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# A tipping point for solar production of hydrogen?

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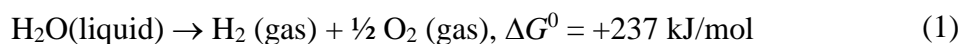
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## Summary

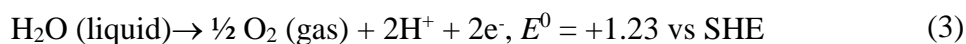
In a recent issue of *Nature*, Zhou *et al.*<sup>1</sup> report an artificial photosynthesis scheme which splits water into hydrogen and oxygen with an overall energy efficiency of nearly 10%, close to the value needed for commercial viability. This Preview provides a technological context for this advancement and discusses needed next steps.

## Narrative

Hydrogen has been proposed as an energy carrier which could prospectively replace the fossil fuels now used for this purpose.<sup>2</sup> If the hydrogen can be generated by “green” methods, such an approach could be a crucial element of a sustainable energy economy.<sup>3</sup> The fixed carbon sources which we now use to power most of the world’s economy – coal, gas, and oil – were originally made by photosynthesis. What if we could engineer systems which could use sunlight in a similar manner to make the energy carriers of the future? This is the premise of artificial photosynthesis (AP), which we illustrate here in its simplest form, water splitting:

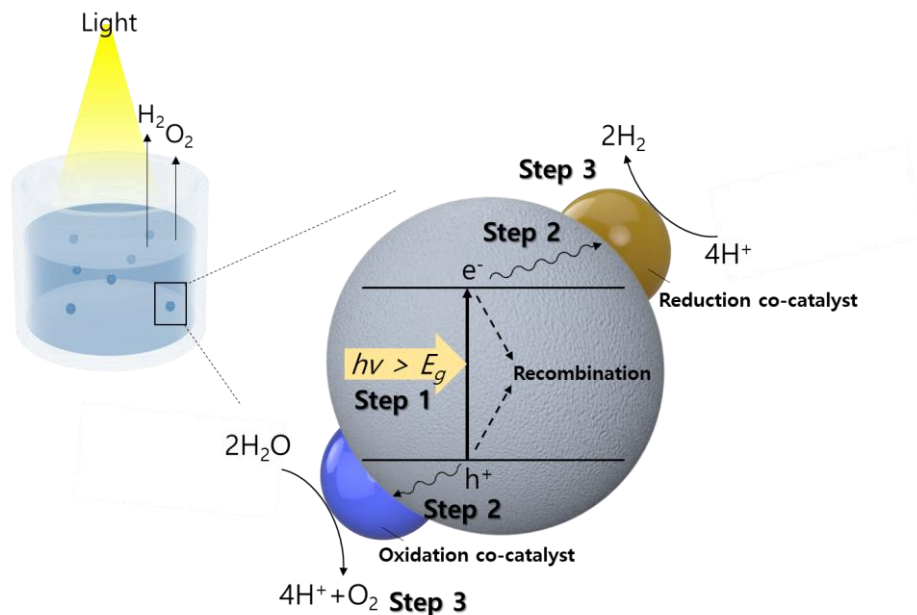


The large and positive free energy change for this reaction under standard conditions is the reason that water does not spontaneously dissociate into hydrogen and oxygen at room temperature. Yet many of us may remember splitting water in our high school chemistry lab using electrodes immersed into a beaker. How was this possible? The key concept is that a new reactant was added, namely the electrons which are available from the metal electrodes. We can rewrite Reaction (1), as two “half reactions,” one of which consumes electrons while the other one generates them to maintain charge balance:



If electrons can be provided two different places with a potential difference of at least 1.23 V, and there is a means to provide proton transport between these places, water splitting into H<sub>2</sub> and O<sub>2</sub> is possible, as the high school experiment showed. This concept is the basis of water electrolysis.

In artificial photosynthesis light-absorbing material is used to drive Reactions (2) and (3) directly. Figure 1 shows how this is possible using a semiconductor particle which can absorb light with energy equal or greater than its band gap to generate electrons and “holes” (the absence of electrons). If the semiconductor is in contact with water, electrons can perform Reaction (2), making H<sub>2</sub>, and holes can perform Reaction (3), making O<sub>2</sub>.



**Figure 1.** Photocatalytic solar water splitting using a semiconductor absorber combined with hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) catalysts. In Step 1, electrons and holes are generated by the absorption of light with energy higher than the band gap of the semiconductor. In Step 2 photon-excited electrons and holes diffuse to the HER and OER catalysts, respectively, with recombination being an undesirable loss process. In Step 3, electrons reduce  $H^+$  to  $H_2$  (Reaction 2), and holes oxidize water to  $O_2$  (Reaction 3).

There are many ways to combine semiconductors and catalysts to couple sunlight to Reactions (2) and (3).<sup>4</sup> However, using a single semiconductor, in small particle or nanoparticle form, integrated with catalysts which facilitate the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), is conceptually the simplest.<sup>5</sup> Moreover, there are compelling arguments that such an approach would be scalable if the photocatalyst were made of earth-abundant elements.

