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WO₃/BiVO₄ composite photoelectrode prepared by improved auto-combustion method for highly efficient water splitting

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ABSTRACT

We report on the improvement in the water splitting efficiency of a WO₃/BiVO₄ composite photoelectrode by the application of an improved auto-combustion method to the preparation of porous BiVO₄ thin films. The unique feature of this preparation method is the addition of both NH₄NO₃, as a strong oxidizing agent, and an organic additive into BiVO₄ precursor solution. The local decomposition heat of the organic additive and oxidizing agent created a porous film with small, highly crystalline BiVO₄ particles. The photoelectrode has many advantages over existing ones, such as the high light-harvesting efficiency (LHE), a single BiVO₄ phase, the facile access of the holes to the photoelectrode/electrolyte interface, and the ease of water and oxygen diffusion. The maximum incident photon-to-current efficiency (IPCE) was estimated to be 64% (at 440 nm, 1.23 V vs. RHE) and the applied bias photon-to-current efficiency (ABPE) reached as high as 1.28%. This ABPE value is highest among all oxide semiconductor photoelectrodes reported previously, except for the case of a stacking photoelectrode system.

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1. Introduction

Ever since water splitting into hydrogen and oxygen by a TiO₂ photoelectrode under ultraviolet illumination was reported [1], various semiconductor photoelectrodes have been studied [2]. Porous n-type semiconductor photoelectrodes, especially, have been vigorously investigated using visible-light responsive metal oxides, as a practical water splitting method using

solar light. This is because oxide semiconductor photoelectrodes are superior in terms of the facility of oxygen evolution, as well as in the simplicity of preparation by a wet-coating and calcining process, and easy hydrogen collection at the counter electrode [2,3].

It is important to improve the applied bias photon-to-current efficiency (ABPE or $\eta_{\text{sun}}^{\text{ex}}$) for practical use of photoelectrodes, but the ABPE values are still very low.

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Approximate ABPE can be estimated from the reported current-potential ($I-V$) curve under simulated solar light [3–5]. The photoelectrodes of WO_3 semiconductor (band-gap energy (E_g) = 2.7 eV) could split water effectively, and the maximum ABPE was estimated to be approximately 0.7% [6]. As for Fe_2O_3 semiconductor, the E_g of Fe_2O_3 is small (E_g = 2.1 eV), hence visible light below about 590 nm can be used. The maximum ABPE of nanostructured Fe_2O_3 , modified by Pt on Au substrate photoelectrode [7], was estimated to be approximately 1.1%. However, higher external voltage on Fe_2O_3 photoelectrodes is required to obtain sufficient photocurrent, because the conduction band potential (E_{CB}) of Fe_2O_3 is more positive than for WO_3 . On the other hand, BiVO_4 is a semiconductor that is attracting attention as an effective candidate material for water splitting [3,8–29]. The E_g of BiVO_4 (E_g = 2.4 eV) is smaller than that of WO_3 , which means it can utilize visible light below approximately 520 nm. It is noted that the E_{CB} of BiVO_4 is more negative than those of WO_3 and Fe_2O_3 . The valence band potential of BiVO_4 is more negative than those of the common oxide semiconductors, because the valence band of BiVO_4 is formed by the hybridization of O-2p and Bi-6s orbitals [3,28,29]. In order to obtain efficient ABPE on BiVO_4 photoelectrodes, various modifications have been reported, such as a thin-film underlayer (SnO_2 [12,13] and WO_3 [14–20]), or the coupling with an oxygen evolution catalyst (cobalt-phosphate [20–23], cobalt-borate [24] and FeOOH [25]). Recently, we have succeeded in greatly improving the efficiency of a $\text{WO}_3/\text{SnO}_2/\text{BiVO}_4$ composite photoelectrode using a highly concentrated carbonate aqueous electrolyte solution [18,19], whose maximum ABPE reached 0.85%. Furthermore, we stacked two of the same photoelectrodes to improve the light-harvesting efficiency (LHE), resulting in an ABPE of 1.35%, however, there was the problem of doubling the cost.

