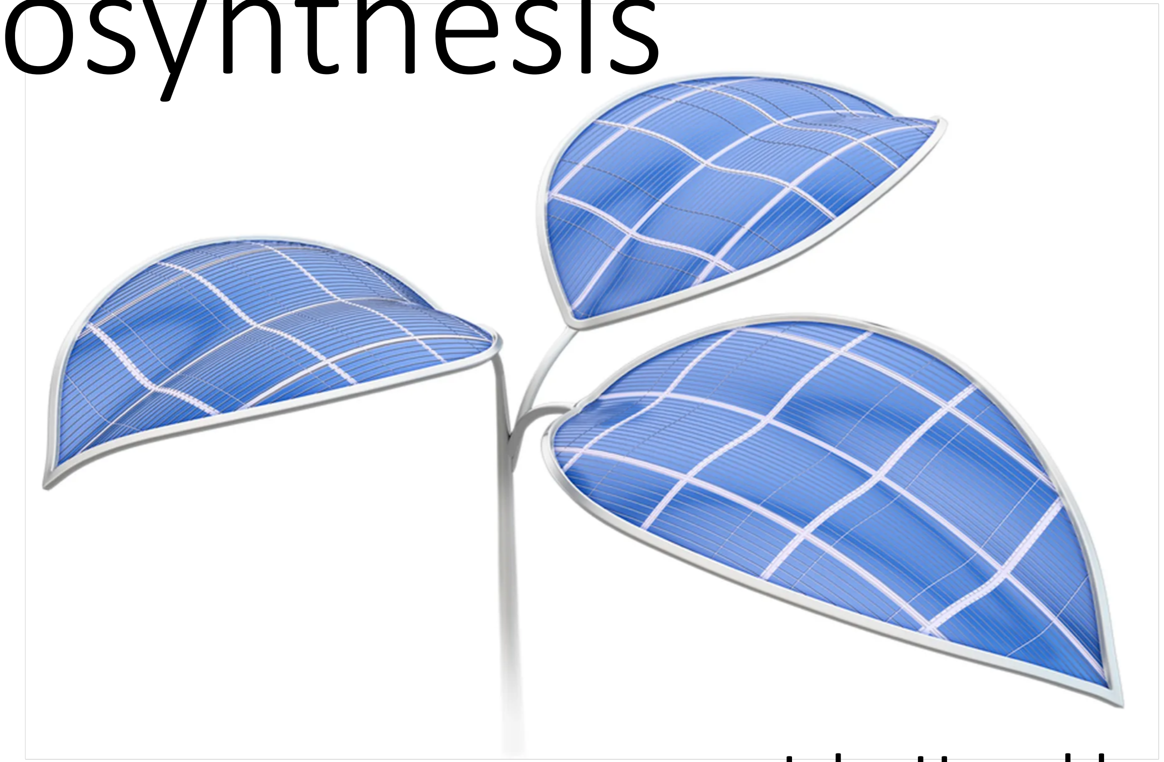
Solar Fuels and Artificial Photosynthesis



John Harrold

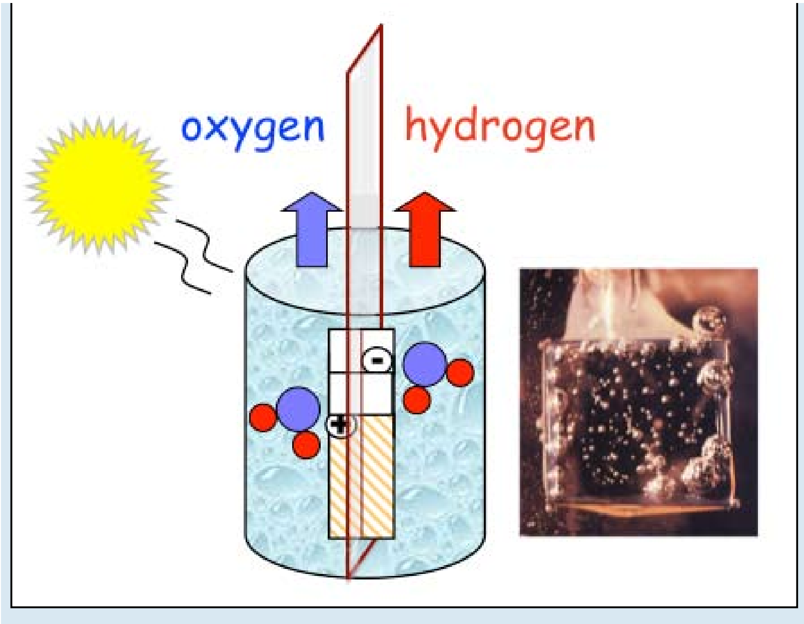
November 5th, 2021

Harvard Energy Journal Club

What are solar fuels?

Solar fuels are made with energy from sunlight stored in a chemical bond, that is designed to be released to supply energy for a process. Estimates indicate that 4.3 x 10^20 J of energy from sunlight strike the earth each hour. If this energy could be harvested is would satisfy the global energy consumption for a year. Much of the focus on conversion of solar energy utilizes photovoltaic systems rely on advanced battery technology for storage. Photosynthesis is a natural process capable of converting light energy into chemical energy by means of light dependent reactions and so called “dark reactions”. Likewise, artificial photosynthesis looks to store the solar energy in a chemical bond using sun, water, and air. These processes can lead to a chemical or solar fuel.

What are solar fuels?

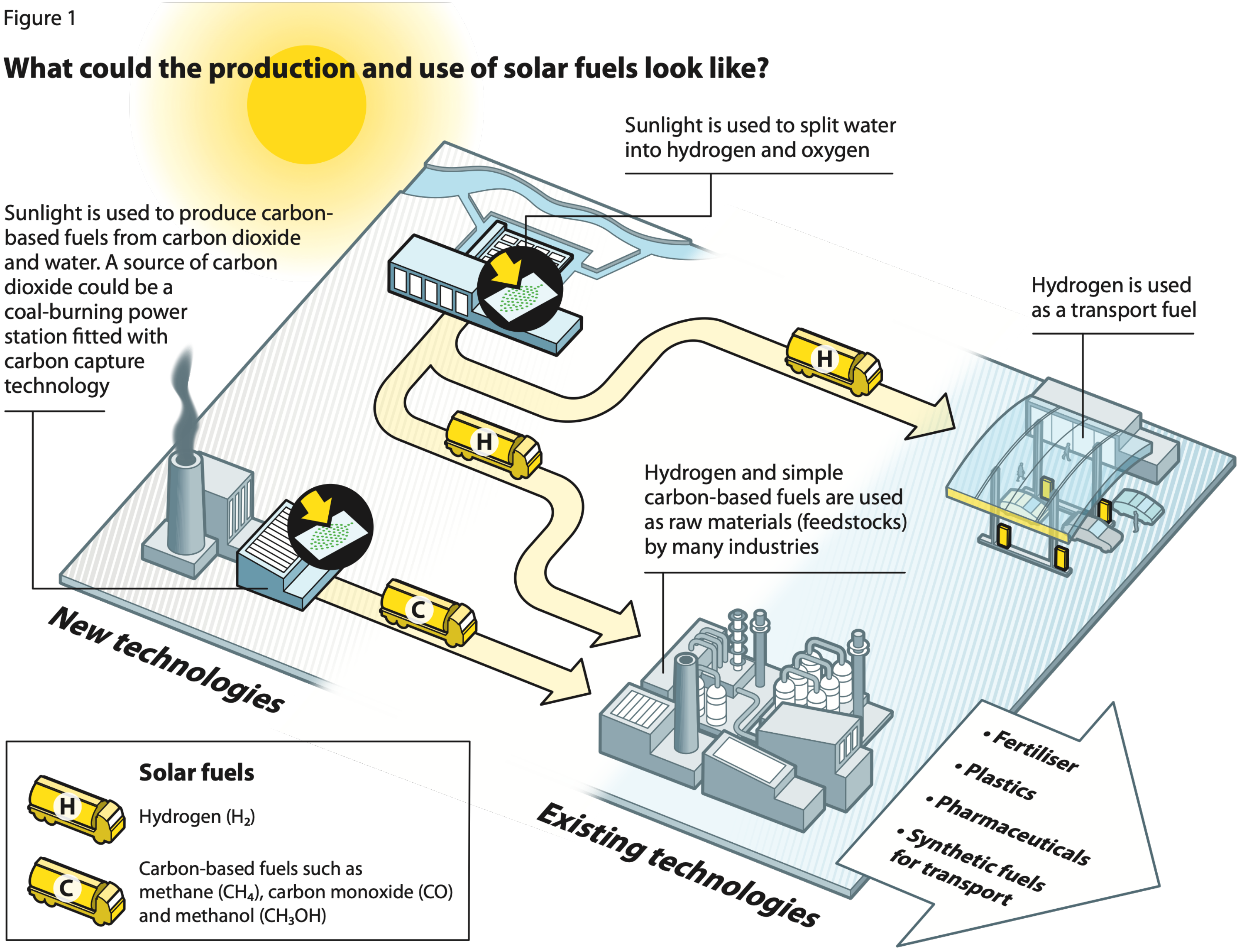


Utilizing sunlight to make fuels directly like hydrogen.

