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Visible-light-promoted gas-phase water splitting using porous $WO_3/BiVO_4$ photoanodes

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ABSTRACT

We recently described the use of Ti(0) microfibers as an anodization substrate for the preparation of TiO_2 nanotubes arrays as porous photoanodes. Here, we report the use of these fibers as a scaffold to build porous photoanodes based on a $WO_3/BiVO_4$ heterojunction. The obtained photoelectrodes show promising results under visible light irradiation for water oxidation both in a typical liquid-phase photoelectrochemical setup and in a gas phase reactor (developed in-house) based on a polymeric electrolyte membrane.

1. Introduction

With the rise of energy and climate concerns, a large number of research teams around the world are working on the development of devices to produce hydrogen from water and solar energy. In the ideal case, these photoelectrochemical (PEC) devices or cells would make possible, under light irradiation, the dissociation of water into its fundamental components, hydrogen and oxygen. In this context, the use of semiconductor-based water-splitting systems is a promising route towards production of “solar hydrogen” at an affordable price [1,2].

The main challenges in the field are the development of efficient photoelectrodes and scalable reactor design [1–3]. This work focuses on the development of a PEC design which resembles polymeric electrolytic membrane (PEM) electrolysers and is thus called PEM-PEC [3]. This type of reactor has the advantage of being compact, robust and easily scalable. However it requires a porous photoelectrode rather than the planar design built on conducting glass substrates used in conventional PEC studies. Up to now only simple photoanodes based on TiO_2 or WO_3 have been developed for PEM-PEC applications [4–6]. These materials can absorb only a small fraction of the solar terrestrial illumination and as a result their performance is very limited [4–6]. In order to adapt the PEM-PEC concept to the visible part of the solar spectrum, the scope of this article is to investigate the possibility of using the well-known heterojunction $WO_3/BiVO_4$ [2,7].

$BiVO_4$ in its scheelite type monoclinic phase possesses promising properties for applications as a photoanode in photoelectrochemical cells. With an ~2.4 eV band gap, it can, in theory, under 1 sun illumination produce photocurrents up to 7 $mA{\cdot}cm^{-2}$ for the water splitting reaction at the thermodynamic potential [1,2]. However, in practice, this material is susceptible to fast hole/electron pair recombination leading to a significant performance drop [7–9]. Some solutions have been tested to overcome this issue: the addition of a doping metal (e.g. W, Mo) [8,9] to diminish the recombination or the association with another semiconductor through the formation of a heterojunction (i.e. $WO_3/BiVO_4$) to enhance the charge separation [7]. WO_3 is a semiconductor with an indirect band-gap around 2.8 eV that provides light absorption in the near UV and at the beginning of the visible spectrum [1] and has recently been reported to be compatible with titanium microfibers as electric back contact [10]. Due to its good charge carrier properties and to the band alignment with the bands of $BiVO_4$, the electrons from the $BiVO_4$ conduction band can be injected into WO_3, enhancing the charge separation and thus the efficiency [1,2,7].

In this study we built $WO_3/BiVO_4$ heterojunctions on porous titanium substrates by combining electrochemical anodization of sputtered tungsten layers and $BiVO_4$ formation via the SILAR (Successive Ionic Layer Adsorption and Reaction) [11] method, and successfully used them to perform gas phase water-splitting. Although most of the common methods (i.e. spin-coating, doctor blade, hydrothermal synthesis) [2] cannot be used in this case, the aforementioned preparation techniques suit the nature and the specific porous morphology of the electrode substrate particularly well.

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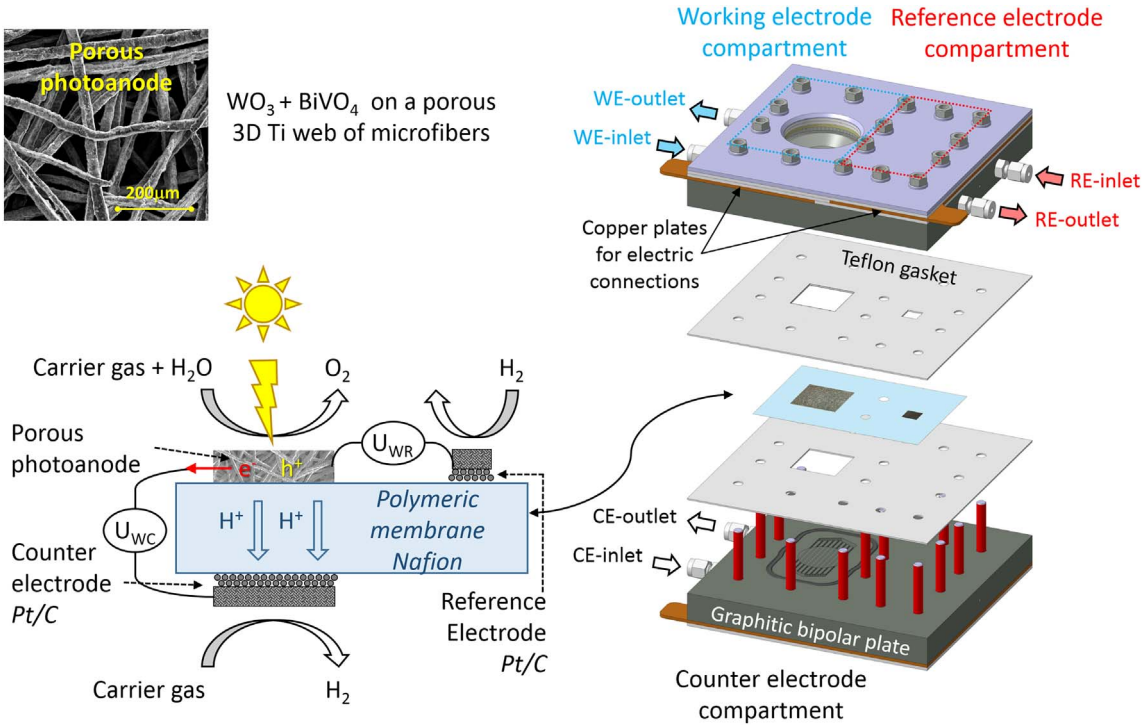

