In Operando Photoelectrochemical Femtosecond Transient Absorption Spectroscopy of WO₃/BiVO₄ Heterojunctions

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ABSTRACT: The WO₃/BiVO₄ heterojunction is a promising photoanode architecture for water splitting applications. Here, the photoinduced charge carrier dynamics occurring in this system in operando photoelectrochemical conditions, i.e. under an applied anodic potential, are studied through femtosecond transient absorption spectroscopy, to unveil the effects of an applied bias on the early charge carrier dynamics following WO₃/BiVO₄ excitation. Electrochromic measurements on BiVO₄ suggest the presence of intra band gap (IBG) states in this oxide which play an important role in the charge carrier dynamics in the heterojunction. The differences observed in WO₃/BiVO₄ with respect to individual BiVO₄ electrodes are rationalized in terms of the electron equilibration between the two oxides at the heterojunction, dominated by the WO₃/BiVO₄ interfacial electric field arising from their band energy offset, and the bias-dependent alteration of the IBG states, both determining the rate of hole transfer and accumulation at the BiVO₄ surface.
Among n-type metal oxide semiconductors with small band gap (BG), BiVO$_4$ (BG = 2.4 eV) is promising as photoanode material for water splitting, exhibiting good visible-light absorption and a valence band (VB) edge (ca. 2.5 V$_{RHE}$) suitable for oxygen evolution.$^{1-7}$ However, pure BiVO$_4$ exhibits a rather poor light-to-current conversion efficiency, unless a strongly anodic bias is applied, typically in excess of 1.3 V$_{RHE}$$^{9-11}$ and a limiting photoanodic performance depending on the kinetic competition for long-living photogenerated holes between surface recombination and oxygen evolution, typically occurring in the millisecond to second timescale.$^{8,12}$

Enhanced photoactivity can be obtained by combining smaller and larger BG semiconductor oxides in heterojunctions.$^{13,14}$ In particular, in the WO$_3$/BiVO$_4$ heterojunction (where WO$_3$ has a BG of 2.7 eV) the two oxides display a staggered (type II) band alignment, the conduction band (CB) minimum and the VB maximum of WO$_3$ (ca. +0.4 and +3.1 V, respectively) both being lower in energy than those of BiVO$_4$ (ca. +0.02 and +2.4 V, respectively). This allows the injection of electrons photoexcited in BiVO$_4$ into the WO$_3$ CB, leading to enhanced spatial separation of charges, lower carrier recombination and hole accumulation in BiVO$_4$, while photoexcited electrons rapidly diffuse to the external circuit thanks to their higher mobility in WO$_3$.$^{15,16}$

Charge carrier dynamics in photoactive materials can be studied through transient absorption (TA) spectroscopy from the picosecond to the second timescale.$^{8,17-25}$ In particular, a close-knit group of papers recently appeared on ultrafast (femtosecond to picosecond) TA of BiVO$_4$-related systems, i.e. pure BiVO$_4$, $^{22,23,26,27}$ W-doped BiVO$_4$, $^{28}$ and the WO$_3$/BiVO$_4$ heterojunction.$^{7,15,24,29}$ However, the charge carrier dynamics has been scarcely investigated so far in operando photoelectrochemical (PEC) conditions which are relevant for water splitting applications, i.e. under an applied bias. In their TA studies on pure BiVO$_4$ Ravensbergen et al.$^{23}$ observed no spectral or kinetic differences by applying a bias voltage, while a comparison between the TA signals obtained, on the microsecond time scale, with and without applied bias very recently appeared for BiVO$_4$ combined with black phosphorene.$^{30}$ Moreover, recent investigations of the WO$_3$/BiVO$_4$ junction under an applied bias on the long (microsecond to second) timescales relevant to water
oxidation reveal that electron transfer from BiVO$_4$ to WO$_3$ occurs in the sub-$\mu$s time range and that an anodic bias (> 0.6 V$_{RHE}$) is required to increase the lifetime and population of the holes that oxidize water. Thus, the important effects of an applied bias on the very fast photoinduced dynamics in the WO$_3$/BiVO$_4$ heterojunction need to be elucidated.

Here we investigate the carrier dynamics in photoexcited BiVO$_4$ and in the WO$_3$/BiVO$_4$ heterojunction under applied bias in an electrochemical cell, i.e. in operando PEC conditions, by combining femtosecond TA spectroscopy with the electrochromic and PEC characterization of the materials.

