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Visible light promoted gas phase water splitting using porous WO₃/BiVO₄ photoanodes

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Abstract

We recently described the use of Ti(0) microfibers as anodization substrate for the preparation of titanium oxide nanotubes array as porous photoanodes. We report here the use of those fibres as scaffold to build porous photoanodes based on the WO₃/BiVO₄ heterojunction. The obtained photoelectrodes exhibit promising performances under visible light irradiation for water oxidation both in a typical liquid-phase photoelectrochemical setup and in an in-house developed gas phase reactor based on polymeric electrolyte membrane.

Keywords: Photoelectrochemical H₂ production, polymeric electrolyte membrane, gas phase water-splitting, WO₃/BiVO₄ photoanode, visible light

1. Introduction

With the rise of energetic and climatic 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 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 semiconductors based water-splitting systems appears to be a promising way to achieve production of “solar hydrogen” at an affordable price^[1,2].

Within this field we recently reported a new photoelectrochemical reactor design for gas phase application based on a polymeric electrolyte membrane assembly (PEM-PEC) and using as photoanode Titanium nanotubes array, obtained via electrochemical anodization^[3]. This approach tackled some of the inherent drawbacks induced by the use of traditional TiO₂ nanoparticles decorated carbon microfibers gas diffusion layer electrodes: strong recombination of the electron-hole pairs at the TiO₂ particles boundaries and degradation upon prolonged operation. However, the use of titania limited us to UV-light irradiation. In order to adapt our 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 WO₃/BiVO₄^[2,4].

BiVO₄ in its scheelite type monoclinic phase possess promising properties for applications as photoanode in photoelectrochemical cells. With a 2.4 eV band gap, it can, in theory, under 1 sun

illumination produce photocurrents up to $7 \text{ mA}\cdot\text{cm}^{-2}$ for the water splitting reaction at the thermodynamic potential^[1,2]. However, in practice, this material is susceptible to fast hole/electron pairs recombination leading to an important performance drop^[4-6]. Some solutions have been tested in the literature to overcome this issue: the addition of a doping metal (e.g. W, Mo)^[5,6] to diminish the recombination or the association with another semi-conductor through the formation of an heterojunction (i.e. $\text{WO}_3/\text{BiVO}_4$) to enhance the charge separation^[4]. 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 been recently reported to be compatible with titanium microfibers as electric back contact^[7]. Due to its good charge carrier properties and to the good band alignment with the bands of BiVO_4 , the electrons from the BiVO_4 conduction band can be injected to WO_3 , enhancing the charge separation and thus the efficiency^[1,2,4].

