

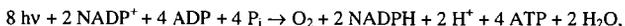
SOLAR HYDROGEN VIA A PHOTOSYNTHETIC Z-SCHEME ANALOGUE BASED ON SEMICONDUCTOR POWDERS

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ABSTRACT

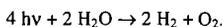
Mother Nature uses solar energy to oxidize water to O₂ and reduce protons onto NADP⁺ via dual photosystems connected by a string of redox agents. By splitting the energetically challenging task of decomposing water between two separate photochemical reactions, more abundant and lower energy solar photons can be employed. This same approach can be utilized with semiconductor powders. Based upon their electronic band structure, semiconductors can be chosen that selectively oxidize or reduce water. One can then select O₂-evolving and H₂-evolving photocatalysts, disperse or immobilize them in separate containers, and use an appropriate reversible redox agent as an electron shuttle between them. We have had some success with this photosynthetic Z-scheme analogue using an alkaline iodate redox electrolyte and a variety of semiconductor compounds, such as TiO₂ and InP. Proof of concept has been demonstrated, but various materials problems underscore the need to identify other photocatalysts.

The scientific community has long marveled at Nature's ability to perform kinetically and/or thermodynamically challenging reactions such as O₂ reduction and N₂ fixation under ambient conditions. In particular, with the rise of mankind's consciousness toward environmental preservation and the need for a sustainable energy supply, we have sought ways to emulate Nature and develop our own approach to the light reaction of photosynthesis, where solar energy is stored by photo-oxidatively decomposing water to O₂ and synthesizing adenosine triphosphate, ATP, and reduced nicotinamide adenine dinucleotide phosphate, NADPH:



where hv refers to light quanta and P_i is a phosphate oxyanion, HPO_4^{2-} .

In particular, we would like to skip the various phosphorylations and nicotinamide reductions and simply photo-decompose water to its constituent elements:



This energy-storing reaction would become the basis of the "Solar-Hydrogen Economy."

Even though the water-splitting reaction is mechanistically less ambitious than the overall photosynthetic reaction, the challenge is the same: how to use abundant, relatively low energy photons to drive a chemical system thermodynamically uphill.

Because the water decomposition process can be described in terms of a redox reaction or half cell reactions, it is convenient to look at the free energy relationships in terms of its voltage equivalent. The cell voltage corresponding the standard Gibbs free energy change for water decomposition is:

$$\begin{aligned} \Delta E^0 &= -\Delta G^0 / nF = -(-56.6 \times 10^3 \text{ cal/mol})(4.184 \text{ J/cal}) / (2 \text{ equiv/mol})(96485 \text{ Coul/equiv}) \\ &= 1.23 \text{ V.} \end{aligned}$$

The various photosynthetic reactions can also be viewed in terms of their redox potentials. The general trend is shown in Figure 1a. Mother Nature has developed two photosystems; one for oxidative water splitting, one for reducing NADP⁺. An electron transfer chain of redox reactions connects them. Note that the redox potential is shifted by an amount corresponding to the energy of the photon that was absorbed. The zigzag shifting of redox potential energy as an electron courses through the photosynthetic light reaction has engendered the appellation "Z-scheme" [1].

To enable water oxidation to occur, a ground state electron must be promoted from an energy level positive of +0.82 V at neutral pH (the standard state value calculated above assumes unit protonic activity, or approximately 1.0 M acid). To reduce the first acceptor state in the electron transfer chain (plastoquinone), one needs a redox potential of about 0.0 V. An excited state electron in chlorophyll *a* at 680 nm has an energy of 1.83 eV; therefore, in analogy to overpotentials in electrolysis, Nature is putting an extra eV of energy into the redox system to make sure there is a driving force on the reaction.

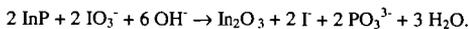
We have been attempting to put together our own water-splitting Z-scheme utilizing immobilized semiconductor powders, or photocatalysts, as our photosystem elements. We needed one material that would be O₂-evolving under illumination, and another that would be H₂-evolving. For this purpose we were able to draw from the wealth of photoelectrochemical work done over the last 25 years. Mainly because of the requirement to exhibit long term aqueous stability, most semiconductor materials are eliminated and only a few choices remain. For the water-oxidizing photocatalyst, there are a number of transition metal oxides that have been used as photoanodes, such as SnO₂, ZnO, WO₃, Fe₂O₃, and TiO₂. For the H₂-evolving photocatalyst, one can consider various photocathode materials; most of these have been metalloid phosphides and arsenides, such as GaP, InP, and GaAs. We chose TiO₂ and InP as the initial photosystem pairing.

To provide an electron transfer chain between our two photosystems, we needed to identify a "redox mediator", a reversible redox couple that would be highly soluble, optically transparent, allow facile charge transfer kinetics between the TiO₂ and InP dispersions. After testing many possible redox couples [2], it was decided to concentrate on the I/IO₃⁻ and Br⁻/BrO₃⁻ systems in alkaline solution. In particular, the IO₃⁻ couple best facilitated an even split of the energy-storing requirement between the two photosystems.

