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Tilley, S David

DOI: <https://doi.org/10.1021/acseenergylett.3c00578>

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Journal Article

Published Version



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Originally published at:

Tilley, S David (2023). Will Cuprous Oxide Really Make It in Water-Splitting Applications? ACS Energy Letters, 8(5):2338-2344.

DOI: <https://doi.org/10.1021/acseenergylett.3c00578>

# Will Cuprous Oxide Really Make It in Water-Splitting Applications?

S. David Tilley\*



Cite This: *ACS Energy Lett.* 2023, 8, 2338–2344



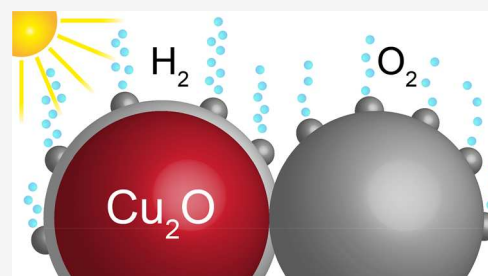
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**ABSTRACT:** For cost-effective solar hydrogen production on an industrial scale, Earth-abundant, low-cost, and easily processable materials are required. In this Perspective, a case is made that cuprous oxide has strong potential for practical large-scale water splitting. Recent research directions for improved efficiency and durability are highlighted, which target both the back and front interfaces of the  $\text{Cu}_2\text{O}$  light absorber as well as protective overlayers and co-catalysts. The translation of high-efficiency thin-film device architectures to photocatalytic sheets or particles is proposed as a disruptive approach to solar hydrogen generation with fertile ground for new scientific discoveries.



A key challenge for enabling widespread penetration of renewable energies into the global economy is cost-effective energy storage. Although battery technologies will be essential for day/night cycles, fuels are likely the only effective option for seasonal or multi-year energy storage.<sup>1,2</sup> Water splitting is an attractive option for storing renewable energies due to the abundance of solar energy and water as a chemical feedstock, which produces renewable hydrogen.<sup>3</sup> In the near term, renewable  $\text{H}_2$  will decarbonize large-scale industrial processes such as Haber–Bosch, which currently rely on fossil  $\text{H}_2$ . In the long term, renewable  $\text{H}_2$  could become the foundation of the global energy economy. There is currently a strong push in this direction due to government initiatives around the world promoting green hydrogen as a way to achieve net-zero carbon emissions.<sup>4,5</sup> Renewable hydrogen could also serve as an intermediate for the synthesis of renewable hydrocarbons via conventional processes such as Fischer–Tropsch as well as unconventional processes that leverage biology to make valuable reduced carbon products.<sup>6</sup> The essential point, however, is that once the solar energy is stored in the hydrogen molecule, we have the ability to store solar energy over centuries, just like fossil fuels.

Solar energy is by far the largest source of renewable energies,<sup>7</sup> and this Perspective focuses on the production of hydrogen fuel via solar water splitting. While the solar resource is immense, the power is dilute, and therefore very large areas of the Earth's surface will need to be covered with solar energy conversion devices. The use of water as the source of electrons and protons for the synthesized fuel is essential due to the tremendously large scale that such fuels will need to attain.<sup>8,9</sup> Figure 1 describes the aim in the most general sense. Water and solar irradiation are fed into Technology X, which produces hydrogen fuel and oxygen as

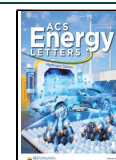
a byproduct. What are the characteristics of Technology X? What would need to be true such that hydrogen is produced at a price that is competitive with fossil fuels? Essentially, the costs of fabricating, operating, and maintaining this technology must be as low as possible. Various technoeconomic analyses find that it is indeed possible to produce solar hydrogen at a price competitive with fossil fuels, even without carbon taxes (though, practically, such financial incentives will accelerate the transition).<sup>10,11</sup> These studies find that efficiency plays a key role due to the areal dependence of solar power collection: higher efficiency devices mean smaller areas of Earth's surface that need to be covered, which saves on the raw materials and fabrication costs of the photovoltaic (PV),<sup>12</sup> photoelectrochemical (PEC),<sup>13</sup> or photocatalytic (PC) devices.<sup>14</sup> The synthesis of the light absorber materials as well as charge-extracting interfaces and/or catalysts in these devices should be low-cost and scalable, which implies the use of Earth-abundant elements. A second major finding of these studies is that the materials must be durable, which targets the operating and maintenance costs of the technology.

