



# Solvent-engineering assisted synthesis and characterization of BiVO<sub>4</sub> photoanode for boosting the efficiency of photoelectrochemical water splitting



Truong-Giang Vo<sup>a,b</sup>, Jian-Ming Chiu<sup>b</sup>, Chia-Ying Chiang<sup>a,\*</sup>, Yian Tai<sup>b,\*</sup>

<sup>a</sup> Sustainable Engineering Lab, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan ROC

<sup>b</sup> Nanohybrid Materials and Devices Lab, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan ROC

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## ABSTRACT

A simple direct, scalable and reproducible approach for preparing photoelectrochemically active BiVO<sub>4</sub> films on fluorine-doped tin oxide (FTO) substrates by hydrothermal method using a mixing solvent of ethylene glycol/water was presented for the first time. As-prepared BiVO<sub>4</sub> thin films were found to have pure monoclinic scheelite structure with a compact, irregular microstructured morphology and strong absorption in the visible-light region with estimated bandgap of 2.4 eV. When applied as an electrode material for water splitting in borate electrolyte solution, a significantly enhanced stability, coupled with a 15-fold increase in photocurrent density (ca. 1.04 mA cm<sup>-2</sup>) are observed compared to those of conventional hydrothermal synthesized films. The BiVO<sub>4</sub> prepared with mixed solvent gave a substantial enhancement of the incident photon to current efficiency (IPCE) and absorbed photon to current efficiency (APCE) during light driven oxygen evolution reaction.

## 1. Introduction

Over the past few decades, many scientists and engineers have dedicated substantial efforts exploiting and developing efficient photocatalysts to deal with energy and environmental problems which have threatened the modern society. Till now, as benchmark materials for photoconversion processes, titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) have been intensively studied for this purpose owing to their high efficiency, nontoxicity, high stability, environmentally friendly and inexpensive materials [1–3]. Nevertheless, their advantageous properties are offset by the fact that they are incapable of absorbing visible light and have high recombination rate of photo-excited species [4,5]. Therefore, many other material systems which absorb visible light such as CdS [6], PdS [7], Se-based compounds (NiSe<sub>2</sub>, CoSe<sub>2</sub>, PdSe<sub>2</sub>) [8] have been recently developed. However, practically they are barely applicable because of the elemental toxicity and accompanied environmental issues during preparation and disposal processes [9,10]. Among various visible-light responsive materials, the binary metal oxide, bismuth vanadate (BiVO<sub>4</sub>), has been recognized as one of the most promising materials because of its earth abundant, relatively nontoxicity, and high stability against chemical and photoelectrochemical (PEC) corrosion [11,12]. Among three BiVO<sub>4</sub> polymorphs (monoclinic, tetra-

gonal and tetragonal-zircon structures), it is well-known that only monoclinic BiVO<sub>4</sub> with relatively low band gap (2.2–2.5 eV) [5,12] shows excellent photocatalytic performance in the decomposition of organic pollutants and photocatalytic evolution of oxygen under visible light irradiation [3,13]. Additionally, it provides well-positioned band edges (conduction band and valence band at ~0 and 2.4 V vs. RHE, respectively) and requires relatively low onset potential for water oxidization [14]. Hence, monoclinic BiVO<sub>4</sub> has been intensively and widely studied for use in both photocatalytic and photoelectrocatalytic applications in recent years.

This interest in BiVO<sub>4</sub> has led to a considerable amount of works on the synthesis of BiVO<sub>4</sub> bulks. Although it is beneficial for in-depth analysis of crystal properties, bulk powders are unsuitable for the practical applications. This drawback has led to a considerable amount of works on the preparation of BiVO<sub>4</sub> films over a conductive substrate. There are many approaches for the fabrication of BiVO<sub>4</sub> on a substrate, including metal organic decomposition [15–19], chemical vapor deposition [20], chemical bath deposition [21], dip coating [22], spray pyrolysis [23], and electrodeposition [24,25]. It cannot be denied that each of these above methods has certain advantages, but they also face some obstacles such as poor substrate adhesion, high reaction temperature (500 °C) or complicate post-treatment [26]. For instance,

\* Corresponding authors.

