Enhanced Charge Carrier Separation in $\text{WO}_3/\text{BiVO}_4$ Photoanodes Achieved via Light Absorption in the $\text{BiVO}_4$ Layer

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ABSTRACT: Photoelectrochemical (PEC) water splitting converts solar light and water into oxygen and energy-rich hydrogen. $\text{WO}_3/\text{BiVO}_4$ heterojunction photoanodes perform much better than the separate oxide components, though internal charge recombination undermines their PEC performance when both oxides absorb light. Here we exploit the $\text{BiVO}_4$ layer to sensitize $\text{WO}_3$ to visible light and shield it from direct photoexcitation to overcome this efficiency loss. PEC experiments and ultrafast transient absorption spectroscopy performed by frontside (through $\text{BiVO}_4$) or backside (through $\text{WO}_3$) irradiating photoanodes with different $\text{BiVO}_4$ layer thickness demonstrate that irradiation through $\text{BiVO}_4$ is beneficial for charge separation. Optimized electrodes irradiated through $\text{BiVO}_4$ show 40% higher photocurrent density compared to backside irradiation.

KEYWORDS: solar water oxidation, heterojunction, ultrafast transient absorption, photoactive layer thickness, filter effect

BiSmuth vanadate, $\text{BiVO}_4$, is a promising semiconductor oxide employed in photoanodes for the oxygen evolution reaction in water-splitting devices.$^{1,2}$ Its stability in contact with aqueous electrolytes,$^{3,4}$ its good visible light-harvesting capability,$^5$ and its simple preparation through cheap wet techniques$^6$ pointed to this material as a possible component of future commercial photoelectrochemical (PEC) cells. Furthermore, in the last 15 years the efficiency of $\text{BiVO}_4$-based photoanodes (in terms of current density) rapidly grew from a few microamps per square centimeter in early reports to 4−5 mA cm$^{-2}$, with prolonged continuous operation of photoelectrodes modified with oxygen evolution cocatalysts.$^{3,4,6−13}$ However, the fast charge recombination of $\text{BiVO}_4$-based electrodes still hampers the efficiency of this material.$^{2,14}$

A way to overcome this intrinsic flaw is to couple $\text{BiVO}_4$ with $\text{WO}_3$ in the $\text{WO}_3/\text{BiVO}_4$ heterojunction where visible light harvesting $\text{BiVO}_4$ sensitizes wider band gap $\text{WO}_3$.$^{15}$ $\text{BiVO}_4$ photoanodes based on this heterojunction achieve the highest current densities among oxide-based photoanodes.$^{10,17}$ The suitable band gap alignment between the two oxides, the efficient electron and hole transport in $\text{WO}_3$ and $\text{BiVO}_4$, respectively, and the spacial charge separation support the high performance of $\text{WO}_3/\text{BiVO}_4$ photoanodes.$^{18−25}$

In previous studies, we investigated the charge carrier dynamics in the $\text{WO}_3/\text{BiVO}_4$ system through transient absorption spectroscopy (TAS) with detection either in the visible range to observe the hole dynamics in $\text{BiVO}_4$ or in the mid-infrared to follow the electron dynamics in $\text{WO}_3$ and $\text{BiVO}_4$.$^{26−28}$ We also identified wavelength-dependent processes by tuning the excitation wavelength across the $\text{WO}_3$ absorption edge (ca. 450 nm).$^{18,26,29}$ Indeed, the type II band alignment between the two oxides (Figure 1A) allows distinct charge transfer processes leading to charge separation or recombination, depending on the excitation wavelength. Under visible light excitation of $\text{BiVO}_4$ electrons promoted in its conduction band (CB) flow into the energetically lower-lying CB of $\text{WO}_3$, while holes remain in the $\text{BiVO}_4$ valence band (VB). This electron transfer process (process ⊙ in Figure 1A) decreases charge recombination and leads to long-living charge carriers that are beneficial for PEC performance.$^{29}$ Conversely, irradiation at wavelengths below 450 nm leads to the excitation of both oxides and opens a detrimental recombination path between the electrons photopromoted in the CB of $\text{WO}_3$ and the holes in $\text{BiVO}_4$ (process ® in Figure 1A). This process results in charge recombination on a ∼200 ps time scale$^{26}$ and becomes more relevant with increasing $\text{WO}_3$ layer thickness.$^{30}$