Cuprous oxide ( $\text{Cu}_2\text{O}$ )<sup>15–18</sup> is a strong candidate material for use in Technology X. It is composed of abundant elements and has a bandgap of about 2.0 eV, which translates to a maximum theoretical solar-to-hydrogen efficiency of about 18%.<sup>19</sup> It can be prepared by simple methods such as electrodeposition,<sup>20</sup>

Received: March 17, 2023

Accepted: April 11, 2023

Published: April 20, 2023



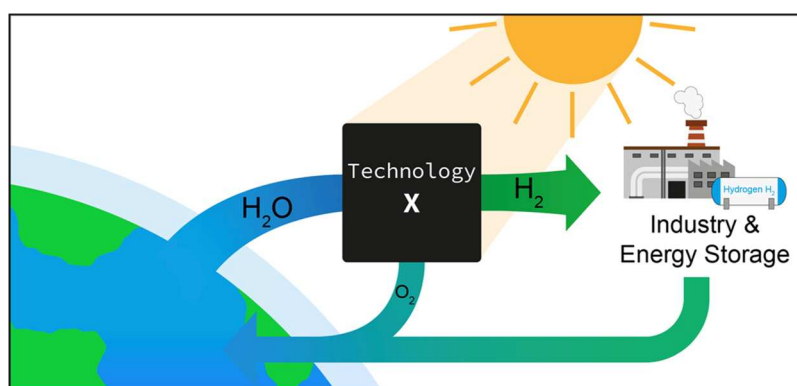


Figure 1. Technology X converts abundant water and sunlight into hydrogen fuel, which powers society and yields water as a byproduct after its use. Artwork by Jan Bühler.

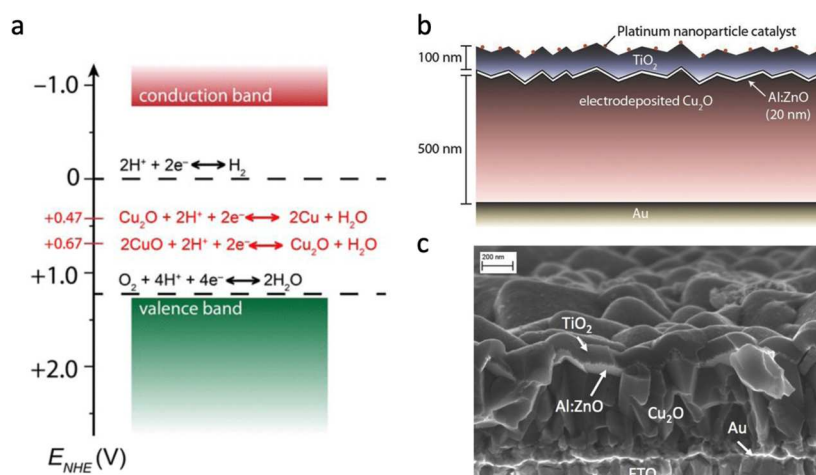


Figure 2. (a) Energetic band positions of  $\text{Cu}_2\text{O}$  as well as the corrosion reactions. Reproduced with permission from ref 15. Copyright 2015 American Chemical Society. (b) Schematic of a  $\text{Cu}_2\text{O}$  light absorber coated with functional overlayers. (c) Cross-sectional SEM image of the photocathode depicted in panel b. The conformal  $\text{TiO}_2$  layer prevents photocorrosion of the  $\text{Cu}_2\text{O}$  photoabsorber layer. Panels b and c adapted from ref 38, Wiley 2013.

hydrothermal synthesis,<sup>21</sup> anodization of metallic copper (a nanostructuring approach),<sup>22</sup> *in situ* electroconversion,<sup>23</sup> and thermal oxidation of copper foils.<sup>24–26</sup> Cuprous oxide can achieve unassisted overall water splitting when paired with a second photoactive material in a tandem configuration.<sup>27–29</sup>

Cuprous oxide is not stable in water under illumination, as the corrosion reactions lie within the bandgap (Figure 2a). For compatibility with water, a protective overlayer strategy was developed. McFarland first studied electron-beam-evaporated  $\text{TiO}_2$  as a protective layer,<sup>30</sup> and later Grätzel et al. investigated protective  $\text{TiO}_2$  layers deposited by atomic layer deposition (ALD) (Figure 2b,c).<sup>31</sup> Although ALD coatings were initially investigated on relatively flat films, ALD is a suitable method for making conformal coatings on nanostructured devices.<sup>22</sup> The use of overlayers greatly improves the durability of  $\text{Cu}_2\text{O}$  photocathodes in aqueous media.

