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Nanoporous Hydrogen-Reduced BiVO₄: better charge separation with Ni-B_i Electrocatalysts for Photoelectrochemical Water Oxidation JI-AYONG GAN, YUEBING ZHENG, Department of Mechanical Engineering, Materials Science and Engineering Program, and Texas Materials Institute, The University of Texas at Austin — $BiVO_4$ as a photoanode material has attracted broad attention recently as an inexpensive and robust semiconductor for potential application for solar water oxidation. However its photochemical activity is limited by poor charge carrier separation. Here we show that this problem can be solved by constructing a nanoporous morphology as well as controlled introduction of oxygen vacancies via hydrogenation. In comparison to pristing $BiVO_4$, the hydrogen-treated $BiVO_4$ $(H-BiVO_4)$ show superior photocurrent and electron-hole separation yield of 0.95 at 1.23 V vs. reversible hydrogen electrode (RHE) due to enhanced carrier density and conductivity. Significantly, we adopt a layer of nickel-borate $(Ni-B_i)$ complex on the $BiVO_4$ surface as an oxygen evolution catalyst. Modification of H-BiVO₄ photoanode with Ni-Bi has yielded a large ($\sim 300 \text{ mV}$) cathodic shift in the onset potential at pH 7. It shows an outstanding performance in the low bias region and the maximum power point for solar water oxidation was achieved at potential as low as 0.75 V vs. RHE with a photocurrent density of 2.25 mA/cm². We attribute these improved PEC performances to the enhanced charge separation, carrier density and conductivity in these photoanodes.

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