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Short Communication

Electrospun Mo-doped $BiVO_4$ photoanode on a transparent conductive substrate for solar water oxidation

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ABSTRACT

Molybdenum-doped porous bismuth vanadate ($BiVO_4$) nanostructures were successfully synthesized on a fluorine-doped tin oxide (FTO) substrate by a simple electrospinning technique. These nanostructures were used as the photoanode for solar water oxidation. Post hot-pressing treatment was crucial in improving the photocurrents of electrospun $BiVO_4$ by contributing to their adhesion on the substrate and for charge separation.

1. Introduction

Photoelectrochemical (PEC) water splitting is a clean and sustainable pathway to produce hydrogen from water using solar energy. By mimicking a natural photosynthesis system, semiconductors in a PEC water splitting system can convert solar energy into chemical energy which can be used as fuels instead of the conventional fossil fuels. [1] However, improvements in conversion efficiency are required for industrial applications. Therefore, research efforts for developing semiconductor materials with efficient light absorption, charge separation, charge transfer, etc. are under progress.

The nanostructures of semiconductors have been intensively studied to improve their PEC activities, because morphology significantly influences their optical, electrical, and catalytic properties. For example, a high surface-to-volume ratio of the porous nanostructure can be favorable in providing a large interfacial surface area between the semiconductor and the electrolyte where photogenerated charge carriers can be separated and catalytic reactions can occur. In addition, a nanoporous structure is considered to be especially superior for $BiVO_4$ because it can overcome its short diffusion length [2]. One-dimensional (1D) nanostructures, such as nanorods, nanowires, and nanoflowers are also advantageous for facile charge transport along the 1D structures as well as for charge separation across their large interfacial surface areas. Moreover, nanostructures can act as light scattering centers to improve light absorption [3].

Electrospinning is a fascinating method for the synthesis of 1D nanofibers wherein their diameters can be easily controlled by modulating the synthetic parameters such as applied electrostatic force, flow rate, and composition of the polymer/metal precursor [4]. It can also introduce porosity in the fiber structures during the calcination process. Electrospinning of several metal oxide nanofibers has been studied for various applications, including photocatalytic degradation [5–7] and PEC water splitting [8,9], because of the unique structures it can generate. Herein, we have focused on $BiVO_4$ because of its visible light absorption capability (bandgap = 2.4–2.5 eV) and excellent stability in a neutral pH electrolyte [10]. Despite the interesting morphology, most of the studies were carried out with the $BiVO_4$ nanofiber suspended in an electrolyte, and not fixed on the electrode presumably due to its poor adhesion on the bottom substrate [11].

We have successfully synthesized $BiVO_4$ nanofibers on a fluorine-doped tin oxide (FTO) glass by electrospinning without a template and have characterized their photoanode performance. Further, the $BiVO_4$ nanofibers were doped with molybdenum followed by post hot-pressing to improve charge separation and contact adhesion on the substrate.

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2. Experimental

2.1. Electrospun $BiVO_4$ photoanode preparation

0.5624 g of $Bi(NO_3)_3 \cdot 5H_2O$ (≥98%, Sigma-Aldrich) and 0.3074 g of $VO(acac)_2$ (98%, Sigma-Aldrich) were dissolved in a 7.73 mL solvent mixture of 3:5:4.2 (by volume ratio) CH_3COOH (≥99.7%, Sigma-Aldrich), ethanol (≥99.9%, J.T.Baker), and N,N-dimethylformamide (≥99.8%, Sigma-Aldrich). Further, 0.35 g of polyvinylpyrrolidone (PVP, Mw = 1,300,000, Sigma-Aldrich) was added. A clean FTO substrate (8 Ω, Pilkington) was placed on the collector of an electrospinning (NanoNC Co., Ltd., Korea) chamber. The distance between the collector and needle was fixed at 15 cm with an applied voltage of 15 kV, and a solution flow rate of 10 μL/min. After electrospinning, it was annealed at 500 °C in air for 1 h. 0.0076 g of $MoO_2(acac)_2$ (99%, Alfa aesar) was added to the precursor solution for Mo doping, and the other electrospinning conditions were maintained. Hot-pressing was performed with preheated metallic plates at 120 °C for 30 s, followed by annealing at 500 °C for 1 h.

2.2. Photoelectrochemical measurements

Currents of the $BiVO_4$ and Mo-doped $BiVO_4$ photoanodes were measured by a potentiostat (Ivium Technologies) in a 0.1 M potassium phosphate (K-Pi) buffered electrolyte (pH 7.0). For the photocurrent measurement, simulated sunlight was produced by a solar simulator (ABET, Sun. 2000) and passed through the quart window of an electrochemical cell to illuminate the working electrodes. The solar simulator was equipped with a 300 W xenon lamp and an air mass (AM) 1.5 filter, and the input power intensity (100 mW cm^{-2}) was confirmed with a reference silicon solar cell. A three-electrode configuration was employed with a Pt counter electrode, an Ag/AgCl reference electrode, and a $BiVO_4$ photoanode as the working electrode. All measured potentials were converted relatively to a reversible hydrogen electrode (RHE) using E (vs. RHE) = E (vs. Ag/AgCl) + 0.209 + 0.0591 V × pH.