It should be noted that, by introducing solid-state overlayers to the  $\text{Cu}_2\text{O}$ , the photoelectrode has become a so-called “buried” junction, where the photovoltage is generated underneath the semiconductor/electrolyte junction. The electrode functions nearly identically to a thin-film PV cell, except that the charge-extracting (ohmic) metal contact of the PV cell has been replaced by a surface catalyst that carries out the reaction of interest (also an ohmic contact, though with higher resistance due to the overpotential required to drive the desired chemistry

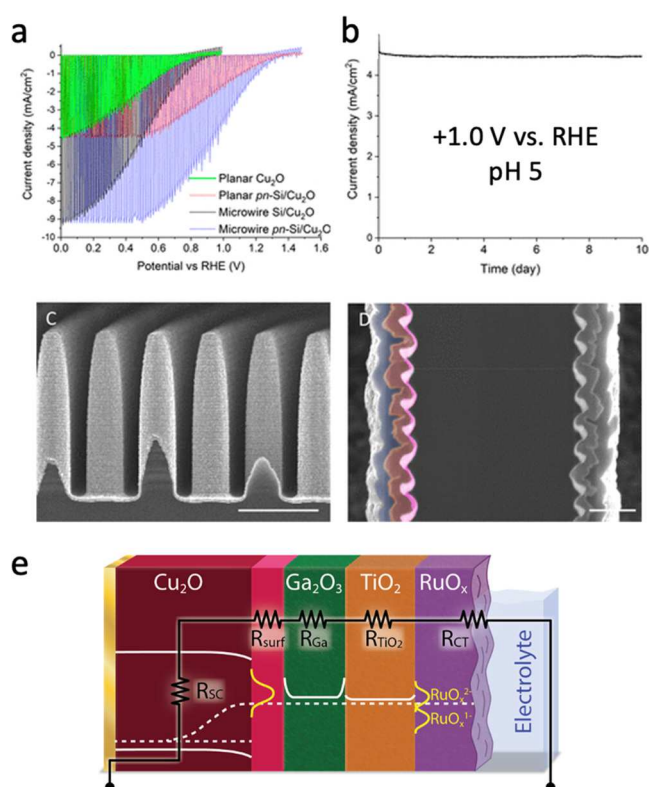
at a reasonable rate). In order to maximize the efficiency of such a system, the same principles can be employed as used for PV cells (e.g., designing selective contacts).<sup>32</sup> As such, the band positions of the photoabsorber on the NHE scale (Figure 2a) and their relation with the thermodynamic water-splitting potentials are not particularly relevant for buried junction systems. This is in contrast to the traditional PEC concept, where the photovoltage is generated at the semiconductor/electrolyte (Schottky) junction.<sup>25</sup> The buried junction strategy often yields a larger photovoltage than systems based on a semiconductor/electrolyte junction<sup>33</sup> and additionally facilitates the use of protective overlayers.  $\text{TiO}_2$  has been widely used for this purpose in photocathode systems due to its transparency in the visible light range, conduction band edge near the hydrogen evolution potential, and high stability in aqueous environments.<sup>34</sup> However, organic layers that offer robust durability have also been employed for water-splitting photocathodes.<sup>29,35,36</sup>

Let us now take a deeper look at various aspects of  $\text{Cu}_2\text{O}$  thin-film devices that are important for continued improvement as well as for the future perspectives considered below. First, the catalytic interface will be discussed, where hydrogen is produced. Next, recent efforts to improve the durability of  $\text{Cu}_2\text{O}$  devices will be detailed, followed by the electron-selective

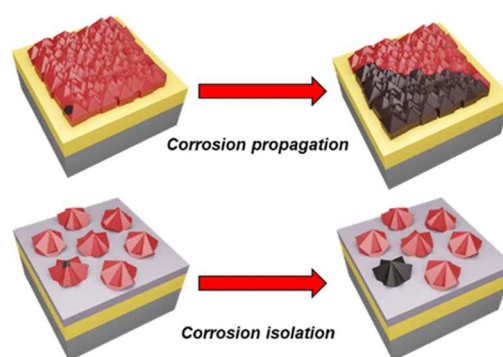
layer (the front contact), and finally the hole-selective layer (the back contact).

