Applied Catalysis A: General xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

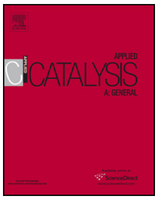

Photo-catalytic activity of $BiVO_4$ thin-film electrodes for solar-driven water splitting

Simelys Hernández[a,b], Sitaramanjaneya Mouli Thalluri[a], Adriano Sacco[b], Samir Bensaid[a], Guido Saracco[a], Nunzio Russo[a,*]

[a] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[b] Center for Space Human Robotics (IIT@POLITO), Istituto Italiano di Tecnologia, C.so Trento 21, 10129 Torino, Italy

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 9 January 2015
Accepted 10 January 2015
Available online xxx

Keywords:
$BiVO_4$
Dip-coating
Thin film
Water splitting
Electrochemical impedance spectroscopy
Photocatalyst

ABSTRACT

There is an ever-increasing attention directed to the development of solar fuels by photo-electrochemical water splitting, given the inexhaustible availability of solar energy. The water oxidation half-reaction is a critical step for the overall water splitting reaction, and the development of suitable photoanodes is therefore required. The present research work focuses on bismuth vanadate thin films' deposition on FTO glass electrodes, through the dip coating technique, and discusses the influence of the film preparation technique on the electrode's photo-electrochemical performance.

The bismuth vanadate thin films were synthesized with thicknesses ranging from 60 to 210 nm, depending on a number of dip coatings from 2 to 15. The structural and optical characterization of the films showed that monoclinic scheelite-type phase was obtained in all samples, with crystal sizes ranging from 24 to 65 nm, at increasing film thicknesses, and corresponding band gaps between 2.55 and 2.35 eV. A maximum photo-current density of about 0.57 mA cm^{-2} at 1.23 V vs. RHE under sunlight illumination was obtained for an electrode thickness of 160 nm. The electrochemical impedance spectroscopy elucidated the transport mechanisms occurring at the electrolyte–electrode interface, as well as inside the film. The estimation of the equivalent circuit parameters showed that an increasing film thickness decreased the resistance associated to the charge transfer between the electrolyte and the electrode (from 1100 to 450 Ω, from 60 to 160 nm layer thickness, respectively), given the higher number of active sites involved in the reaction. However, excessive film thicknesses increase the probability of charge recombination within the film and, in the specific case here investigated, can also be associated to film imperfections arising from several deposition-calcination cycles, which further act as traps. These concurring phenomena are of high relevance to isolate the rate-determining step of the water oxidation half-reaction, in the perspective of an optimization of bismuth vanadate film coating on FTO to obtain photo anodes.

1. Introduction

The most promising technology for the production of hydrogen from renewable energy sources is photo-electrochemical water splitting exploiting solar light [1,2]. However, the greatest challenge of this technology is that anodic electrodes are needed to overcome the high over-potential required to perform the water oxidation four-electron reaction, which is responsible for the slow kinetics of such a photo-electrochemical system [3]. There is an ever increasing need to develop efficient and robust light harvesters, water oxidation catalysts and photo-catalysts in order to develop a commercially viable photo-electrochemical cell (PEC) for H_2 production, with a efficiency higher than 10%. Therefore, an improvement in charge generation, separation and transfer at the electrodes is required to enhance the efficiency of the PEC system, which is currently lower than photovoltaic cells coupled to electrolyzers [4].

Semiconductor materials for this kind of approach have been studied extensively since the first report on photo-electrochemical water splitting with TiO_2 by Fujishima and Honda in 1972 [5]. Of all the different kinds of semiconductor materials [6] that are available, metal oxides have attracted a great deal of interest thanks to their cost effectiveness and stability. Among these metal oxide semiconductors, bismuth vanadate has demonstrated to be a promising material for water oxidation [7–9]. $BiVO_4$ presents three crystal systems: a Scheelite structure with monoclinic (s-m)

---

* Corresponding author. Tel.: +39 011 0904710.
E-mail address: nunzio.russo@polito.it (N. Russo).

http://dx.doi.org/10.1016/j.apcata.2015.01.019
0926-860X/© 2015 Elsevier B.V. All rights reserved.

Please cite this article in press as: S. Hernández, et al., Appl. Catal. A: Gen. (2015), http://dx.doi.org/10.1016/j.apcata.2015.01.019

(highly active), tetragonal (s-t) phases, and a zirconia structure with a tetragonal (z-t) phase [8]. Some of the commonly quoted advantages of $BiVO_4$ are: (i) a low band gap of about 2.4 eV (for monoclinic scheelite), which roughly corresponds to a 520 nm wavelength that allows a good visible-photon absorbance capability [8,10]; (ii) a valence band (VB) position which is sufficiently negative (ca. 2.4 V vs RHE) with respect to water oxidation, and a conduction band (CB) that is around 0 V vs. RHE, thus implying a thermodynamic level close to H_2 [8,10–12]; (iii) the effective masses of the electrons and holes have been estimated to be lower than similar semiconductors (e.g. In_2O_3 or TiO_2), and this, in principle, would result in improved separation and extraction processes of the electron–hole pairs [8,10,12]; and (iv) it is composed of inexpensive elements and is non-toxic [11,12].

Although the synthesis of $BiVO_4$ powders is useful for an in-depth analysis of crystal properties, these powders are actually unsuitable from the practical application point of view. For this reason, photoelectrodes are dealt with the development of devices for solar water oxidation. The photoelectrode concept has become popular, compared to the direct utilization of powder, since the compartmentalization of O_2 and H_2 is simpler. Different approaches with diverse performances and efficiencies have been applied to date. In general, the formation of a thin film over a conductive substrate, usually fluorine-doped tin oxide (FTO) or the more expensive indium tin oxide (ITO), is achieved via a solution-based method [13], electrochemical deposition [14], direct crystal growth [15] or powder synthesis (as described above) and later impregnation of these as films [16].

