



## Role of the electrode morphology on the optimal thickness of BiVO<sub>4</sub> anodes for photoelectrochemical water splitting cells



S. Hernández<sup>a,b</sup>, G. Saracco<sup>b</sup>, G. Barbero<sup>a,d</sup>, A.L. Alexe-Ionescu<sup>\*,a,c</sup>

<sup>a</sup> Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 29, Torino 10129, Italy

<sup>b</sup> Istituto Italiano di Tecnologia, Centre for Sustainable Future Technologies, CSFT@PoliTo, Corso Trento, 21, Torino 10129, Italy

<sup>c</sup> Department of Physics, University Politehnica of Bucharest, Splaiul Independentei 313, Bucharest 060042, Romania

<sup>d</sup> National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoye shosse 31, Moscow 115409, Russian Federation

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### ABSTRACT

Photoelectrochemical (PEC) water splitting is one of the most promising technologies able to exploit renewable resources such as water and sunlight for the sustainable production of energy carriers (*i.e.* H<sub>2</sub>, solar fuels). Recently, it was demonstrated that the currents through a PEC water splitting cell present a maximum for a specific thickness of the photocatalytic anode film (*J. Electroanal. Chem.* 2017, 788, 61–65), which is related to the attenuation of the light in the semiconductor layer and to the applied bias potential. In this work, it is shown that this non-monotonic behavior is not only due to the trade-off between the absorption length of light and thickness of a photocatalyst (*e.g.* BiVO<sub>4</sub>) film, but mainly to the porous nature of the semiconducting material. A theoretical analysis of such behavior for an ideal compact medium shows a very broad maximum, in contrast to the experimental values that present steeper slopes both at low and large thicknesses (*e.g.* for films prepared by dip-coating method). There have been taken into account, subsequently, the loss of useful current at grain boundaries, due to an increased number of recombination centers, the reduction of specific area (less porosity) as the grains increase in size when increasing the number of dip-coatings, the possible non-uniform coverage of the substrate by the BiVO<sub>4</sub> for a low number of coatings, and the partial blocking of pores with oxygen bubbles under operation. For each of these considerations, a normalized current plot in terms of the number of coatings has shown a remarkably good concordance to the experimental data.

### 1. Introduction

Photoelectrochemical (PEC) water splitting aims to mimic the natural photosynthesis process as a sustainable way of converting solar energy into chemical energy. The development of this technology could contribute to tackle the environmental issues (*i.e.* global warming and its related consequences) that resulted from the increasing amount of greenhouse gases emissions, consisting in about 65% of CO<sub>2</sub> emitted to the atmosphere during the use of fossil fuels for energy generation [1,2]. Commonly, semiconductor photoelectrodes are used as catalysts in PEC devices. They would enable the harvesting and conversion of the abundant but intermittent solar energy into a form that can be stored [3,4]. Indeed, the PEC water splitting is an alternative way to directly produce hydrogen and oxygen from water, or to produce other solar fuels, such as syngas (CO and H<sub>2</sub> mixtures), methanol or methane, through the electrochemical CO<sub>2</sub> reduction [5,6].

However, a PEC water splitting cell is a very complicated device, the constitutive parts of which are quite different one from the other. They

represent various aggregation states (solid, liquid, gas, electronic plasma) and follow various physicochemical laws. A key part of a PEC cell is the anode that is made of a thin layer of semiconducting porous inorganic metal-oxide. Its porous structure, the way it anchors on the substrate, and its intrinsic semiconductor properties make a comprehensive *ab initio* calculation very complex. Density Functional Theory models are usually employed to predict the physico-chemical properties, but not the photoelectrochemical behavior of semiconductor photocatalyst materials [7,8]. Therefore, the creation of simplified models, which are able to explain and predict the multiphase phenomena taking place in photoelectrodes, has a great importance for fastening the progress toward the development of an efficient PEC water splitting device.