Like storing sun in a bottle

Figure 1

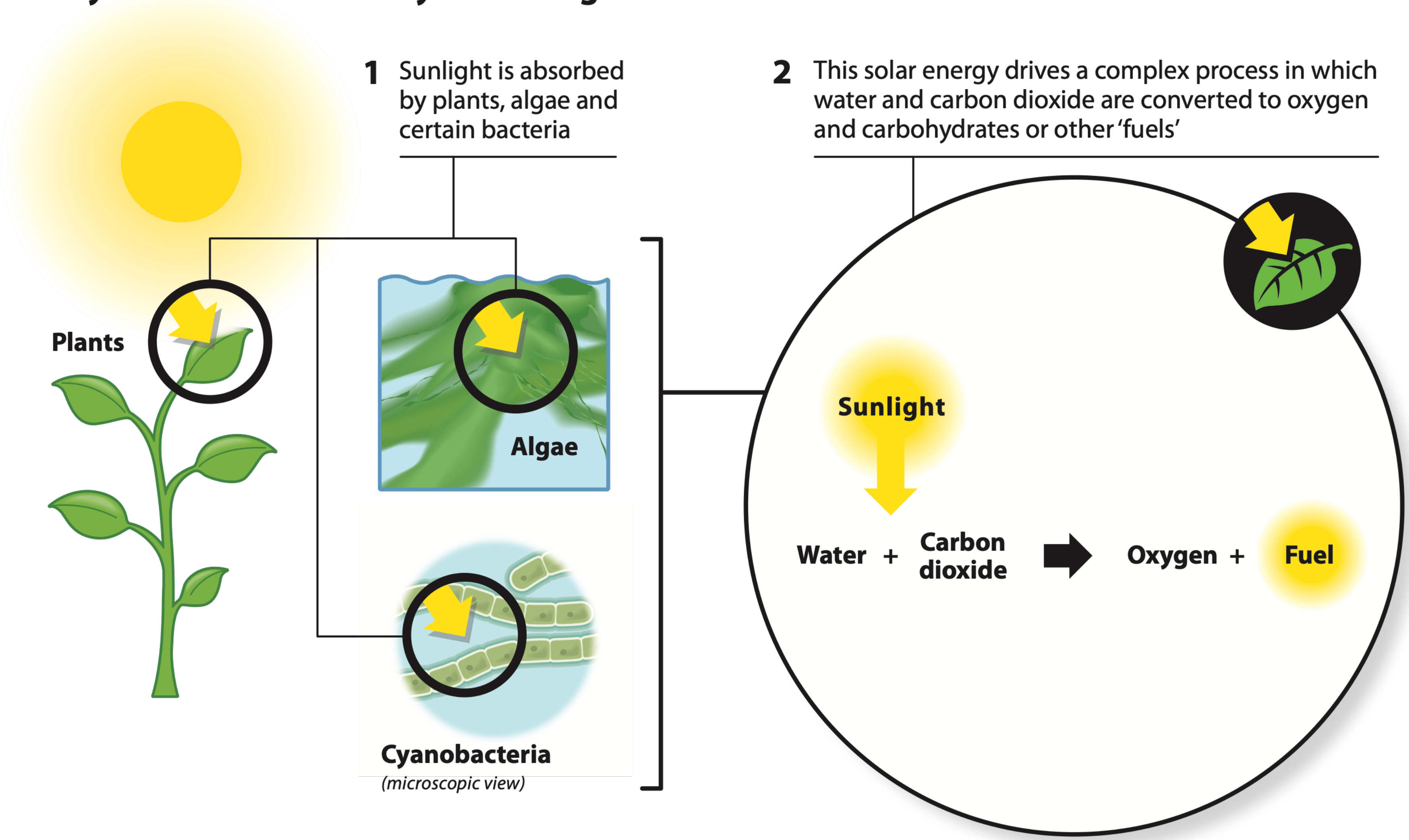
What could the production and use of solar fuels look like?



Alan Heeger, Solar Fuels and Artificial Photosynthesis, 2012 www.rcs.org

Natural Photosynthesis

Photosynthesis: Nature's way of making solar fuel



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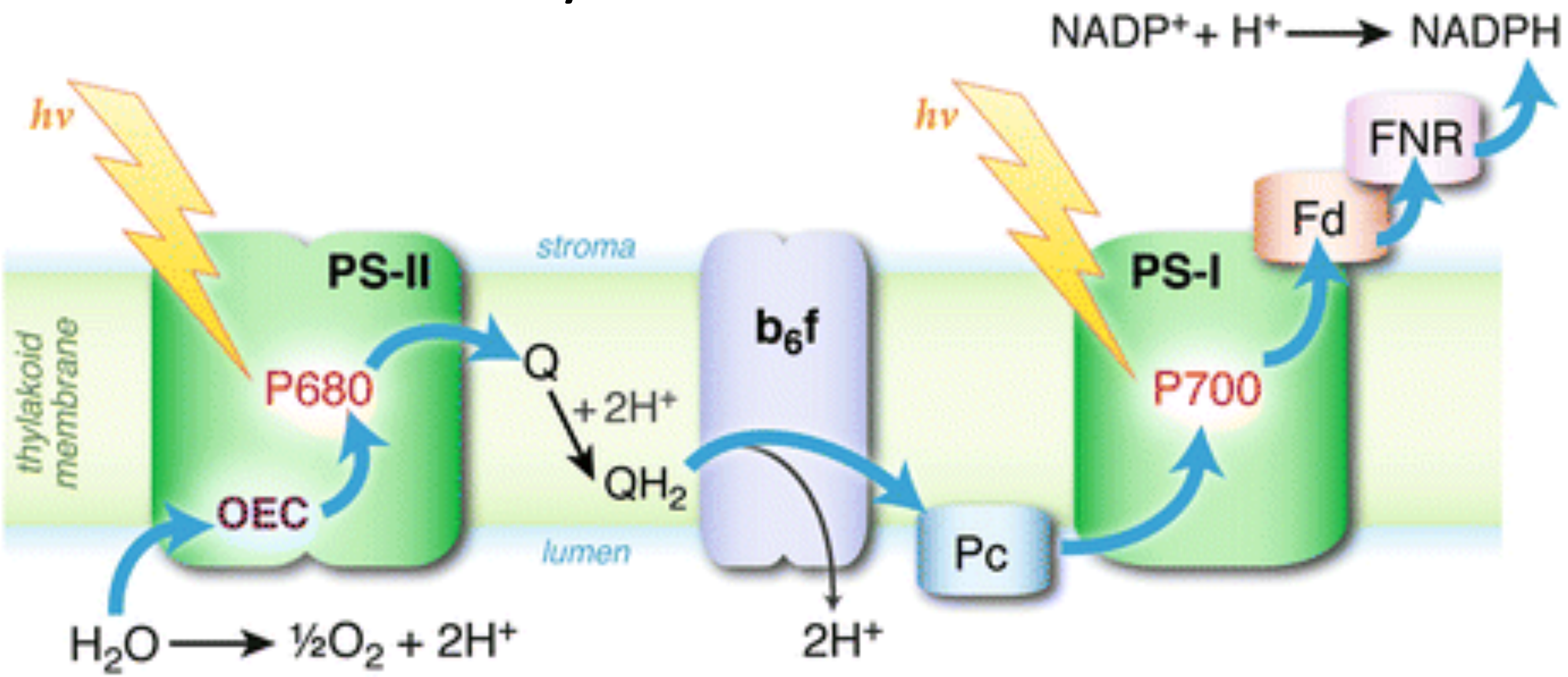
Natural Photosynthesis



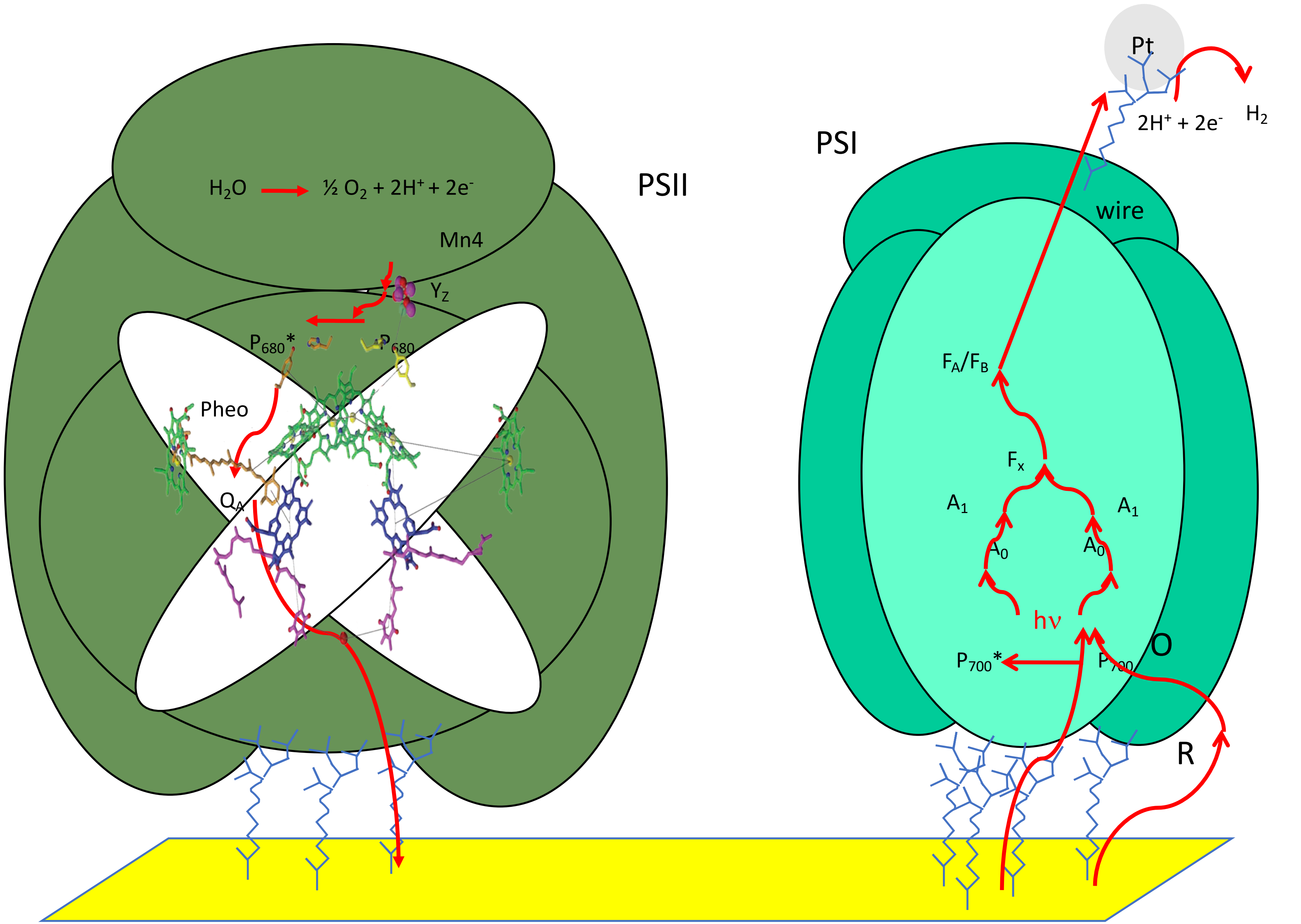
Components of the light-dependent reactions and electron transfer in oxygenic photosynthesis. *Blue arrows* indicate the flow of electrons from H_2O to NADPH. *Q*plastoquinone, *Pc* plastocyanin, *Fd* ferredoxin, *FNR* ferredoxin-$NADP^+$ reductase