E-mail addresses: [cychiang@mail.ntust.edu.tw](mailto:cychiang@mail.ntust.edu.tw) (C.-Y. Chiang), [ytai@mail.ntust.edu.tw](mailto:ytai@mail.ntust.edu.tw) (Y. Tai).

Kang et al. have described the poor adhesion and coverage of BiVO<sub>4</sub> deposited on conducting glass, fluorine-doped tin oxide (FTO), by electrodeposition method [25]. Luo et al. reported a procedure to fabricate BiVO<sub>4</sub> microelectrode by chemical bath deposition that requires post-annealing at 580 °C for 24 h [21]. Alarcón-Lladó and coworkers presented the synthesis of BiVO<sub>4</sub> by chemical vapor deposition using even higher temperature of 900 °C [20]. Such high temperature process limits the option of substrates that can be utilized. To solve those difficulties, herein, we report a simple, convenient, relatively low temperature, and reproducible hydrothermal treatment process for fabricating BiVO<sub>4</sub> thin film on FTO substrate. The hydrothermal method has advantages over other wet chemistry methods, including the potential for generating highly crystalline and narrow size distribution products, and high morphology control ability by tuning process parameters or precursor compositions [27]. Simultaneously, ethylene glycol (EG) is widely accepted as a green solvent with high viscosity and chelate ability which can control crystal growth. In the present study, we employed a mixture of water and EG as solvent for the hydrothermal synthesis of BiVO<sub>4</sub>. This approach results in a dense, homogeneous and high crystalline hydrophilic BiVO<sub>4</sub> film with robust substrate adhesion, leading to remarkable PEC performances.

## 2. Experimental

### 2.1. Materials

FTO-coated glass (15 Ω/sq, 14 mm×18 mm) was employed as the substrate for thin film electrode fabrication. Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Acros, 99.9%), NH<sub>4</sub>VO<sub>3</sub> (Alfa Aesar, 98%), VO(acac)<sub>2</sub> (Strem, 98%), acetic acid (Sigma, 99.7%), 2,4-pentanedione (Sigma, 99.5%), HNO<sub>3</sub> (Sigma, 65%), NaOH (Sigma, 97%), ethylene glycol (Acros, 99.9%), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Showa, 99%) were used directly without any further purification.

### 2.2. Fabricating BiVO<sub>4</sub> film

FTO-coated glass was cleaned by sonication in de-ionized (DI) water, acetone and isopropanol alcohol (20 min each), and following by nitrogen (N<sub>2</sub>) gas flux drying. To orientate and to boost high-density growth, a seed layer was deposited on FTO-coated glass by previous spin-coating procedures [16] with slight modification. The spin-coating precursor was made as follows. Equimolar amounts of bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, 0.25 mmol) and vanadyl acetylacetonate (VO(AcAc)<sub>2</sub>, 0.25 mmol) were added to a 5 mL solution of 1:8.25 acetic acid and 2,4-pentanedione, following by sonication for 15 min to obtain the stable dark green solution. Prior to coating, the resulting solution was filtered with a 0.22 μm nylon filter (Thermo Scientific), then a small amount of precursor solution being spread over an area of 0.64 cm<sup>2</sup> in the FTO substrate (previously masked with the aids of Scotch tapes to leave some non-coated FTO available for the electrical contacts). Spin coating parameters were set at 2500 rpm for 20 s. After drying in air, coated glass was annealed in a muffle furnace at 500 °C for 10 min with the ramping rate of 2 °C min<sup>-1</sup>.

The synthetic route of BiVO<sub>4</sub> films is illustrated in Fig. 1a. In a typical synthesis procedure, for control purpose, 1.0 mmol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 20 mL of HNO<sub>3</sub> 1 M and 10 mL of ethylene glycol (EG) to form solution A. Meanwhile, 1.0 mmol NH<sub>4</sub>VO<sub>3</sub> was dissolved in 20 mL of NaOH 0.5 M and 10 mL of EG to form solution B. After stirring for 30 min at room temperature, solution B was added slowly to solution A with continuous stirring for an additional 30 min. A piece of FTO glass slide (14 mm x 18 mm) was then immersed in this yellow suspension with its conductive side down. Afterward, the 60 mL of the mixture was transferred to a 100 mL Teflon-lined stainless autoclave and then put in an oven at 180 °C under autogenous pressure for 12 h. After that, the autoclave was cooled naturally to ambient temperature, the sample was taken out and washed with acetone and blown dry using an N<sub>2</sub> stream. For convenience, BiVO<sub>4</sub> film prepared

from the mixed solvent system was termed as MIX-BVO. Also, to confirm the effect of EG, the comparative experiments using pure water without EG (denoted as H<sub>2</sub>O-BVO) and pure EG without water (EG-BVO) were also carried out. It should be mentioned that for a fair comparison in photoelectrochemical performance, H<sub>2</sub>O-BVO samples with relatively controlled thickness were grown by adjusting the hydrothermal deposition duration time while keeping other parameters constant.

