Photocatalysis in solar fuel production

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With the increasing concerns on energy and environmental problems caused by the combustion of fossil fuels, solar energy becomes vitally important because it is the only viable renewable energy source that can replace the fossil fuels in vast volume. The research on photocatalysis for solar fuel production, especially H₂ production by photocatalytic splitting of water and conversion of CO₂ to chemical fuels such as CO, CH₃OH, CH₄, etc., is regarded as the most ideal way for solar energy conversion, storage and utilization. In view of the current research status and the near future practical applications, particulate semiconductor photocatalyst (PSP), photoelectrochemical cell (PEC) cell and photoelectrochemical cell coupled with photovoltaics (PEC-PV) system are the three most promising solutions for solar fuel production.

The best PSP reported so far for water splitting under UV light irradiation is La doped NaTaO₃ loaded with Ni/NiOₓ cocatalyst, reaching quantum efficiency (QE) of 56% [1]. Because UV light takes only less than 5% of the solar spectrum, solar energy conversion by UV-active photocatalyst is rather limited. Since visible light occupies more than 40% in the solar spectrum, development of visible light active photocatalyst is necessary. The best visible light photocatalyst for water splitting is (Ga₁ₓZnₓ)(N₁₋ₓOₓ) semiconductor photocatalyst loaded with Rh₂₃CrₓO₃ cocatalyst, which can reach QE of 5.6% under visible light irradiation (λ > 420 nm) [2]. Visible light QE of 6.3% has also been reported for a ZrO₂/TaON and PtOₓ/WO₃ coupled system with 1⁻/IO₃⁻ as the shuttle reduct mediator. Though it is still far from the practical application requirement of at least 10% solar energy conversion...
efficiency ($\eta_{\text{STH}}$), these results already demonstrated that photocatalytic water splitting is a promising solution for solar energy to chemical conversion and storage.

In order to achieve high solar energy conversion efficiency, the efficiencies of light absorption, charge separation and surface redox reactions should be harmonically and simultaneously achieved. Among them, efficient charge separation is the vital factor for solving the energetically uphill solar energy conversion reactions. Interface (junction) engineering has been demonstrated to be efficient approach for achieving high charge separation. For example, $\text{CaFe}_2\text{O}_4/\text{TaON}$ heterojunction photoanode has been demonstrated for efficient photoelectrochemical water oxidation [3]. Formation of surface phase junction between $\alpha$- and $\beta$-phase $\text{Ga}_2\text{O}_3$ can also enhance overall water-splitting activity under visible light irradiation (Fig. 1a) [4].

Cocatalysts [5] play important roles in the assembly of efficient semiconductor photocatalyst (Fig. 1b). It was found that photogenerated electrons and holes may be spatially separated on the $\{010\}$ and $\{110\}$ facets of $\text{BiVO}_4$ crystal. Upon selective photodeposition of reduction cocatalysts (Pt, Au, Ag, etc.) on $\{010\}$ facet and oxidation cocatalysts of transition metal oxides (MnO$_2$, CoO$_2$, NiO$_2$, etc.) on $\{110\}$ facets, water oxidation activity was increased more than two orders of magnitude higher [6]. The intrinsic nature of charge separation between different facets of $\text{BiVO}_4$ together with the synergistic effect of dual cocatalysts plays a key role in photocatalytic activity enhancement. This opens up a new avenue for the assembly of semiconductor-crystal-based artificial photosynthesis system by selectively loading of dual cocatalysts on the different facets (Fig. 1c).

Alternative approaches other than PSP should be also highly considered, such as PEC and PEC-PV systems. A $\text{Ta}_3\text{N}_5$ photoanode coated with ferrihydrite (Fh) layer on which $\text{Co}_3\text{O}_4$ water oxidation cocatalyst ($\text{Co}_3\text{O}_4/\text{Fh}/\text{Ta}_3\text{N}_5$) was deposited, could yield a photocurrent of 5.2 mA cm$^{-2}$ at a potential of 1.23 V versus RHE under AM 1.5G simulated sunlight irradiation. And remarkably, about 94% of the initial activity could be maintained even after 6 h irradiation, which is due to the avoidance of the $\text{Ta}_3\text{N}_5$ corrosion via efficient hole storage and transfer by the Fh layer [7]. A self-biased PEC-PV system consisting of FeOOH/Mo:$\text{BiVO}_4$ photoanode and a Pt/p-Si solar-cell-based photocathode showed $\eta_{\text{STH}}$ of 2.5% under parallel irradiation [8]. A triple junction amorphous silicon photovoltaic coupled with Ni-MoZn alloy and cobalt borate cocatalysts can achieve $\eta_{\text{STH}}$ of 4.7% for a wired configuration and 2.5% for a wireless configuration when illuminated with 1 sun of air mass 1.5 simulated sunlight [9]. Based on these results, concept of ‘artificial leaf’ has been proposed. Recently, it has been also reported that a solution processed perovskite tandem solar cell coupled with a NiFe-layered double hydroxide electrocatalyst exhibited a water-splitting photocurrent density of around 10 mA cm$^{-2}$, corresponding to a $\eta_{\text{STH}}$ of 12.3% [10], but the stability of the perovskite is a problem.