Krewald V., Retegan M., Pantazis D.A. (2015) Principles of Natural Photosynthesis. In: Tüysüz H., Chan C. (eds) Solar Energy for Fuels. Topics in Current Chemistry, vol 371. Springer, Cham. https://doi.org/10.1007/128_2015_645Solar Energy for Fuels: Harun Tüysüz and Candace K. Chan 2015

Methods of generating solar fuels

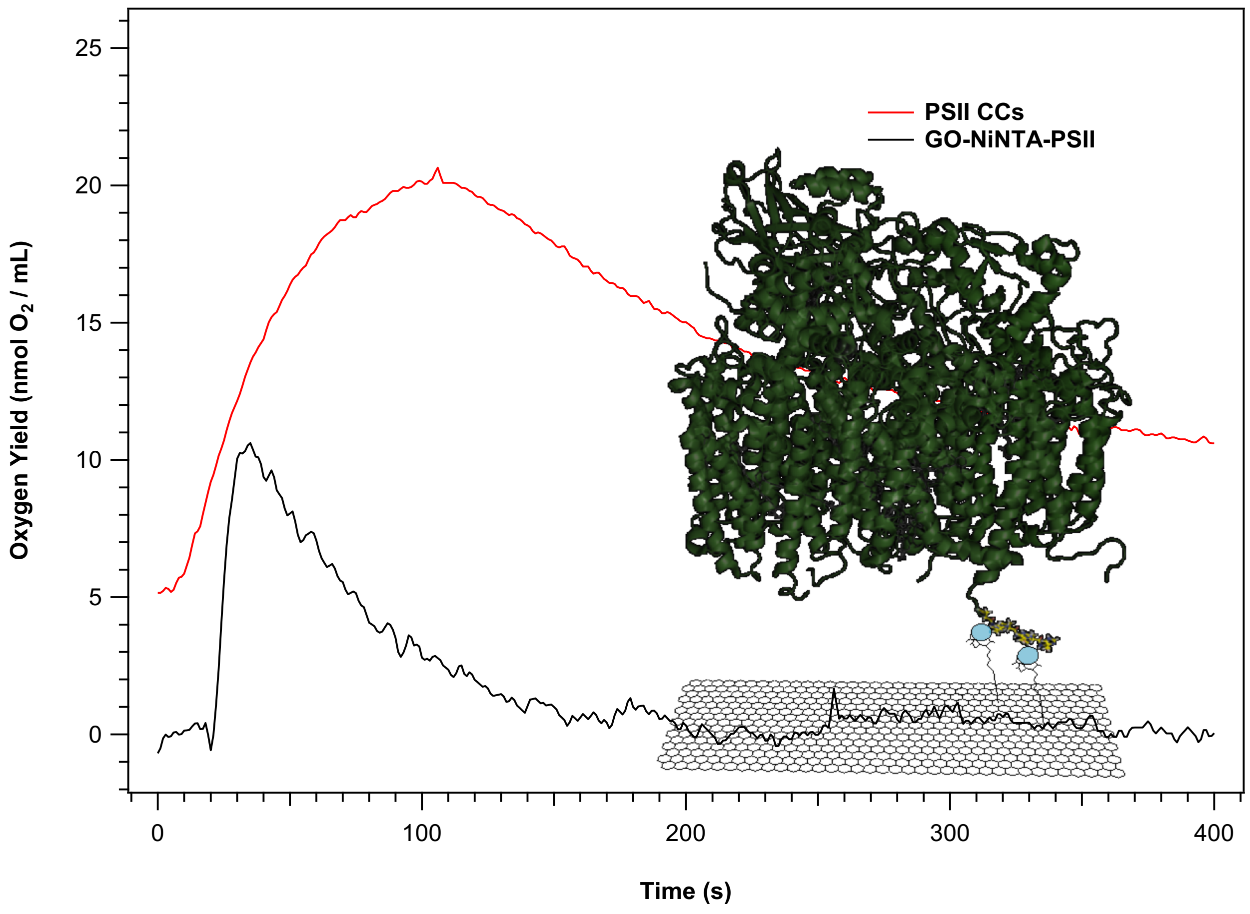
- Biohybrid Solar cells
- Biomimetic Water-Oxidation Catalysts
- Solar Water Splitting Using Semiconductor Photocatalyst
- Solar concentrators

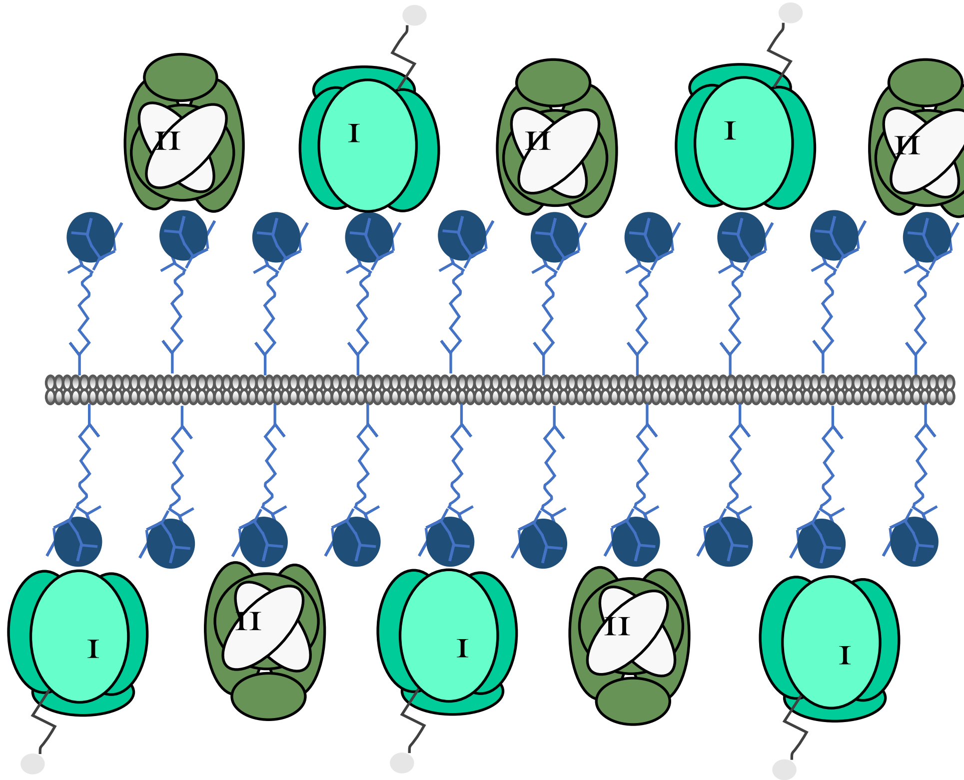
Biohybrid solar system example



Harrold Jr, J.W., 2014. *Assembly of natural photosynthetic components on graphene oxide and gold surfaces for light energy transduction*. Rutgers The State University of New Jersey-New Brunswick.

