Harnessing sunlight by photocatalysis: a sustainable pathway for renewable fuels and clean water

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Photocatalysis has been known since the early 20th century from the flaking of paints and the degradation of fabrics incorporating TiO_2 under sunlight.¹ However, significant research on photocatalysis did not initiate until early 1970s, when Fujishima and Honda demonstrated splitting of water to H_2 and O_2 under near-UV using a titania photoanode and a platinum cathode.^{2,3} Interestingly, this breakthrough came at the verge of oil crisis, which thereafter stimulated a rapid growth of the scientific literature on photocatalysis over a decade.⁴

Photocatalysis allows direct harvesting of solar radiation – the largest energy reservoir accessible to mankind – by absorbing the solar photons first and subsequently channeling the absorbed energy to a chemical reaction by means of photogenerated electrons and holes. Therefore, a diversity of chemical processes, uphill or activated in energy, can be directly driven by solar energy.

Recent years have seen a boosting interest in the exploration of this promise of photocatalysis, particularly in storage of solar energy in sustainable chemical fuels, decomposition and removal of environmental pollutants and disinfection of water. However, the success of photocatalytic systems are largely impeded by competing mechanisms, instability and stringent requirement of efficient optical absorption and charge transfer at the same time.^{4–7} In an effort to help address these challenges, the present issue of *Nanomaterials and Energy* compiles a variety of emerging approaches to photocatalytic materials, processes and devices.

Although the sun exposes the earth with 10,000 times more power than the world's population consumes today, nourishing our civilization from this gigantic energy reservoir remains a challenge. For instance, at its maximum value of 1 kW/m^2 , solar radiation incident on a car or plane is too low to power these vehicles.⁸

Furthermore, irradiance varies significantly across the globe, and it is absent at night. Therefore, storage of solar energy in the form of a useful fuel is a logical choice to help solve the problems associated with the large variation in energy usage.

An ideal carrier of solar energy should involve inexpensive, earth-abundant materials that can be transformed between states that absorb and emit energy in a sustainable cycle. One common option consists of paired half cycles: (A) $\text{fuel} + \text{O}_2 \rightarrow \text{products} + \text{usable energy}$ and (B) $\text{products} + \text{solar energy} \rightarrow \text{fuel} + \text{O}_2$. With fossil fuels as the prime fuel in our current energy landscape, step A (consumption) is dramatically faster than step B (replenishment = photosynthesis + fossilization). Some argue that the earth's oil reserves may run out during the present century. Due to the imbalance between the steps A and B, there is accumulation of products in the atmosphere, one of which (CO_2) has a major environmental drawback and results in global warming. Although biofuels (if they could be realized on a massive scale) might offer a solution to the balancing of steps A and B (regenerate as much as you burn), they increase the nitrogen burden on the soil and water of the earth that is already feeding a population of 7 billion with the aid of artificial fertilizers.

An alternative is the water cycle: (A) $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{energy}$ and (B) $\text{H}_2\text{O} + \text{sunlight} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. Rather than using carbon-based fuels, water's photolytic energy cycle does not interfere with the carbon and nitrogen cycles of the biosphere, making it more sustainable as well as renewable. Molecular hydrogen, H_2 , is the cleanest and smallest carrier of chemical energy, yet it has the highest energy content per unit weight among all fuels (120 MJ/kg).⁸ H_2 can be directly utilized as fuel in internal combustion engines or for generation of electric power in fuel cells.⁸ As H_2O is the final product of the $\text{H}_2 + \text{O}_2$ reaction, no pollutants or greenhouse gases are produced. Therefore, H_2 generation from water and sunlight

hints at the ‘holy grail’ of fully renewable and sustainable fuel production. Hydrogen-powered buses and prototype H₂-filling stations are already in service in Japan and Europe.⁸

Photocatalysis has also emerged as a promising approach to recycling of wastewater and water purification for protecting both human health and the environment. Pollutants and toxins in water can be decomposed into environmentally friendly species directly or by highly reactive hydroxyl radicals generated by photocatalytic reactions.⁹ In developing countries, about a billion people have no access to safe drinking water and close to 3 billion lack adequate sanitation.¹⁰ Millions die each year, mostly children, from preventable diseases, because they do not have access to clean water and proper sanitation.¹⁰ In addition, a growing concern for the environment in both developing and developed countries is the contamination of fresh water sources, such as lakes, rivers and groundwater with chemicals from industrial waste to pesticides and pharmaceuticals. Hence, energy-saving green technologies are needed for water recycling and purification. A sustainable solution is through photocatalytic reactions driven by sunlight.

For this themed issue of *Nanomaterials and Energy* (NME), we had the opportunity of conducting an exciting interview with Dr. Todd G. Deutsch. Dr. Deutsch is a Senior Scientist in the Hydrogen Technologies and Systems Center at the National Renewable Energy Laboratory in Golden, CO, USA. He has answered our questions about the promise and challenges of hydrogen production from sunlight and water. He has also shared with us his peer opinion on various controversies in photolysis of water. Among such controversies is whether sustainable hydrogen generation should adopt directly photocatalysis or ‘photovoltaics + electrolysis’. Similarly, an ongoing debate is between oxide semiconductors or compound semiconductors such as III–V, II–VI and I–III–VI, as sustainable photocatalysts for splitting of water. Dr. Deutsch also advises new researchers in the field about emerging technologies and potential mistakes.