The photoelectrodes were prepared by spin coating BiVO$_4$ or WO$_3$ followed by BiVO$_4$ on fluorine doped tin oxide, as previously detailed (see Supporting Information), and consisted of 100 nm thick monoclinic WO$_3$, 60 nm thick monoclinic scheelite BiVO$_4$ and (100+60) nm thick WO$_3$/BiVO$_4$ films with high optical quality. Their absorption spectra are shown in Figure 1A. Under an applied potential, WO$_3$ and BiVO$_4$ photoanodes generate moderate photocurrents, while the WO$_3$/BiVO$_4$ heterojunction generates larger photocurrents (see J-V curves reported in Figure S1), resulting in a higher internal quantum efficiency of the heterojunction in the visible (\( \lambda > 400 \) nm), as shown in Figure 1B.

**Figure 1.** A) Steady-state absorption spectra of the WO$_3$, BiVO$_4$ and WO$_3$/BiVO$_4$ electrodes. B) Internal Quantum Efficiency (IQE) as a function of the irradiation wavelength at an applied potential of 1.23 V vs. RHE of the WO$_3$, BiVO$_4$ and WO$_3$/BiVO$_4$ photoanodes in 0.5 M Na$_2$SO$_4$. 
We preliminarily performed spectro-electrochemical experiments by recording the absorption changes induced in BiVO₄ and WO₃/BiVO₄ by anodic bias at potentials comparable to those used in PEC and in operando TA experiments. Steady-state spectra have previously been collected for BiVO₄ with an applied bias. The differential absorption ($\Delta A$) spectra of BiVO₄ at different potentials, recorded after 60 s applied bias in the electrolyte solution detailed in Section 1.3 of the Supporting Information, are shown in Figure 2A. The spectra were obtained by subtracting the absorption spectrum recorded at the open circuit potential (OCP, i.e. without applied bias) from the absorption spectrum measured at each applied bias in contact with an electrolyte solution.

![Figure 2. Spectro-electrochemical analyses performed in 0.1 M tetrabutyl ammonium hexafluoro phosphate in acetonitrile solution of A) BiVO₄ and B) WO₃/BiVO₄ photoanodes, showing the spectral changes occurring under anodic bias. $\Delta A$ is the difference between the absorption spectrum at each applied potential and that recorded under open circuit potential conditions. At low applied potentials (0.4 V) the $\Delta A$ signal is close to the measurement baseline, while at biases higher than 0.8 V_RHE a well-defined band peaking at 470 nm appears. As the applied potentials are anodic with respect to the flat band potential, which is $\sim 0.02$ V_RHE, the appearance of this band indicates that it originates from the oxidized form of intra band gap (IBG) states at energy a few hundred of meV below the CB of BiVO₄. In the absence of an electrochemical bias, these IBG states are occupied by electrons, while they are depopulated under the application of an anodic bias, and a new optical transition involving the promotion of electrons from the most...
populated VB states (see the density of states of BiVO$_4$ sketched in Scheme 1) to fill IBG states appears peaking at ca. 470 nm (transition $\beta$ in Scheme 1A), which has been attributed to trapped holes.$^{7,8,22}$ At high anodic potentials a positive $\Delta A$ band at wavelengths shorter than 400 nm appears, which may be tentatively assigned to surface transformation of BiVO$_4$ into Bi$_2$O$_3$ and V$_2$O$_5$, both absorbing in this wavelength range,$^2$ or to a transition to IBG states from VB states at largely positive energy.

On the other hand, the electrochromic tests on the WO$_3$/BiVO$_4$ system (see Figure 2B) show a progressive absorption decrease in the visible region upon increasing anodic bias, and only at potential larger than 2.0 $V_{\text{RHE}}$ the signal of BiVO$_4$ holes appears at 470 nm. Visible light absorption in WO$_3$ is ascribed to the excitation of electrons trapped at W$^{5+}$ sites to the CB$^{29,35}$ (see Scheme 1A). However, at potentials up to 2.0 $V$ - i.e. more positive than WO$_3$ CB -, no bias-induced absorption change was evidenced with WO$_3$ in the 300-800 nm range, as shown in Figure S2 of the Supporting Information. This suggests that in the ground state of the heterojunction electrons from BiVO$_4$ are trapped in WO$_3$ at W$^{5+}$ states and they are depleted under applied bias, as demonstrated by the negative $\Delta A$ signal at wavelengths above ca. 450 nm in Figure 2B. For the highest bias voltages, a weak $\Delta A > 0$ band peaked at 470 nm, attributed to hole injection into the IBG states of BiVO$_4$, overlaps to this broad background.

