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).

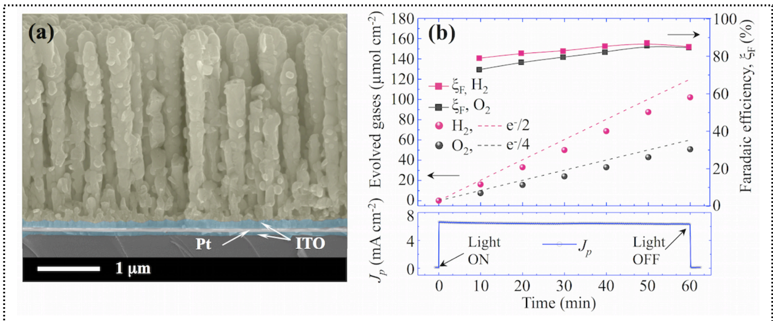

Fig. 1. SEM image of a WO_3-NRs/$BiVO_4$ photoanode (a). Evolution of H_2/O_2 gases measured by gas chromatography with faradaic efficiency on the right axis and photocurrent for the same photoanode at 1.23V_{RHE} under standard solar simulated light of 1Sun (b). All measurements have been performed at a standard 3 electrodes configuration cell in a potassium phosphate buffer solution (pH 7.0) with WO_3-NRS/$BiVO_4$ as a working electrode, Pt- counter and Ag/AgCl- reference electrodes, respectively.