Photoinduced Charge Transfer Dynamics in WO₃/BiVO₄ Photoanodes Probed through Mid-IR Transient Absorption Spectroscopy

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Supporting Information Placeholder

ABSTRACT: The dynamics of photopromoted electrons in BiVO₄, WO₃ and WO₃/BiVO₄ heterojunction electrodes has been directly probed by transient absorption (TA) mid-infrared (mid-IR) spectroscopy in the picosecond to microsecond time range. By comparing the dynamics recorded with the two individual oxides at 2050 cm⁻¹ with that of the heterojunction system after excitation at different wavelengths, electron transfer processes between selectively excited BiVO₄ and WO₃ have been directly tracked for the first time. These results support the charge carrier interactions which were previously hypothesized by probing the BiVO₄ hole dynamics through TA spectroscopy in the visible range. Nanosecond mid-IR TA experiments confirmed that charge carrier separation occurs in WO₃/BiVO₄ electrodes under visible light excitation, persisting up to the microsecond timescale.

Harvesting energy from sunlight and producing solar fuels by photon-to-chemical energy conversion is a promising approach to fulfill the challenge of a sustainable energy economy. Along this line, one of the most attractive goals is the development of photovoltaic cells for water splitting.¹ Due to its ~ 2.4 eV relatively narrow band gap, bismuth vanadate (BiVO₄) has been intensively studied as photoanode material for oxygen evolution.²,³ However, its main drawback is the significant recombination of photogenerated electron-hole pairs mainly due to its poor electrical conductivity, the slow hole transfer for water oxidation and surface recombination.⁴,⁵ In the WO₃/BiVO₄ composite heterojunction, efficient electron-hole separation may occur due to the favorable type II band alignment between the two oxides, with the exploitation of both the good charge transport properties of WO₃ and the strong absorption of visible radiation by BiVO₄.⁶

The complex processes occurring in the WO₃/BiVO₄ heterojunction after band gap excitation have been investigated through transient absorption (TA) spectroscopy by probing the hole dynamics in BiVO₄ in the visible range.⁷,⁸,¹⁴ on the basis of the results obtained for pure BiVO₄ in this spectral window.⁹,¹³,¹⁷ Here, direct information on the charge carrier dynamics in the WO₃/BiVO₄ heterojunction is provided by tracking the photoexcited electrons on the picosecond to microsecond time scale through mid-infrared transient absorption (mid-IR TA) spectroscopy.¹⁸,¹⁹ The crucial role of WO₃ in mediating the electron extraction from photoexcited BiVO₄ is highlighted, leading to efficient electron-hole separation in the WO₃/BiVO₄ heterojunction.

The dynamics of electrons in several semiconductors, such as TiO₂, ZnO, WO₃, Fe₂O₃ and CdSe, can be followed in the IR range.²⁰,²¹ Upon reduction, the oxides show a characteristic coloration due to optical transitions involving the excitation at wavelengths longer than their band gap of either free conduction band (CB) electrons,²² or electrons from intraband gap trap sites to the CB edge.²³,²⁴ Indeed, we verified that the photoreduction of WO₃ films immersed in ethanol as hole scavenger resulted in mid-IR spectral changes attributable to CB electrons (Figure S1).

Also for BiVO₄ we found that a new mid-IR absorption feature extending in the 4000-1400 cm⁻¹ range appears upon chemical reduction (see SI for details). Figure 1 shows the IR spectra recorded with a BiVO₄ film immediately after contact with an aqueous NaBH₄ solution and at different time during exposure to air up to the complete relaxation.

Figure 1. Spectral evolution in a BiVO₄ film exposed to air after reduction in aqueous NaBH₄. Asterisks indicate CO₂ absorption peaks. The red and the black traces were recorded right after BiVO₄ reduction and after 6 h-long exposure to air, respectively. Inset: difference absorption spectra during BiVO₄ re-oxidation.
The difference absorption spectra, obtained by subtracting the spectrum of the fully recovered film from the spectra recorded at different time during exposure to air (Figure 1, inset), show that the IR spectrum of reduced BiVO₄ uniformly relaxes in contact with air. This is confirmed by a comparison between the decay profiles recorded at 3350 and 2050 cm⁻¹ (Figure S2). Reduced BiVO₄ reversibly undergoes oxidation in the presence of oxygen, while when it is stored under N₂ it retains its broad mid-IR absorption spectrum. Broad and featureless IR absorption, similar to that here observed in BiVO₄, is ascribed to free electrons.¹⁸,³⁰