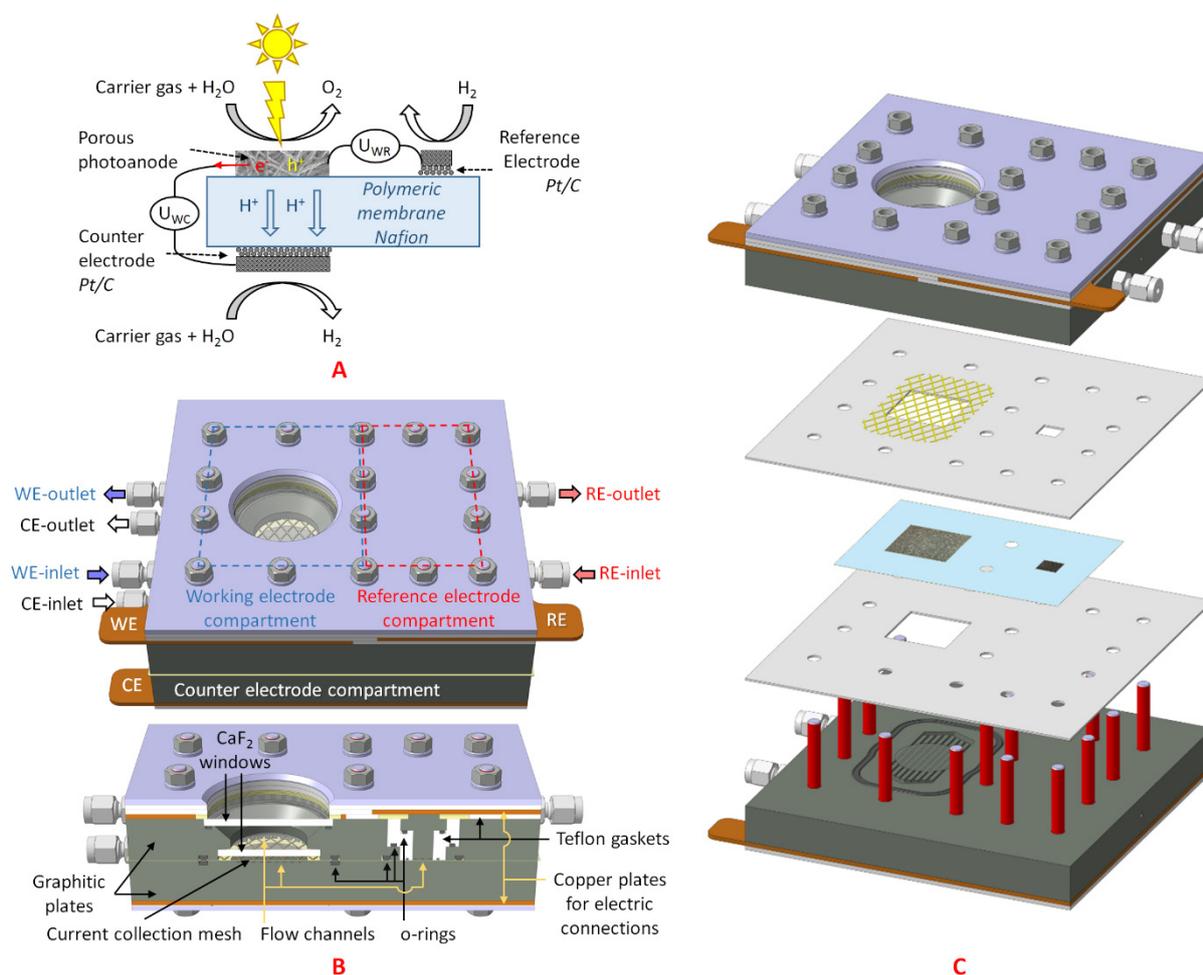


Fig.1 (A) Configuration and operation of the membrane (photo)electrode assembly. (B,C) Novel PEM-PEC reactor design with three compartments for accommodating photoanode, cathode and reference electrodes. Intersection and break out of the PEM-PEC reactor presenting the sealing and the electrical isolation between the compartments.

In this study we built $\text{WO}_3/\text{BiVO}_4$ heterojunctions, on porous titanium substrates by combining electrochemical anodization of sputtered tungsten layers and BiVO_4 formation via SILAR (Successive Ionic Layer Adsorption and Reaction)^[8] method, and successfully used them to perform gas phase water-splitting. The aforementioned preparation techniques suit particularly well with the specific morphology of the electrode substrate both in terms of reproducibility and achieved performances, while most of the common methods (i.e. spin-coating, doctor blade, hydrothermal synthesis)^[2] were hardly controllable or simply not suitable for the electrode geometry.

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)^[3]. W-deposition was carried out with base pressure $\sim 10^{-8}$ mbar, target-substrate distance of 95mm at 25°C, an 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 a solution containing 0.3 wt% NH_4F and 2% vol% H_2O in ethylene glycol. Then the electrode was rinsed with water prior to a calcination step (500°C for 1h). 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 1 min, rinsed in miliQ water for 30 s and dried 30 s. Once the desired number of cycles is reached the samples are calcined at 550°C for 1h and then etched for 20 min in 1M KOH solution to remove the unwanted vanadium binary oxide (V_2O_5)^[9]. The amount of deposited BiVO_4 is therefore controlled by the number of performed cycles.

