can be a powerful tool. Often, in addition to reducing the kinetic overpotentials by facilitating charge transfer, the catalyst can alter the electronic states on the surface, leading to drastically different behaviors under photocatalytic conditions. For instance, the performance of hematite has been shown to improve dramatically after the deposition of amorphous $NiFeO_x$.[12] In an interesting twist, despite the fact that $NiFeO_x$ is an outstanding water oxidation catalyst, the performance enhancement was found to be due to better charge separation rather than faster charge transfer from hematite to H_2O. In this case, $NiFeO_x$ could be regarded as a "passivation" layer rather than a catalytic layer in that its application mainly functions positively by reducing interface charge recombination.

Importantly, the hematite/$NiFeO_x$ system is by no means unique in terms of its working mechanisms. The most recent example that supports this understanding comes from a paper by Boettcher and co-workers, who used potential-sensing electrochemical atomic force microscopy to measure the potential change of cobalt (oxy)hydroxide phosphate (CoPi) on a hematite surface under solar water oxidation conditions.[13] The results revealed the complex functions of CoPi both in helping charge separation by collecting holes and in promoting hole transfer to water by acting as a catalyst. In another recent publication, our group showed that unique mechanisms such as photochemical radical processes can be used to form new and better photoelectrode-catalyst interfaces for better performance.[14] The prototypical material platform for this demonstration was Ta_3N_5, another material that features high photocurrent densities (>12 mA/cm^2) but suffers from rapid performance decay. Only under PEC conditions could we observe a rare performance improvement when $Co(OH)_2$ was used as a coating on Ta_3N_5. Studies on the interface of light absorbers and catalysts will prove fertile as we move forward with direct solar fuel production.

The last piece of the triangle shown in Figure 1 is advanced engineering for direct solar fuel production. In comparison with research on materials and catalysis, it is much less developed, chiefly because the basis for device-level optimization is not quite ready yet. Nevertheless, one cannot overemphasize the importance of this component for the final implementations. To this end, the recent *Joule* paper by Domen and co-workers makes important advances.[4] In this article, the authors build upon the progress that the Domen group has made over the past few decades in identifying high-performance light absorbers (e.g., Al-doped $SrTiO_3$) and the application of catalysts (e.g., $RhCrO_x$) and take a critical step forward by designing and testing panels on the scale of 1 × 1 m, paving the way for large-scale implementations given that these 1 m^2 modules can be readily connected.

Interestingly, the authors took a rather unorthodox approach to this demonstration in that they performed panel-based photocatalytic water splitting. Previous efforts to utilize particulate photocatalyts were mostly guided toward suspension-based implementations, and panel-like designs were mostly proposed for PEC approaches. Domen and co-workers argued compellingly in this demonstration that implementing a photocatalytic panel can be equally practical. The trick was a method for embedding powder photocatalysts onto glass substrates by drop casting with the help of SiO_2 nanoparticles as binders. Compared with the traditional suspension approach, the new design features several advantages: (1) better light harvesting without stirring, (2) a reduced amount of water, and (3) simplified systems to sustain operations by a suspension (such as the need for filtration or centrifugation). The panel-type reactor achieved an STH efficiency of 0.4% under natural sunlight irradiation. Stable H_2/O_2 evolution was demonstrated for over 150 hr. Furthermore, when a hydrophilized quartz window was applied as the cover for the panel reactors, the gas evolved during water splitting could be effectively removed even at a rate corresponding to 10% STH efficiency with just a 1 mm water layer. This demonstration presents a new possibility of direct solar fuel production. How to effectively separate the H_2 and O_2 mixture and how to reduce the involvement of scarce and expensive elements (such as Rh) will be issues for future research to address.

As exciting as this new progress might be, we have a long way to go for the goal of direct solar fuel synthesis as a practical technology. The two demonstrations highlighted here both deal with hydrogen generation. Society has yet to come up with a sustainable infrastructure for storing, transporting, and utilizing hydrogen on a large scale. The science needed for selective, high-efficiency hydrocarbon synthesis from CO_2 reduction still requires significant development. Precisely for these reasons, the field will remain fertile for research in the years, if not decades, to come.

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