The procedures here employed for the preparation of WO₃, BiVO₄ and WO₃/BiVO₄ photoanodes and for the photoelectrochemical experiments are reported in the SI, together with their steady state UV-Vis absorption characterization (Figure S3). All WO₃ and BiVO₄ films on FTO were 410 and 45 nm thick, respectively. The photoelectrochemical responses of WO₃ and BiVO₄ electrodes are compared with that of the WO₃/BiVO₄ composite electrode in Figure 2A. With respect to the individual oxides, a significantly enhanced photocurrent is observed in the entire potential range for the composite electrode. This activity enhancement has been attributed to the favorable band alignment between the two oxides, which allows the injection of photopromoted electrons from the BiVO₄ CB to the WO₃ CB, where they can exploit the better charge mobility of the latter material.⁵,⁹

Furthermore, the incident photon to current efficiency (IPCE) measured with the WO₃/BiVO₄ coupled system outperforms the sum of the IPCE curves measured with the two individual oxides (see Figure S4) at wavelengths longer than the WO₃ absorption onset (ca. 460 nm). In contrast, for wavelengths shorter than 400 nm, the IPCE of the heterojunction system falls below the sum of the IPCE curves measured with the two individual semiconductors. Previous fs-TA measurements in the visible region to track BiVO₄ hole dynamics¹¹ indicate that charge recombination of electrons photopromoted in WO₃ with BiVO₄ holes may occur upon simultaneous BiVO₄ and WO₃ excitation.

Direct evidence of photoinduced charge transfer occurring in the WO₃/BiVO₄ heterojunction is here obtained by directly probing electrons in WO₃, BiVO₄ and WO₃/BiVO₄ films through IR-TA spectroscopy. The dynamics of photopromoted electrons in BiVO₄ after visible excitation was followed by TA in the 2300-1700 cm⁻¹ range (Figure S5). These time-resolved spectra show an essentially flat induced absorption, similar to the steady-state IR spectra of chemically reduced BiVO₄ (Figure 1).

The mid-IR transient signal of BiVO₄ (Figure 2B) decays within few hundreds of picoseconds and shows a faster dynamics than the holes signal previously monitored in the visible,³ which exhibits a ΔA tail extending longer than the fs-TA time window. This discrepancy was recently observed with pure BiVO₄ powders and ascribed to the free electrons fast relaxation to states not observable in the mid-IR region.⁵ On the other hand, in WO₃ and in the WO₃/BiVO₄ coupled system, the 2050 cm⁻¹ TA signal exhibits a relatively slower decay (Figure 2B). Quantitative information on the dynamics involved in BiVO₄ and in the other two systems was obtained by fitting the decay traces with a bi- and a tri-exponential equation (eq. S2 and S3), respectively. The resulting parameters are reported in Table 1.

Upon excitation at 410 nm, most of the electrons photopromoted in BiVO₄ alone decay with a time constant τ₁ of ~10 ps, while the remaining free electrons decay with a ca. 170 ps τ₂ time constant. Thus the TA signal disappears within the temporal window of our experiments, in line with the results of recent studies.³¹ Power dependence measurements carried out on BiVO₄ (Figure S6 and SI) indicate that the initial part (< 10 ps) of the mid-IR signal decay becomes progressively faster with increasing pump power at 410 nm. This corroborates the hypothesis that the ultrafast decay exhibited by the mid-IR TA signal in BiVO₄ can be mainly ascribed to trapping and cooling of free electrons into IR unobservable states, not to electron-hole recombination. In fact, the longer lasting relaxation of trapped holes was found to be independent of the pump power.¹⁴ Charge recombination cannot be excluded and may be active during the first tenths of picoseconds, as for Fe₂O₃.³²

![Figure 2](image)

**Figure 2.** (A) Photocurrent density recorded in linear sweep voltammetry under simulated solar light with the WO₃ (brown), BiVO₄ (blue) and WO₃/BiVO₄ (green) electrodes in contact with 0.5 M Na₂SO₄. (B) IR-fs TA traces recorded at 2050 cm⁻¹ with the WO₃ (red circles), BiVO₄ (blue squares) and WO₃/BiVO₄ (orange stars) electrodes upon 410 nm excitation (270 nJ/pulse) and with WO₃/BiVO₄ upon 500 nm excitation (300 nJ/pulse; green triangles).

