Multilayer WO₃/BiVO₄ Photoanodes for Solar-Driven Water Splitting Prepared by RF-Plasma Sputtering

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Abstract: A series of WO₃, BiVO₄ and WO₃/BiVO₄ heterojunction coatings were deposited on fluorine-doped tin oxide (FTO), by means of reactive radio frequency (RF) plasma (co)sputtering, and tested as photoanodes for water splitting under simulated AM 1.5 G solar light in a three-electrode photoelectrochemical (PEC) cell in a 0.5 M NaSO₄ electrolyte solution. The PEC performance and time stability of the heterojunction increases with an increase of the WO₃ innermost layer up to 1000 nm. A two-step calcination treatment (600 °C after WO₃ deposition followed by 400 °C after BiVO₄ deposition) led to a most performing photoanode under back-side irradiation, generating a photocurrent density of 1.7 mA cm⁻² at 1.4 V vs. SCE (i.e., two-fold and five-fold higher than that generated by individual WO₃ and BiVO₄ photoanodes, respectively). The incident photon to current efficiency (IPCE) measurements reveal the presence of two activity regions over the heterojunction with respect to WO₃ alone: The PEC efficiency increases due to improved charge carrier separation above 450 nm (i.e., below the WO₃ excitation energy), while it decreases below 450 nm (i.e., when both semiconductors are excited) due to electron–hole recombination at the interface of the two semiconductors.

Keywords: WO₃/BiVO₄ heterojunction; RF-plasma sputtering; photocatalytic water splitting; photoelectrochemical cell

1. Introduction

With the rapid increase in the global energy demand and the tremendous climate concerns due to combustion of the limited fossil fuels reserves, there is an urgent need for clean and renewable energy sources [1,2]. The exploitation of hydrogen as an energy vector of the future is thought as an ideal solution for these problems [3,4]. However, to date, most of its production is based on steam reforming of natural gas which still involves massive amounts of CO₂ emission, resulting environmentally unsustainable [5]. In this context, photoelectrochemical (PEC) water splitting is considered one of the most promising and green routes to harvest and convert solar energy through the production of H₂ [6].

Among plenty of semiconductor materials suitable for the PEC water splitting reaction, BiVO₄ has received significant attention in the last years due to its remarkable theoretical efficiency under visible light irradiation [7,8]. This is due to its narrow band gap of 2.4 eV, that extends its photoactivity up to 510 nm, and favorable band edges position. However, BiVO₄ usually suffers low photocatalytic efficiency due to poor charge carriers mobility [9]. A possible solution to overcome this limitation is to couple BiVO₄ with another semiconductor in order to form a heterojunction at the interface, achieving a spatial charge separation. Several semiconductors can be combined with BiVO₄, including WO₃ [10], SnO₂ [11], Fe₂O₃ [12] and CdS [13]. Among these, WO₃/BiVO₄ is one of the most promising...
heterostructure, because both the valence and conduction bands of BiVO$_4$ are located at a higher energy than those of WO$_3$. Hence, a type II heterojunction is generated at the interface between the two semiconductor materials that allows efficient photo-promoted electron–hole separation [14]. Moreover, WO$_3$ possesses a good electron transport ability of 12 cm$^2$ V$^{-1}$ s$^{-1}$ with a moderate length of hole diffusion of ca. 150 nm [15]. Thus, in WO$_3$/BiVO$_4$ heterojunction, BiVO$_4$ primarily acts as an excellent visible-light harvester up to 510 nm (i.e., ca. 30% of sunlight), while WO$_3$ acts as efficient electron conductor. Several morphologies and preparation methods influencing the PEC activity of the WO$_3$/BiVO$_4$ heterojunction have been widely investigated and reported in literature so far. These include dense [10,14,16] and porous films [17,18], nanorods [19,20], helix [21] and inverse opal [22] structures. In particular, the highest photocurrent density reported so far (ca. 6.72 mA cm$^{-2}$ at 1.23 V vs. RHE under 1 sun illumination) has been achieved over core-shell WO$_3$/BiVO$_4$ nanorods arrays decorated with a Co-Pi water oxidation co-catalyst system [23]. The WO$_3$ nanorods arrays were prepared by RF magnetron sputtering under glancing angle deposition.