Scheme 1. Scheme of the energy levels and of the transitions occurring A) in separate WO$_3$ and BiVO$_4$, B) in the WO$_3$/BiVO$_4$ heterojunction in contact with air, and C) in the WO$_3$/BiVO$_4$ heterojunction in contact with the electrolyte and under anodic bias. $\Phi_{D1}$: diffusive flux of holes generated by the pump in BiVO$_4$; $\Phi_{2}$: additional flux of holes in the WO$_3$/BiVO$_4$ heterojunction, consisting of a diffusive component $\Phi_{D2}$ due to
the population imbalance between the VBs of WO$_3$ and BiVO$_4$, and a migration component $\Phi_M$ due to the electric field at the BiVO$_4$ and WO$_3$ junction.

**Figure 3.** Transient absorption (TA) spectra and time traces measured under applied bias with the electrode in contact with a 0.5 M Na$_2$SO$_4$ aqueous solution or with air. (a,b) TA spectra recorded 10 ps after the pump
excitation at 400 nm and normalized with respect to the bleaching maximum for a) BiVO₄ and b) WO₃/BiVO₄. (c-f) TA dynamics monitored at (c,d) 470 nm and (e,f) 530 nm for (c,e) BiVO₄ and (d,f) WO₃/BiVO₄, normalized with respect to the signal maximum.

Figures 3a and 3b show the ultrafast TA spectra of BiVO₄ and WO₃/BiVO₄ films recorded at different applied potentials, as well as at OCP and in air, following excitation by a 100-fs pulse at 400 nm through BiVO₄, and probing by a broadband white light continuum. All reported spectra refer to a pump-probe delay of 10 ps and are normalized to the photo bleaching (PB) minimum. Delay dependent TA spectra and TA dynamics at selected wavelengths for BiVO₄ and BiVO₄/WO₃ at 1 V bias are reported in Figure S3 of the Supporting Information.

The TA signals in both systems essentially originate from BiVO₄, since WO₃ films do not show any signal in the relevant time and wavelength range,⁷ and can be divided into three regions. As better explained in the Supporting Information, where all dynamics are described in detail, region I) consists in a negative TA signal in the 410-450 nm range (negative band α), implying a decrease of transition α (band gap absorption) in Scheme 1A, and corresponds to PB due to VB depopulation and consequent CB filling resulting in Pauli blocking of the corresponding transitions. The positive TA signal range can be divided into two regions, labeled as II) and III) in Figures 3a and 3b. Region II) covers the 450-530 nm range with the characteristic band peaking at 470 nm (band β) ascribed to transitions from the VB to IBG trapped hole states (transition β in Scheme 1A), while in region III) a broad feature extending to longer wavelengths appears, labeled as band γ, which has been attributed to holes²³ in BiVO₄, possibly resulting from intraband transitions within the VB, though also transitions within the CB band or involving IBG states³⁶ at different energy cannot be excluded. In this region a low intensity tail of band β also persists. Bands α and γ appear instantaneously with the pump pulse, while band β grows within the first tens of picoseconds.

A comparison between Figures 3a and 3b evidences that in WO₃/BiVO₄ band β has a lower relative intensity than in BiVO₄ (see also Figure S4). This difference can be explained by considering that in the heterojunction electrons have spilled from the IBG states of BiVO₄ to the W⁶⁺ trap states of WO₃ as a consequence of the band alignment (see Scheme 1B) and it is
perfectly in line with the electrochromic tests on WO₃/BiVO₄ reported in Figure 2B. In fact, in WO₃/BiVO₄ the ground state electron population of the IBG states is lower than in BiVO₄. This implies that transition β may occur also in the unperturbed heterojunction, with a consequent decrease of band β intensity in the TA spectra of WO₃/BiVO₄ with respect to single BiVO₄.

Upon increasing anodic bias, the TA spectrum of BiVO₄ displays only minor changes, with a slight contraction on the long wavelengths side of the 470 nm peak (see inset of Figure 3a) and a slight decrease of the γ band (see also Figure S5A). On the other hand, the TA spectrum of WO₃/BiVO₄ (Figure 3b) shows a stronger bias-dependence, with the intensity of trapped hole band β decreasing with increasing bias, while band γ increases and tends to become slightly peaked around ca. 650 nm (Figure 3b and Figure S5B). WO₃ contributes to the red portion of the TA spectrum in region III), since reduced WO₃ shows a characteristic absorption feature at wavelengths longer than 550 nm, due to the optical transition involving electrons from W⁵⁺ states to the WO₃ CB. Anodic bias fosters the electron injection from BiVO₄ to WO₃ at very short times, with a consequent increase of the TA band γ in region III) with respect to unbiased experiments. It is worth noting that an applied bias at potentials lower than the OCP (i.e. 0.1 V RHE, Figure 3b) produces opposite effects on the TA spectra with respect to bias above the OCP, implying that under such conditions the IBG states have a larger population with respect to OCP conditions.