**The Catalytic Interface.** The protective overlayers that interface with the electrolyte solution in water-splitting cells (e.g.,  $\text{TiO}_2$  or organic layers) typically have a large overpotential for the hydrogen evolution reaction (HER), and so co-catalysts are added to facilitate this reaction. As many systems are designed for illumination through the overlayer, there is a trade-off between parasitic light absorption by a surface catalyst and enhanced catalytic activity through higher catalyst loading. Initially, electrodeposited Pt nanoparticles were used (Figure 2b),<sup>37</sup> since Pt has a very low overpotential for the HER. However, the stability of the photocurrent degraded on the order of tens of minutes. Further experiments identified the problem as not degradation of the  $\text{Cu}_2\text{O}$  photoabsorber but degradation of the catalytic interface. It was proposed that the Pt nanoparticle catalysts were either dislodged from the surface during operation or poisoned by impurities in the buffer salts used to prepare the electrolyte solutions, since re-platinization often completely restored the performance following degradation. When the photoelectrons that arrive at the  $\text{TiO}_2$ /electrolyte interface are unable to be injected into the electrolyte solution (via the HER), then reduction of the  $\text{Ti}^{4+}$  centers in the  $\text{TiO}_2$  layer to  $\text{Ti}^{3+}$  occurs (coupled with proton intercalation), which facilitates further degradation of the protective layer. Thus, a robust physical and electronic connection between the overlayer and catalyst is critical for the long-term durability of the photoelectrode.

**Durability of  $\text{Cu}_2\text{O}$ -Based Photocathodes.** One strategy that improved the durability of the overlayer/catalyst interface was the use of  $\text{RuO}_x$  as an HER catalyst, which is more resistant than Pt to poisoning by impurities in the electrolyte solution (e.g., sulfur-containing species or trace metal ions that electrodeposit onto the Pt and are not catalytic for the HER).<sup>38,39</sup> Continuous PEC hydrogen production for 10 days with essentially no loss in photocurrent was demonstrated using a high-photovoltage  $\text{Cu}_2\text{O}$  absorber layer with  $\text{RuO}_x$  catalyst on top of a microstructured Si substrate (Figure 3),<sup>40</sup> suggesting that industrially relevant durability can be achieved even for light absorbers that are unstable in water. Another strategy for improving the durability focused on the  $\text{TiO}_2$  layer itself, which is typically amorphous when deposited by ALD. High-temperature annealing of an ALD- $\text{TiO}_2$ -coated silicon photocathode resulted in an electrode that produced  $\sim 21 \text{ mA/cm}^2$  of hydrogen evolving photocurrent for 3 continuous weeks.<sup>41</sup> Unfortunately, high-temperature annealing of  $\text{Cu}_2\text{O}$ -based heterojunctions ( $\geq 200 \text{ }^\circ\text{C}$ ) degrades the photovoltaic properties. For this reason, alternative methods to crystallize the amorphous layer on temperature-sensitive substrates were sought. While hydrothermal treatment of electrodeposited  $\text{Cu}_2\text{O}$ -based photocathodes in an aqueous bath completely dissolved the layers, steam treatment resulted in vastly improved durability.<sup>42</sup> Interestingly, the  $\text{TiO}_2$  layer remained amorphous, and the improved durability was attributed to healing of cracks and/or pinholes in the overlayer as well as an improvement in the homogeneity of the surface-deposited co-catalyst. An innovative third approach based on pixelation was recently demonstrated to prolong the lifetime of  $\text{Cu}_2\text{O}$ -based photocathodes. In typical thin films of  $\text{Cu}_2\text{O}$ , a single pinhole in the protective layer will lead to eventual degradation of the entire film. By pixelating the  $\text{Cu}_2\text{O}$  absorber, defects in the protective overlayer lead only to corrosion of individual pixels, preventing global degradation (Figure 4).<sup>43</sup>