In a photoelectrochemical cell, it is expected that current (*I*) curves show a monotonic increasing behavior with respect to the bias potential (*V*), higher current densities corresponding to both higher potentials or higher available surface of the catalysts material. However, analyzing the *I*–*V* curves of different semiconducting photoanodes (such as

\* Corresponding author at: Department of Physics, University Politehnica of Bucharest, Splaiul Independentei 313, Bucharest 060042, Romania.  
E-mail address: [anca-luiza.ionescu@physics.pub.ro](mailto:anca-luiza.ionescu@physics.pub.ro) (A.L. Alexe-Ionescu).

TiO<sub>2</sub> [9], WO<sub>3</sub> [10] and BiVO<sub>4</sub> [11–13]), an anomalous behavior have been observed as soon as the constitutive film thickness overpasses a certain value. For any fixed bias value, the recorded current density increases when the thickness increases, but only up to a critical value, then, the current density decreases.

Simplified models of the porous semiconducting films, strongly guided by the experimental results, could eventually explain why there is an optimal thickness of the anodic photocatalysts in terms of the photocurrent. In our previous work [14], a theoretical model able to describe the dependence of the photocurrent on the thickness of the active layer was presented, which takes into consideration the attenuation of the light in the porous semiconductor layer and the bias voltage. However, the agreement between the theoretical predictions of the model proposed in Ref. [14] and the experimental data is rather poor, indicating that some important ingredient has not been taken into account. In this work, a more detailed analysis is performed considering that the non-monotonic behavior of the current density is not only due to the trade-off between the absorption length of light and thickness of a photocatalyst film, but mainly to the porous nature of the semiconducting material. Firstly, a theoretical analysis is made for an ideal compact medium, which is then compared to experimental values that present steeper slopes, both at low and large thicknesses. The case of BiVO<sub>4</sub> films prepared by dip-coating method [12] is analyzed and used to validate the model. Subsequently, the porosity of the film have been considered through: *i*) the loss of useful current at grain boundaries, due to an increased number of recombination centers, *ii*) the reduction of specific area (less porosity) as the grains increase in size when increasing the number of deposited layers, *iii*) the possible non-uniform coverage of the substrate by the BiVO<sub>4</sub> for a low number of coatings, and *iv*) the partial blocking of pores with oxygen bubbles under operation. For each of those considerations, normalized current plots were compared with experimental data at different thicknesses of a state-of-the-art BiVO<sub>4</sub> photocatalyst material [12].

## 2. Experimental

BiVO<sub>4</sub> films were prepared in Fluorine-doped Tin Oxide (FTO, 7 ohm/sq) substrate covering an area of 2 cm<sup>2</sup> by dip-coating method, following a procedure described elsewhere [12]. In the typical synthesis, 1.121 g of Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O and 0.292 g of NH<sub>4</sub>VO<sub>3</sub> were mixed in 50 ml of 1 M HNO<sub>3</sub> until a clear homogenous solution was obtained. The so obtained solution was then filtered to obtain a clear solution, which was used to dip-coat the FTO-glass substrates at a controlled speed of 1 mm s<sup>-1</sup>. A series of BiVO<sub>4</sub> photoelectrodes with different thicknesses was prepared by varying the number of dip-coated layers ( $\kappa$ ) from 2 to 15. After depositing each layer, a calcination step was performed at 450 °C for 20 min in air. A final calcination was performed on all of the samples at 450 °C for 2 h in air.

The morphology of the BiVO<sub>4</sub> films was investigated by using a field emission scanning electron microscopy FE-SEM MERLIN ZEISS, which was employed to evaluate crystals sizes, external porosity of the films and their thickness. Further physico-chemical and photoelectrochemical characterizations are reported elsewhere [12]. In Fig. 1, the top views and cross sections of some representative BiVO<sub>4</sub> samples are shown. The porous nature of the films that is observed up to 8 layers is represented in the Fig. 1a, while more compact structures are noted from 10 to 15 coated layers (see Fig. 1b, c).