The TA dynamics at 470 and 530 nm for BiVO₄ and WO₃/BiVO₄ are shown in panels (c-f) of Figure 3. In BiVO₄, the presence of an electrochemical bias does not substantially change the dynamics at 470 nm (Figure 3c) as also evidenced from the Global Analysis (see Table 1 and Figures S6-S7), while it leads to considerable effects at 530 nm (the absorption onset of BiVO₄), see Figure 3e, where the spectral component characterized by a build-up (band β) starts to be less significant and the maximum TA is attained during the pump pulse.

On the other hand, an applied bias yields more dramatic effects on the WO₃/BiVO₄ heterojunction. Indeed, as shown in Figure 3d, the ΔA maximum at 470 nm occurs earlier at a potential larger than 0.4 V RHE and the buildup almost completely disappears at 1.0 V RHE. This is a consequence of the fact that the hole-trapping component of the TA signal becomes progressively
weaker with increasing applied potential, as evidenced in Figure 3b, so that the TA signal at 470 nm reaches its maximum within the pump pulse. The dynamics in the WO3/BiVO4 system is even more influenced by bias if it is monitored at 530 nm (Figure 3f), with the ΔA signal always being maximized impulsively under applied bias.

Global Analysis\textsuperscript{37,38} was carried out with all datasets, as detailed in the Supporting Information (Figures S6-S9). For both BiVO4 and WO3/BiVO4 the time-dependent TA spectra exhibit a characteristic sequence of four kinetic components with different time constants (see Figures S10-S12 and Table 1).\textsuperscript{23} The first time constant τ₀ is below 0.5 ps and accounts for the impulsive build-up of the TA signal, which cannot be resolved with our experimental setup. For this reason τ₀ values are not reported in Table 1. Time constant τ₁ accounts for the hole trapping process, which results in the characteristic build-up at 470 nm (band β), and in air it is shorter for the heterojunction (2.2 ps) with respect to BiVO4 (3.5 ps). This difference can be explained in terms of electronic structure of the heterojunction system, as shown in Scheme 1. In BiVO4 alone, the dynamics of IBG hole-trapping can be depicted as a diffusive flux \( \Phi_D \) of the holes generated by the pump from the bulk to surface traps.\textsuperscript{22} This flux is purely diffusive when BiVO4 is in contact with air, i.e. in the absence of band-bending. In WO3/BiVO4 \( \Phi_D \) is accompanied by a second flux \( \Phi_2 \) of holes from WO3, which involves a diffusive component \( \Phi_{D2} \) within WO3 and a migration component \( \Phi_M \) due to the electric field at the interface between BiVO4 and WO3, resulting from the type-II band alignment. The increased build-up rate of band β in the heterojunction thus arises from the additional flux \( \Phi_2 \). These results are consistent with previous wavelength-dependent femtosecond TA experiments.\textsuperscript{15} Furthermore, as shown in Figure S13, the build-up of the β band is clearly faster in WO3/BiVO4 only when both oxides are excited (i.e. when holes are also formed in WO3), whereas it is identical in the two systems upon selective excitation of BiVO4 at 500 nm.

Time constant τ₂ accounts for the recombination between trapped holes and free electrons (see Figure S12B-C) which in WO3/BiVO4 is slower than in BiVO4 (in air τ₂ is ca. 12 ps for BiVO4 and ca. 15 ps for WO3/BiVO4). This effect might be explained by the presence of an additional loss channel
for free electrons excited in the CB of BiVO₄, which can be injected into the CB of WO₃. This process partially prevents the recombination of free electrons with BiVO₄ trapped holes. In fact, the fraction of electrons injected into the CB of WO₃ experiences a longer and thus slower recombination path with BiVO₄ holes with respect to the direct recombination between free electrons and holes in BiVO₄ alone. As a consequence of the longer τ₂ in the coupled system the disappearance of band β is delayed.

