

# Photonics Society Image Winners Present: Blossom in Photosynthesis

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## 1. Background

Due to the ever-increasing consumption rate of energy in the world, scientists and engineers are seeking to harness renewable energy sources such as sunlight, wind, geothermal heat, tides, and biomass. As exemplified by photosynthesis in plant leaves, sunlight can be harnessed to produce oxygen and carbohydrates from water and carbon dioxide [1], where energy conversion efficiency can reach 7% [2]. Different from the fossil fuels, which has caused numerous environmental and health problems [3, 4], the solar-to-chemical energy conversion is a green process [5, 6, 7].

Inspired by nature, researchers have been exploring artificial photosynthesis in various forms for the solar-to-chemical energy conversion [8]. One of the promising examples is hydrogen production via photoelectrochemical (PEC) water splitting using sunlight. In the PEC cells, semiconductor materials that work as electrodes are optically excited to drive the water splitting and solar energy is stored in the form of hydrogen, which is regarded as a new-generation clean energy carrier (Figure 1). With the solar-to-hydrogen efficiency around 5% [9], PEC cells need be further improved to compete with fossil fuels. The development of better electrodes is the key to the improvement.

Following the initial demonstration of PEC cell consisting of a single-crystalline  $\text{TiO}_2$  anode and a Pt cathode [10], researchers have made significant progresses in developing new electrode materials to improve the power conversion efficiency. In particular, nanomaterials have proved as promising candidates for the PEC electrodes due to their unique physical and chemical properties that are tailorable by the size, shape, and morphology [11–14].

## 2. Plasmonic PEC Water Splitting

With their capability of manipulating light at the nanoscale, metal nanostructures can be incorporated into semiconductor electrodes to improve the water splitting by enhancing the light harvesting, charge generation and separation,



and kinetics of chemical reactions, which is known as plasmonic PEC water splitting [15]. Firstly, the excitation of surface plasmon resonances (SPRs) at metal nanostructures helps concentrate sunlight at the metal-semiconductor interfaces to enhance the light absorption in the semiconductors [16]. Therefore, thin films of semiconductors can be employed as electrodes in the PEC cells to reduce the exciton recombination rate and lower the production cost.

Secondly, hot electrons from the decay of surface plasmons on metal nanostructures can also contribute to the chemical reactions in PEC water splitting. The hot electrons ejected from metal nanostructures enter the conduction band of semiconductors and interact with protons to form hydrogen, while the holes in the metal nanostructures accept electrons from electrolyte for oxygen production [17]. Since SPRs of metal nanostructures can be tuned to cover a broad range of

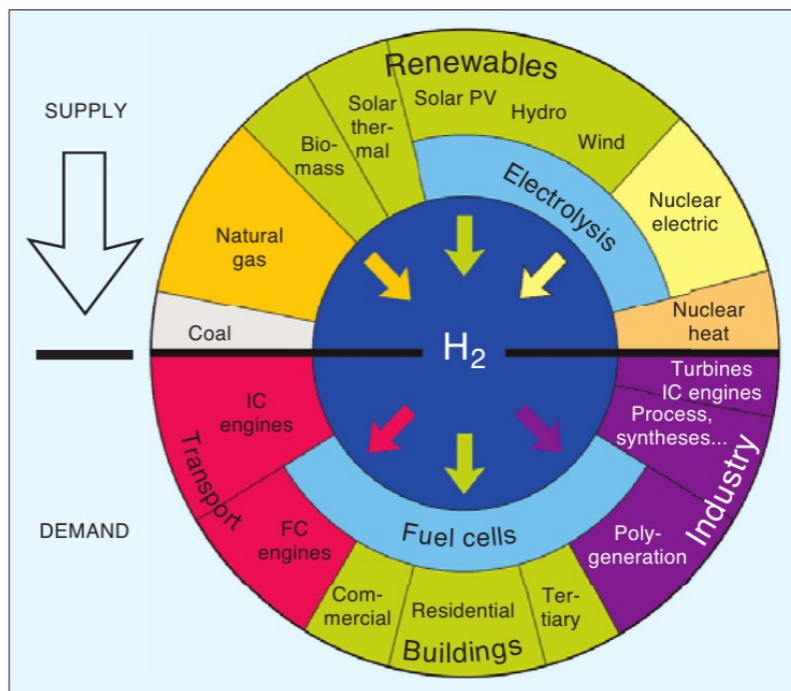


Figure 1. An overview of hydrogen production and utilization.

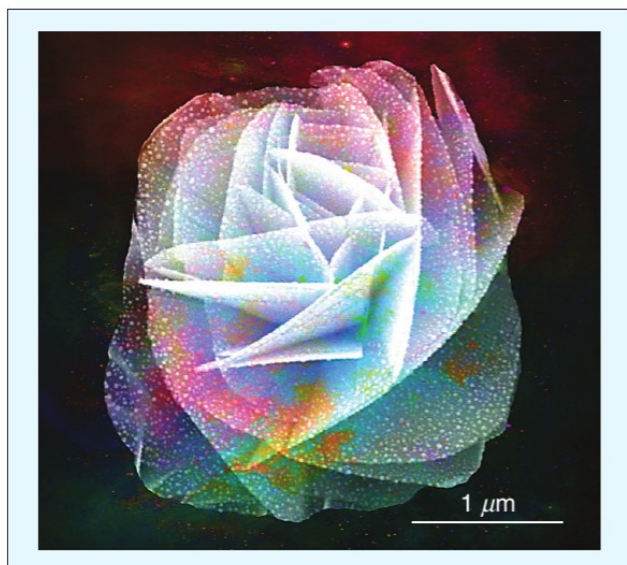


Figure 2. Scanning electron micrograph of a representative microscale “rose” of BiVO<sub>4</sub> dotted with Au nanoparticles that exhibits efficient photosynthesis.

sunlight spectrum [18, 19], one can use the hot electrons to sensitize wide-band semiconductors to harness the visible and near-infrared lights that are otherwise wasted.