Low cost and scalability are expected to play key roles in realization of photocatalysis in harnessing of the solar energy. As such, the present themed issue features a novel photocatalyst developed at Indian Institute of Technology, Kanpur, India. Kunal Mondal, Jitendra Kumar and Ashutosh Sharma demonstrate fabrication of their photocatalyst in three subsequent steps: (i) dispersing TiO₂ nanoparticles in polyacrylonitrile (PAN) solution; (ii) spin-casting the mixed solution on a Si substrate and (iii) pyrolysis of PAN film to carbon. The macroporous carbon thin film immobilizes the TiO₂ nanoparticles in its pores and facilitates efficient reactant/product transport through its interconnected pore network for the photocatalytic reactions. The photocatalytic function of the composite structure is verified by photodecomposition of RhB dye.

In a photocatalyst, the instrumental mechanistic steps are the absorption of a photon by a ground + excited energy-level system

and subsequent transfer of photogenerated carriers, while the ground + excited energy levels does not have to be in a semiconductor. Indeed, molecules can do the job. Furthermore, the ability to change the electron conjugation length in molecules or molecular complexes offers the potential to tailor the absorption spectrum as well as energetics for optimum charge transfer in photocatalytic reactions. To this end, we have a distinct mini review from Johannes Kepler University Linz, Austria. Engelbert Portenkirchner, Kerstin Oppelt, Günther Knör and Niyazi Serdar Sarıçiftçi provide several examples of rhenium and rhodium complexes with modified ligand structures for electro- and photo-catalytic applications toward CO₂ reduction and NAD⁺ cofactor regeneration. The electrocatalysis is studied by cyclic voltammetry and controlled potential electrolysis for determining the overpotentials, Faradaic efficiencies and reaction rate constants. The authors discuss photophysics of these compounds based on UV-visible absorption, photoluminescence and infrared absorption spectroscopy.

In their interesting work on remediation of wastewater by photocatalysis, Dr. Özlem Esen Kartal and her student Gülistan Turhan of İnönü University (Malatya, Turkey) used La³⁺-doped TiO₂ nanostructures prepared by a sol-gel method. The photocatalytic activity is investigated in terms of decolorization and degradation efficiencies of Acid Orange 7 dye. It is found that doping with La³⁺ enhances the photocatalysis of TiO₂. The authors utilize X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy and nitrogen adsorption measurements to show that doping with La³⁺ inhibits the transformation of anatase phase to rutile during calcination treatment and the growth of crystallite size where La is incorporated in the form of La₂O₃ at the surface of TiO₂. The authors demonstrate efficient decolorization and degradation of Acid Orange 7 under solar radiation.

The present themed issue of *NME* closes with a unique review contributed by Dr. Nitin Chopra and his student Wenwu Shi of University of Alabama. The authors review nanoscale heterostructures, which are designed for photoelectrochemical water splitting and degradation of pollutants/contaminants. The heterostructures are classified according to charge-transfer mechanisms. In addition, the authors discuss multifunctional attributes of the heterostructures, such as light absorption enhancement in the presence of plasmonic metal nanostructures. Also included in the article is a review of the characterization techniques, commonly used for photocatalytic heterostructures.

In summary, sunlight and water are the most abundant resources on our planet. Indeed, life has evolved around water and sunlight. Combining the two resources through photocatalysis offers a potential solution for our vital problems, concerning energy and clean water sustainability. In particular, storage of solar energy in a renewable clean fuel will be a major milestone for humankind. Furthermore, with continuing increase in fresh water consumption

and pollution each year, energy-saving green technologies are highly demanded for water recycling and purification. To this end, harnessing of solar energy through photocatalysis is a promising and sustainable pathway.

REFERENCES

1. Keidel, E. Die beeinflussung der lichtechtheit von teerfarblacken durch titanweiss [Influence of titanium white on the fastness to light of coal-tar dyes]. *Farben-Zeitung* **1929**, *34*, 1242–1243.
2. Fujishima, A.; Honda, K.; Kikuchi, S. Photosensitized electrolytic oxidation on semiconducting n-type TiO₂ electrode. *Kogyo Kagaku Zasshi* **1969**, *72*, 108–113.
3. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
4. Bard, A. J.; Fox, M. A. Artificial photosynthesis: solar splitting of water to hydrogen and oxygen. *Accounts of Chemical Research* **1995**, *28*, 141–145.
5. Osterloh, F. E.; Parkinson, B. A. Recent developments in solar water-splitting photocatalysis. *MRS Bulletin* **2011**, *36*, 17–22.
6. Grimes, C. A.; Ranjan, S.; Varghese, O. K. *Light, Water, Hydrogen*. New York: Springer Science + Business Media LLC, 2008.
7. Gratzel, M. Photoelectrochemical cells. *Nature* **2001**, *414*, 338–344.
8. Schlapbach, L. Hydrogen-fuelled vehicles. *Nature* **2009**, *460*, 809–811.
9. Pichat, P. (ed.) *Photocatalysis and Water Purification*. Weinheim: Wiley-VCH Verlag GmbH & Co., 2013.
10. Rosenberg, T. The burden of thirst. *National Geographic*, **2010**, *4*.