Table 1. Time constants and corresponding confidence intervals estimated from the Global Analysis of TA spectra recorded upon excitation at 400 nm of BiVO₄ and WO₃/BiVO₄ in air and in operando in contact with a Na₂SO₄ 0.5 M aqueous solution. Potentials are vs. RHE. For τ₁ the confidence interval (0.1 ps) is determined by the instrumental response function of the system.

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<th>BiVO₄</th>
<th>Applied potential/V</th>
<th>τ₁/ps</th>
<th>τ₂/ps</th>
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<td>in air</td>
<td>3.5 ± 0.1</td>
<td>11.9 ± 0.1</td>
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<td>OCP (0.23 V)</td>
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<td>14.6±0.1</td>
<td>512±2.5</td>
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<tr>
<td>0.4</td>
<td>4.8 ± 0.1</td>
<td>13.5±0.12</td>
<td>500±3.0</td>
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<tr>
<td>0.7</td>
<td>4.5 ± 0.1</td>
<td>15.0±0.12</td>
<td>513±3.1</td>
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<tr>
<td>1.0</td>
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<th>τ₂/ps</th>
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<td>in air</td>
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Finally, time constant $\tau_3$, corresponding to the recombination of trapped holes with thermalized electrons occurring in the nanosecond time scale ($\tau_3$ values in Table 1, with accuracy limited by the maximum available delay of 1500 ps), appears to be almost unaffected by the presence of the WO$_3$ layer and also by the applied bias, under excitation at 400 nm through the BiVO$_4$ layer.

*In operando*, i.e. under the application of an anodic bias, the TA spectra of BiVO$_4$ and WO$_3$/BiVO$_4$ differ considerably both in kinetics and spectral features with respect to those measured in air, i.e. in the absence of band bending at the solid/liquid junction. This is reflected by the time constant values reported in Table 1, obtained from Global Analysis. While time constant $\tau_1$ does not show a clear trend with voltage in BiVO$_4$, it dramatically decreases in the heterojunction, with increasing bias down to ca. 1.41 ps at 1 V$_{RHE}$, indicating a faster hole accumulation at the BiVO$_4$ surface. The anodic polarisation on the one hand oxidizes the IBG states, thus increasing their hole population; on the other hand, it gives rise to an upwards band bending. In principle, the increase of hole concentration in the IBG and band bending have opposite effects on hole injection to the IBG, but the latter effect is found to dominate, resulting in a higher overall flux, in turn leading to a decrease of $\tau_1$. On the other hand, the recombination time constant $\tau_2$ of trapped holes with free electrons becomes longer with increasing applied bias, both in BiVO$_4$ and in WO$_3$/BiVO$_4$. The anodic bias, giving rise to an upward band bending (Scheme 1C), tends to withdraw mobile electrons from the BiVO$_4$ CB and a smaller concentration of free electrons in the CB thus results in a lower recombination rate with trapped holes, thus explaining the observed increase of $\tau_2$ with increasing anodic voltage. Finally, the recombination of trapped holes with thermalized electrons, occurring in the nanosecond time scale ($\tau_3$ values in Table 1, with accuracy limited by the maximum available delay of 1500 ps), appears to be almost unaffected by the presence of the WO$_3$ layer and also by the applied bias.
In conclusion, both spectro-electrochemical and TA measurements performed in the present study provide direct evidence of the spillover of the electrons from the IBG states of BiVO$_4$ to WO$_3$ when the WO$_3$/BiVO$_4$ heterojunction is formed. Furthermore, *in operando* PEC TA measurements show that the dynamics of photogenerated charge-carriers in BiVO$_4$ and WO$_3$/BiVO$_4$ is strongly affected by the application of an external bias, the latter system being more sensitive, as a consequence of the electric field built-in at the WO$_3$/BiVO$_4$ heterojunction. Indeed, in the heterojunction system the hole trapping rate increases by ca. 50\% and the rate of electron-hole recombination almost halves on a relatively short timescale (below 1 ns). This effect is amplified in the presence of the applied anodic bias leading to an accumulation of surface trapped holes beneficial for water oxidation.

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publication websire at DOI: xxxx. Experimental, preparation of photoelectrodes, photo- and spectro-electrochemical characterization, TA and *in operando* TA spectroscopy, Global Analysis, Comparison of the TA spectra of BiVO$_4$ and WO$_3$/BiVO$_4$, Global Analysis representative DAS and fittings, TA dynamics in BiVO$_4$, TA experiments upon excitation at different wavelength.

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