WO$_3$-NRs/BiVO$_4$ core-shell nanostructure for enhanced photocatalytic H$_2$ production

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Bismuth vanadate (BiVO$_4$) is one of the most promising photocatalytic materials for water splitting with theoretical solar to hydrogen (STH) efficiency of 9.2%. Despite being a good light absorber with a direct bandgap, BiVO$_4$ is characterized by a high recombination rate of photogenerated carriers. As a result, the carrier diffusion length ($L_d$) is much shorter than the thickness required for sufficient light absorption. In our previous work, Pihosh et al. Small (2014), we demonstrated that this issue can be effectively resolved by using core-shell WO$_3$/BiVO$_4$ heterojunction nanorods fabricated by the Glancing Angle Deposition (GLAD) technique, where the BiVO$_4$ absorber layer is thinner than the $L_d$ while its optical thickness is reestablished by light trapping in high aspect ratio nanostructures. Such photoanode resembles the well-known concept of an Extremely Thin Absorber (ETA) solar cell. Our results showed that the ETA concept offers a promising strategy toward efficient photocatalytic systems with a highly stable photocurrent of 3.2 mA cm$^{-2}$. However, in that case the BiVO$_4$ layer covers only the top parts of the WO$_3$-NRs in a form of caps that utilize only ~25-30% of the nanorods’ surface to form a heterojunction. Apparently, there is a clear possibility to further improve the efficiency of the photoanode by covering the WO$_3$-NRs along the whole length with a conformal layer of BiVO$_4$.

At present work we demonstrated that the WO$_3$-NRs prepared by GLAD provide highly efficient pathways for photogenerated electrons and outlined that further optimization of a WO$_3$-NRs/BiVO$_4$ core-shell structure toward better conformality of the BiVO$_4$ ETA layer should lead to an enhanced photocurrent. We fabricated a WO$_3$-NRs/BiVO$_4$ core-shell structure photoanode by a combination of GLAD of WO$_3$-NRs and subsequent Electrochemical Deposition (ED) of BiVO$_4$ and Co-Pi (Fig.1a). The fabricated photoanode demonstrated an ultimate water splitting photocurrent of 6.72 mA cm$^{-2}$ measured under 1 sun illumination at 1.23V$_{RHE}$ that corresponds to ~90% of the theoretically possible value for BiVO$_4$, where H$_2$ and O$_2$ gases evolved at the expected stoichiometric ratio with the generation rates of 102 and 51 µmol h$^{-1}$ cm$^{-2}$, respectively, with a saturated faradaic efficiency of 85% (Fig.1b).