## 3. Model

When a photoelectrode (*n*-type semiconductor) is in contact with an electrolyte, electron transfer takes place until electrochemical potential of electrons in the semiconductor electrode (Fermi level  $E_F$ ) and the redox potential of the liquid electrolyte are equal. Electrons from photoanode are transferred to the solution and thus a positively charged photoelectrode appears, this charge being distributed in a

space-charge region near the surface and a layer of negative ions (anions) sets in the Helmholtz zone of the electrolyte. The conduction and the valence band edges are bent due to the generation of the space-charge region creating a potential barrier against further transfer of electrons into electrolyte. The direction of the field is such that the holes generated in the space charge region move toward the interface and excess electrons move toward the bulk.

The space-charged region within the semiconductor as well as the Helmholtz zone are not sensitive to the geometry of the surface (due to the liquid properties of the electrolyte and to the large ionic concentration of it), and it should be true even in the case of porous semiconductors such as BiVO<sub>4</sub>. Thus, both the inner surface of one pore inside a semiconductor and the Helmholtz layer in the electrolyte are electrically equipotential. From the electrical point of view, this drawing could represent the real BiVO<sub>4</sub> film. Yet, this model must be improved by adequately adding the contributions from the photoelectrode porosity and the grains dimensions.

We consider a BiVO<sub>4</sub> layer delimited by two planar surfaces: semiconductor/electrolyte (SE) at  $x = 0$ , and semiconductor/back contact at  $x = 6r$  (the back contact surface is actually equipotential). The FE-SEM (Fig. 1) and X-ray diffraction measurements referring to the thickness of the photoelectrode and the size of the grains (crystallites) [12], respectively, show that, on average, a film is made up of three layers of (approximately) round grains of radius  $r$  and has two grain boundaries at  $x = 2r$  and  $x = 4r$ , as depicted in Fig. 2 [14]. The contorted SE interface was stretched into a large plane at  $x = 0$  and the back contact surface was increased, accordingly (being an equipotential surface, it does not support in-plane currents, but only transversal ones).

The charge transport in a nanostructured BiVO<sub>4</sub> photoelectrode can depend substantially on the size of the grains and on the number of the grain boundaries on the transport path [15]. The crystallite joints introduce high rates of trapping and recombination that diminish the carrier lifetime and mobility. The grain size is one of the various ingredients that influence the efficiency of the charge transport in these photoelectrodes.

When the semiconductor is a very thin porous film, the effective surface,  $A_{eff}$ , (i.e. the area of the semiconductor–electrolyte interface where the redox reaction could take place) can be quite large. Obviously, it depends on the actual porosity of the film along its thickness, which is a function of the synthesis method. For instance, considering that a 3D structure is built up of close-packed spheres of radius  $r$ , and ignoring the void space, the specific area  $A_s$  (area/volume) is  $3/r$ . Building up an anode porous film out of a certain number of  $\kappa$  coatings, the effective area could no longer be proportional to  $\kappa$ , even if the specific area  $A_s$  is not changed. In the here analyzed case, when  $\kappa$  is small (up to 6, 7, 8), the effective area is still considered to be proportional to the number of coatings [12], due of the 3D orientation of the channels, as shown in Fig. 1. On the contrary, for larger  $\kappa$ , the film became less porous, due to the subsequent annealing steps that caused the sintering of the nanoparticles, and thus its specific area is smaller. In addition, for larger  $\kappa$ , more channels could be obstructed by the formed oxygen bubbles attached on the electrode surface during its operation. That is, the effective area of  $\kappa$  coatings is less than  $\kappa$  times the effective area of one coating.

As emphasize before, on average, a film is made up of three layers of (approximately) round grains of radius  $r$ . Increasing the number of coatings does not increase the number of grain layers but, rather, their dimension  $r$ . From the experimental data [12], the radius of the grains is proportional to  $\kappa$ , whereas the thickness of the film,  $\zeta(\kappa)$ , to  $\sqrt{\kappa}$  (as will be reported later, in Fig. 4). Since the grains are about three times smaller than the photoelectrode thickness, the electrons pass through two grain boundaries (oriented along the applied bias) before going to the FTO substrate.

As in Ref. [14], we consider a one dimensional problem. The cartesian reference frame has the  $x$ -axis normal to the interface between the photoanode and the electrolyte, directed to the back contact. The

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