Lastly, metal nanostructures on semiconductor electrodes can help suppress optical reflection to enhance the light utilization. The high refractive indices of semiconductors result in a large reflection loss of incident light at the electrode surfaces. Metal nanoparticles can reduce the reflection by preferentially scattering the light into the semiconductors. Metal nanostructures in rationally designed arrays can even lead to a negligible reflection at the electrodes, significantly enhancing the light absorption and energy conversion efficiency [20].

### 3. A Glimpse into Recent Developments

Tremendous progresses have been achieved in the plasmonic PEC water splitting. Various metal-semiconductor hybrid nanostructures have been developed as new electrodes that benefit from the plasmonic enhancements [21,22]. As an example, we have designed PEC photoanodes consisting of BiVO<sub>4</sub> nanoplates decorated with Au nanoparticles. As shown in Figure 2, the BiVO<sub>4</sub> nanoplates and Au nanoparticles can form the rose-like microstructures. With the high surface area and small thickness of the BiVO<sub>4</sub> nanoplates, as well as the plasmonic enhancements of Au nanoparticles, the hybrid photoanodes can achieve an AM 1.5G photocurrent density of  $5.1 \pm 0.1$  mA/cm<sup>2</sup> at 1.23 V versus reversible hydrogen

electrode and >99% Faraday efficiency. The enhanced PEC performance is mainly attributed to the hot electrons from Au nanoparticles. With their unique properties and the continuous research efforts from scientists and engineers in the multiple fields such as materials science, engineering, chemistry, physics, and biology, hybrid metal-semiconductor nanostructures will continue to blossom in photosynthesis.

### References

- [1] J. Barber, *Chem. Soc. Rev.* 2009, 38, 185.
- [2] Blankenship *et al.*, *Science*, 2011, 332, 805.
- [3] V. I. Ugursal, *Appl. Energ.*, 2014, 130, 783.
- [4] M. M. Aman, K. H. Solangi, M. S. Hossain, A. Badarudin, G. B. Jasmon, H. Mokhlis, A. H. A. Bakar, S. N. Kazi, *Renew. Sust. Energ. Rev.*, 2015, 41, 1190.
- [5] N. Armaroli, V. Balzani, *Angew. Chem., Int. Ed.*, 2007, 46, 52.
- [6] A. J. Esswein, D. G. Nocera, *Chem. Rev.*, 2007, 107, 4022.
- [7] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, V. Pellegrini, *Science*, 2015, 347, 6217.
- [8] Y. Umena, K. Kawakami, J.R. Shen, N. Kamiya. *Nature*, 2011, 473, 55.
- [9] F. F. Abdi, L. Han, A. H. M. Smets, M. Zeman, B. Dam, R. van de Krol, *Nat. Commun.*, 2013, 4, 2195.
- [10] A. Fujishima, K. Honda, *Nature*, 1972, 238, 37.
- [11] R. Plass, S. Pelet, J. Krueger, M. Grätzel, *J. Phys. Chem. B*, 2002, 106, 7578.
- [12] C. Ampelli, G. Centi, R. Passalacqua, S. Perathoner, *Catal. Today*, 2015, doi:10.1016/j.cattod.2015.07.020
- [13] Han *et al.*, *ChemSusChem*, 2014, 7, 2832.
- [14] J. Gan, X. Lu, B. B. Rajeeva, R. Menz, Y. Tong, Y. Zheng, *ChemElectroChem*, 2015, DOI: 10.1002/celec.201500091.
- [15] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.*, 2010, 110, 6503–6569.
- [16] K. L. Kelly, *J. Phys. Chem. B*. 2003, 107, 668.
- [17] H. M. Chen, C. K. Chen, C.-J. Chen, L.-C. Cheng, P. C. Wu, B. H. Cheng, Y. Z. Ho, M. L. Tseng, Y.-Y. Hsu, T.-S. Chan, *ACS Nano*, 2012, 6, 7362.
- [18] L. Lin, Y. B. Zheng, *Opt. Lett.*, 2015, 40, 2060.
- [19] Y. B. Zheng, B. Kiraly, P. S. Weiss, T. J. Huang, *Nanomedicine*, 2012, 7, 751.
- [20] W. F. Xu, M. Y. Pan, P. H. Fu, S. W. Li, D. W. Huang, P. K. Wei, *J. Mater. Chem. C*, 2015, DOI: 10.1039/C5TC01462J.
- [21] Z. Liu, W. Hou, P. Pavaskar, M. Aykol, S. B. Cronin, *Nano Lett.*, 2011, 11, 1111.
- [22] Z. Zhang, L. Zhang, M. N. Hedhili, H. Zhang, P. Wang, *Nano Lett.*, 2013, 13, 14.