In Figure 1b, the corresponding energy level diagram for the photocatalytic system is shown. The valence band edge of TiO₂ becomes the ground state electronic energy for the reaction center in Photosystem II. The photogenerated hole is easily capable of performing water oxidation. The conduction band is the excited state donor level that injects electrons into the electron transfer chain, which in our case is simply IO₃⁻ ion. Having been reduced to I, the redox mediator migrates to the InP dispersion, or Photosystem I, where it is reoxidized by valence band holes in the InP photocatalyst. Photogenerated electrons in the conduction band of InP are energetically capable of reducing water to H₂.

We have studied each photocatalytic system separately and confirmed that the TiO₂/IO₃⁻ system evolved O₂ and only O₂, and that the InP/I system evolved H₂ and only H₂. Data for O₂-evolution from various TiO₂ particle dispersions are shown in Table I. The positive effect of adding a 1.0% by weight coating of noble metal co-catalyst is clearly evident. It is also clear that IO₃⁻ or some other electron acceptor must be present to achieve a reasonable photoreaction rate. While TiO₂ is satisfactory in terms of showing proof of concept, with a band gap of 3.0 eV, it is not an effective absorber of solar radiation. Narrower band gap materials need to be identified.

The InP, while showing initial H₂ evolution, would slow to virtually nothing after about an hour of photolysis. This was initially thought to be a form of photocorrosion, but after some control experiments, it became clear that the InP was being attacked by photogenerated IO₃⁻:



Thus alternatives to the H₂-evolving photocatalyst also need to be identified.

In both the natural photosynthetic and photocatalytic schemes, there needs to be some type of ordered, spatial arrangement of the photosystems and the electron transport chain to enable efficient charge and product separation. The photosynthetic organelle is the chloroplast. In higher plants, they appear as discs or flat ellipsoids 3-10 μm across. Within the chloroplast are many stacked arrays of flattened, sac-like membranes or thylakoids. Each stack, or granum, is about 500 nm in diameter. Both photosystems are embedded in the thylakoid membrane. They consist of bundles of several hundred chlorophyll molecules and associated species forming a 175 Å particle, as shown in Figure 2.

With a formal redox potential of -0.32 V (vs NHE) at pH 7.0, NADPH would be easily oxidized by O₂. However, this reaction is prevented because they are generated on opposite sides of the thylakoid membrane. The thylakoid membrane could be thought of as a semiconductor electrode, with a directed flow of charge carriers through it.

For the photocatalytic system, we have opted to disperse the two semiconductor powders in separate modules, or beds, as shown in Figure 3. A pump circulates a working fluid containing the redox mediator between them. The product gases are thus evolved at the macro scale in separate containers. This avoids the issue of how to safely separate the H₂ and O₂ co-evolved in a 2:1 ratio, well within the combustibility range.

Theoretical studies on the solar spectrum versus photovoltaic efficiency have shown that the optimum band gap for a single material is 1.3 eV. Efficiency can be improved upon by using multiple semiconductor materials in a tandem arrangement. By carefully lining up the band edges, so that the hole current in one layer feeds the electron current in the next, one can achieve a summation of individual voltages that can have a much higher efficiency. This comes from minimizing the energy lost in thermalizing a high energy charge carrier inside a wide energy band. In particular for water-splitting, the more efficient semiconductor materials, when used as a photoelectrode, cannot generate sufficient voltage to drive the electrolysis. The use of tandem electrodes, however, has made this possible. Work by Rocheleau on triple junction a-Si pin cells [3] and by Turner on GaAs/GaInP₂ cells [4] have demonstrated water decomposition using a single photoelectrode. Reported efficiencies have recently exceeded 12.8% [5].

The dual bed photocatalytic system can be "tandemized" as well by folding one bed underneath the other as shown in Figure 4. This would be feasible as long as: 1) the top layer photocatalyst has a wider band gap than the lower layer, so that light not absorbed in the first layer is transmitted underneath; and 2) the upper photocatalyst is finely dispersed, minimizing scattering losses. One may further be able to minimize mass transport problems by finely perforating the support membrane. The redox mediator would then travel through micro-channels instead of across the top face of the membrane in one direction and then back underneath. The resulting perforated, photocatalytic tandem membrane would then no longer require a circulating fluid, eliminating that parasitic loss.

It is interesting to note that Nature decided not to tandemize her photosynthetic apparatus, i.e., Photosystems I and II have nearly the same, instead of complementary, absorption spectra. Instead, the spectral gaps between the chlorophyll maxima at 650-700 and 430-470 nm are filled by secondary pigments, such as the carotenes, phycobilins, and xanthophylls. Perhaps the lesson here is that if solar power conversion efficiency percentages in the single digit range are acceptable, then concentrating on absorbing as much light as possible and then letting all the charge carriers thermalize to an energy band edge that can do useful chemistry is the preferred approach.

