Photovoltaic Designs for Integrated and Spontaneous Solar Water Splitting

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A practical method to use sunlight to generate liquid transportation fuels would be a carbon-neutral energy source which could dramatically change the landscape of global energy generation and storage. "Artificial photosynthesis" systems which convert sunlight to energy in the form of chemical bonds are an attractive approach to address this challenge. This presentation will focus on an integrated approach to perform solar driven water splitting to H_2 and O_2 using unconcentrated sunlight.

The minimum potential required to split water into H_2 and O_2 is 1.23 V (values for reducing CO_2 to methanol or to methane are similar). The JCAP photovoltaic approach uses photocathodes (H_2 or hydrocarbon producing) and photoanodes (O_2 producing) linked in a tandem geometry. The photocathode and photoanode provide the same functionality as PS I and PS II in natural photosynthesis.

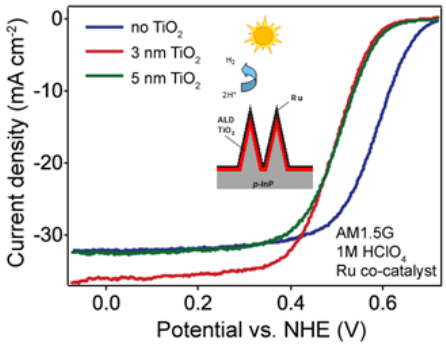

Fig. 1. InP nanopillar photocathodes were produced by reactive ion etching (inset). Using a Ru co-catalyst, nanopillar photocathodes produce H_2 at a current density >30 mA cm^{-2} with an open circuit potential close to 700 mV. Atomic layer deposited TiO_2 is used to provide passivation for long term stability. Adapted from M. H. Lee *et al*. [1].

For reducing protons to make H_2, high efficiencies can be obtained. We have shown that p-InP photocathodes optimized by surface nanostructuring and stabilized by conformal oxide coatings can have current densities exceeding 30 mA cm^{-2} under AM 1.5G illumination. The onset potential for H_2 generation measured with respect to RHE is 650 mV, which is approximately half of the total required for overall water splitting [1]. Our most recent work in developing scalable synthesis approaches for InP and in increasing the onset potential with alternative materials choices will be presented.

Water oxidation by photoanodes is more challenging from an efficiency point of view. Monoclinic $BiVO_4$ is a promising materials choice [2]. It has a band gap of approximately 2.4 eV and has been shown to have an onset potential of up to 1 V vs. the oxygen evolution potential, which makes it very attractive for use in an integrated "no bias" solar to fuel conversion device. We have developed a number of approaches including reactive sputtering, chemical vapor deposition, and hydrothermal synthesis to produce both thin film and nanostructured $BiVO_4$ photoanodes. These allow us considerable control over the Bi/V stoichiometry, doping, contact design, and catalyst integration, all of which will be shown to influence the performance of $BiVO_4$ as a photoanode.

The onset potential of $BiVO_4$ is sufficiently large to allow spontaneous (no-bias) water splitting with a series-connected InP photocathodes. Initial experimental results of this configuration will be presented and the influence of the electrolyte and co-catalyst choices on performance and long-term stability will be discussed.

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[1] M. H. Lee, K. Takei, J. Zhang, R. Kapadia, M. Zheng, Y.-Z. Chen, J. Nah, T. S. Matthews, Y.-L. Chueh, J. W. Ager and A. Javey, *Angew. Chemie Int. Ed.* **51**, 10760 (2012).
[2] Y. Park, K. J. McDonald and K.-S. Choi, *Chem. Soc. Rev.* **42**, 2321 (2013).