Nanostructured Photoanodes Based on $BiVO_4$ Modified Inverse Opals and Glass Coupled to Earth-Abundant Oxygen Evolution Catalysts for Solar Water Splitting

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Abstract

Hydrogen produced by splitting water using sunlight at a semiconductor electrode can offer a continuous and clean energy source to meet the global energy demand and limit reliance on fossil fuel. Research into finding efficient and stable photoelectrodes and multielectron catalysts for solar water splitting has continued for four decades since it was first reported at a TiO_2 electrode. In this research project, we propose to design a photoanode based on $BiVO_4$ (E_g = 2.4 eV) inverse opal or inverse glass architecture and investigate the mechanism by which coupling with earth-abundant electrocatalysts improves water photooxidation at the photoanode. In the first aim, we will fabricate a photoanode as an inverse opal or as a disordered inverse glass based on $BiVO_4$ doped with Mo and W, or where $BiVO_4$ is deposited on TiO_2 (E_g = 3.2 eV) or WO_3 (E_g = 2.7 eV) inverse opal or inverse glass and investigate its photoelectrochemistry. The photoanode is predicted to benefit from internal light trapping, thin walls and large pores to enhance hole separation, a junction to drive electron separation and a pathway that facilitates transport. The novelty is to interrogate possible light trapping in disordered glass and ordered inverse opal films for solar-to-hydrogen generation, and the effect of the nanostructured heterojunction in this architecture. In the second Aim, oxygen evolution catalysts, based on Ni, with Fe and Al mixed metal oxide systems, will be coupled to $BiVO_4$ photoanodes fabricated in Aim 1 and the mechanism by which co-catalysis enhances water photooxidation will be interrogated using photoelectrochemical and spectroscopic measurements. The work will address key fundamental questions on coupling co-catalysts and surface modification of semiconductor electrodes, and will have a direct impact on structure design for photovoltaics, photocatalysis for environmental remediation, and solar-to-hydrogen to generate a clean fuel.