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Based on these dynamics, we posited that an efficient heterojunction system needs to direct charges along process \( \circ \) and disfavor off-track routes such as process \( \bullet \). Still, solar light includes photons energetic enough to excite WO\(_3\) (\( \sim 4\% \) of the solar spectrum is at wavelengths below the absorption edge of bulk WO\(_3\)). Therefore, a portion of photogenerated charges in WO\(_3/\)BiVO\(_4\) systems may be wasted through process \( \bullet \). On the other hand, BiVO\(_4\) efficiently absorbs light beyond the absorption edge of WO\(_3\), up to 520 nm, allowing us to exploit a larger fraction of the solar spectrum. Therefore, in this work we pursue the strategy of using the BiVO\(_4\) sensitizer to shield WO\(_3\) from direct photoexcitation.

We assembled a series of heterojunction electrodes with a WO\(_3\) scaffold layer of fixed thickness (ca. 150 nm) coated with BiVO\(_4\) overlayers with different thickness (15–160 nm) to tune the amount of light absorbed by BiVO\(_4\). First, a systematic PEC study allowed us to probe whether the irradiation mode (through WO\(_3\) or BiVO\(_4\), backside or frontside irradiation, respectively, Figure 1B) affects the overall PEC efficiency of the electrodes. Then, transient absorption spectroscopy (TAS) with a pump in the UV region (387 nm) and detection in the visible range was employed to assess the effects of the irradiation mode on the lifetime of photogenerated holes in BiVO\(_4\). These tests allowed us to evaluate the extent of charge recombination induced by process \( \bullet \) and its impact on the PEC performance of the heterojunction photoanodes as a function of the BiVO\(_4\) layer thickness.

The WO\(_3/\)BiVO\(_4\) photoanodes were prepared through spin coating using fluorine-doped tin oxide (FTO) as the conductive glass substrate (see the Supporting Information). The absorption spectra of the two electrode series are shown in Figures S1 and S2; the thickness of the BiVO\(_4\) layer was estimated using the absorption coefficient at 420 nm, \( \alpha_{420} = 6.7 \times 10^4 \text{ cm}^{-1} \). XRD analyses confirm the successful synthesis of WO\(_3\) and BiVO\(_4\) (Figure S3) and FESEM images...
Figure 3. Internal quantum efficiency (IQE) 3D contour plots (color scale) vs the incident wavelength and the BiVO$_4$ film thickness of the WO$_3$/BiVO$_4$ electrodes, obtained in contact with a 0.5 M Na$_2$SO$_4$ aqueous solution at 1.23 V$^\text{SHE}$ under (A) frontside or (B) backside irradiation; (C) IQE plots under backside and frontside irradiation obtained with the best performing electrode (with a 75 nm thick BiVO$_4$ layer).

demonstrate the uniform coating of the photoanodes (Figure S4).

In order to explore the shielding hypothesis, we carried out PEC experiments on the electrodes. Figure 2A, B shows the photocurrent density generated with the WO$_3$/BiVO$_4$ electrodes under simulated solar light irradiation in 0.5 M Na$_2$SO$_4$ solution under back- and frontside irradiation at different applied potentials. The linear sweep voltammetry plots are reported in Figures S5 and S6. As a general trend, all heterojunction photoanodes outperform control pure BiVO$_4$ electrodes (see Figure S7). Furthermore, the better light exploitation achieved with increasing the BiVO$_4$ layer thickness drives the photocurrent increase under both irradiation conditions up to a 75 nm thick BiVO$_4$ layer.

Under frontside simulated solar light irradiation (Figure 2A), the heterojunction photoanodes generate considerably higher photocurrent than in backside mode (Figure 2B). The best performing electrode with a 75 nm thick BiVO$_4$ layer thickness (Figure 2C), when irradiated frontside shows a ca. 40% increase in the current density, from 1.0 to 1.38 mA cm$^{-2}$, with respect to backside irradiation, at the formal H$_2$O/O$_2$ redox potential of 1.23 V vs the standard hydrogen electrode (V$^\text{SHE}$).