In the present work, a BiVO$_4$ thin film was deposited by radio-frequency (RF) plasma co-sputtering [24] over a bilayer WO$_3$ n–n heterojunction already optimized in our previous work [25]. The latter was obtained by plasma reactive sputtering, by depositing two consecutive layers of WO$_3$ at different pressures. In fact, it was demonstrated that the deposition pressure affects the position of the conduction band (CB) energy of the material, resulting in a built-in electric field at the interface between the two WO$_3$ layers. This obviously enhances the photo-promoted electron transfer.

The obtained WO$_3$/BiVO$_4$ system can, in principle, exploit the visible-light photoactivity of BiVO$_4$ together with the efficient charge transport properties of the previously optimized WO$_3$.

The effect that the WO$_3$ bilayer thickness and the post calcination temperature have on the performance of WO$_3$/BiVO$_4$ photoanodes for water splitting was investigated under simulated AM 1.5 G solar light irradiation. The individual materials were also tested for comparison.

2. Materials and Methods

2.1. Photoanodes Preparation

The WO$_3$ and BiVO$_4$ individual photoanodes were prepared by RF diode plasma sputtering [26] and RF magnetron plasma co-sputtering [24], respectively. Both semiconductors were deposited on 10 x 10 mm$^2$, 2 mm thick fluorine-doped tin oxide (FTO) conductive glass. For WO$_3$ photoanodes preparation, the substrates were placed at 4.5 cm from the W (99.9%) metal target in a reactive environment (40% O$_2$/Ar). The reactor was evacuated to less than 10$^{-4}$ Pa before deposition. The sputtering power was set to 140 W and 1500 V of DC self-bias voltage. WO$_3$ was grown with a bilayer deposition strategy using two different gas pressures. The first layer was deposited at 3 Pa, followed by the deposition of the second layer at 1.7 Pa. The deposition time was set in order to obtain three samples with a thickness of 200, 500 and 1000 nm. Each photoanode was formed by two layers with the same thickness. The photoelectrodes were then calcined in air at 600 °C for 2 h.

The BiVO$_4$ films were deposited with a co-sputtering approach using separate bismuth oxide (Bi$_2$O$_3$, 99.9%) and metal vanadium (V, 99.99%) targets, 3.0 in. in diameter (Testbourne Ltd., Basingstoke, UK), with two separate power supplies in order to tune their power independently. The RF power of the metal vanadium target was fixed at 300 W (ca. 6 W/cm$^2$), while that of Bi$_2$O$_3$ was fixed at 20 W (ca. 0.44 W/cm$^2$). The FTO substrate was placed at 10 cm distance from the targets on a rotating substrate holder (1.5 rev/min) to guarantee a uniform deposition. The chamber was evacuated to less than 10$^{-4}$ Pa before deposition. The deposition was performed in a 10% O$_2$/Ar reactive mixture at a constant pressure of 1.7 Pa and for a deposition time necessary to achieve a thickness of 200 nm. The obtained photoelectrodes were then annealed in air at 400 or 600 °C for 2 h.

A series of heterojunction photoelectrodes was prepared by depositing a 200 nm-thick BiVO$_4$ layer above the WO$_3$ bilayer pre-calcinated at 600 °C for 2 h, with different thicknesses. After BiVO$_4$ deposition, the photoelectrodes were calcinated at 400 °C for 2 h. Finally, one more heterojunction
photoelectrode was prepared by depositing a 200 nm-thick BiVO$_4$ layer above a pristine (i.e., not pre-annealed at 600 °C) 1000 nm-thick WO$_3$ double layer and subsequently calcined at 600 °C for 2 h.

2.2. Photoanodes Characterization

In order to measure the film thickness, a portion of sample was covered with a silicon mask during deposition. After taking it away, the height difference between the deposited and non-deposited parts was measured with a P15 surface profilometer (KLA Tencor, San Jose, CA, USA).

The morphology of the photoelectrodes was investigated by scanning electron microscopy (SEM) using a LEO 1430 microscope (Zeiss, Jena, Germany) equipped with an INCA Energy Dispersive X-Ray Spectroscopy (EDX) Detector (Oxford Instruments, Buckinghamshire, UK) and by atomic force microscopy (AFM) in air by means of a Nano-RTM System Pacific Nanotechnology (Santa Clara, CA, USA). The AFM images were acquired in contact mode and the measurements were recorded at a scan speed of 0.5 µm/s for a scanned area of 5 × 5 µm$^2$.