In this study, we have prepared BiVO_4 film of $\text{WO}_3/\text{BiVO}_4$ composite photoelectrodes using an improved auto-combustion method, with both an organic additive and NH_4NO_3 (a strong oxidizing agent) added into the BiVO_4 precursor solution. The auto-combustion method is suitable for low-temperature synthesis of single-phased and porous materials, as well as nanoparticles of composite oxide due to the local decomposition heat of the organic additive and the oxidizing agent [30]. We report here that this preparation method improved both LHE by achieving efficient optical confinement structure and charge-transfer property. The maximum IPCE (incident photon-to-current efficiency) was improved to 64% (at 440 nm, 1.23 V vs. RHE) and the ABPE reached 1.28% without stacking.

2. Experimental details

2.1. Preparation of $\text{WO}_3/\text{BiVO}_4$ composite photoelectrodes

We prepared $\text{WO}_3/\text{BiVO}_4$ composite photoelectrodes by spin-coating on conductive glass as follows. First, the WO_3 underlayer (optimal thickness of about 190 nm) was coated twice on F-doped SnO_2 (FTO) conductive glass substrate

(surface resistance $10 \Omega \text{ sq}^{-1}$, Nippon Sheet Glass Co., Ltd.) at 1000 rpm for 15 s. The WO_3 precursor was 0.7 mol dm^{-3} peroxotungstic acid aqueous solution, as reported previously [31]. The films were then calcined at 500 °C for 30 min for each coating. Subsequently, the BiVO_4 layer was coated six times onto the WO_3 underlayer using a spin-coater (1000 rpm, 15 s). The BiVO_4 layer was prepared by an improved auto-combustion method. The BiVO_4 precursor solution was prepared by mixing of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and V_2O_5 in 2 mol dm^{-3} HNO_3 aqueous solution [11]. The concentration of the BiVO_4 precursor solution was 0.07 mol dm^{-3} (Bi:V = 1:1). Furthermore, Triton X-100 ($\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$, $n = 9-10$, non-ionic surfactant, 0.5 v/v %) and a large amount of NH_4NO_3 aqueous solution (5.52 mol dm^{-3} , 9.9 v/v %) were added as an organic additive agent and oxidation agent, respectively. The films were calcined at 550 °C for 30 min for each coating. Triton X-100 improves the film uniformity. We refer to this photoelectrode as “ $\text{BiVO}_4\text{-TN}$ ”. As reference samples, we also prepared the photoelectrodes with only NH_4NO_3 aqueous solution ($\text{BiVO}_4\text{-N}$), only Triton X-100 ($\text{BiVO}_4\text{-T}$), and no additives ($\text{BiVO}_4\text{-non}$) in the BiVO_4 precursor solution.

2.2. Photoelectrochemical measurements and characterizations

$I-V$ curves were measured by an electrochemical analyzer (BAS. Inc. ALS630A) using a three-electrode cell with an Ag/AgCl reference electrode and a Pt coil counter electrode. Potential sweeps (scan rate, 50 mV s^{-1}) were carried out in a direction from positive to negative to avoid overestimating ABPE. We used a 0.1 mol dm^{-3} or saturated (ca. 2.8 mol dm^{-3}) KHCO_3 aqueous solution with bubbling CO_2 gas as an electrolyte in a Pyrex glass cell with an antireflection film on the irradiation side. The working electrode with a black mask (aperture area of 0.28 cm^2) and back reflection plate was irradiated from the BiVO_4 film side (front illumination), because of the larger photocurrent than from the FTO side (back illumination). We used a solar simulator (JIS-A-class, SAN-EI ELECTRIC Co.) as a light source. The light intensity of the solar simulator (Supporting information, Fig. S1a) was calibrated to AM-1.5 (1 SUN, 100 mW cm^{-2} , Fig. S1b) using a solar simulator spectroradiometer (SOMA Optics, Ltd), immediately after calibration using a standard light source (certification body, Japan Electric Meters Inspection Corporation, JEMIC).

We also investigated the amount of H_2 and O_2 evolved from the photoelectrochemical cell by a closed gas-circulating system with online gas chromatography (Shimadzu Co., GC-8A, TCD, 5A molecular sieves, Ar carrier). The photoelectrochemical cell consists of a $\text{WO}_3/\text{BiVO}_4$ composite photoelectrode, a Pt counter electrode and 0.1 mol dm^{-3} KHCO_3 aqueous electrolyte solution.

Light-harvesting efficiency (LHE) was calculated from equation (1).

$$\text{LHE} = 1 - R - T \quad (1)$$

Transmittance (T) and reflectance (R) was measured using an integrating sphere (Jasco, V-570, ISN-470).

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