Fig. 1. (Left) Configuration and operation of the membrane (photo)electrode assembly. (Right) Novel PEM-PEC reactor design with three compartments for accommodating photoanode, cathode and reference electrodes [3].

2. Experimental

W thin films were deposited by DC magnetron sputtering (Kurt J. Lesker) from a 2 in. metallic W target (Kurt J. Lesker) on Ti substrates (Bekaert) of 0.3 mm thickness, 80% porosity, 20 µm microfibers and 99.9% purity [3]. W-deposition was carried out with base pressure ~ 10^{-8} mbar, a target–substrate distance of 95 mm at 25 °C, under Ar pressure of 1 Pa, and a power of 100 W. The resulting W-film thickness was 200 nm. WO_3 layers were formed through anodization of the 200 nm layer of W(0). To form the oxide a potential of 30 V was applied for 2 min in an ethylene glycol solution containing 0.3 wt% NH_4F and 2 vol% H_2O. Then the electrode was rinsed with water prior to a calcination step (500 °C for 1 h). One SILAR cycle for the $BiVO_4$ deposition is described as follows: the electrode is dipped for 1 min in a 0.05 M $BiNO_3$ solution, dried for 1 min, rinsed in miliQ-water for 30 s, dried for 30 s, dipped in 0.05 M ammonium metavanadate (NH_4VO_3) (pH = 2) solution for 1 min, dried for 1 min, rinsed in miliQ water for 30 s and dried for 30 s. Once the desired number of cycles has been reached the samples are calcined at 550 °C for 1 h and then etched for 20 min in 1 M KOH solution to remove the unwanted vanadium binary oxide (V_2O_5) [12]. The amount of deposited $BiVO_4$ is therefore controlled by the number of cycles performed.

Surface morphologies of the photoanodes were characterized using a scanning electron microscope (FEI Quanta 3D FEG instrument) at an acceleration voltage of 30 keV and a working distance of 10 mm. The crystal phases were analyzed by X-ray diffraction (Brucker D8 Advance Eco) using a Cu K_α tube. Diffuse reflectance spectra were obtained using a UV–Vis spectrophotometer (PerkinElmer-Lamda 1050) with an integrating sphere attachment (150 mm InGaAs). A Hiden QGA quadrupole mass spectrometer (M/S) operating in selected ion mode with a SEM detector was used for the detection of oxygen and hydrogen in the anodic and cathodic gas streams. Raman spectroscopy measurements were performed with a Renishaw Raman microscope equipped with a 514 nm laser, a grating with 1800 lines/mm, and a CCD detector, and with a measurement step size of 1.7 cm^{-1}. The laser power during measurements is fixed at 0.3 $W{\cdot}mm^{-2}$.

The photoelectrodes (geometrical area ca. 1 cm^2) were illuminated using a 150 W Xe lamp (66477-150XF-R1, Newport) with a UV cut-off filter (< 395 nm) and an IR removal water filter, where the light intensity was adjusted with a reference cell and meter certified by Newport (91150V) to 100 $mW{\cdot}cm^{-2}$ on the photoelectrode surface. The lamp in both cases was positioned at the same distance (3 cm) from the photoelectrode surface and the illumination density was measured in both conventional and PEM-PEC reactors to ensure that the power was the same. The dark current and photo-current of the working electrode versus the external bias voltage were recorded using an Ivium-CompactStat potentiostat, at a 10 $mV{\cdot}s^{-1}$ scan-rate. Liquid phase photoelectrochemical water-splitting experiments were performed at pH = 1 (0.1 M H_2SO_4) in a conventional PEC cell while gas phase experiments were carried out in our novel PEM-PEC cell (Fig. 1) both are described in detail in a previous paper [3]. Each compartment of the PEM-PEC was fed with gaseous streams, made by bubbling He or air for anodic, He for cathodic and H_2 for reference compartment (at 50 $ml{\cdot}min^{-1}$) through thermostatted gas saturators (at 25 °C) containing H_2O, leading to 3.5 vol% H_2O in the feeds.

3. Results and discussion

3.1. Structural analysis

Five samples were characterized: pure Ti/TiO_2 substrate (Ti_{web}), and substrates covered with W(0), WO_3, $BiVO_4$ and WO_3/$BiVO_4$. Fig. 2A shows the XRD patterns of the different samples. Typical diffraction peaks from the titanium substrate (black line) are clearly observed for all the samples, along with some smaller signals that can be attributed to a thin over-layer of rutile TiO_2 [3]. In the XRD pattern of the W(0) sputtered sample (blue line) three new signals can be seen at 44, 58 and 74° in good agreement with literature [2,4]. Those peaks are still present after the anodization plus annealing processes (green line), suggesting the formation of a thin WO_3 layer since none of its typical peaks are detected.