X-ray diffraction (XRD) patterns of the deposited coatings were recorded with a PW3020 powder diffractometer (Philips, Amsterdam, the Netherlands), using the Cu K radiation (λ = 1.5418 Å).

UV-Vis diffuse reflectance spectra (DRS) were recorded in the 220–800 nm range with a UV3600 Plus spectrophotometer (Shimadzu, Kyoto, Japan) equipped with an ISR-603 integrating sphere, using barium sulfate as blank.

2.3. Photoelectrocatalytic Water Splitting Tests

The PEC activity was tested using a three-electrode homemade PEC cell, with the film deposited on FTO as working electrode, a Pt wire as counter electrode and a saturated calomel electrode (SCE) as reference. They were all connected to an Amel (Milan, Italy), mod. 2549 potentiostat/galvanostat and immersed in a 0.5 M Na$_2$SO$_4$ electrolyte solution. All measurements were performed under N$_2$ bubbling into the electrolyte solution; N$_2$ bubbling always started 20 min prior to the beginning of the tests. The samples were tested by means of linear sweep voltammetry (LSV, scan speed 5 mV s$^{-1}$) and chronoamperometry (CA), both under simulated AM 1.5 G solar light (300 W LOT-qd Xe lamp, equipped with an AM 1.5 G filter). The photoanodes were placed at ca. 50 cm from the light source in order to have an incident power of 100 mWcm$^{-2}$ on the photoactive surface. The incident photon to current efficiency (IPCE) curves were measured using the set-up described elsewhere [25]. The incident power was measured with a calibrated Thorlabs S130VC photodiode connected to a Thorlabs PM200 power meter. The electrodes were tested under both front- and back-side (i.e., through the FTO support) irradiation.

3. Results and Discussion

3.1. Photoanodes Characterization

The WO$_3$ and BiVO$_4$ coatings prepared as above described display the characteristic XRD peaks of the orthorhombic and monoclinic crystal structures, respectively, as already reported in our previous works [24,25]. The SEM micrograph of the cross section of the multilayer WO$_3$/BiVO$_4$/FTO photoanode (Figure 1a) confirms an overall film thickness of 1.28 µm due to a ca. 1.05 µm thick WO$_3$ double layer and a ca. 238 nm-thick BiVO$_4$ layer on top of it.

The EDX spectrum of the BiVO$_4$ coatings reveals a V:Bi atomic ratio of 0.8, i.e., the coatings obtained under the adopted experimental conditions are Bi-rich. This result reflects the difficult tuning of the V:Bi atomic ratio during the co-sputtering process. The average surface roughness of the coating is 20 nm according to AFM measurements (Figure 1b). The UV-vis DRS spectra reported in Figure 1c show that the absorption edge of the individual WO$_3$ coating is located at ca. 450 nm while that of BiVO$_4$, calcined at either 400 or 600 °C, extends up to ca. 500 nm. The two heterojunction samples are dominated by the absorption properties of BiVO$_4$. The direct band gap energy determined by the Tauc plot (Figure 1d) confirms that the two heterojunction samples show a band gap value
similar to that of the single BiVO₄ coating (i.e., ca. 2.5 eV; corresponding to a photon wavelength of 496 nm). The individual WO₃ coating possesses a larger band gap energy of 2.8 eV, corresponding to a 443 nm wavelength.

![Figure 1](image-url)  
**Figure 1.** (a) Cross section SEM and (b) top view AFM images of WO₃/BiVO₄ 400 °C; (c) UV-vis reflectance spectra and (d) Tauc plots for direct band gap of the investigated samples.

### 3.2. PEC Performance of Individual WO₃ and BiVO₄ Photoanodes

The effect of the WO₃ thickness on the LSV chopped curves is reported in Figure 2. The photocurrent density as a function of the applied potential on the as-prepared samples was recorded under both front (Figure 2a) and back (Figure 2b) irradiation. Similar PEC performances were obtained for the two modes of irradiation, proving an excellent photo-promoted electron transfer through the WO₃ bilayer. The film thickness apparently does not significantly affect the PEC performance. However, during the subsequent chronoamperometry (CA) test at 1.0 V vs. SCE (Figure 2c), the photocurrent density significantly increases along the 3 h irradiation time, revealing a clear effect of the film thickness at the end of the run, the WO₃ 1000 nm-thick photoanode being the most performing one. This is reasonably due to the increasing light absorption capability with an increase of film thickness. The increasing PEC performance with increasing WO₃ film thickness is further proved by the LSV curves recorded after CA tests (Figure 2d).