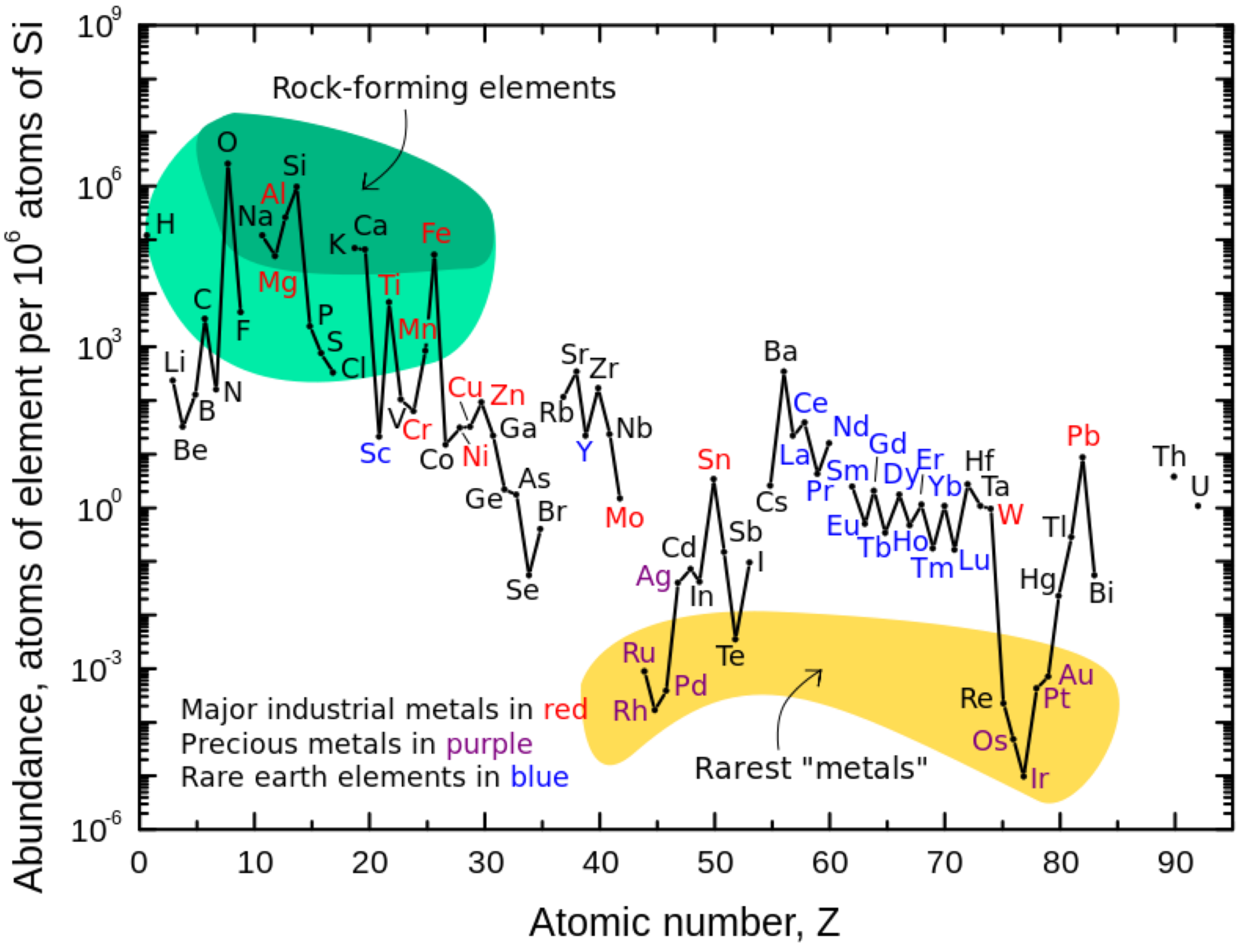
Photosynthetic core complexes



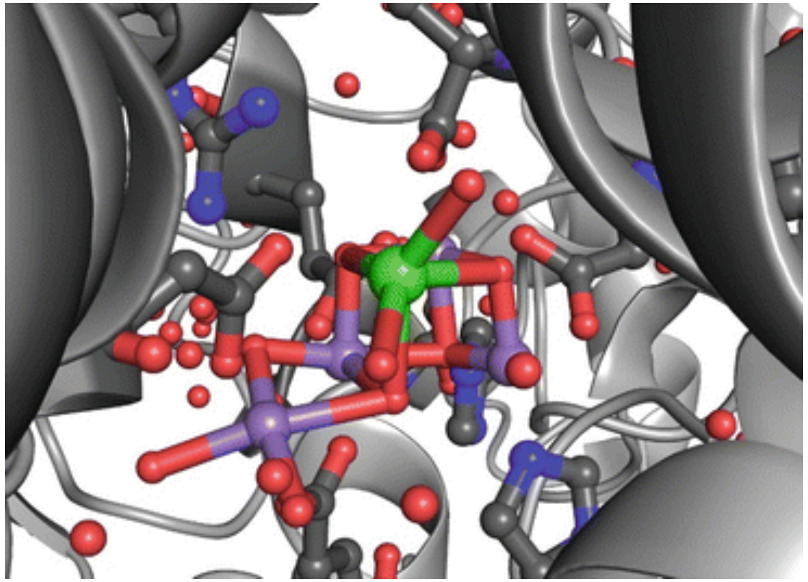


Harrold Jr, J.W., 2014. *Assembly of natural photosynthetic components on graphene oxide and gold surfaces for light energy transduction*. Rutgers The State University of New Jersey-New Brunswick.

Earth Abundance of Elements



Biomimetic Water-Oxidation Catalysts

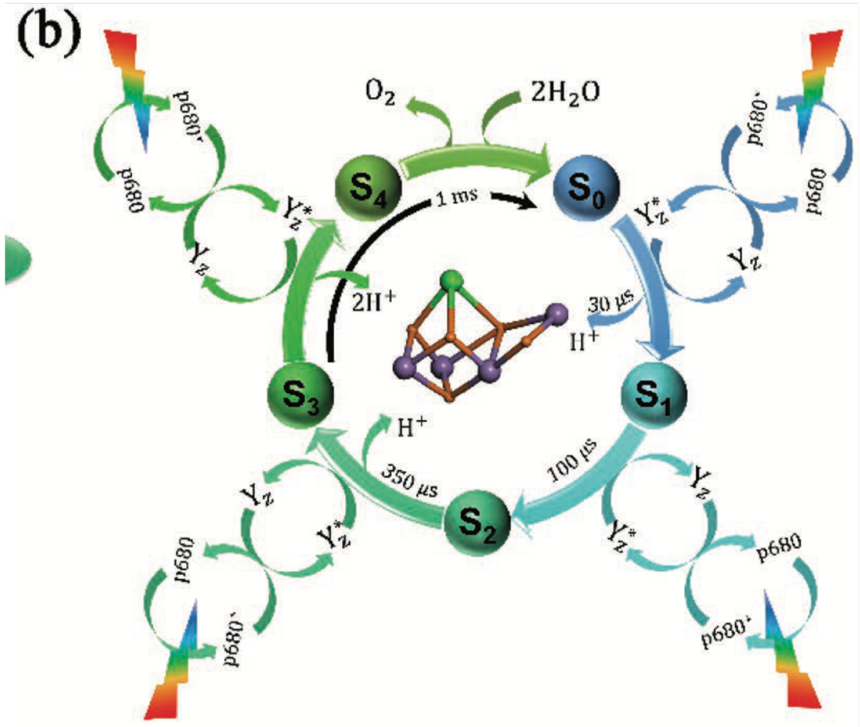


Architecture of the oxygen-evolving-complex (OEC) of Photosystem II, coordinates Suga et al.

Mn: *purple*; Ca: *green*; O: *red*; C: *grey* and N: *blue*. As hydrogen atom coordinates could not be directly detected, *red spheres* might indicate the O positions for O^{2-}, OH^- or H_2O

Biomimetic Water-Oxidation Catalysts: Manganese Oxides, Philipp Kurz
Solar Energy for Fuels, 2015 Harun Tüysüz and Candace K. Chan.

Suga, M., Akita, F., Hirata, K., Ueno, G., Murakami, H., Nakajima, Y., Shimizu, T., Yamashita, K., Yamamoto, M., Ago, H. and Shen, J.R., 2015. Native structure of photosystem II at 1.95 Å resolution viewed by femtosecond X-ray pulses. *Nature*, *517*(7532), pp.99-103.



b) The Kok cycle showing a consecutive series of five intermediate S-states (S_0, S_1, S_2, S_3, and S_4) along with the redox reactions and release of protons.

Ye, S., Ding, C., Liu, M., Wang, A., Huang, Q. and Li, C., 2019. Water oxidation catalysts for artificial photosynthesis. *Advanced Materials*, *31*(50), p.1902069.

