



Photoanode characteristics of multi-layer composite BiVO₄ thin film in a concentrated carbonate electrolyte solution for water splitting

Rie Saito, Yugo Miseki, Kazuhiro Sayama*

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, Japan

ARTICLE INFO

Article history:

Received 5 December 2012
Received in revised form 7 February 2013
Accepted 25 February 2013
Available online 14 March 2013

Keywords:

Bismuth vanadate
Tungsten oxide
Tin oxide
Photoelectrochemical cell
Solar energy conversion

ABSTRACT

The improvement of the solar energy conversion efficiency is important for the solar hydrogen production using semiconductor photoelectrodes. In this paper, the photoelectrochemical properties of multi-layer composite photoelectrodes of thin film BiVO₄ in various electrolyte solutions were investigated in detail. The improvement of photocurrent and the decrease of onset potential were observed on BiVO₄ composite electrodes in carbonate electrolyte solution as well as bare BiVO₄ electrode. The LHE (light-harvesting efficiency) and photocurrent were significantly improved by the light trapping structure of the double stacked photoelectrodes. The photocurrent was increased by insertion of an optimum SnO₂ intermediate layer. The decrease of resistance at the BiVO₄ composite electrodes was observed comparison with the bare BiVO₄. In the BiVO₄/SnO₂/WO₃ photoelectrode, the highest IPCE (incident photon to current efficiency) was 53% at 420 nm. The H₂ and O₂ were evolved stoichiometrically. The maximum value of the applied bias photon-to-current efficiency (ABPE) was 1.35%. The reaction mechanism of carbonate anions, mainly affecting the BiVO₄ layer, was discussed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The solar splitting of water into H₂ and O₂ using a photoelectrochemical cell composed of an n-type semiconductor photoanode and H⁺-reducing cathode has been widely investigated for application on solar energy conversion and storage [1–3]. Some nano-crystalline oxide semiconductor photoelectrodes with narrow band-gap energy (E_g) [2,4,5], such as Fe₂O₃ ($E_g = 2.1$ eV), WO₃ ($E_g = 2.7$ eV) and BiVO₄ ($E_g = 2.4$ eV) on a conductive glass substrate, are easily prepared by wet coating process and calcination under an air atmosphere. These photoelectrodes have significant advantages for the practical production of solar hydrogen, including simple preparation, H₂ gas accumulation and large area production. These nano-crystalline photoelectrodes offer an improved photocurrent. Augstynski et al. reports the ca. 2.7 mA cm⁻² (at 1.23 V_{RHE}) using the nano-crystalline WO₃ photoelectrode [6]. Grätzel et al. reported that in the case of a modified Fe₂O₃ film photoelectrode consisting of a perpendicularly oriented dendritic nanostructure [7–10], the best photocurrent reached ca. 3.2 mA cm⁻² (at 1.23 V_{RHE}) [9]. Moreover, Pt-doped Fe₂O₃/Pt nanorod arrays on a gold substrate photoelectrode was developed by Park et al., and the photocurrent at 1.23 V_{RHE} was very high (ca. 7.0 mA cm⁻²) [11]. On the other hand, the solar energy conversion efficiency (η_{sun}) value is still low

and the improvement of η_{sun} poses the greatest challenge. Several equations have been used to calculate the value of η_{sun} [5,12,13], and a η_{sun} considering the energy loss resulting from the external bias in a two-electrode system, that is, applied bias photon-to-current efficiency (ABPE or $\eta_{\text{sun}}^{\text{ex}}$), is calculated by the following equation [5].

$$\text{ABPE (\%)} = \left[\frac{J_{\text{opt}} \times (1.23 - E_{\text{opt}})}{Int} \right] \times 100 \quad (1)$$

where J_{opt} /mA cm⁻² is the photocurrent density at E_{opt} ; E_{opt} /V is the applied voltage at the optimal operating conditions between the working and counter electrodes; Int /mW cm⁻² is the intensity of incident solar light under A.M. 1.5, 1 Sun condition; and 1.23 V vs. reversible hydrogen electrode (RHE) is the standard electrode potential of H₂O.