Among the available in situ thin-film deposition techniques, dip coating has attracted a great deal of attention because of its advantages. Dip coating is in fact a simple method of depositing a uniform liquid thin film which then solidifies into a coating on a substrate [13]. Many reports have been written on the fabrication of thin $BiVO_4$ films by the available techniques [8,14,17,18], but there is still an urgent need to address the importance of the thickness of $BiVO_4$ films and their characteristics regarding the photocatalytic activity of the system.

The simple fabrication of stable and reproducible thin films of pure $BiVO_4$ on FTO conducting glass electrodes, employing a dip coating procedure, and their use as photoanodes for the water oxidation reaction are herein reported. Insights are provided, from electrochemical impedance spectroscopy, about the different types of processes that occur in the film as a function of the thickness of the as-synthesized $BiVO_4$ film. In particular, the quantification of the different charge transfer and transport mechanisms, namely the electrolyte–electrode charge transfer as well as the charge transport inside the bismuth vanadate film, has been done in the perspective of capturing the rate-determining steps of the water oxidation half-reaction, at the different operating conditions here investigated. These images have clearly pointed out that the thickness of the film is a key factor for the performance of the catalyst.

2. Experimental

2.1. Materials

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), ammonium metavanadate (NH_4VO_3) and nitric acid (HNO_3) were purchased from Sigma Aldrich. The conductive FTO glasses, with a sheet resistance of 7 $\Omega\,cm^{-2}$, were obtained from Solaronix Inc.

2.2. Synthesis of thin $BiVO_4$ films

The raw materials involved in this process are bismuth nitrate, ammonium metavanadate and nitric acid. 1.121 g of $Bi(NO_3)_3{\cdot}5H_2O$ and 0.292 g of NH_4VO_3 were mixed in 50 ml of 1 M HNO_3 until a clear homogenous solution was obtained. The solution was then filtered through Whatman filter paper to obtain a clear solution. This solution was employed in the dip coating procedure. The FTO electrodes were cleaned in acetone, ethanol and then with distilled water using an ultrasound bath. The dip coating process was performed at a controlled speed of 1 mm s^{-1}. A series of electrodes with different thicknesses was prepared by varying the number of layers through the dip-coating procedure. Thereafter, each sample is designated as BV-*n*, where *n* stands for the number of deposited layers. A calcination step was performed at 450 °C for 20 min in air after each dipping. A final calcination was performed on all of the samples at 450 °C for 2 h in air.

2.3. Characterization

The $BiVO_4$ samples were characterized through X-ray diffraction (XRD) using an X'Pert Phillips diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 30 mA. All the patterns were recorded in the 5–60° range, with a step size of 0.02°. The crystallite sizes of the samples were estimated using the Scherrer formula [13,19]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the average crystallite size (nm), λ is the wavelength of the X-ray radiation, K is the shape factor (0.9), β is the peak width at half-maximum height, corrected for instrumental broadening, and $2\theta = 30.6°$. The UV–vis diffuse reflectance spectra were recorded on a UV–vis Varian Cary 5000 spectrophotometer equipped with an integrating sphere. The morphology of the samples was investigated by means of scanning electron microscopy (SEM) using an FE-SEM MERLIN ZEISS equipped with an energy-dispersive analysis system (EDS), which was employed to obtain an insight into the bulk element composition of the sample.

2.4. Photo-electrochemical characterization

The photoelectrochemical characterizations of the $BiVO_4$ electrodes used as photoanodes for the water oxidation reaction were carried out in an aqueous 0.1 M Na_2SO_4 electrolyte solution (pH ~ 6.2), employing a multi-channel VSP potentiostat/galvanostat made by BioLogic. A three-electrode system, consisting of the $BiVO_4$ material as the working electrode, a platinum counter electrode and an Ag/AgCl (3 M) as the reference electrode, was used. Linear scan voltammetries (LSVs) were performed in the dark and under simulated solar light, using a 450 W Xe lamp by Newport with an AM 1.5 filter and a water filter. The intensity of the light was maintained at 100 mW cm^{-2} by adjusting the distance between the source and the PEC. Chrono-amperometry (I–t) measurements were performed at 0.6 V vs. Ag/AgCl over continuous light on–off cycles. Electrochemical impedance spectroscopy (EIS) measurements were conducted in the 100 mHz to 1 MHz frequency range, with an amplitude of 25 mV, under different applied DC potentials in the −0.3 to 0.9 V vs. Ag/AgCl range, with 0.3 V steps. The EIS data were modeled using ZSimpWin (EChemSoftware). Incident-photon-to-current-efficiency (IPCE) was recorded using a Newport Xe lamp (150 W) coupled to a monochromator (Cornestone 130 by Newport), by varying the wavelength of the incident light from 300 to 570 nm (step size: 10 nm), at an applied potential of 0.6 V vs. Ag/AgCl. The electrochemical data presented in the work refer to the reversible hydrogen electrode (RHE) potential, calculated with $E_{RHE} = E_{Ag/AgCl} + 0.209\,V + 0.059{\cdot}pH$.

Please cite this article in press as: S. Hernández, et al., Appl. Catal. A: Gen. (2015), http://dx.doi.org/10.1016/j.apcata.2015.01.019