We used single-wavelength efficiency measurements to gather further information on this PEC performance increase. Specifically, internal quantum efficiency (IQE, Figure 3 and Figures S8 and S9), measuring the efficiency of absorbed photons, was calculated from the incident photon to current conversion ratio at wavelengths above the absorption onset (Figure 3C).

Figure 3A shows the transient decay signal at 470 nm to trapped holes in BiVO$_4$ based on experiments in the presence of hole scavengers. TAS proved an essential tool for studying charge carrier dynamics and diffusion in photocatalysis and photovoltaics. Therefore, TAS with detection at 470 nm was here employed to investigate the dynamics of photogenerated holes in both pure BiVO$_4$ and WO$_3$/BiVO$_4$ electrode series upon backside and frontside excitation at 387 nm.

The DA signals recorded with pure BiVO$_4$ electrodes were analyzed first. For this system, similar transient dynamics were obtained in the two irradiation modes. Figure S12 reports representative transient absorption spectra, while Figure S13 shows the transient decay DA profiles at 470 nm, which were fitted according to a biexponential decay model (eq 1).

$$\Delta A = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + \Delta A_0$$

In this equation, $\tau_1$ and $\tau_2$ are the lifetimes of the faster and slower decay processes typical of BiVO$_4$ respectively, $A_1$ and $A_2$ are the weighted coefficients that represent the contribution of each of the two processes to the overall decay and $\Delta A_0$ is the offset (set at zero in the fitting). The fitting parameters for the BiVO$_4$ electrodes (Table S1) are in line with literature...
Figure 4. Comparison between the normalized TAS decay signals in (A–C) WO$_3$/BiVO$_4$ electrodes with different BiVO$_4$ thicknesses recorded under backside (through WO$_3$, black squares) or frontside (through BiVO$_4$, red triangles) irradiation and in (D–F) WO$_3$/BiVO$_4$ (red triangles) and pure BiVO$_4$ films (blue diamonds) with the same BiVO$_4$ thickness recorded under frontside irradiation. The solid lines are the fitting curves according to eq 1 (BiVO$_4$ films) or eq 2 (WO$_3$/BiVO$_4$ films). Excitation pump at 387 nm, TAS signal monitored at 470 nm.

Table 1. Fitting Parameters of the TAS Dataset Collected with the WO$_3$/BiVO$_4$ Electrodes under Backside Excitation at 387 nm$^a$

| BiVO$_4$ thickness (nm) | $A_1$ (%) | $\tau_1$ (ps) | $A_2$ (%) | $\tau_2$ (ps) | $A_3$ (%) | $\tau_3$ (ps) |
|------------------------|----------|--------------|----------|--------------|----------|--------------|
| 15                     | 30 ± 1   | 7.4 ± 0.8    | 32 ± 3   | 170 ± 22     | 38 ± 3   | 0.98 ± 0.07  |
| 30                     | 26 ± 2   | 6.2 ± 1.1    | 34 ± 3   | 189 ± 27     | 40 ± 3   | 1.9 ± 0.2    |
| 50                     | 24 ± 2   | 7.8 ± 1.2    | 39 ± 2   | 156 ± 30     | 57 ± 2   | 1.99 ± 0.11  |
| 75                     | 22 ± 1   | 15.8 ± 1.8   | 17 ± 2   | 215 ± 48     | 61 ± 3   | 1.44 ± 0.07  |
| 115                    | 23 ± 2   | 22 ± 3       | 19 ± 2   | 210 ± 25     | 58.0 ± 0.3| 3.57 ± 0.11  |
| 160                    | 18 ± 1   | 13.1 ± 1.7   | 15 ± 1   | 159 ± 26     | 67.4 ± 0.9| 3.05 ± 0.11  |

$^a$Data fitted according to eq 2.

