Strategies to improve the efficiency of photoelectrochemical water splitting systems

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Direct solar water splitting is an attractive option for the generation of hydrogen as a energy vector for both chemical energy storage and clean fuel. The general idea is to use a semiconductor material to absorb sunlight, generating free electrons in the conduction band and free holes in the valence band, which are eventually used to reduce and oxidize water, respectively. In order to achieve efficient and sustained conversion of solar energy to hydrogen, however, several critical conditions need to be fulfilled: (i) The semiconductor must be stable under illumination in an aqueous solution; (ii) the semiconductor must absorb a significant fraction of the solar spectrum; and (iii) the electron and holes generated need to be efficiently separated and transferred to the aqueous solution, in order to prevent recombination. History has shown that achieving these conditions is very challenging and we are currently nowhere near the implementation of a commercially viable system.

Metal oxide (MO) semiconductors based on abundant, low-cost materials are attractive for solar water splitting systems related to their perceived inherent stability, specifically against oxidation. In addition, taking into account the wide variety of compositions of ternary, quaternary, etc. systems, ample versatility in terms of physical and chemical properties may be achieved. Many systems have been evaluated for photo-oxidation of water in the past 10 years, with some of the more popular materials being Fe_2O_3, WO_3, $BiVO_4$, TiO_2, etc.

In order to improve the efficiency of a solar water splitting system, the specific loss mechanisms need to be elucidated. In general, in addition to standard photoelectrochemical methods, non-steady state methods need to be applied. Intensity-modulated photocurrent spectroscopy (IMPS) is a powerful technique to study the carrier dynamics in a photoelectrochemical system: the photocurrent admittance corresponds to the frequency-dependent external quantum efficiency, and time constants for charge separation, charge transfer and surface recombination can be deduced. Based on the results, strategies can be designed to improve the performance of the system by specifically addressing the main cause of the low efficiency.

In this presentation, a variety of systems will be discussed and strategies to improve their performance are presented: (i) planar, compact WO_3 / $BiVO_4$ heterojunction systems *versus* nanorod array WO_3 / $BiVO_4$ heterojunctions; (ii) $CuBi_2O_4$ with and without catalysts, and an alternative electron acceptor; and (iii) specific examples of other materials to highlight the proposed interpretations.