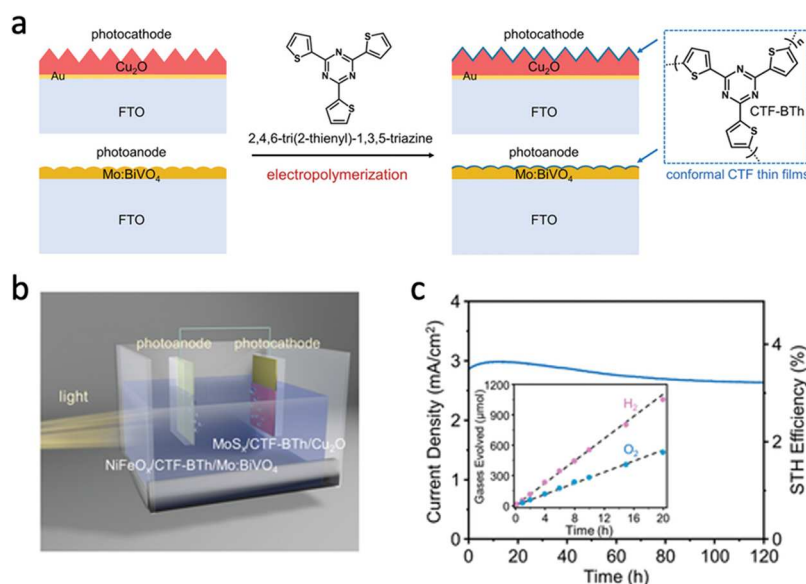
**Figure 3.** (a) *JV* curves of  $\text{Cu}_2\text{O}$ -based photocathodes. (b) Durability measurement of the microwire  $\text{pn-Si/Cu}_2\text{O}$  photocathode. (c) Cross-sectional SEM image of the  $\text{pn-Si/Cu}_2\text{O}$ . (d) FIB-TEM cross-section of one of the microwires, with the  $\text{Cu}_2\text{O}$  photocathode false colored. Panels a–d adapted from ref 40 under a CC-BY-NC-ND 4.0 Creative Commons license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>). No changes were made to the panels. (e) Schematic of the  $\text{Cu}_2\text{O}$  portion of the electrode. Reproduced from ref 64 under a CC BY 3.0 Creative Commons license (<https://creativecommons.org/licenses/by/3.0/>). No changes were made to the panel. The  $\text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3$  heterojunction provides up to 1 V of photovoltage in water-splitting systems.



**Figure 4.** A pixelation approach prevents global degradation of the film in the presence of defects in the protective overlayer. Reproduced with permission from ref 43. Copyright 2022 American Chemical Society.

**The Electron-Selective Layer.** With regard to the efficiency of  $\text{Cu}_2\text{O}$ -based electrodes, perhaps the most important factor is the choice of heterojunction partner (i.e., the electron-selective layer). Minami et al. have investigated a variety of heterojunction partners for  $\text{Cu}_2\text{O}$ , tuning the conduction band offset and achieving photovoltages as high as





**Figure 5.** (a) An electropolymerized covalent triazine framework serves as a robust protective layer for both Cu<sub>2</sub>O and BiVO<sub>4</sub> photoelectrodes. (b) Schematic of the stacked tandem cell architecture. (c) Durable overall water splitting exceeding 3.2% solar-to-hydrogen efficiency is achieved. Adapted from ref 29, Wiley 2021.

1.10 V with Cu<sub>2</sub>O/Zn<sub>0.38</sub>Ge<sub>0.62</sub>O junctions.<sup>24</sup> An alternative strategy to finding a suitable junction material is to shift the band positions of the p-n junction with molecular dipoles placed at the interface. As TiO<sub>2</sub> can serve as both the n-type heterojunction partner and protective layer, the molecular dipole approach can be used to tune the band offset for any p-type photoabsorber for maximal efficiency. For example, a thin layer of phosphonic acid on silicon, Cu<sub>2</sub>O, and Sb<sub>2</sub>Se<sub>3</sub> photocathodes enabled improved photovoltages in water-splitting systems.<sup>44</sup> More recently, it was demonstrated that a polyethylenimine ethoxylated (PEIE) layer between a photoabsorber material and TiO<sub>2</sub> can also be used as a tunable interface dipole for improved efficiency.<sup>45</sup>