### 2.3. Morphology and crystal structure characterization

The morphology of the samples prepared as described above was analyzed by field emission scanning electron microscope (JEOL JSM6700) equipped with an energy-dispersive X-ray spectroscopy (EDS) analysis, which was employed to obtain an insight of the bulk element composition of the sample. The crystal phase of as-synthesized samples was characterized by Bruker D2 Phaser XRD in the region of 2θ=10–70° using Cu Kα radiation (λ=0.15418 nm) with a step size a 0.02° and a scanning rate at 0.1° s<sup>-1</sup>. The absorption spectra and the light-harvesting efficiency (LHE) of the electrode were measured and calculated using a doubled-beam ultraviolet-visible (UV-Vis) spectrophotometer (Jasco V670, Japan) using bare FTO as a reference. The Raman spectra and images were taken with a microscopic Raman system (MRI, Protrustech Co, Ltd., Taiwan). The 532-nm line of a laser with a laser power of 50 mW was used as the excitation wavelength. A motorized xy stage was applied for Raman mapping, a technique that yields information on the spatial distribution of the different crystalline parts that are located on the surfaces of the film. The photoluminescence (PL) spectra of the samples were recorded on Fluorolog-Tau-3 spectrofluorometer (Jobin Yvon, USA) with an excitation wavelength of 325 nm. X-ray photoelectron spectroscopy (XPS) (VG ESCA Scientific Theta Probe & VG Scientific ESCALAB 250) was used for the surface element composition analysis.

### 2.4. PEC measurements

The PEC performance of synthesized BiVO<sub>4</sub> electrodes as photoanodes for water oxidation reaction was carried out in a three-electrode, single-compartment quartz cell connecting with an electrochemical analyzer potentiostat (Autolab PGSTAT302N, Switzerland). Notably, the PEC cell has two sides of quartz for preventing light absorbance. The BiVO<sub>4</sub> thin film with working area of 0.64 cm<sup>2</sup> (8 mm for both length and width) was used as the working electrode while a 2.5 cm×2.5 cm Pt mesh (100 mesh) and an Ag/AgCl (3 M KCl) electrode were employed as counter and reference electrodes, respectively. 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> aqueous solution (pH 9.3) was used as the electrolyte. In the cases of studying BiVO<sub>4</sub> surface reaction kinetics, 0.1 M sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) was added into the electrolyte as a hole scavenger. Linear scan voltammetry (LSV) was conducted in the dark and under irradiation by a solar simulator with a 300 W Xenon lamp (Model 66905, Newport) and an AM 1.5 G filter. The light intensity of the lamp was calibrated with a reference silicon solar cell and a readout meter for solar simulator irradiance (Model 91,150 V, Newport) to warrant that light intensity was fixed at 100 mW cm<sup>-2</sup> in all experiments. Unless stated otherwise, the light was irradiated through the BiVO<sub>4</sub> semiconductor side (front-side). Photocurrents were measured while sweeping the potential from -0.6 to 0.7 V vs. Ag/AgCl (3 M KCl) in the positive direction with a scan rate of 10 mV s<sup>-1</sup> and step potential of 0.0244 V. At least three samples were tested to obtain the significant statistical results for all experiments unless otherwise noted. Cyclic voltammetry (CV) scans were performed for five cycles with similar settings as described for LSVs. Mott-Schottky plot was obtained by using a potentiostat (Autolab, Netherlands) in the dark with the applied frequency of 1 kHz and amplitude of 10 mV. The electrochemical impedance spectroscopy (EIS) were conducted at 0.5 V vs. Ag/AgCl with an AC amplitude of 10 mV, frequency of 100 kHz–

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