Biomimetic Water-Oxidation Catalysts

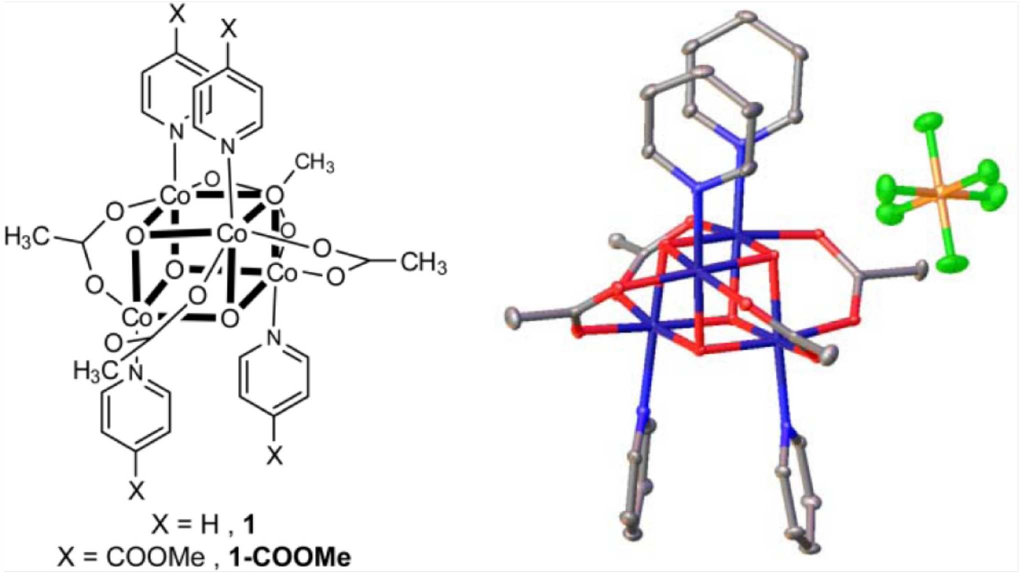
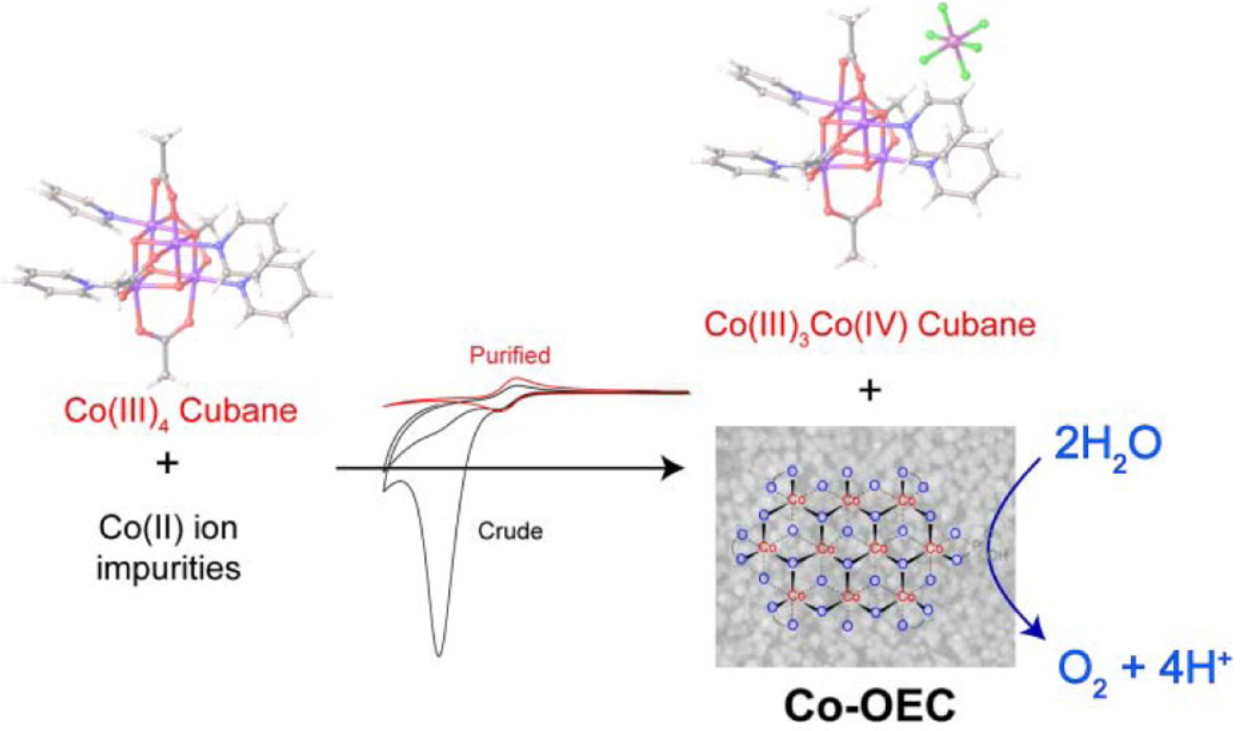
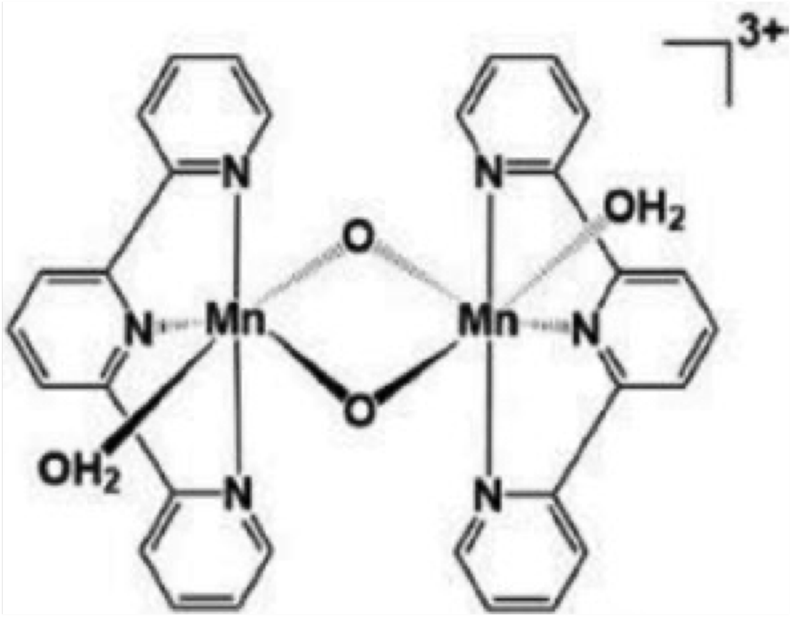


Figure 1. (left) Molecular structure of Co_4O_4 cubane structure **1** and (right) thermal ellipsoid representation at the 50% probability level of the one-electron oxidized cubane, **1**[$\mathbf{PF_6}$]. Hydrogen atoms and an acetonitrile molecule have been omitted for clarity. Atoms are color-coded: gray (carbon), blue (nitrogen), red (oxygen), dark blue (cobalt), green (fluorine), and yellow (phosphorus).

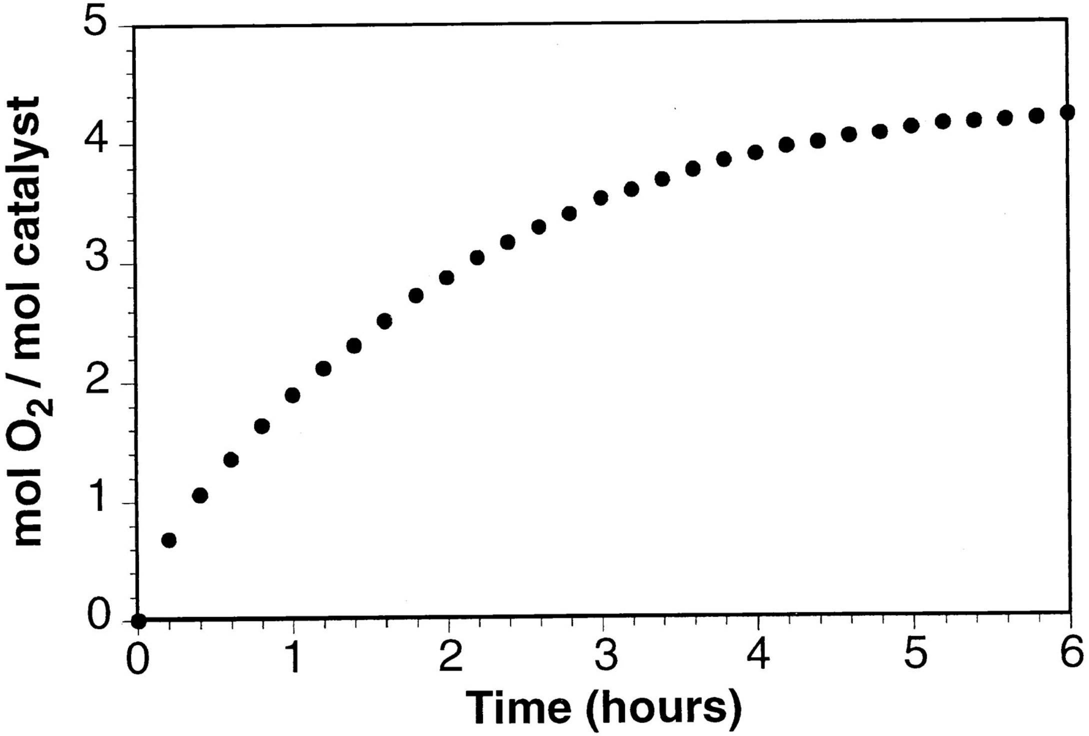


Ullman, A.M., Liu, Y., Huynh, M., Bediako, D.K., Wang, H., Anderson, B.L., Powers, D.C., Breen, J.J., Abruña, H.D. and Nocera, D.G., 2014. Water oxidation catalysis by Co (II) impurities in Co (III) 4O4 cubanes. *Journal of the American Chemical Society*, *136*(50), pp.17681-17688.

