



Comment

Recent developments in photocatalytic solar water splitting

Jiming Bao

University of Houston, Department of Electrical and Computer Engineering, N 308 Engineering Building 1, Houston, TX 77204-4005, United States

Jiming Bao looks at some examples of how the emergence of new materials has increased the efficiency of this important technique for renewable energy

The generation of hydrogen through photocatalytic water splitting is a clean and sustainable technique to produce renewable fuels. Compared with photovoltaics, solar water splitting does not suffer from electricity storage problem, moreover, it can provide an important feedstock – hydrogen for the chemical industry. However, the energy conversion efficiency has remained much lower than that of photovoltaics. The solar water splitting process has two more steps than photovoltaics: hydrogen evolution and oxygen evolution. Thus, the improvement of efficiency relies on new materials for efficient solar energy harvesting as well as active co-catalysts for hydrogen and oxygen evolutions. In recent years the world has witnessed the emergence of many new materials and approaches with increased water splitting efficiency, in the Comment we look at some representative examples.

The most important step in improving efficiency is to develop lower bandgap photocatalysts. The main effort has focused on reducing the bandgaps of wider semiconductors through doping or alloying. These engineered materials are solid solutions containing four or more elements. $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ and Ta-based semiconductors are two well-known examples of such semiconductor

alloys [1]. Plasmonic nanostructures are a totally new type of visible light energy harvesting material. Surface plasmon resonances are widely used to enhance local electromagnetic field, to guide light and funnel energy to the active regions of devices. Recently, plasmonic nanostructures have been shown to donate electrons to the attached co-catalysts. By integrating plasmonic gold nanorods with hydrogen and oxygen co-catalysts, overall water-splitting has been demonstrated [2]. In addition, a wide range of the solar spectrum can be harvested by tuning the resonance of surface plasmon resonances.

Two-dimensional (2D) nanomaterials are finding more and more applications in solar water splitting. 2D materials have the potential to be excellent catalysts because of their high surface to volume ratio. But 2D materials can do much more: they can harvest solar energy and generate electrons and holes, and they can also provide paths for the separation and diffusion of photoexcited carriers. One important achievement that has been recently reported is that functionalized graphene oxides can perform overall water splitting without co-catalysts and a sacrificial reagent [3].

Following the discovery of CoPi as an efficient oxygen evolution catalyst, cobalt oxides (CoO and Co_3O_4) have emerged as new promising oxygen evolution catalysts [1,4]. When decorated on the surface of other photocatalysts, cobalt oxides have been shown to greatly increase the lifetime of photoexcited electrons, leading to enhanced oxygen evolution efficiency. Further, CoO thin films have shown to enormously enhance the oxygen evolution activity of hematite.

Nanoparticles continue to exhibit surprisingly higher activity than their bulk counterparts. They can be synthesized using laser ablation without any precursors or surfactants, and they can be as small as 5 nm. Co_3O_4 nanoparticles have exhibited a huge enhancement in oxygen evolution activity compared to micropowders [5]. More surprisingly, CoO nanoparticles have demonstrated a high efficiency overall water splitting without any co-catalysts and sacrificial reagents although CoO bulk is not active [6].

Looking forward, we expect to see more breakthroughs in many fronts of solar water splitting; and ultimately, the efficiency has to reach 10% benchmark in order to be competitive. Although, in past, materials discovery has largely been made through trial and error, we are going to see more novel materials and rational device designs based on theory and simulations.

Further reading

- [1] T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.* (2014), <http://dx.doi.org/10.1039/c3cs60378d>.
- [2] S. Mubeen, et al. *Nat. Nanotechnol.* 8 (2013) 247–251.
- [3] T.-F. Yeh, et al. *Adv. Mater.* (2014), <http://dx.doi.org/10.1002/adma.201305299>.
- [4] S.C. Riha, et al. *ACS Nano* 7 (2013) 2396–2405.
- [5] J.D. Blakemore, et al. *ACS Catal.* 3 (2013) 2497–2500.
- [6] L. Liao, et al. *Nat. Nanotechnol.* 9 (2014) 69.