Photoelectrochemical water splitting for solar hydrogen production over oxide semiconductors: A perspective

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Abstract: Oxide semiconductor solids are promising materials as photoelectrodes for photoelectrochemical water splitting to produce solar hydrogen because they are intrinsically stable in water and of low cost made of earth-abundant elements. But they have poor charge mobility, and multiple modifications are needed to minimize recombination of generated photoelectrons and holes, and to realize full potential of the materials. The stategies include heterojunction formation, band engineering, metal or anion doping, low-dimensional nano-structuring, and loading co-catalysts. Finally, a stand-alone solar fuel production system is needed by combining with a solar cell in tandem, which provides bias voltage needed for unassisted solar fuel production utilizing only solar energy. The presentation summarizes the progress made in my research group to provide a perspective of the practical applications.

Keywords: Photoelectrochemical water splitting, Oxide semiconductor photocatalysts, Unassisted solar fuel production.

1. Introduction

About 400 semiconductor solids are known to have photocatalytic activity for water splitting. Yet they could not satisfy all the requirements for practical use: i) suitable band gap energy (~ 2 eV) for high efficiency, ii) proper band position for reduction/oxidation of water, iii) long-term stability, iv) low cost, v) high crystallinity, and vi) high conductivity. We have selected intrinsically stable metal oxide semiconductors made of earth-abundant elements. But because of their poor charge mobility, we employ multiple modifications strategy to minimize recombination of generated photoelectrons and holes, and extract full potential of the materials. The strategies include; i) heterojunction photoanodes for effective charge separation, ii) band engineering to extend the range of light absorption, iii) metal or anion doping to improve conductivity of the semiconductor and, iv) one-dimensional nanomaterials to secure a short hole diffusion distance and vectoral electron transfer, and v) loading co-catalysts for facile charge separation. A stand-alone solar fuel production system by photoelectrochemical (PEC) water splitting is consructed by combining with a solar cell in tandem, which provides bias voltage needed for unassisted solar fuel production utilizing only solar energy..

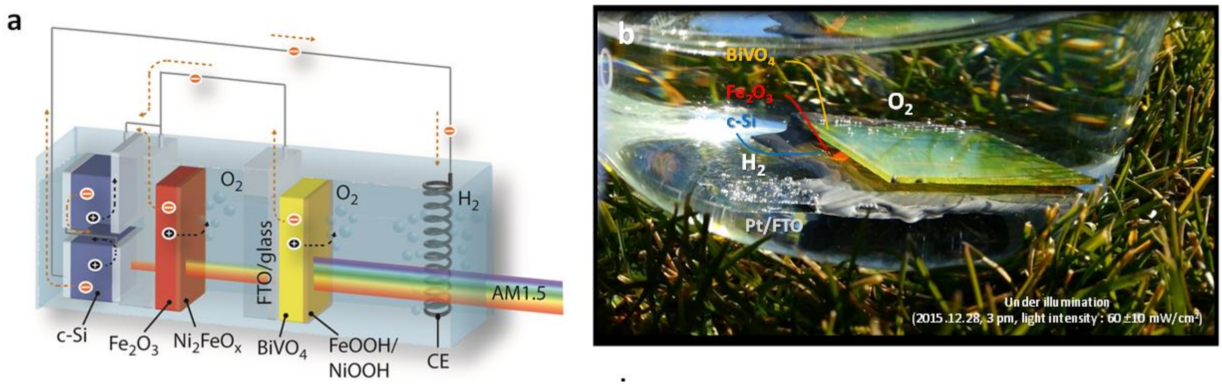
2. Experimental

The base $BiVO_4$ electrode was fabricated by a metal-organic deposition (MOD) method. Then, 1 at% (optimized) Mo doping and partial reduction treatment were performed to increase mainly the bulk charge separation efficiency as reported in our recent work[8]. The reduction treatment *via* a borohydride decomposition method induced $V_o^{\cdot\cdot}$ defects that effectively increase the charge carrier density in $BiVO_4$ lattice. Hence, the partial reduction and extrinsic Mo doping treatments synergistically improve the n-type conductivity of $BiVO_4$. The other photoanode, hematite Fe_2O_3, was synthesized by a nitrate decomposition method. This photoanode was doped with 0.5 at% (optimized) Ti, and also partially reduced by the borohydride decomposition.

3. Results and discussion

In order to enhance the light harvesting in two semiconductors of different E_g's, here we introduce a concept of 'hetero-type dual photoelectrode (HDP)' containing two independent liquid-semiconductor junctions. By using the large E_g semiconductor as the top absorber and the small E_g semiconductor at the bottom, both thermalization and non-absorption losses could be minimized. The advantage of our HDP concept is that current-matching of the two electrodes is not required unlike multi-junction solar cells and heterojunction photoelectrodes**.** Thus we can independently optimize each photoelectrode and the performance of the HDP device becomes the simple sum of the individual performance of the two. As a result, the spectral range of light harvesting in the solar spectrum utilized for PEC water splitting is extended.

Thus we have implemented the concept of the HDP using $BiVO_4$ as the front and α-Fe_2O_3 as the back photoanodes for PEC water splitting. To extract the best possible performance of the single photoanodes, we need bulk and surface modifications by doping and co-catalyst, respectively, to improve the charge separation/transfer properties of these semiconductors [1-5]. As a result, a PEC device made of modified $BiVO_4$ and α-Fe_2O_3 as dual photoanodes in Figure 1 shows stable photocurrents of 7.0±0.2 mA cm^{--2} at 1.23 V_{RHE} under 1 sun irradiation utilizing visible light up to 610 nm [5]. A tandem cell composed with HDP – silicon solar cell demonstrates unbiased water splitting efficiency of 7.7 % [1].



Under illumination
(2015.12.28, 3 pm, light intensity: 60±10 mW/cm^2)

Figure 1. Unassisted solar water splitting with a HDP − PV tandem cell.

4. Conclusions

A hetero-type dual photoelectrode has been adopted as a new strategy to fabricate a stand-alone, highly efficient solar water splitting system. With a HDP of $BiVO_4 \,||\, Fe_2O_3$, we obtained a water oxidation photocurrent density of 7.0±0.2 mA cm^{-2} at 1.23 V_{RHE}, which sets a new performance benchmark for metal oxide photoanodes. The HDP photoanode was successfully incorporated into a tandem cell with a c-Si solar cell for unbiased solar water splitting to demonstrate a stable and reproducible η_{STH} of 7.7 %.

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