EDITORIAL : Proteins as a source for Hydrogen Fuel

Sumit O. Bajaj, Ph.D.

Department of Chemistry and Chemical Biology, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA. Email: sobajaj@scripps.edu/sumitbajaj16@gmail.com

To accommodate the increasing energy demands, new techniques for the production, conversion and storage of energy are required. Solar energy is a natural, free and abundant source of energy from the sun and can be converted to various forms. As hydrogen possesses ~120-140 MJ/kg storage capacity and is a clean energy source, it can be studied as a future efficient and eco-friendly fuel. Studies directed towards converting solar energy for H₂ production using catalysts are currently underway, but locating a fit catalyst is challenging. Dr. Soltau's review covers emerging opportunities using natural protein structures as a booming source towards the conversion of solar energy to H₂ production.

Hydrogen, after treatment with oxygen, forms water and releases energy allowing hydrogen to act as a zero-emission fuel which can be used as power source for vehicles, boats, propulsion of space aircraft and electric devices. Naturally produced photocatalytic H₂ will have a greater positive impact on the environment and could be more cost effective. Dr. Soltau, the September issue's Postdoc of the month award winner, focuses on research related to H₂ production using protein sources. Her review talks about the various sources involved in H₂ production as described below.

Synthetic catalysts

In the past, various H_2 evolution reaction (HER) catalysts have been developed using synthetic catalysts from first generation noble metals, or second generation transition metals. Recent research focuses on synthetic organic catalysts for H_2 production. The electrocatalytic system has few limitations, most of which can be overcome by the use of photocatalytic sources (photosensitizers) by capturing photons and converting them to fuel via solar energy. Photocatalytic systems are either a) multimolecular systems (Fe, Ni, Co) as a basic starting point, b) supramolecular complexes that use cobaloximes linked axially or equatorially to $Ru(bpy)_3^{2+}$, although these suffer from shortcomings for scalable H₂ production, or c) nanoparticles, a promising source for the bulk scale photocatalytic H₂ production.

Protein based¹

A natural approach for H₂ production includes enzymes that have low over-potential (hydrogenases as an encouraging source). Hydrogenases are metalloenzymes- containing various metal centers [Ni-Fe], [Fe-Fe], [Fe]. Several biologically inspired catalysts have also been developed for H₂ production using a combination of metal catalysts with synthetic/semi-synthetic proteins to make artificial hydrogenases. Protein based hydrogen fuel production is of potential interest; it includes catalysts attached to peptides, [Fe-Fe]hydrogenase enzymes from algae and cobaloxime porphyrins catalysts bound to myoglobin for hydrogen production.

Bio-hybrids for solar hydrogen production and photocatalytic artificial hydrogenases: Biohybrids use Photosystem I (PSI), a large membrane protein complex to drive solar fuel production from a nickel diphosphine molecular catalyst. This bio-inspired hybrid produces more H_2 than the synthetic methodology upon light exposure. It further establishes strategies for constructing functional, inexpensive, earth abundant solar fuel-producing PSI hybrids that use light to rapidly produce hydrogen directly from water. For photocatalytic artificial hydrogenases, research is being done towards the development of a protein-catalyst framework.^{1,4} The Fe metal center in the Rubredoxin (Rd) protein was replaced by Nickel and used for H₂ production (>100 TON) using $Ru(bpy)_{3}^{2+}$ as a photosensitizer. The heme center of the myoglobin and cytochrome was replaced with Co porphyrins producing H₂. The biohybrid protein system Ru-Fd-Co produces hydrogen via direct photocatalysis. Dr. Soltau's research² shows that novel solar fuels for H_2 production can also be prepared using ferrodoxin (protein source), ruthenium (photosensitizer) along with cobaloxime (catalyst) and there is an extreme potential for the solar fuel production using protein source.

The future of the hydrogen production using proteins is stimulating in eco-friendly manner and further research for large scale fuel production is highly appreciated to meet the increasing energy needs.

References:

1. Sarah R. Soltau; Photocatalytic Hydrogen Production by Protein Systems, Journal of Postdoctoral Research, <u>2016</u>, <u>4(9)</u>, <u>3-14</u>

2. S.R. Soltau, J. Niklas and et al; Aqueous light driven hydrogen production by a Ru-Ferredoxin-Co biohybrid, Chem. Commun., 2016, 51, 10628 http://dx.doi.org/10.1039/C5CC03006D PMid:26051070

Bryan E. Barton and et al; Artificial Hydrogenases, Curr Opin Biotechnol. 2010, 21(3), 292
<u>http://dx.doi.org/10.1016/j.copbio.2010.03.00</u>
<u>3</u> PMid:20356731 PMCid:PMC2903054

4. Feng Wang and et al; Exceptional Poly(acrylic acid)-Based Artificial [FeFe]-Hydrogenases for Photocatalytic H2 Production in Water, Angew.

Chem. Int. Ed. 2013, 52, 8134 http://dx.doi.org/10.1002/anie.201303110 PMid:23788433