ACKNOWLEDGEMENT

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Table I. O₂ Evolution from TiO₂/IO₃⁻ Suspensions

250 mg photocatalyst
50 ml 1.0 N NaOH, 0.2 M KIO₃
1000 W Xe lamp irradiation
6 hour photolysis

Photocatalyst:	TiO ₂	Pt-TiO ₂	Ir-TiO ₂	Ir-TiO ₂ w/o IO ₃ ⁻
O ₂ evolved (ml):	0.58	1.3	2.5	< 0.02

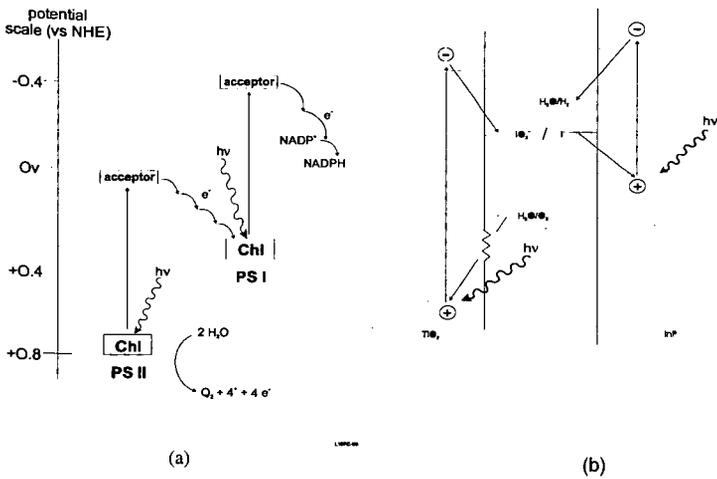


Figure 1. Energy level diagrams of: a) photosynthetic Z-scheme; and b) dual module water-splitting using semiconductor particulates.

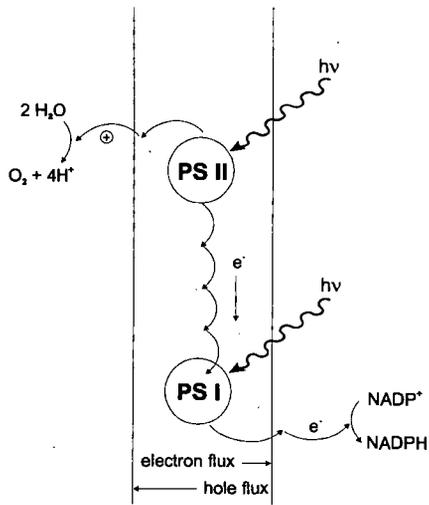
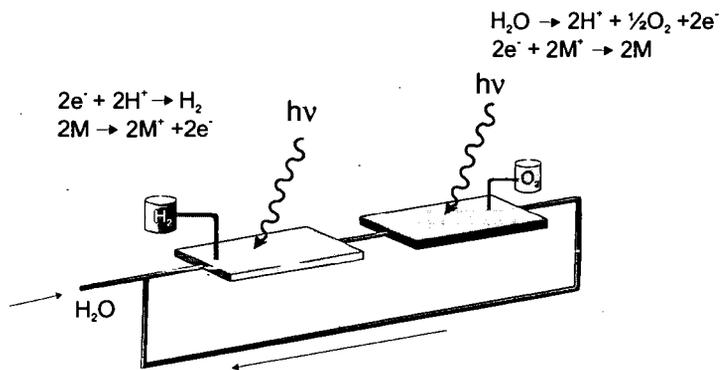


Figure 2. Schematic showing spatial arrangement of photosystems and charge flows in the thylakoid membrane of a chloroplast.



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Figure 3. Schematic of a dual bed photocatalytic water-splitting system.

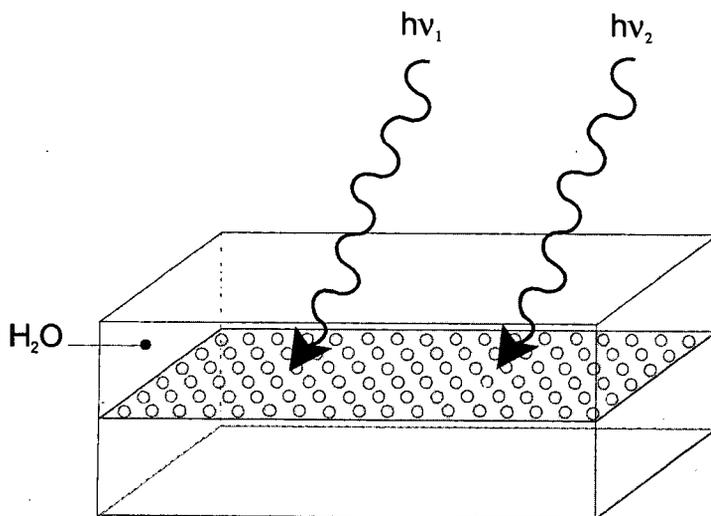


Figure 4. Schematic of a perforated, photocatalytic tandem membrane system.