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 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 WO$_3$/BiVO$_4$ 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 H$_2$ production, polymeric electrolyte membrane, gas phase water-splitting, WO$_3$/BiVO$_4$ 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 TiO$_2$ nanoparticles decorated carbon microfibers gas diffusion layer electrodes: strong recombination of the electron-hole pairs at the TiO$_2$ 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 WO$_3$/BiVO$_4$.$^{[2,4]}$

BiVO$_4$ 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 mA.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. WO\(_3\)/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 WO₃/BiVO₄ heterojunctions, on porous titanium substrates by combining electrochemical anodization of sputtered tungsten layers and BiVO₄ formation via SILAR (Successive Ionic Layer Adsorption and Reaction) 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 ~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. WO₃ 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% NH₄F and 2% vol% H₂O in ethylene glycol. Then the electrode was rinsed with water prior to a calcination step (500°C for 1h). One SILAR cycle for the BiVO₄ deposition is described as follows: the electrode is dipped for 1 min in a 0.05 M Bi(NO₃)₃ solution, dried for 1 min, rinsed in miliQ water for 30 s, dried for 30 s, dipped in 0.05 M ammonium metavanadate (NH₄VO₃) (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 (V₂O₅)[9]. The amount of deposited BiVO₄ 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 (Brucker D8 Advance Eco) using a Cu Kα tube.

A xenon arc lamp (66477-150XF-R1, Newport) was used to illuminate the photoelectrode at a light intensity of 100 W/cm² with a UV cut-off filter (>395nm). 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. Liquid phase photoelectrochemical water-splitting experiments were performed at pH=1 (0.1 M H₂SO₄) 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/TiO$_2$ substrate (Ti$_\text{web}$), and substrates covered with W(0), WO$_3$, BiVO$_4$ and WO$_3$/BiVO$_4$. Fig. 2A shows the XRD patterns of the different 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 TiO$_2$ [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). WO$_3$ peaks were not detected due to thin thickness of the obtained oxide.

The analysis of the Ti$_\text{web}$/BiVO$_4$ 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 BiVO$_4$ deposition process onto the WO$_3$. Due to the multiple annealing step for the WO$_3$/BiVO$_4$ fabrication, additional peaks at 24 and 29 degrees are observed which is attributed to WO$_3$ [4].

The surface morphology of the samples was studied using a scanning electron microscope. Except for some rare cracks, the WO$_3$ layers look highly homogeneous (Fig. 2C).

Fig. 2 SEM images of (A) WO$_3$ covered Ti$_\text{web}$ and (B) of the WO$_3$/BiVO$_4$ covered Ti$_\text{web}$. (C) XRD diffraction pattern of the initial Ti$_\text{web}$ and with different added layers.
They show a low roughness, and seem to cover the titanium substrate efficiently. The SILAR obtained BiVO₄ 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 WO₃ and BiVO₄ 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 WO₃/BiVO₄ heterojunction. As it is shown of the Fig.3A, under irradiation the two semiconductors individual give relatively low currents 0.10 and 0.25 mA cm⁻², for WO₃ and BiVO₄ respectively, while a strong synergistic effect is observed for WO₃/BiVO₄ since their combination can reach up to 2.5 mA cm⁻².

To reach those photocurrents, we studied the effect of the BiVO₄ loading onto the WO₃ layers (Fig.3B). To achieve that, we compared the activity of the WO₃/BiVO₄ 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

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[^4]: Reference to the literature where the synergic association of WO₃ and BiVO₄ has been described.
the 10-cycles sample give the lowest photocurrent with 0.65 mA cm\(^{-2}\) while the maximum activity, i.e. 1.9 mA 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 mA cm\(^{-2}\) at the thermodynamic potential) and regarding the photocatalytical onset (+0.4 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 WO\(_3\)/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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**6. References**