The quality of the heterojunction interface is also very important, and the synthesis method of the overlayer plays a large role in the interface quality. A study of Cu<sub>2</sub>O/ZnO junctions demonstrated that very different band-bending situations (and therefore efficiencies) arise depending on the deposition conditions, due to varying interface states and/or dipoles.<sup>46</sup> For instance, if the cuprous oxide is exposed to air prior to deposition of the heterojunction partner, the surface is oxidized to generate Cu<sup>2+</sup> states, which serve as recombination centers in the device. The surface oxidation can potentially be reversed when using ALD to deposit the overlayer, as the precursor molecules are typically highly reducing (e.g., diethylzinc),<sup>47</sup> though the amount of precursor dosed into the reactor must be carefully controlled to avoid over-reduction to Cu metal. Small amounts of metallic Cu at the interface, invisible even by X-ray photoelectron spectroscopy (XPS), are sufficient to degrade the photovoltaic properties of the junction. The Ga<sub>2</sub>O<sub>3</sub> ALD precursor is also highly reducing, but reduction of the surface to Cu metal can be avoided if CuO formation is prevented, as the kinetics for reduction of Cu<sub>2</sub>O to Cu is much slower than for CuO.<sup>48</sup>

**The Hole-Selective Layer.** Optimization of the contact at the back interface (i.e., the hole-selective layer) is another research target for Cu<sub>2</sub>O photocathodes. Typically, gold is employed because it is stable, forms an ohmic contact with Cu<sub>2</sub>O, and serves as a reflector layer for transmitted light in thin (e.g., electrodeposited) Cu<sub>2</sub>O films. In order to reduce the

amount of gold required for scaling up, very thin layers of gold (nominally 3 nm) on fluorine-doped tin oxide (FTO) were employed, which resulted in transparent cuprous oxide samples that were suitable for use as the front electrode in a stacked tandem cell architecture.<sup>28,40</sup> The FTO provided the conductivity to extract charge over the centimeter dimensions of the device, while the gold served as an ohmic contact to facilitate hole injection into the FTO (since FTO does not form an ohmic contact to Cu<sub>2</sub>O). While this approach has proven successful for reducing the amount of gold required, others have sought to replace the gold with a hole-selective contact, which can additionally reduce recombination at the back interface. Son et al. demonstrated that a copper–nickel mixed oxide has a suitable alignment to the valence band of Cu<sub>2</sub>O and reported improved PEC performance over gold.<sup>49</sup> Pan et al. demonstrated that an electrodeposited CuSCN layer on FTO could be used to fabricate high-performance Cu<sub>2</sub>O photocathodes, which were suitable for demonstrating a solar-to-hydrogen (STH) efficiency exceeding 4.5% when paired with a perovskite solar cell in a stacked tandem architecture.<sup>50</sup>

A state-of-the-art, all-oxide photoabsorber tandem cell is depicted in Figure 5, which pairs a high-photovoltage Cu<sub>2</sub>O photocathode with a BiVO<sub>4</sub> photoanode.<sup>29</sup> An electropolymerized organic protective layer was employed, which offered a good band alignment to both the Cu<sub>2</sub>O and BiVO<sub>4</sub> and enabled STH efficiencies exceeding 3.2% to be achieved for 120 h. The overall efficiency is limited by the relatively large bandgap of the BiVO<sub>4</sub> (2.4 eV). For optimal dual photoabsorber tandem cells, the cuprous oxide should be paired with a smaller bandgap partner.<sup>50,51</sup>

**Future Research with Cu<sub>2</sub>O.** High-efficiency and durable cuprous oxide photosystems have thus far been achieved using thin films. Since high-quality Cu<sub>2</sub>O can be achieved through thermal oxidation of copper foils, scaling up such devices could be relatively straightforward (starting from larger copper foils), assuming protective overlayer technology advances to the point where pinhole formation over large areas can be eliminated. While it is not impossible that such an advance can be achieved at low cost, it seems unlikely. Moreover, pathways forward to

cost-effective solar water splitting based on thin-film PEC devices are challenging.<sup>10</sup> In contrast, photocatalytic systems can potentially generate low-cost solar hydrogen with only modest efficiency and durability requirements.<sup>10</sup> Although many researchers have considered the co-generation of hydrogen and oxygen gases non-viable for safety reasons, Domen et al. have already demonstrated a 100 m<sup>2</sup> photocatalytic panel reactor that operated safely for more than one year.<sup>52</sup> Intentional explosion tests of the H<sub>2</sub>/O<sub>2</sub> gas mixtures in various parts of the system were surprisingly undramatic, compared to the Hindenberg image that one typically conjures. Relaxation of the constraint to keep the evolved gases separated in the water-splitting device has important implications for reactor design and cost. Efficient and safe separation of H<sub>2</sub> from H<sub>2</sub>/O<sub>2</sub> gas mixtures is therefore a topic of high interest in enabling new disruptive water-splitting technologies to emerge.