The BiVO₄ photoanode shows a clear difference in photocurrent density between the two illumination conditions (Figure 3a,b), generating higher photocurrent when irradiated through FTO (back-side irradiation). This confirms the poor mobility of photo-promoted electrons through the BiVO₄ material [27]. Moreover, the sample post-calcined at 600 °C shows a slightly higher performance than that calcined at 400 °C. The photoactivity of this BiVO₄ coating is lower with respect to that of the best performing one reported in our previous work [24] prepared under similar sputtering conditions, due the Bi-rich atomic ratio of the here investigated material, revealed by EDX analysis. Indeed, the performance of BiVO₄ is strongly affected by the Bi:V atomic ratio, stoichiometric 1:1 ratio materials being best performing. The time stability test (CA at 1.0 V vs. SCE, Figure 3c), though confirming the higher performance of the sample calcined at 600 °C, also reveals a partial loss of activity along the irradiation time. Interestingly, when the light is turned on the two samples generate a similar
photocurrent density, but the BiVO$_4$ coating post calcined at 600 °C shows a marked increase during the first 20 min of irradiation.

Figure 2. Effect of the WO$_3$ film thickness on chopped Linear Sweep Voltammetry (LSV) curves under (a) front and (b) back irradiation of as-prepared samples; (c) chronoamperometry (CA) stability test at 1.0 V vs. SCE; (d) chopped LSV curves under back irradiation recorded after CA tests (panel c). All measurements were made in a 0.5 M Na$_2$SO$_4$ electrolyte solution under simulated AM 1.5 G solar irradiation.

Figure 3. Effect of the post calcination temperature (400 or 600 °C) of the BiVO$_4$ film on chopped Linear Sweep Voltammetry (LSV) curves under (a) front and (b) back irradiation of as-prepared samples; (c) chronoamperometry (CA) tests at 1.0 V vs. SCE; (d) chopped LSV curves under back irradiation recorded after CA tests (panel c). All measurements were made in a 0.5 M Na$_2$SO$_4$ electrolyte solution under simulated AM 1.5 G solar irradiation.
However, contrarily to WO$_3$, when irradiation is chopped off (5 min in the dark), the gain of activity is progressively lost and stabilized after the fourth cycle of 30 min long irradiation. The LSV recorded under back irradiation after CA tests (Figure 3d) shows a decreased performance of the aged samples, as expected by the observed CA trend. Moreover, being the LSV a transient experiment, the performance of the two samples is similar, as expected by the similar photocurrent density generated during the CA experiment as the light is turned on.

3.3. PEC Performance of the WO$_3$/BiVO$_4$ Heterojunction

Figure 4 shows the PEC performance of the WO$_3$/BiVO$_4$ heterojunction as a function of the WO$_3$ film thickness. All samples were annealed at 600 °C after WO$_3$ deposition and at 400 °C after BiVO$_4$ deposition. The PEC performance of the heterojunction electrodes shows a behavior partly common to those of individual WO$_3$ and BiVO$_4$ electrodes, namely: (i) Backside irradiation leads to higher generated photocurrent, as in the case of BiVO$_4$ (Figure 4a,b); (ii) the PEC performance increases during CA tests, as in the case of WO$_3$ (Figure 4c); and (iii) the performance increases with an increase of the WO$_3$ double layer thickness. The highest photocurrent density (i.e., 1.05 mA cm$^{-2}$ at 1.4 V vs. SCE) was attained with the 1000 nm-thick WO$_3$ film illuminated from the backside.

![Figure 4.](image)

Figure 4. Effect of the WO$_3$ film thickness on the photoelectrochemical (PEC) performance of the WO$_3$/BiVO$_4$ heterojunctions: Chopped Linear Sweep Voltammetry (LSV) curves under (a) front and (b) back irradiation of as-prepared samples; (c) chronoamperometry (CA) tests at 1.0 V vs. SCE; (d) chopped LSV curves under back irradiation recorded after CA tests (panel c). All samples were post calcined at 400 °C for 2 h after BiVO$_4$ deposition. All measurements were made in a 0.5 M Na$_2$SO$_4$ electrolyte solution under simulated AM 1.5 G solar irradiation.