Water-Oxidation Catalysts



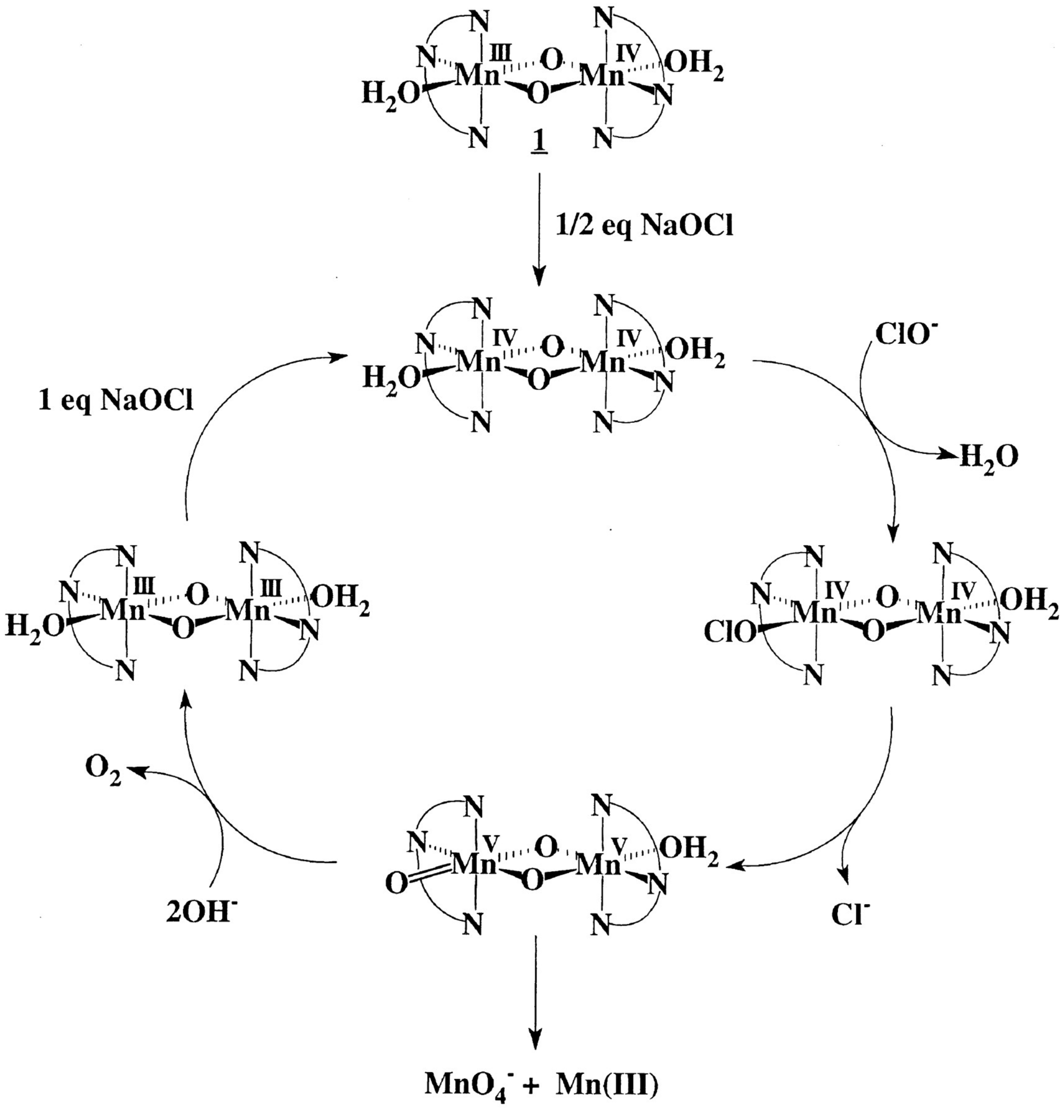
Limburg, J., Vrettos, J.S., Liable-Sands, L.M., Rheingold, A.L., Crabtree, R.H. and Brudvig, G.W., 1999. A functional model for OO bond formation by the O2-evolving complex in photosystem II. *Science*, *283*(5407), pp.1524-1527. via DOI: 10.1002/adma.201902069



O_2 evolution versus time for a solution containing 0.05 µmol of **1** in 4 ml of 0.07 M NaClO at pH = 8.6 ([**1**] = 12.5 µM).

Water-Oxidation Catalysts

A simplified proposal for the reaction mechanism of the formation of O_2 from the reaction of **1** with NaClO. A Mn(V)=O dimer is produced by the oxidation of the IV/IV dimer, and then, the O–O bond-forming step could involve a nucleophilic attack of OH^- on the oxo group. Permanganate would form by the disproportionation of the V/V dimer.



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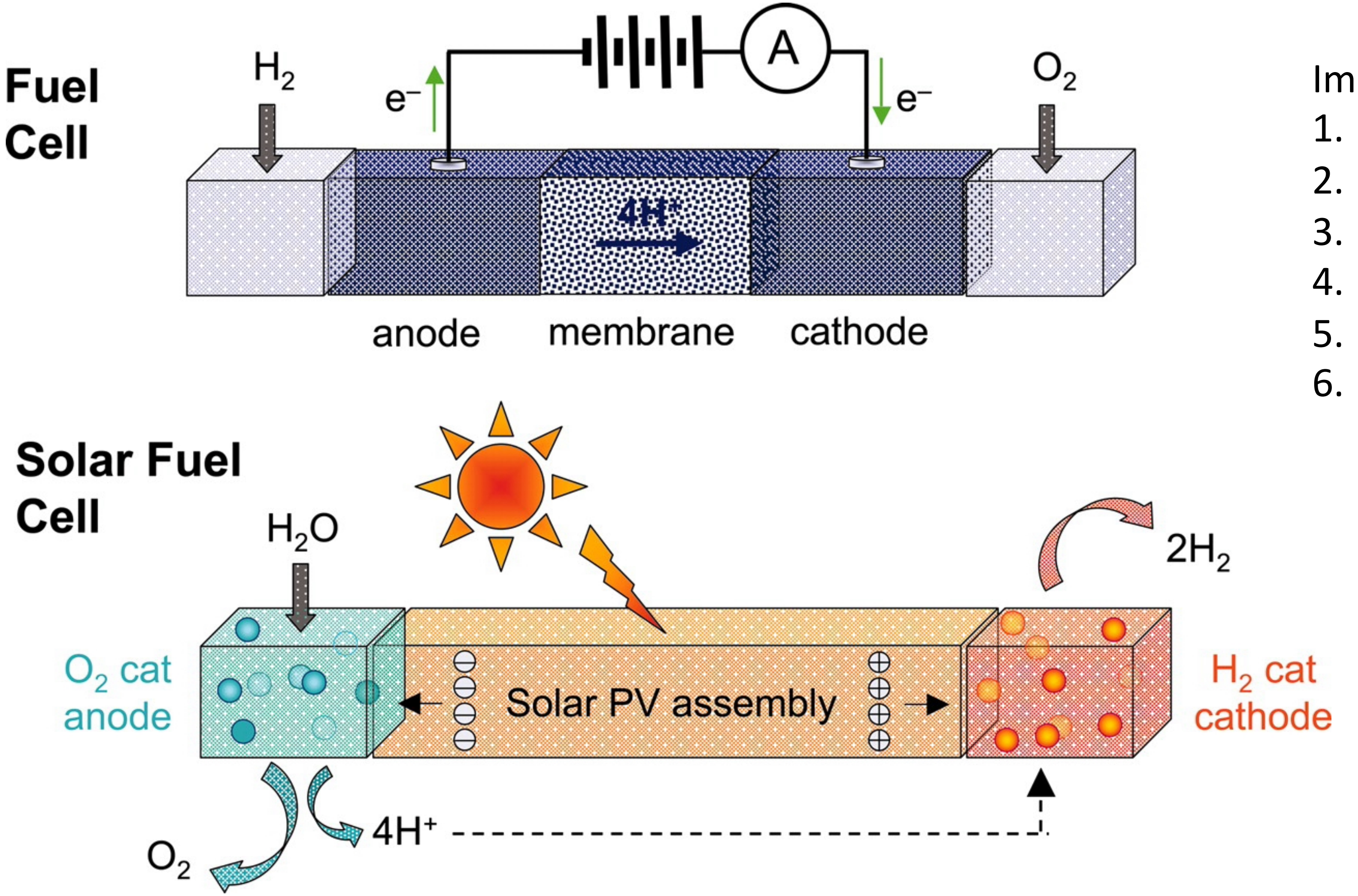
Semiconductor Photocatalyst

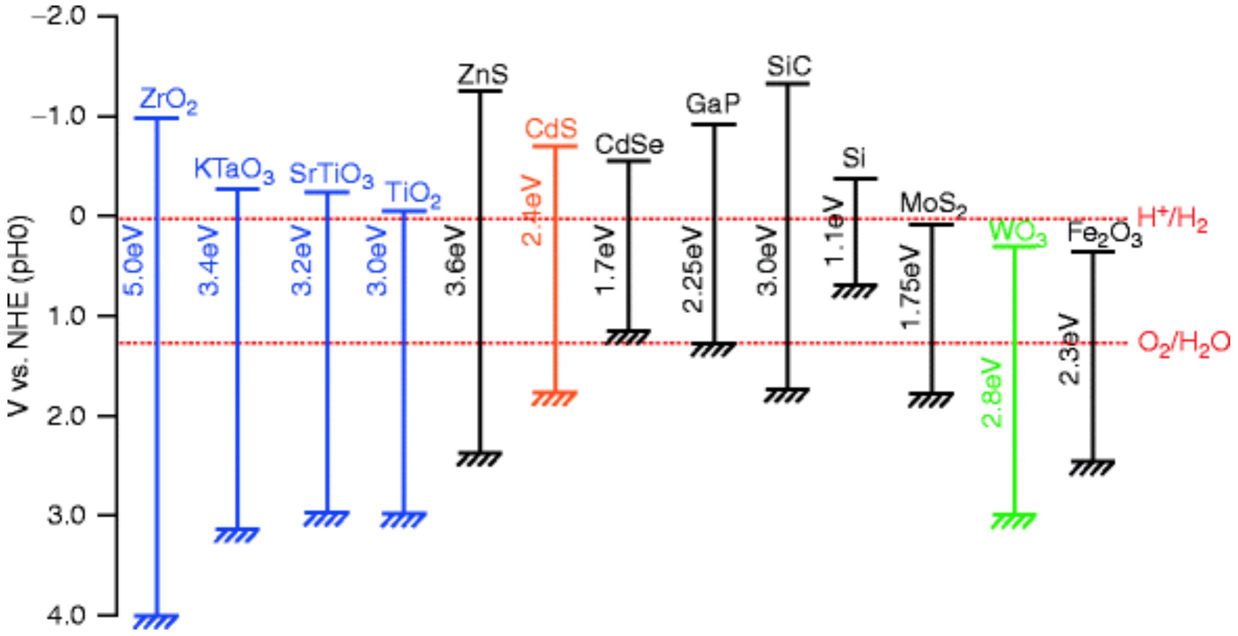


Important Parameters

1. Photon Absorption
2. Exciton separation
3. Carrier diffusion
4. Carrier transport
5. Catalytic efficiency
6. Mass transfer of reaction