Electrochemical impedance spectroscopy (EIS) and other material characterization methods are described in ESI†.

3. Results and discussion

The morphology of the electrospun 1D nanofibers was obtained by scanning electron microscopy (SEM) images (Fig. 1). The smooth surface of nanofibers became rougher during calcination at 500 °C in air because PVP was eliminated and the remaining Bi and V precursors were oxidized to form porous nanofibers similar to the other electrospun fibers (Fig. 1(a)–(b)).

Mo is one of the most effective dopants in improving the PEC performance of the $BiVO_4$ photoanode as it influences electronic properties such as carrier concentrations [12]. Therefore, to increase the PEC activity, Mo-doped $BiVO_4$ (Mo:$BiVO_4$) was prepared by adding molybdenum oxide in the precursor solution. SEM image (Fig. 1(c)) showed that the morphologies of the 1D nanofibers were not affected by the molybdenum precursor. The thickness of the electrospun films was ~8.2 μm (Fig. S1 in ESI†) for both the $BiVO_4$ and the Mo:$BiVO_4$ nanofibers. Efficient light absorption was expected and as shown in UV–Vis spectra (Fig. 1(d)), the almost identical light absorption spectra of the $BiVO_4$ and the Mo:$BiVO_4$ nanofibers indicate that Mo doping does not change the light absorption property including the bandgap. The $BiVO_4$ nanofiber films absorbed up to ~500 nm wavelength of light, corresponding to a 2.5 eV bandgap for $BiVO_4$, consistent with the reported value.

X-ray diffraction (XRD) patterns (Fig. 2(a)) showed that the electrospun $BiVO_4$ and Mo:$BiVO_4$ nanofiber films had monoclinic scheelite-type $BiVO_4$ crystal structure, a popular and active phase for photocatalysts. Monoclinic $BiVO_4$ is known to have the highest

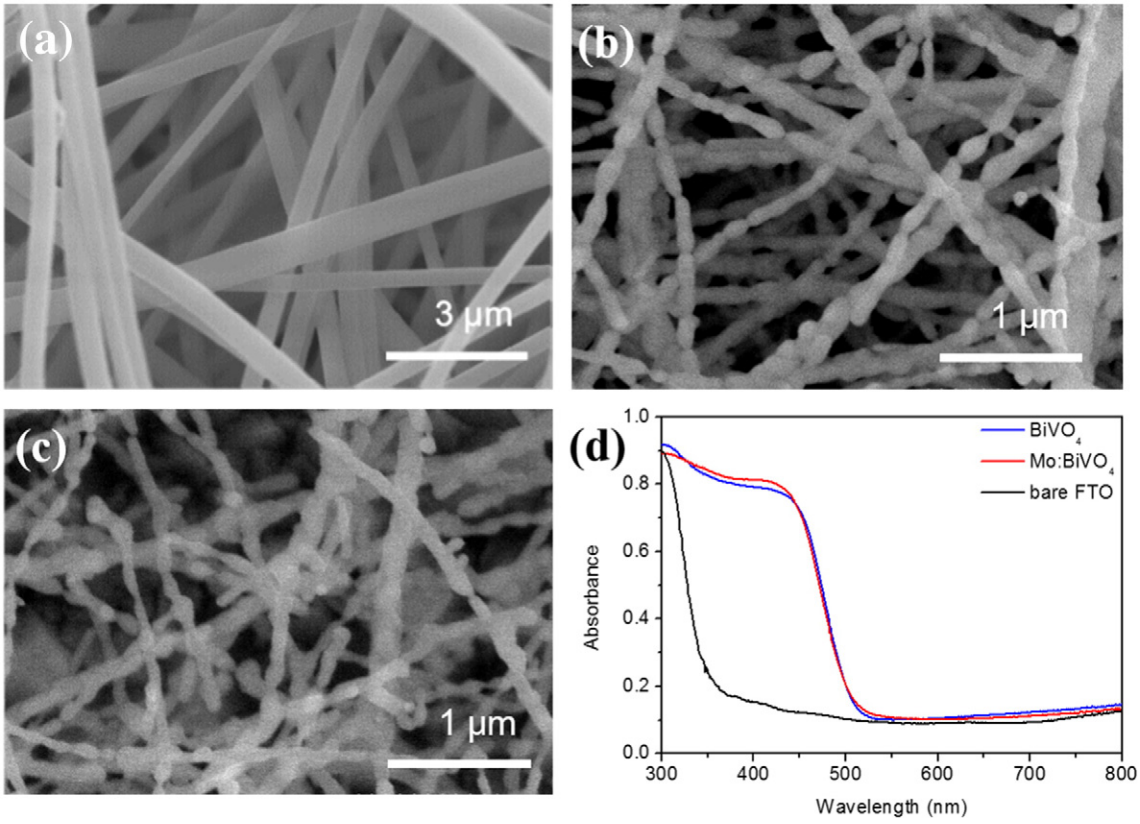

Fig. 1. SEM images of (a) electrospun fibers before annealing, (b) $BiVO_4$ fibers after annealing, (c) Mo:$BiVO_4$ fibers, and (d) UV–Vis absorbance of the bare FTO and $BiVO_4$, Mo:$BiVO_4$ fiber films on the FTO substrates.