To improve ABPE, decreases of E_{opt} and onset potential, and an improvement of I - V curve shape are very important factors of the research as well as an increase in the photocurrent. The applied bias and the onset potential are influenced by the conduction band potential (E_{CB}) of semiconductors. In the case of the Fe₂O₃ photoelectrodes, it was reported that large applied bias was needed to get high photocurrent due to the positive E_{CB} . Recently, the BiVO₄ photoelectrode has been attracting considerable attention. It is noteworthy that the E_{CB} of BiVO₄ (-0.4 V vs. NHE, pH = 7 [14]) is higher than that of WO₃, and is close to that of TiO₂. The photocurrent of BiVO₄ was significantly increased by the addition of an under-layer coating of WO₃ [14–16] or SnO₂ [17,18]

* Corresponding author. Tel.: +81 29 861 4760; fax: +81 29 861 4760.
E-mail address: k.sayama@aist.go.jp (K. Sayama).

on a conducting glass. However, the photocurrent of these BiVO₄ multi composite photoelectrodes is still low. Lee et al. reported that the photocurrent at 1.23 V_{RHE} of heterojunction BiVO₄/WO₃ electrodes reached ca. 1.4 mA cm⁻² [14]. Moreover, various surface treated and modified BiVO₄ photoelectrodes were developed [19–25] and Choi et al. reported that the photocurrent at 1.23 V_{RHE} of FeOOH/BiVO₄ photoelectrodes reached ca. 2.3 mA cm⁻² [24].

We have investigated the improvement of the photoelectrochemical properties of bare BiVO₄ photoelectrode in a carbonate electrolyte [26], as opposed to the sulfate electrolyte that has generally been used. Recently, we reported BiVO₄ composite electrodes and the effect of introducing a SnO₂ intermediate layer between the BiVO₄ and WO₃ layers (i.e., BiVO₄/SnO₂/WO₃ photoelectrode) in a carbonate electrolyte [27]. The photocurrent and ABPE were found to increase by the insertion of a SnO₂ intermediate layer and by carbonate ion effect.

In this study of a multi-layer composite thin-film BiVO₄ photoelectrode, we investigated the effects of the BiVO₄ and SnO₂ film thickness, photoelectrochemical properties on composite electrodes in various electrolyte solution, and light trapping structure on the photoelectrochemical and optical properties in detail. The photocurrent was prominently affected by the film thickness of the BiVO₄ upper layer and the SnO₂ intermediate layer. Regarding the effect of the light trapping structure, it was found that the incident photon-to-current conversion efficiency (IPCE) was improved in the visible light region. The reaction mechanism of effect of the carbonate anions was also discussed.

2. Experimental

2.1. Photoelectrodes preparations

BiVO₄/WO₃ and BiVO₄/SnO₂/WO₃ photoelectrodes were prepared as follows. The precursor solutions of each oxide semiconductor were coated on a F-doped SnO₂ (FTO) conductive glass substrate (surface resistance 10 Ω/sq, Nippon Sheet Glass Co. Ltd.) using a spin coater (1000 rpm, 30 s) and then calcinated at 500 °C for 30 min for each coating. Initially, a WO₃ layer was coated on a FTO glass with subsequent multiple coatings of the SnO₂ film (in the case of the inserted intermediate layer) and the BiVO₄ upper layer. The precursor solution used the following. In the case of the WO₃, it was 1.4 M peroxotungstic acid, as reported previously [28]. In the case of the BiVO₄, bismuth oxide and vanadium oxide of EMOD (Enhanced Metal Organic Decomposition) materials provided by Symetrix Co., USA were mixed with Bi:V = 1:1 and then these were diluted with butyl acetate. The SnO₂ precursor solution was EMOD materials of tin oxide provided by Symetrix Co. (USA) and diluted with xylene.

2.2. Photoelectrochemical measurements and characterizations

The main photoelectrochemical properties were measured by an electrochemical analyzer (BAS. Inc. ALS660B). The *I*–*V* and the time dependence of the photocurrent measurements for the photoanode characteristics were assessed using a three-electrode cell with an Ag/AgCl reference electrode and a Pt coil counter electrode. The *I*–*V* curves of the forward and backward scans of potential should overlap in the steady state. The scan rate was slow (50 mV s⁻¹). The gas measurement for water splitting and the *I*–*V* measurement for the ABPE calculation were performed using a two-electrode cell without a reference electrode. These electrodes were soaked in 80 mL of an electrolyte aqueous solution containing KHCO₃ with CO₂ gas bubbling in a Pyrex glass cell. Previously, we reported that the photocurrent of the BiVO₄ photoelectrode was increased with bubbling CO₂ gas into the carbonate