In principle, any semiconductor with a bandgap of greater than 1.23 eV (corresponding to wavelengths shorter than 930 nm) can generate electrons with a sufficiently negative potential to perform Reaction (2) and holes with a sufficiently positive potential to perform Reaction (3), although a larger bandgap will be required for the conversion rate to be appreciable. As discussed in Zhou *et al.*<sup>1</sup> and more rigorously in Fontaine *et al.*<sup>6</sup> the theoretical maximum conversion efficiency of sunlight to the free energy of  $H_2$  and  $O_2$  can approach the detailed balance limit for single junction solar cells, i.e. 30%.

More practically, both techno-economic and life cycle energy balance analyses predict that a minimum efficiency of 10% and 5-10 year operational lifetime will be necessary for large-scale deployment.<sup>7</sup> However, in stark contrast to photovoltaic power generation, the dream of large-scale artificial photosynthesis has yet to be realized. Researchers have struggled to reduce the rate of recombination of the electrons and holes depicted in Figure 1, which makes them unavailable for the water splitting reactions at the photocatalyst surface. For this reason, the highest reported efficiencies for water splitting performed with particulate photocatalysts are on the order of a few percent or less,<sup>7</sup> falling well short of what is required.

In this context, the report of Zhou *et al.*<sup>1</sup> is highly notable for its claim of 9% solar to hydrogen

(STH) conversion efficiency in the laboratory and 6% outside using natural sunlight. Not only are these values much larger than all prior reports using particulate photocatalysts, they also exceed the photovoltaic power conversion efficiencies reported for the same semiconductor absorber they used.<sup>8</sup> Below, we will discuss some of the fundamental insights which led to this “world record” report and also discuss some limitations of the study.

First, Zhou *et al.*<sup>1</sup> employed a semiconductor absorber with a smaller bandgap compared to the many of the metal oxides which have been used in prior work. Their absorber, which is composed of alloys of InN and GaN (InGaN) grown in nanowire form on silicon, has a range of bandgaps, the lowest being about 1.9 eV, allowing the wires to capture a significant fraction of the solar spectrum. The InGaN quality is exceptionally high, which reduces carrier recombination, and the charge transfer to the HER (Cr<sub>2</sub>O<sub>3</sub>/Rh) and OER (Co<sub>3</sub>O<sub>4</sub>) catalysts appears to be effective.

Secondly, the authors employed concentrated solar light for illumination (up to 38x), which is easily achieved using inexpensive Fresnel lenses. This not only increases the rate at which electrons and holes are generated and made available for Reactions (2) and (3), it can also reduce their recombination by filling the “trap” states which mediate this process.

Finally, importantly, the work emphasizes the importance of suppressing the reverse of Reaction 1, which is strongly downhill.<sup>9</sup> This is done by reducing the activity of the O<sub>2</sub> and H<sub>2</sub> which appear on the product side of (1), in a nice demonstration of Le Chatelier's principle. This is experimentally implemented by operating the reactor at reduced pressure, with the headspace of the reactor being, initially, water vapor only. Interestingly, when the reactor is operated in this way, the initial efficiency is high but declines and drops to zero after 40-50 minutes when the forward rates of (2) and (3), which are driven by light, are balanced by the reverse of (1) as the O<sub>2</sub> and H<sub>2</sub> activities increase. Reapplying the vacuum, which has the effect of degassing the water, resets the system, and high efficiencies can be observed again. Over 70 cycles of operation were demonstrated in this way.

Further, they investigated, with electronic structure calculations, the ability of the surfaces of the materials they used to catalyze H<sub>2</sub> and O<sub>2</sub> recombination via the reverse of reaction (1). The reaction is predicted to be slow on Cr<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> (adsorbed water blocks the surface) but fast on Rh. Authors posit the rate of this reverse reaction will decrease with temperature and find, consistent with this hypothesis, that the initial STH efficiency increases with temperature up to about 70 °C. Heating of the reactor is synergistic with the solar concentration they employed and was accomplished in their large-scale outdoor demonstrations by simply insulating the reactor.

On a fundamental level, this work shows the importance of considering losses due to H<sub>2</sub> and O<sub>2</sub> recombination in photocatalytic water splitting. This loss channel is possible because H<sub>2</sub> and O<sub>2</sub> are co-generated in closed proximity to each other as opposed to being separated by membrane barriers or other means as in photoelectrocatalysis and electrolysis. It is possible that the findings of Zhou *et al.*<sup>1</sup> might apply more generally such that previously studied photocatalysts would have substantially higher initial STH efficiencies if operated under conditions which suppress the activity of the H<sub>2</sub> and O<sub>2</sub> products. The work might also inspire a rethinking of the choice of catalysts, optimizing not only the activity for HER and OER but, at the same time, suppressing the activity for H<sub>2</sub>/O<sub>2</sub> recombination. It is possible that some of the extensively investigated non-precious metal catalysts might have these properties.

Technologically, the attainment of close to 10% STH efficiency is exciting, as it approaches benchmark values for commercialization. Still, some caution is in order. It is noted that while

high temperature operation increases the initial STH efficiency, the steady-state of zero net H<sub>2</sub> production appears to be reached more quickly such that more frequent pumping cycles will be required. For this reason, until the energy costs of operating the system in this cyclic manner are quantified, efficiency numbers should not be compared directly to those from systems which operate continuously or are able to accumulate H<sub>2</sub> and O<sub>2</sub> to reasonable partial pressures.<sup>10</sup>

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