The effect of the WO$_3$ layer thickness becomes more evident after their stability test (Figure 4c,d). In fact, the WO$_3$ 1000 nm/BiVO$_4$ sample benefits most from the “photo-assisted activation”, reaching a
maximum photocurrent of 1.7 mA cm\(^{-2}\) at 1.4 V vs. SCE (Figure 4c), with an 80% increase with respect to the as-prepared heterojunction electrode. This corresponds to ca. two-fold and to ca. five-fold increase compared to the photocurrent produced by individual 1000 nm-thick WO\(_3\) (0.8 mA cm\(^{-2}\)) and BiVO\(_4\) (0.35 mA cm\(^{-2}\)), respectively. Moreover, the overall photocurrent density generated by the heterojunction electrode significantly exceeds the sum of the photocurrent densities generated by the individual semiconductors (Figure 5). Thus, it confirms the capability of the heterojunction structure to attain an efficient space separation of the charge carriers due to the optimal band alignment of these two semiconductor materials.

![Figure 5](image-url)

**Figure 5.** Effect of the post calcination temperature (400 or 600 °C) on the photoelectrochemical (PEC) performance of the WO\(_3\)/BiVO\(_4\) heterojunctions: Chopped Linear Sweep Voltammetry (LSV) curves under (a) front and (b) back irradiation of as-prepared samples; (c) chronoamperometry (CA) stability tests at 1.0 V vs. SCE; (d) chopped LSV curves under back irradiation recorded after CA tests (panel c). The WO\(_3\) and BiVO\(_4\) film thicknesses were 1000 and 200 nm, respectively. All measurements were made in a 0.5 M Na\(_2\)SO\(_4\) electrolyte solution under simulated AM 1.5 G solar irradiation.

Finally, we explored the effect of the post calcination temperature on the PEC performance of the heterojunction photoanodes (Figure 5).

Two samples were prepared under the same WO\(_3\) and BiVO\(_4\) sputtering conditions. One sample was post annealed at 600 °C for 2 h after WO\(_3\) deposition over FTO and then at 400 °C for 2 h after BiVO\(_4\) deposition (as the above investigated series of samples). This sample is labelled as WO\(_3\)/BiVO\(_4\)\(_{400\text{C}}\). The other sample was subjected to a single-step post calcination treatment at 600 °C for 2 h after BiVO\(_4\) deposition above WO\(_3\) (WO\(_3\)/BiVO\(_4\)_600C). Figure 5 shows that the post calcination procedure strongly affects the PEC performance of the heterojunction. Surprisingly, WO\(_3\)/BiVO\(_4\)_600C displays similar efficiency under both front and backside irradiation, reaching ca. 1 mA cm\(^{-2}\) photocurrent density at 1.4 V vs. SCE over the as-prepared sample. Moreover, the sample annealed at 600 °C generates ca. two-fold photocurrent density with respect to that annealed at 400 °C under front irradiation,
while the two samples show similar activity under backside irradiation. The post calcination protocol affects the time stability of the samples as well. WO$_3$/BiVO$_4$ suffers from partial deactivation along the irradiation time similar to that of BiVO$_4$$_{600}$C (Figure 5c). Hence, the sample calcined at 600 °C shows a similar activity to WO$_3$ after CA tests, which is half of the photocurrent generated by WO$_3$/BiVO$_4$$_{400}$C (Figure 5d).

The IPCE curves recorded after CA tests (Figure 6) help to get a deeper insight into the different PEC performances of these two heterojunction samples.

![Figure 6](image)

**Figure 6.** Incident photon to current efficiency (IPCE) curves recorded with WO$_3$ (red line), WO$_3$/BiVO$_4$$_{400}$C (green line), WO$_3$/BiVO$_4$$_{600}$C (blue line) and BiVO$_4$$_{600}$C (black line) photoanodes under (a) front- and (b) back-side irradiation at 1.0 V vs. SCE in a 0.5 M Na$_2$SO$_4$ electrolyte solution.