Lewis, N.S. and Nocera, D.G., 2006. Powering the planet: Chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences*, *103*(43), pp.15729-15735.

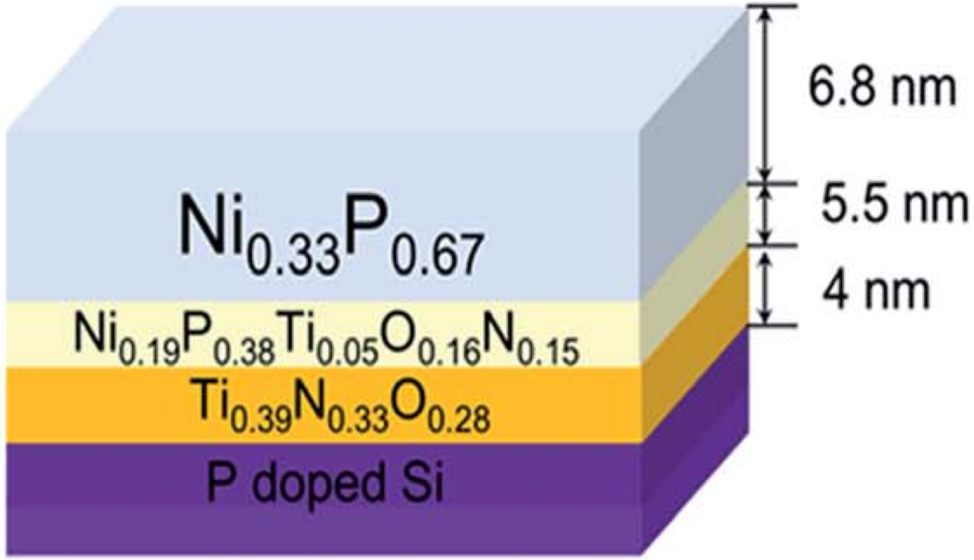
Semiconductor Photocatalyst



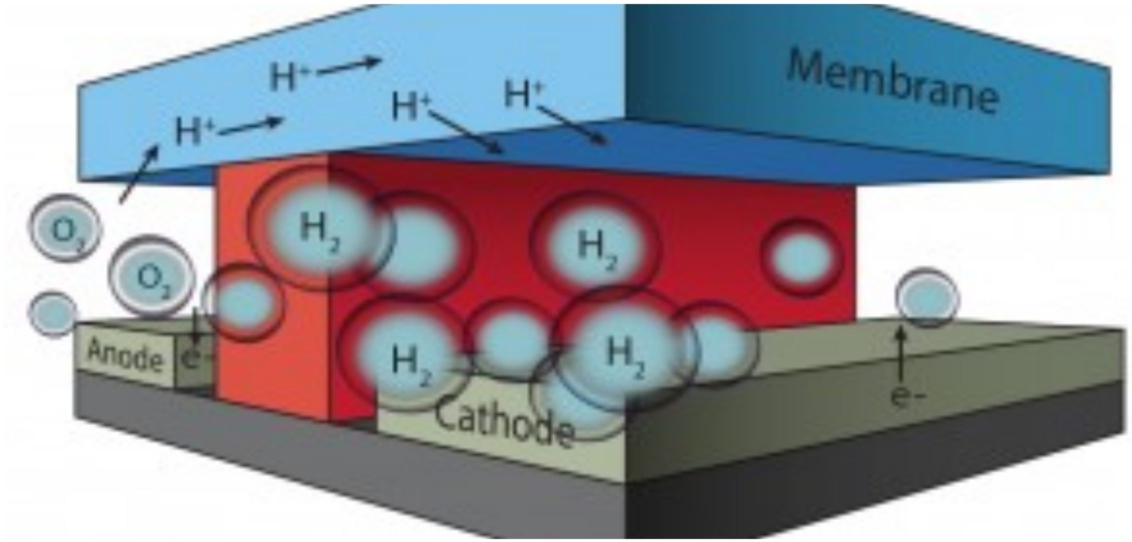
Band structures of common semiconductor photocatalysts relative to NHE. Note that in this representation, the valence band is at the bottom and the conduction band is on the top.

Kudo, A. and Miseki, Y., 2009. Heterogeneous photocatalyst materials for water splitting. *Chemical Society Reviews*, *38*(1), pp.253-278.
via https://doi.org/10.1007/978-1-4419-7991-9_46

Semiconductor Photocatalyst

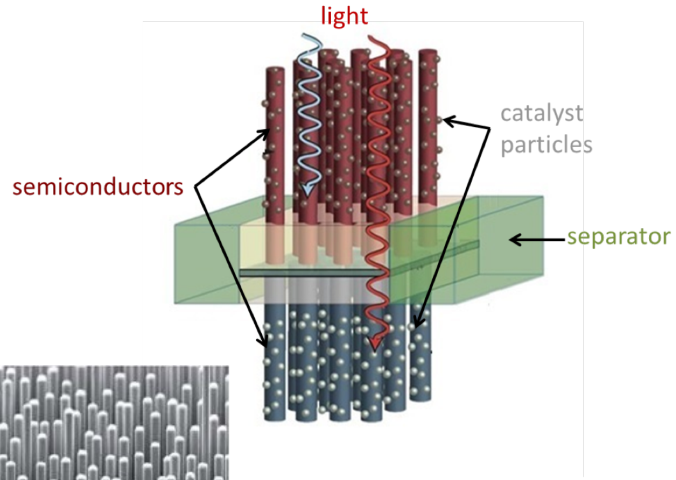


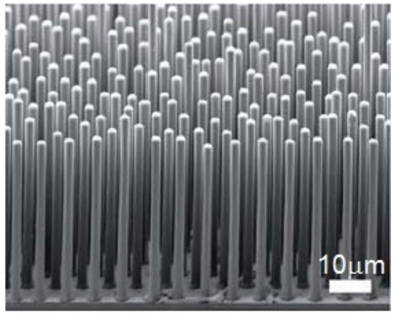
Hwang, S., Porter, S.H., Laursen, A.B., Yang, H., Li, M., Manichev, V., Calvinho, K.U., Amarasinghe, V., Greenblatt, M., Garfunkel, E. and Dismukes, G.C., 2019. Creating stable interfaces between reactive materials: titanium nitride protects photoabsorber–catalyst interface in water-splitting photocathodes. *Journal of Materials Chemistry A*, *7*(5), pp.2400-2411.

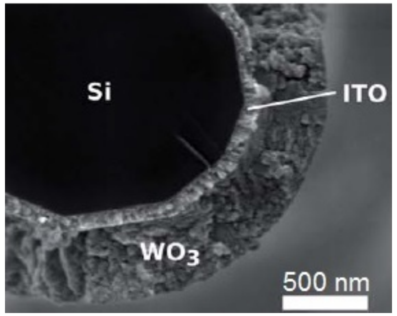


Joint Center for Artificial Photosynthesis (JCAP). Fully integrated microfluidic test-bed for evaluating and optimizing solar-driven electrochemical energy conversion systems.