reports on pure BiVO$_4$. Regardless of the BiVO$_4$ thickness, $A_1$ and $A_2$ account for ~30 and 70% of the hole decay, respectively. The fast decay lifetime, which is associated with the recombination of trapped holes in BiVO$_4$ with photopromoted free electrons, is independent of the BiVO$_4$ layer thickness ($\tau_1$, ~20 ps), because all electrodes are excited at the same pump wavelength (i.e., with the same energy excess with respect to the BiVO$_4$ CB). On the other hand, $\tau_2$, which is ascribed to the recombination of trapped holes with trapped electrons, increases from ~1 to 6.5 ns with increasing BiVO$_4$ layer thickness as more holes get trapped in bulk.

The decay signal of photoproduced holes in the BiVO$_4$ layer of the WO$_3$/BiVO$_4$ electrodes series recorded at 470 nm under backside and frontside irradiation are reported in Figure 4 and Figures S14 and S15. Under frontside excitation, the $\Delta A$ signals decay slower than under backside excitation (Figure 4A–C). Indeed, under backside irradiation mode a significant fraction of 387 nm photons is absorbed by WO$_3$, leading to photoexcitation of electrons into its CB (the individual WO$_3$ layer absorbs ca. 16% of 387 photons, Figure 1C). Therefore, many photoproduced charge carriers recombine through process $\circledR$ (Figure 1A). This additional recombination channel leads to the abrupt $\Delta A$ drop observed during the first 400 ps following backside photoexcitation (Figure 4A). Furthermore, under frontside irradiation the $\Delta A$ signal recorded with the WO$_3$/BiVO$_4$ heterojunctions becomes progressively slower and comparable with those recorded with pure BiVO$_4$ (Figure 4D–F and Figure S13).

In previous studies on the WO$_3$/BiVO$_4$ heterojunction, we evaluated the contribution of process $\circledR$ to the overall $\Delta A$ decay signal by fitting the $\Delta A$ decay traces including an additional decay component in eq 1, to take into account also process $\circledR$. Here, we used the same approach to assess its contribution to the charge carrier dynamics in the two irradiation modes and fitted the $\Delta A$ decay with eq 2.

$$\Delta A = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3} + \Delta A_0$$

where $\tau_i$ is the lifetime of the recombination process $i$. Here, $A_3$ accounts for the additional recombination process and $A_1$ is its weighted contribution.

We first fitted the dynamics recorded in the WO$_3$/BiVO$_4$ electrodes under backside excitation. The fitting parameters are reported in Table 1. In this configuration, the WO$_3$ layer is
Table 2. Fitting Parameters of the TAS Dataset Collected with the \( \text{WO}_3/\text{BiVO}_4 \) Electrodes under Frontside Excitation at 387 nm

| BiVO\(_4\) thickness (nm) | \( A_1 \) (%) | \( \tau_1 \) (ps) | \( A_2 \) (%) | \( \tau_2 \) (ps) | \( A_3 \) (%) | \( \tau_3 \) (ns) |
|--------------------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|
| 15                       | 25 ± 1         | 13 ± 1          | 20 ± 1         | 170             | 55 ± 1         | 1.55 ± 0.03     |
| 30                       | 23 ± 3         | 15 ± 2          | 27 ± 3         | 189             | 50 ± 3         | 2.8 ± 0.4       |
| 50                       | 21 ± 3         | 19 ± 7          | 13 ± 5         | 156             | 66 ± 2         | 3.0 ± 0.3       |
| 75                       | 23 ± 3         | 10 ± 3          | 12 ± 4         | 215             | 65 ± 2         | 3.1 ± 0.4       |
| 115                      | 20 ± 1         | 24 ± 4          | 4 ± 2          | 210             | 76.3 ± 0.8     | 5.4 ± 0.3       |
| 160                      | 27 ± 1         | 21 ± 2          | -              | -               | 73.1 ± 0.3     | 10.6 ± 1.2      |

“Data fitted according to eq 2 using the \( \tau_r \) values reported in Table 1.

irradiated directly and absorbs the same amount of light in all electrodes. Therefore, we expect that process \( \circledast \) has a comparable effect on the charge carrier dynamics at each BiVO\(_4\) layer thickness. Indeed, this process accounts for ca. 23 ± 8% of the holes decay, with a time constant \( \tau_r \) of ∼200 ps (Table 1).