The onset photoactivity of WO$_3$ and of BiVO$_4$ are below 450 and 500 nm, respectively, in agreement with their band gap energy determined by the Tauc plot. BiVO$_4$$_{600}$C shows higher IPCE under backside irradiation with a maximum of 6% at 350 nm. On the other hand, the WO$_3$ double layer confirms to be a good performing photoanode, with a maximum IPCE of 90% at 350 nm under backside irradiation. Both heterojunction samples post-calcined at different temperatures display a significantly improved photoactivity in the 450–500 nm range (i.e., in the photon energy range below the WO$_3$ absorption onset). This result highlights the role of the WO$_3$ double layer in improving the photoactivity of BiVO$_4$ by providing a downhill pathway in the CB levels that allows an efficient electron–hole separation, as shown in Scheme 1a. Interestingly, the IPCE of the WO$_3$/BiVO$_4$$_{600}$C sample in this spectral region is higher than the IPCE of the WO$_3$/BiVO$_4$$_{400}$C sample, especially under front-side irradiation. However, at higher photon energy (i.e., below the WO$_3$ absorption threshold), both heterojunction photoanodes exhibit an IPCE lower than the WO$_3$ coating alone. This phenomenon has been already reported in the literature [14,28] and attributed [29,30] to an electron–hole recombination path occurring at the interface when both semiconductors are excited, as depicted in Scheme 1b. Interestingly, the two heterojunction samples display very different behaviors in the high photon energy region ($\lambda < 450$ nm) under front- or back-side irradiation. Indeed, the WO$_3$/BiVO$_4$$_{600}$C sample keeps a relatively high IPCE under front-side irradiation, reaching a maximum of 23% at 370 nm, with a minor loss with respect to single WO$_3$. In contrast, under back-side irradiation the same photoelectrode shows a maximum IPCE of 27% at 440 nm (i.e., in correspondence of the WO$_3$ absorption onset), followed by a dramatic loss of efficiency at lower wavelengths, while WO$_3$/BiVO$_4$$_{400}$C shows an increasing IPCE up to 60% at 350 nm (though lower than that of WO$_3$ alone). This dramatic loss of efficiency of the WO$_3$/BiVO$_4$$_{600}$C sample below 450 nm is responsible for its relative low PEC performance under simulated solar light, as shown in Figure 5c,d. This result suggests that the single step post annealing treatment at 600 °C very likely produces a better contact at the interface between the two semiconductor materials that favors a more efficient electron transfer at $\lambda > 450$ nm (Scheme 1a),
but also a higher probability of charge carriers recombination (according to Scheme 1b) when both semiconductors are excited (i.e., $\lambda < 450 \text{ nm}$). The higher IPCE attained with this sample under front-side irradiation reflects its intrinsic higher efficiency, because under this irradiation mode, even at $\lambda < 450 \text{ nm}$, the largest part of the photons are absorbed by the outermost BiVO$_4$ layer, thus reducing the probability of electron–hole recombination at the interface.

![Scheme 1](image)

**Scheme 1.** Effect of the irradiation wavelength on the pathways of photogenerated electron–hole pairs in multilayer WO$_3$/BiVO$_4$ photoanodes: Spatial electron–hole separation at the WO$_3$/BiVO$_4$ heterojunction under irradiation at wavelengths (a) above and (b) below 450 nm. Under excitation of both semiconductors, a possible recombination channel opens at the interface, between electrons photo-promoted in the WO$_3$ conduction band (CB) and holes photoproduced in the BiVO$_4$ valence band (VB), hindering the overall PEC performance.

4. Conclusions

Reactive RF plasma (co)sputtering demonstrates to be an effective technique for the deposition of multilayered WO$_3$/BiVO$_4$ heterojunction photoanodes for solar-driven water splitting. This can open the way to a future scale-up of the PEC technology by deposition of large surface area photoanodes. The thickness of the WO$_3$ double layer, the post annealing treatment and the irradiation mode (back- or front-side) strongly affect the efficiency of the WO$_3$/BiVO$_4$ heterojunction. In this work, the best performing heterojunction was obtained by a two-step annealing treatment (i.e., over a 1000 nm-thick WO$_3$ double layer calcined at 600 °C followed by deposition of a 200 nm-thick BiVO$_4$ layer further calcined at 400 °C). The electron–hole recombination at the interface between the two semiconductors occurring at photon energy above the WO$_3$ band gap was confirmed to be the main drawback of this system, especially for heterojunction photoanodes prepared in a single-step calcination treatment at 600 °C. Nonetheless, coupling two semiconductor materials with appropriate bands alignment confirms to be a very promising approach to improve charge carrier separation and, hence, significantly increase the PEC performance under solar light irradiation.

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