electrolyte [26]. The electrochemical impedance spectroscopy (EIS) used CIMPES-system 1 (ZAHNER/ZENNIUM, XPOT, Germany). The Mott–Schottky plots of the photoelectrode was analyzed by result of the impedance-potential. In the main case of the *I*–*V* measurement, the working electrode was irradiated through a black mask/aperture (0.31 cm⁻²) from the side of BiVO₄ film (front side irradiation) using a solar simulator (JIS-A-class, SAN-EI ELECTRIC Co.) through a light chopper. Sometimes, photoanode properties were measured under the light irradiation from the side of a glass substrate (back side irradiation) for the comparative experiment. The light intensity of the solar simulator was calibrated to A.M. 1.5 (1 Sun, Supporting Information, Fig. S1) using a solar simulator spectroradiometer (SOMA Optics, Ltd.), immediately after calibration using a standard light source (certification body, Japan Electric Meters Inspection Corporation, JEMIC). The mismatch between the A.M. 1.5 (1 Sun) and the solar simulator spectra was precisely corrected by the spectral mismatch factor (MMF) method [29]. The IPCE was automatically measured by a quantum efficiency-IPCE system (EKO Instruments Co. Ltd.) with a Xe lamp (USHIO INC). The photon flux of the monochromatic light was measured by a Si photodiode detector (Hamamatsu Photonics K. K. and this Si photodiode detector was calibrated by National Metrology Institute of Japan, NMIJ). The IPCE was calculated from Eq. (2).

$$\text{IPCE} = \frac{1240 \times \text{photocurrent density (mA cm}^{-2}\text{)}}{\text{wavelength (nm)} \times \text{photon flux (mW cm}^{-2}\text{)}} \quad (2)$$

The LHE (light-harvesting efficiency) of the electrode was calculated from transmittance (*T*) and reflectance (*R*) using an integrating sphere (Jasco, V-570, ISN-470) (Eq. (3)).

$$\text{LHE} = 1 - R - T \quad (3)$$

The amount of H₂ and O₂ evolved from the photoelectrochemical cell, which consisted of a photoanode and a Pt cathode, was investigated by a closed gas-circulating system with on-line gas chromatography (Shimadzu Co., GC-8A, TCD, 5A molecular sieves, Ar carrier).

The characterization of samples was investigated by a scanning electron microscopy (SEM, Hitachi S-800, SE mode), transmission electron microscopy (TEM, Hitachi High Technologies HD-2700), X-ray fluorescence spectroscopy (XRF, Rigaku ZSXmini), and X-ray photoelectron spectroscopy (XPS, Ulvac-Phi XPS-1800). A stylus-type step measuring instrument (Surfcoorder ET-3000, Kosaka Laboratory Ltd.) was used to the evaluation of film thickness.

The solar energy conversion efficiency has various derivations [5,12,13]. We used the ABPE by Eq. (1) [5]. The point, where size of photocurrent (at *E*) × potential (*E*) of obtained *I*–*V* curves became to the maximum, was chosen as the *E*_{opt} and *J*_{opt}.

3. Results and discussion

3.1. Morphology and optical properties of the BiVO₄/WO₃ photoelectrode

To investigate the effect of BiVO₄-upper layer film thickness on photoelectrochemical properties, we prepared multi-layer composite BiVO₄ photoelectrodes with several different BiVO₄-upper-layer film thicknesses maintaining the WO₃-under-layer film thickness (190 nm). The adjustment of the BiVO₄-upper-layer film thickness was carried out by changing the coating number of times of the BiVO₄ precursor solution. The BiVO₄ film thickness was ca. 60, 100, 150 and 200 nm. Fig. 1 shows the SEM photographs of the WO₃ and the BiVO₄/WO₃ photoelectrode surface. The nanocrystalline WO₃ film surface was very smooth. With an increase in the film thickness of the BiVO₄, the BiVO₄ particle grew and the interparticle crevice widths became narrower. The amounts of Bi

Download English Version:

<https://daneshyari.com/en/article/27691>

Download Persian Version:

<https://daneshyari.com/article/27691>

[Daneshyari.com](https://daneshyari.com)