BiVO₄/WO₃/FTO nanostructured photoelectrodes for photoelectrochemical water oxidation

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Introduction

To reduce the dependence of fossil fuels and to decrease the emission of CO₂, there has been a demand for the sustainable sources of energy. In this direction, hydrogen production via photoelectrochemical water splitting is a promising option as it utilizes sunlight to produce high energy density fuel in its clean form. Fujishima and Honda demonstrated the production of chemical fuels via harvesting sunlight using semiconductor photoelectrodes (TiO₂) through water splitting reaction.¹ Although, TiO₂ has been well explored as photoelectrode for PEC water splitting, it absorbs only UV part of the solar spectrum. Revival of interest in improving the overall efficiency of water splitting is based on the development of visible light active semiconductor photoelectrodes. In this direction, WO₃ having band gap of 2.5 to 2.8 eV, has received much attention as a promising photoelectrode for water splitting application.² Several approaches have been explored to improve the water oxidation activity of WO₃ photoelectrodes. Of particular interest is based on designing nanostructured electrodes, coupling with a suitable semiconductor to design tandem configuration. Recently, BiVO₄ has shown particular promise for water oxidation with moderate band gap between 2.4-2.6 eV.³ In this study, we developed a promising heterojunction photoelectrode BiVO₄/WO₃ NR/FTO by integration of porous BiVO₄ layer with the nanostructured WO₃ film (WO₃ NR). Thermal decomposition method was utilized to synthesize nanostructured WO₃ NR. Metal-organic decomposition method was utilized to prepare BiVO₄ layer on top of nanostructured WO₃ electrodes.

Materials and Methods

A spray deposition followed by calcination under controlled atmosphere method was utilized to deposit WO₃ NR on top of FTO substrate. Further, a layer of porous BiVO₄ was deposited on top of nanostructured WO₃ by a surfactant assisted metal organic decomposition method.⁴ The precursor solution for the deposition of the film was obtained by mixing solutions of Bi (Bi(NO₃)₃.5H₂O), and V (vandium (V) tri-propoxy oxide ) in the presence of a structure directing agent, sodium dodecyl sulfate (SDS). The two solutions were mixed in a 1:1 stoichiometric ratio of Bi to V and stirred for 0.5 h. The resulting precursor solution with the desired atomic percentage ratios of Bi: V as 1: 1 was spray-coated on FTO glass using a Grex Tritium double action air brush and consequently annealed at 500°C for 6 h in an air atmosphere to get BiVO₄/FTO. Bare WO₃ NR and BiVO₄ were also deposited on FTO with similar thickness as that of heterojunction electrodes, in order to see the effect of heterojunction configuration. Photoelectrochemical measurements were carried out at room temperature in a three-electrode cell with a flat glass window using a Solartron 1287 potentiostat interfaced to a computer. BiVO₄/WO₃ NR/FTO, WO₃ NR/FTO or BiVO₄/FTO electrodes were used as the working electrode with Pt sheet (~ 3 cm²) and Ag/AgCl (3M KCl) as counter and reference electrodes, respectively. A 1.0 M Na₂SO₄ aqueous solutions (pH7 phosphate buffer) were used as the electrolytes for the PEC measurements.

Results and Discussion

The crystal structure of as synthesized electrodes was determined by X-ray diffraction (XRD) using a Philips X’pert X-ray diffractometer using Cu-Ku radiation.

![XRD patterns of BiVO₄/FTO and WO₃ NR/FTO and BiVO₄/WO₃ NR/FTO, electrodes.](Image)

Figure 1. XRD patterns of BiVO₄/FTO and WO₃ NR/FTO and BiVO₄/WO₃ NR/FTO, electrodes.

XRD patterns of all electrodes studied showed strong peaks for SnO₂ originating from FTO substrate. The WO₃ electrodes exhibited diffraction peaks corresponding to a monoclinic structure (JCPDS card no. 75-2072). After deposition and annealing of a BiVO₄ layer the BiVO₄/WO₃/FTO films exhibited peaks corresponding to BiVO₄ and WO₃. The bare BiVO₄ electrodes correspond to a monoclinic scheelite type crystal structure (JCPDS card no. 14-0688).

Significance

WO₃ having band gap of 2.5 -2.8 eV can capture ~12% of the solar spectrum compared to 4% by TiO₂. Improving overall efficiency of WO₃ is necessary to achieve high water splitting efficiency. In this direction, the present work which utilizes nanostructured WO₃ electrodes has great potential as it can enhance electrode/electrolyte interfacial area. Further, by designing BiVO₄/WO₃/FTO heterojunction electrode, the photogenerated electrons in the conduction band of BiVO₄ were efficiently transferred into the conduction band of WO₃ and consequently improved photocurrents have been achieved.

References