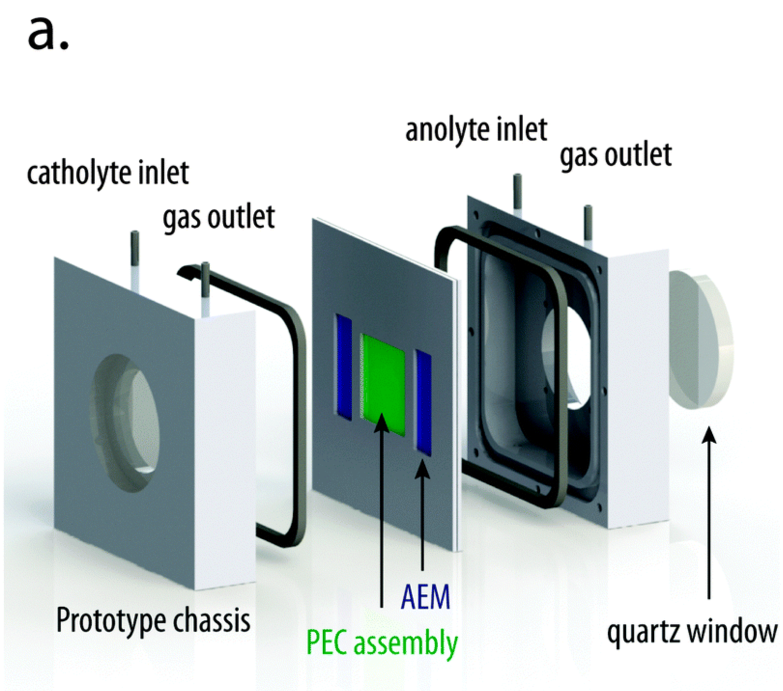
Semiconductor Photocatalyst

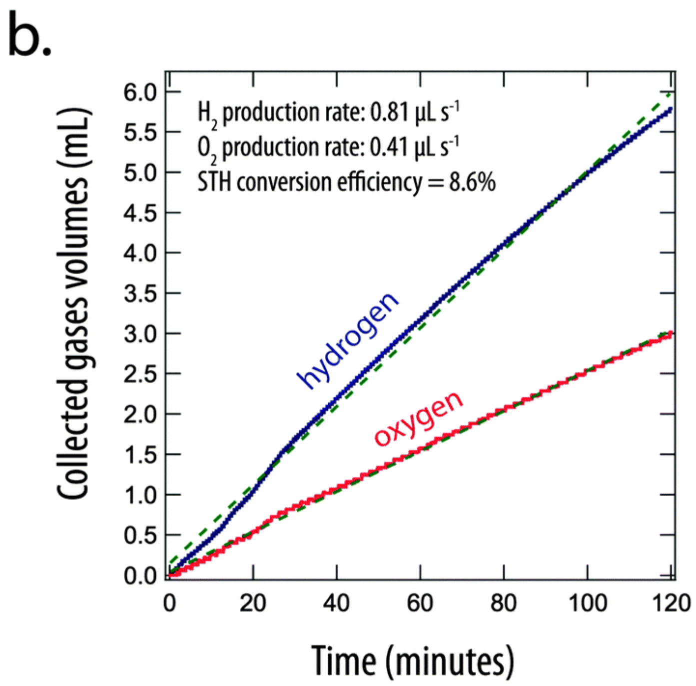






http://nsl.caltech.edu/

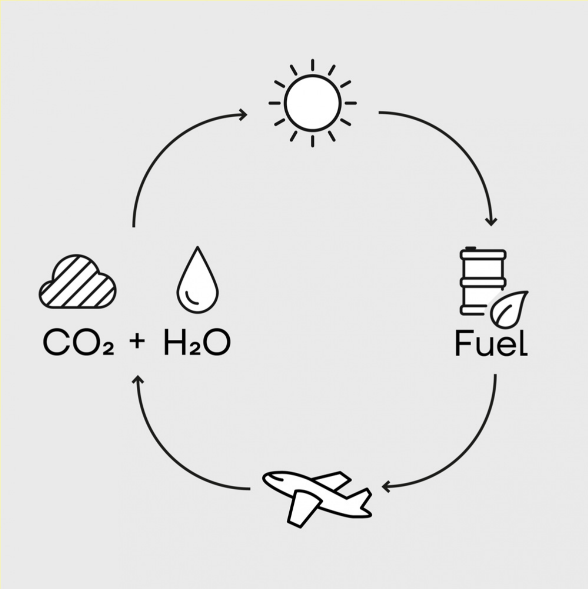


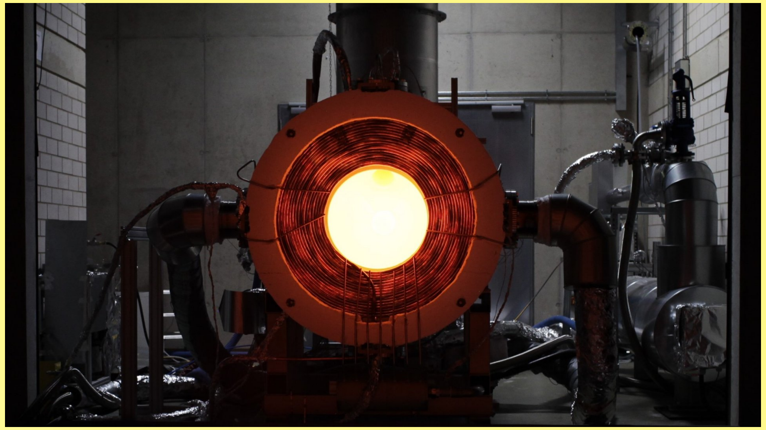


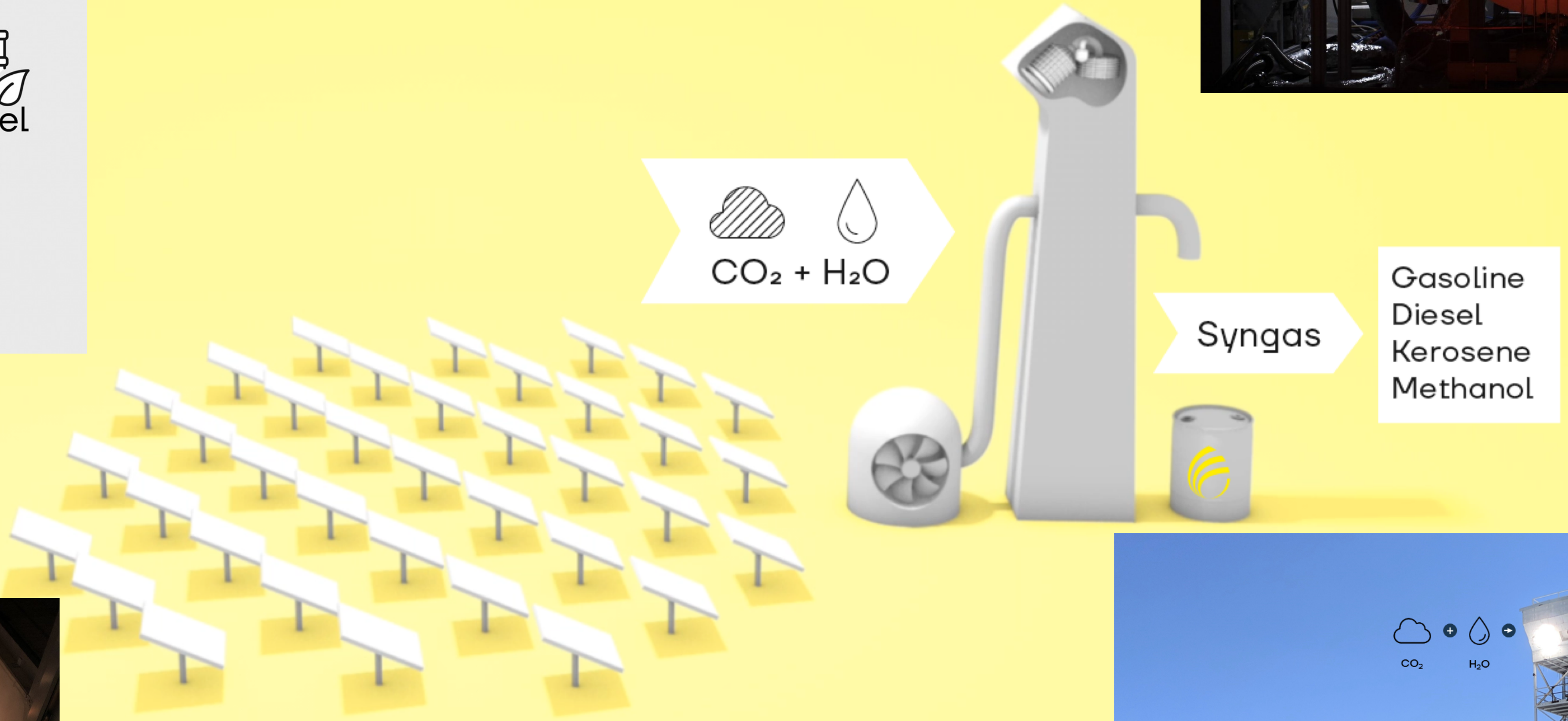
(a) Schematic illustration of a fully monolithically integrated intrinsically safe, solar-hydrogen system prototype. (b) Collected hydrogen and oxygen as a function of time for the integrated prototype

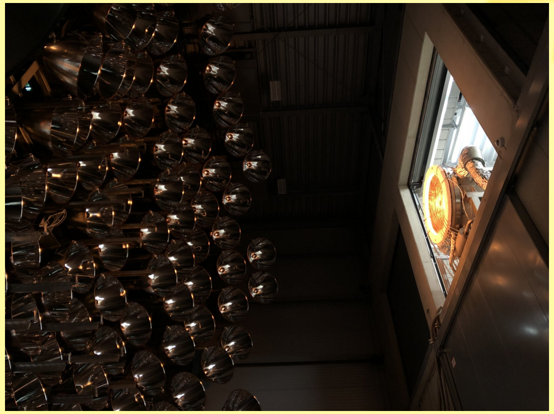
Verlage, E., Hu, S., Liu, R., Jones, R.J., Sun, K., Xiang, C., Lewis, N.S. and Atwater, H.A., 2015. A monolithically integrated, intrinsically safe, 10% efficient, solar-driven water-splitting system based on active, stable earth-abundant electrocatalysts in conjunction with tandem III–V light absorbers protected by amorphous TiO 2 films. *Energy & Environmental Science*, *8*(11), pp.3166-3172.

Solar Concentrators









Synhelion

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