Surface morphologies of the photoanodes were characterized with a Scanning electron microscope (FEI Quanta 3D FEG instrument) at an acceleration voltage of 30 keV and working distance of 10mm. The crystal phases were analyzed by X-ray diffraction (Bruker D8 Advance Eco) using a Cu K_α tube.

A xenon arc lamp (66477-150XF-R1, Newport) was used to illuminate the photoelectrode at a light intensity of 100 W cm^{-2} with a UV cut-off filter ($>395\text{nm}$). The dark current and photo-current of the working electrode versus the external bias voltage were recorded using an Ivium-CompactStat potentiostat, at a scan-rate 10 mV s^{-1} . Liquid phase photoelectrochemical water-splitting experiments were performed at pH=1 (0.1 M H_2SO_4) in conventional PEC cell while gas phase experiments were carried out in our novel PEM-PEC cell, both are precisely described in a previous paper^[3].

3. Results and discussion

3.1. Structural analysis: Five samples were characterized: pure Ti/TiO₂ substrate (Ti_{web}), and substrates covered with W(0), WO₃, BiVO₄ and WO₃/BiVO₄. Fig.2A shows the XRD patterns of the different prepared 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 TiO₂^[3]. In the XRD pattern of the W(0) sputtered sample (blue line) three new typical signals can be seen at 44, 58 and 74 degrees in good agreement with literature^[2,4]. Those peaks are still present after the anodization process (green line). WO₃ peaks were not detected due to thin thickness of the obtained oxide.

The analysis of the Ti_{web}/BiVO₄ sample (yellow line) shows additional peaks for a monoclinic scheelite structure^[2,4]. Those signals are still visible on the complete multilayered sample XRD pattern (red line) confirming the success of the BiVO₄ deposition process onto the WO₃. Due to the multiple annealing step for the WO₃/BiVO₄ fabrication, additional peaks at 24 and 29 degrees are observed which is attributed to WO₃^[4].

The surface morphology of the samples was studied using a scanning electron microscope. Except for some rare cracks, the WO₃ layers look highly homogeneous (Fig.2C).