Efficient and safe separation of H<sub>2</sub> from H<sub>2</sub>/O<sub>2</sub> gas mixtures is a topic of high interest in enabling new disruptive water-splitting technologies to emerge.

While there is substantial literature on Cu<sub>2</sub>O for photocatalysis (dye degradation, H<sub>2</sub> evolution, and CO<sub>2</sub> reduction),<sup>53–56</sup> the photostability remains a challenge. Nevertheless, the photocatalytic approach is particularly advantageous for materials that are intrinsically unstable in water, such as cuprous oxide. In thin films of Cu<sub>2</sub>O, a single pinhole in the protective layer will lead to eventual degradation of the entire film. Photocatalytic sheets or particle reactors represent a pixelation approach analogous to Figure 4, where imperfectly protected Cu<sub>2</sub>O particles will corrode, and the others will survive and perform. Moreover, particle reactors can operate in pure water (pH 7) without electrolyte salts, as the protons do not need to move very far, which is expected to improve the durability of overlayers and surface co-catalysts. A new exciting research direction is the development of cost-effective and simple corrosion protection methods for high-quality Cu<sub>2</sub>O particles<sup>57,58</sup> and their combination with photoanode particles, either in dual-particle photocatalytic sheets<sup>59</sup> or as Janus particles.<sup>60</sup> A key challenge will be to find interface treatments and/or protection layer strategies that are compatible with the photoanode particles that are coupled to the Cu<sub>2</sub>O photocathode particles.

Thin-film studies of these materials will still be essential to enable powerful *in situ* or *operando* characterization of novel material combinations (i.e., protective overlayers and co-catalysts) such as dual working electrode<sup>61,62</sup> and impedance spectroscopy,<sup>63,64</sup> which can then inform the synthesis of photocatalytic systems, where characterizing the internal processes is much more challenging. The large body of work described above on thin-film Cu<sub>2</sub>O provides many strategies for translation to photocatalytic sheets or particles. For example, how can one ensure an ohmic and/or charge-selective contact to the sheet material or to the other particle? For Cu<sub>2</sub>O, prior work points to Au, a copper–nickel mixed oxide, or CuSCN. How can one ensure a good photovoltage in the particle? Surface etching combined with a Ga<sub>2</sub>O<sub>3</sub> layer and/or a molecular dipole layer buried underneath a protective TiO<sub>2</sub> layer might work. How to ensure durability? TiO<sub>2</sub> and different organic layers have proven effective. Again, any pinholes in the protective overlayer will result in corrosion of the Cu<sub>2</sub>O particle, but due to the effective

pixelation, those particles without pinholes will likely meet the durability requirements for low-cost solar hydrogen with the photocatalytic particle approach (~1 year).<sup>10</sup>

There is much work to be done, and it is not a priori clear how to translate the state-of-the-art thin-film Cu<sub>2</sub>O photocathode device to a particle configuration, or which photoanode partner material will provide the right balance of efficiency, Earth abundance, and cost. Moreover, the two particles that make up the sheet will likely have different work functions, and forming an ohmic contact to each particle with a single sheet material may be challenging. But that is the fun part, which will require creativity and new discoveries along the way. It is my hope that rapid progress on this technology will be made in the near future to enable the large-scale production of cost-competitive green hydrogen without the need for subsidies.

## AUTHOR INFORMATION

### Corresponding Author

S. David Tilley – Department of Chemistry, University of Zurich, Zurich 8057, Switzerland; [orcid.org/0000-0002-7542-1147](https://orcid.org/0000-0002-7542-1147); Email: [david.tilley@chem.uzh.ch](mailto:david.tilley@chem.uzh.ch)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acseenergylett.3c00578>

### Notes

The author declares no competing financial interest.

## ACKNOWLEDGMENTS

The author thanks the University of Zurich and the University Research Priority Program LightChEC for financial support of our research. The author additionally thanks Jan Bühler for preparing Figure 1.

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