Solution-processed p-type photocathodes for solar water splitting

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A device that can convert solar energy into a chemical fuel with good efficiency while also offering high stability and the capability to be constructed with widely available materials using inexpensive processing techniques is urgently needed. A promising system that accomplishes this is a photoelectrochemical (PEC) water splitting tandem cell. Our group has previously shown that an inexpensive oxide-based photoanode, particularly hematite (Fe_2O_3)[1] or tungsten oxide, in tandem with a dye sensitized solar cell (DSC) can achieve solar-to-hydrogen conversion efficiencies up to 3.1%.[2] A more practical device would be achieved with the n-type photoanode in tandem with an inexpensive p-type photocathode that could directly reduce water into hydrogen.[3] Here we present progress in the development of solution-processed photocathodes and their application toward overall photoelectrochemical water splitting tandem cells.

Firstly, the feasibility of n-type $BiVO_4$ and p-type Cu_2O for photoanode/photocathode tandem cell is evaluated. By employing water oxidation and reduction catalysts (Co-Pi and RuOx, respectively) together with an operating point analysis we show that an unassisted solar photocurrent density on the order of 1 mA cm^{-2} is possible in a tandem cell and moreover gain insight into routes for improvement. We further demonstrate the unassisted 2-electrode operation of the tandem cell in this system and show that light harvesting is an important limiting factor.

As the light harvesting in a PEC tandem cell can be improved by using a photocathode with smaller bad-gap energy, we next describe efforts toward the development of a delafossite-type $CuFeO_2$ and Cu_2ZnSnS_4 (CZTS) photocathodes. Both of these materials have a band-gap energy of ca. 1.5 eV, suggesting that STH efficiencies higher than 10% are feasible in a tandem device.[3] Moreover their composition from earth abundant atoms accords with solar energy on a global scale. However, specific drawbacks have limited their application to water splitting to date.

For the delafossite-type $CuFeO_2$ the poor charge carrier conductivity has limited it application. Moreover the inconvenience of the solid-state reactions typically used to produce delafossites has previously prevented the facile preparation of thin-film $CuFeO_2$ electrodes. To overcome these issues, we here report the development a solution-based method to afford stable p-$CuFeO_2$ thin-films. Prepared films were characterized by physical and electrochemical techniques, and were tested as photocathodes for water splitting. Initial photocurrents were stable over many days and in the 500 μA cm^{-2} range under AM 1.5G. The photocurrent onset at +0.8 V vs RHE further demonstrated its suitability for a tandem cell. Subsequently, we show that the performance can be drastically improved through doping with oxygen to champion photocurrents of 1 mA cm^{-2}.

In contrast to $CuFeO_2$, CZTS has already attracted much attention in the photovoltaic field because of its outstanding optoelectronic properties. However, its application to water reduction is complicated by the need to employ charge extraction layers not typically suitable for application in a water-based device. Herein, we present two different approaches to overcome these issues and implement CZTS as a photocathode. On the one hand, the electrodeposition of the CZTS is tested, showing the critical role of overlayers such as CdS, AZO and TiO_2 to improve the charge extraction and protect the materials against photocorrosion. On the other, CZTS colloidal inks offer the prospect of a straightforward synthesis and phase control, as well as excellent building blocks for the fabrication of high surface area electrodes. Given the dramatic importance of buffer layers to promote charge extraction, CZTS photocathodes prepared with colloidal inks were examined with alternative overlayers by measuring the photoelectrochemical performance (photocurrents and open circuit potential measurements). Results indicate that CdSe and non-toxic ZnSe outperforms the ubiquitous CdS buffer layer, boosting the charge extraction when ultrathin layers are employed. Likewise, surface modification with methylviologen demonstrates to further enhance the yield of charge separation with a double role: (1) to mediate in electron funneling toward the electrolyte and (2) to shift downward the flat band potential of the film. Alternatively, a novel low-temperature approach for fabricating high surface area CZTS films from nanocrystal inks based on the thermal decomposition of a surfactant in inert atmosphere is introduced. The enhancement in photocurrent and photopotential corroborate the premise that minimizing the minority carrier transit distance can drastically enhance charge separation.

Overall this work demonstrates the viability of fabricating tandem cells in a cost-effective way using inexpensive materials. While traditionally-used systems exhibit poor light absorption as the major limitations, we have demonstrated that narrow band-gap p-type materials such as $CuFeO_2$ and CZTS have strong potential to advance PEC tandem cells toward the 10% STH goal. Moreover, our work defines new paths for the fabrication of inexpensive photocathodes with optimum light harvesting for various applications in solar energy conversion.

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