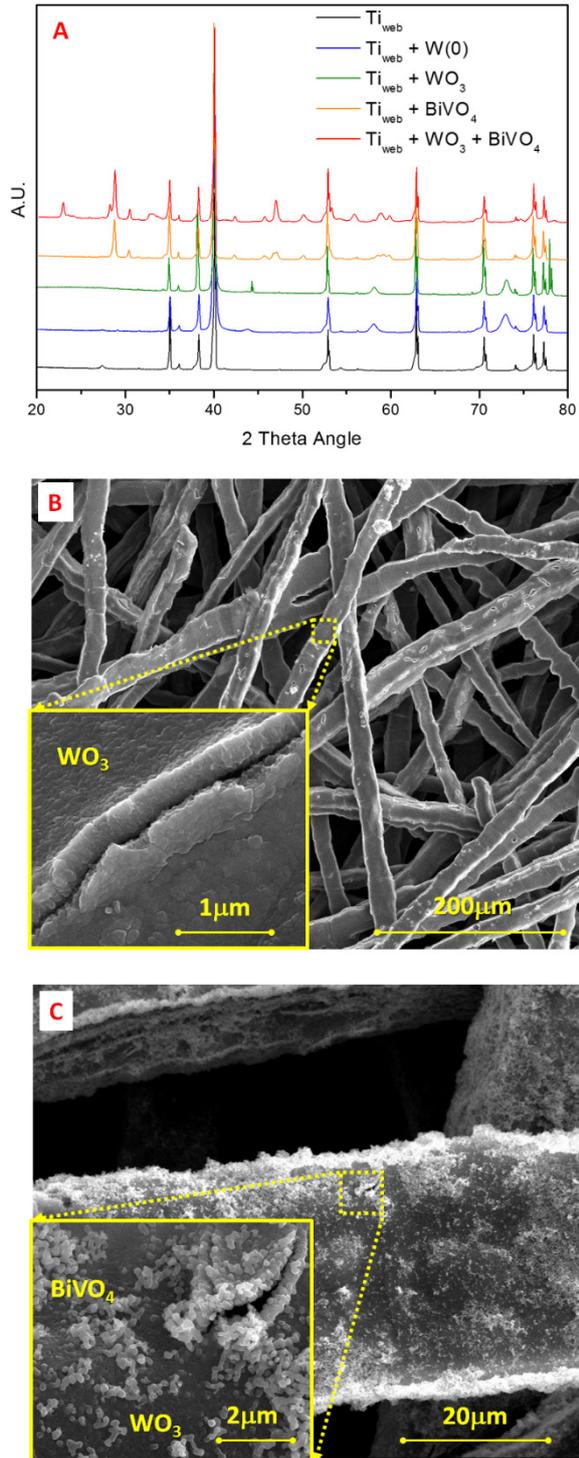


Fig.2 SEM images of (A) WO₃ covered Ti_{web} and (B) of the WO₃/BiVO₄ covered Ti_{web}. (C) XRD diffraction pattern of the initial Ti_{web} and with different added layers.

They show a low roughness, and seem to cover the titanium substrate efficiently. The SILAR obtained BiVO_4 particles measure around 180 nm and are well distributed on the surface, providing good nanostructuring, even if few agglomerates can be observed in some regions (Fig.2C).

3.2. Photoelectrochemical Characterisation:

The synergic association of WO_3 and BiVO_4 has been already well described in the literature^[4]. However, since the type of electrode support and the deposition techniques are different in our case, we initially compared the activities of each photoactive layer separately and prior to the measurement of combined layers.

The obtained results in the aqueous phase confirm that our fabrication process does form a $\text{WO}_3/\text{BiVO}_4$ heterojunction. As it is shown of the Fig.3A, under irradiation the two semiconductors individual give relatively low currents 0.10 and 0.25 $\text{mA}\cdot\text{cm}^{-2}$, for WO_3 and BiVO_4 respectively, while a strong synergistic effect is observed for $\text{WO}_3/\text{BiVO}_4$ since their combination can reach up to 2.5 $\text{mA}\cdot\text{cm}^{-2}$.

To reach those photocurrents, we studied the effect of the BiVO_4 loading onto the WO_3 layers (Fig.3B). To achieve that, we compared the activity of the $\text{WO}_3/\text{BiVO}_4$ assemblies after successive steps of 10-SILAR-cycles until 60-cycles.

All the samples share the same photocurrent onset (about +0.4 V vs RHE) and exhibit a linear current increase through the scanned potentials. At the thermodynamic water oxidation potential