It can be seen that great progresses in solar fuel production have been achieved in the past decades. However, there is still no promising solution for practical application in terms of efficiency, stability and cost effectiveness. In order to further improve the solar fuel production efficiency, in-depth understanding the nature of the energetically uphill photocatalytic reactions is necessary. We should learn from the mother nature, since the natural photosynthesis system has well-resolved all of the uphill energy conversion problems. And addition to the current researches focusing on material engineering for efficient light harvesting and charge separation, the thermodynamic and kinetic aspects of water activation should be also extensively investigated.

Compared to the other approaches of solar energy utilization, such as conversion of solar energy into electricity
(photovoltaics) and thermal energy (solar heat), solar energy to chemical energy conversion to produce solar fuels by photocatalysis has some unique advantages in terms of energy storage, transportation and utilization, because the photocatalytically converted chemicals (solar fuels) can be conveniently activated for use. Though current research on this field is still in the stage of laboratory research, it can be envisioned that some breakthroughs may be achieved in the near future with extensive research input. And it is necessary to take the research on solar fuel production in a high priority to secure the national renewable energy development.

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REFERENCES
1. Kudo, A, Nishiro, R and Kato, H et al. Chem Phys 2007; 339: 104–10.
2. Maeda, K, Inoue, Y and Domen, K et al. Nature 2006; 440: 295.
3. Kim, ES, Domen, K and Lee, JS et al. J Am Chem Soc 2013; 135: 5375–83.
4. Wang, X, Han, HX and Li, C et al. Angew Chem Int Ed 2012; 51: 13089–92.
5. Yang, JH, Han, HX and Li, C et al. Acc. Chem. Res. 2013; 46: 1900–09.
6. Li, RG, Zhang, FX and Li, C et al. Nat Commun 2013; 4: 1432.
7. Liu, GJ, Shi, JY and Li, C et al. Angew Chem Int Ed 2014; 53: 7285.
8. Ding, CM, Shi, JY and Li, C et al. Phys Chem Chem Phys 2014; 16: 15608.
9. Kanan, M and Nocera, DG. Science 2008; 321: 1072–5.
10. Luo, JS, Im, JH and Grätzel, M. Science 2014; 345: 1593–6.

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CHEMISTRY

Special Topic: Catalysis—Facing the Future

Studying birth, life and death of catalytic solids with operando spectroscopy

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Catalytic solids are arguably the most important catalysts used in pharmaceutical, (petro) chemical and environmental industries: most transportation fuels, materials as well as fine and bulk chemicals are produced by heterogeneous catalysts [1,2]. Despite their widespread use, the intricate details how they are composed, function, change and ultimately deactivate are still not well understood. One of the reasons is that catalytic solids are hierarchically structured, multicomponent and multielemental materials. They are very dynamic under true reaction conditions, which often comprise high temperatures and pressures. This dynamic aspect is further underlined by the fact that most often a freshly prepared catalyst material loaded in a chemical reactor structurally changes during a period of activation. Such period of reaction environment-induced changes, very similar to the behavior of a chameleon, can easily take a few days in an industrial setting, a period in which the catalyst unfortunately suboptimally performs. These inherent dynamics make it a real tour de force to study and understand how catalytic solids are formed (‘birth’), function (‘life’) and deactivate (‘death’), an ambition which is already around since the early days of catalysis.

Fig. 1 pictorially illustrates how catalyst scientists may use of a ‘photocamera’ to make real-life 3D movies of the entire lifespan of a heterogeneous catalyst. This photocamera including an extremely powerful lens should have the potential to zoom-in and -out with the capability to focus on both the chemical reactor and individual catalyst particles. Moreover, it should track individual atoms and molecules in real-time, while bond-breaking and -making processes are occurring. All this has then do be done under realistic reaction conditions. Unfortunately, such powerful ‘photocamera’ is not yet on