Electronic structure and defect passivation by H_2 annealing of bismuth vanadate photoanodes

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Over the past decade, bismuth vanadate ($BiVO_4$) has been intensely investigated as a promising photoanode material in photoelectrochemical (PEC) water splitting devices. However, little is known about native or impurity defects in this system, their effects on PEC performance, and possible passivation schemes. In this work, a detailed understanding of both the valence band and conduction band orbital character has been achieved using a combination of experimental and theoretical means. In particular, complimentary optical and X-ray spectroscopies, supported by density functional theory calculations, have been applied to high quality monoclinic $BiVO_4$ thin films deposited by chemical vapor deposition, spin coating, and sputtering. The results demonstrate that the 2.5 eV bandgap is indirect with a higher lying 2.7 eV direct gap. Sub-bandgap radiative recombination is observed by temperature dependent photoluminescence measurements, which reveal the presence of a 620 meV deep trap. Annealing thin films of $BiVO_4$ in a H_2 atmosphere significantly reduces the sub-bandgap photoluminescence, which is correlated with an improvement by ~100-200 meV of the onset potential for photoanodic current, an increase of the fill factor, and elimination of photocurrent losses under frontside compared to backside illumination. These results on thin films, together with XPS of the thin films and solid state ^{1}H NMR analysis of powders, suggest important parallel roles for hydrogen in $BiVO_4$. We find that its substitutional incorporation at oxygen vacancy sites leads to passivation of associated deep level defects. In addition, interstitial hydrogen acts as a shallow level donor and beneficially increases conductivity in functional photoanodes. The results highlight that detailed understanding and controlling of carrier trapping in metal oxides, which often exhibit complex native defect properties due to compositional non-uniformities, provide significant opportunity for increasing PEC water splitting performance.