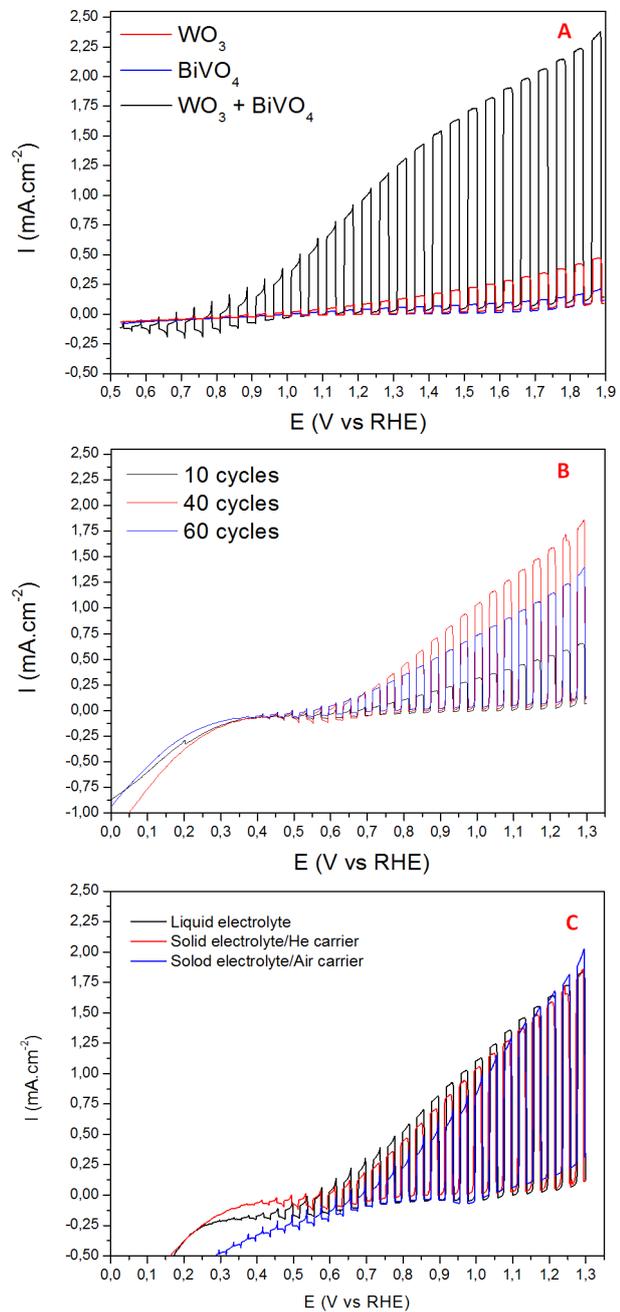


Fig. 3 : Linear voltammetry sweeps (2.5 mV/s) of various photoanodes under chopped illumination for water splitting (A) Independent BiVO_4 and WO_3 and their coupled counterpart, (B) Activity of $\text{WO}_3/\text{BiVO}_4$ photoanodes for different BiVO_4 loading (C) $\text{WO}_3/\text{BiVO}_4$ liquid vs gas phase activity.

the 10-cycles sample give

the lowest photocurrent with $0.65 \text{ mA}\cdot\text{cm}^{-2}$ while the maximum activity, i.e. $1.9 \text{ mA}\cdot\text{cm}^{-2}$, is reached after 40-cycles. Further SILAR cycles lead to a current drop, thus we consider that the electrode surface starts to get saturated after 40-SILAR-cycles.

Fig.3C depicts the activity comparison between liquid and solid electrolyte operation (i.e. in PEM-PEC cell). The photoelectrochemical performances are almost identical in terms of photocurrent profile and intensity ($1.9 \text{ mA}\cdot\text{cm}^{-2}$ at the thermodynamic potential) and regarding the photocatalytical onset ($+0.4 \text{ V}$ vs RHE). This is several orders of magnitude higher than any other visible light activated solid state electrolyte system described in the literature^[3,7,10-12], confirming the strong potential of our reactor and electrodes design.

PEM-PEC cell could be used to capture water molecules from ambient air via natural convection of humidified air. This concept is nicely described by Ronge et al^[10]. Therefore, in order to investigate the air based PEM-PEC operation in our study apart from He, air was used as carrier gas. The presence of oxygen molecules acts as a mediator for recombination and thus causes back reactions which deteriorate photoefficiency^[10]. However the performance of our photoanode in this operation mode is very close to the one when He is used as carrier gas, showing a high potential for implementation in air based PEM-PEC applications.

The obtained results show the good compatibility between the photoanodes and the solid electrolyte PEM-PEC cell design, e.g. the porosity is high enough to maintain the activity while the substrate is exposed at the gas phase reactants.

4. Conclusion:

A new preparation method of highly porous $\text{WO}_3/\text{BiVO}_4$ photoanodes was demonstrated. The photoanodes are efficient under gas phase operation and compatible with our innovative solid electrolyte photoelectrochemical setup. Using our concept, this is the first time that gas phase water splitting exhibits performances similar to those of classical liquid electrolyte photoelectrochemical cells under visible light irradiation and without the use of a co-catalyst.

5. Acknowledgments

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