Under frontside irradiation, the BiVO\(_4\) layer in the heterojunction electrodes shields WO\(_3\) from light absorption as the BiVO\(_4\) layer thickness increases. Indeed, the percent amount of incident 387 nm photons absorbed by the WO\(_3\) underlayer in the coupled system progressively decreases (Figure 1C). Therefore, we sought to quantify the shielding effect of the BiVO\(_4\) layer in decreasing the extent of process \( \circledast \) in the WO\(_3)/\text{BiVO}_4\) electrodes. By assuming that process \( \circledast \) operates with its intrinsic time constant \( \tau_r \) regardless of the excitation mode, we fitted the decay dynamics recorded under frontside irradiation by employing the \( \tau_r \) previously extracted from the TAS signals recorded upon excitation in backside mode (Table 1). Because of the reduced amount of charge carriers generated in WO\(_3\), the weight of process \( \circledast \) in terms of the \( A_r \) parameter (Table 2) decreases with increasing the BiVO\(_4\) layer thickness. Additionally, as fewer charge carriers undergo process \( \circledast \), \( A_r \) increases, suggesting that a larger number of photogenerated charge carriers recombines through the slower process. A 160 nm thick BiVO\(_4\) layer almost entirely absorbs the pump (Figure 1C), preventing WO\(_3\) excitation. Due to the lack of photoexcited electrons in the CB of WO\(_3\), the electrons photopromoted in the BiVO\(_4\) CB can only recombine with trapped holes in BiVO\(_4\) or flow into WO\(_3\) CB via process \( \circledast \), resulting in better charge carrier separation. Consequently, the holes photogenerated in the BiVO\(_4\) layer of the WO\(_3)/\text{BiVO}_4\) heterojunction live longer than those in the individual 160 nm thick BiVO\(_4\) electrode (Figure 4F). This condition is akin to selective BiVO\(_4\) excitation in WO\(_3)/\text{BiVO}_4\) at wavelengths beyond WO\(_3\) absorption edge, which we previously observed extending the hole lifetimes compared to individual BiVO\(_4\)\(^{26,29}\).

Thus, TAS and PEC experiments suggest that light absorption by the BiVO\(_4\) layer in WO\(_3)/\text{BiVO}_4\) electrodes selectively suppresses process \( \circledast \) and promotes process \( \circledast \), which leads to an increase of trapped hole lifetime in BiVO\(_4\). However, despite the promise of long-living holes in the heterojunction electrode with a 160 nm thick BiVO\(_4\) layer, it performs poorly compared to the most active heterojunction with the 75 nm thick BiVO\(_4\) layer. This latter electrode possesses an optimal matching between (i) WO\(_3\) sensitization to the visible light, (ii) photogenerated charge separation at the heterojunction, and (iii) efficient charge extraction toward the external circuit and the electrolyte. Indeed, thinner BiVO\(_4\) layers limit the electrode performance due to the low visible light absorption, while thicker films may suffer from a greater charge recombination owing to hole accumulation in the BiVO\(_4\) bulk under operando conditions.

In conclusion, we identified a shielding strategy to suppress the internal charge recombination occurring in the WO\(_3)/\text{BiVO}_4\) heterojunction due to WO\(_3\) excitation. Optimized light absorption in BiVO\(_4\) layers considerably suppresses this recombination channel. The best performing electrode tested in this work shows a 40% increase in the PEC performance under frontside irradiation compared to backside irradiation. Furthermore, these findings suggest that methods to suppress undesired wavelength-dependent recombination processes and optimize charge transport and surface catalysis are required to design efficient photoelectrodes based on type-II heterojunctions.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.2c02597.

Experimental details, absorption spectra, XRD and FESEM analyses, linear sweep voltammetry tests, IQE and IPCE plots, TAS decay profiles, and fitting parameters (PDF)

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