Multijunction Photoanode of Mo:$BiVO_4$ Layered with TiO_2 Inverse Opal and NiB_i Oxygen Evolution Catalyst to Trap Light and Enhance Water Splitting

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Thin-film photoelectrodes can benefit from mechanisms to trap light to increase absorbance and from multi-electron co-catalysts to facilitate charge transfer kinetics. This study examined photonic and catalytic effects in bismuth vanadate photoanodes coupled with a photonic crystal and oxygen evolution catalyst to enhance light energy conversion. A bilayer photoanode was fabricated by depositing a TiO2 inverse opal (i-TiO2-o) with various stopbands, replicated from polystyrene opals assembled from 227, 282, and 305 nm spheres, on top of a thin Mo-doped BiVO4 film. To assess photonic effects, the photoelectrochemical behavior was examined in the presence of sulfite sacrificial hole scavenger. An average gain in excess of twofold in the visible photon-to-current conversion efficiency was measured with i-TiO2-o having a stopband to the red of or coinciding with BiVO4 absorbance. The effects of a heterojunction with TiO2 and of disorder and the open structure were interrogated using a non-scattering nc-TiO2 layer or a disordered TiO2 inverse photonic glass (i-TiO2-g282) having the same air hole size as i-TiO2-o282, and neither was found to cause the gain. The periodicity was found to be key to enhance the photocurrent, and the gain is attributed to light trapping in different parts of the structure, increasing absorbance of bismuth vanadate coupled to the inverse opal. i-TiO2-o282 on top of Mo:BiVO4 also enhanced water photooxidation in borate buffer but to a lesser extent than with sulfite as the kinetics of oxygen evolution remains the predominant limitation. After modification with Ni(Fe)-oxo/hydroxo complex in borate (termed NiBi), the gain in the photon-to-current conversion efficiency reached twofold at the bilayer relative to the parent Mo:BiVO4. Photocurrents increased at low and high bias, which may be caused by reduced recombination and catalytic reactivity after hole transfer to the co-catalyst. Improved light harvesting upon coupling to the photonic crystal with a hole scavenger in solution or the oxygen evolution reaction catalyst on the surface was the highest for bismuth vanadate films that exhibited initially low light-to-current conversion efficiency, presenting a unique promise for thin photoelectrodes.