### Table 1. Fitting parameters of the decay traces obtained with the investigated materials upon excitation at 410 nm or 500 nm.

<table>
<thead>
<tr>
<th></th>
<th>WO₃ 410 nm</th>
<th>BiVO₄ 410 nm</th>
<th>WO₃/BiVO₄ 410 nm</th>
<th>WO₃/BiVO₄ 500 nm</th>
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<tr>
<td>A₀ (%)</td>
<td>45±2</td>
<td>70±4</td>
<td>54±2</td>
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<td>τ₁ (ps)</td>
<td>1.9±0.2</td>
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<tr>
<td>A₁ (%)</td>
<td>28±2</td>
<td>30±9</td>
<td>39±2</td>
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<tr>
<td>τ₂ (ps)</td>
<td>105±15</td>
<td>171±26</td>
<td>39±3</td>
<td>81±8</td>
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<tr>
<td>A₂ (%)</td>
<td>27±2</td>
<td>7±1</td>
<td>27±1</td>
<td></td>
</tr>
<tr>
<td>τ₃ (ns)</td>
<td>11±3</td>
<td>3.4±0.9</td>
<td>5.3±0.6</td>
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</tr>
<tr>
<td>Red. χ²</td>
<td>1.0×10⁻³</td>
<td>1.3×10⁻³</td>
<td>3.5×10⁻⁴</td>
<td>6.0×10⁻⁴</td>
</tr>
</tbody>
</table>

As shown in Table 1, in the case of the WO₃ and WO₃/BiVO₄ electrodes, even if almost 50% of the photogenerated signal de-
The fastest decay component found in WO$_3$ may be ascribed either to its free carriers intrinsically living shorter than in other oxides, for example TiO$_2$ and BiVO$_4$,

31,32 or to power dependent second order electron-hole recombination. 33 Remarkably, the $\tau_1$ time constant found in the WO$_3$/BiVO$_4$ system upon 500 nm excitation is equal to that observed in WO$_3$ and smaller with respect to those obtained in BiVO$_4$ upon 410 and 500 nm excitation. This suggests that the electron transfer between BiVO$_4$ photoxcited at 500 nm and WO$_3$ is faster than the response function of our experimental set-up (~200 fs). Moreover, the $\tau_2$ value found for the coupled system upon 410 nm excitation is intermediate between the $\tau_1$ values obtained for the two separate oxides upon 410 nm excitation. This can be explained considering that the WO$_3$ CB gets partially filled under 410 nm excitation and thus electron injection from excited BiVO$_4$ CB may be partly hindered by coulombic repulsion.

The second component, $\tau_2$, is much shorter in WO$_3$/BiVO$_4$ than in either WO$_3$ or BiVO$_4$. Under 410 nm pump, both oxides are excited and the shorter $\tau_2$ value obtained for the coupled system with respect to BiVO$_4$ is in line with the hypothesis that a recombination process opens between electrons photopromoted in WO$_3$ and BiVO$_4$ valence band (VB) holes. 14 The effect of 410 nm vs. 500 nm excitation is even more apparent on $\tau_2$. Selective excitation of BiVO$_4$ with the 500 nm pump in the WO$_3$/BiVO$_4$ heterojunction electrode leads to a striking increase of the lifetime of photopromoted electrons. Indeed $\tau_2$ and $\tau_3$ show a two-fold increase, while the $A_1$ weighing coefficient is almost four times larger, with respect to 410 nm excitation (see Table 1 and the green and orange traces in Figure 2B), with time constant values closely matching those obtained with WO$_3$ (red trace in Figure 2B). On the other hand, the IR signal decay found by exciting individual BiVO$_4$ at 500 nm was even faster than under 410 nm excitation (Figure S7). This excludes the hypothesis that the slower mid-IR signal decay observed upon exciting WO$_3$/BiVO$_4$ at 500 nm instead of at 410 nm is merely due to an excitation wavelength dependent charge dynamics in BiVO$_4$.

The lifetime in of trapped electrons in WO$_3$/BiVO$_4$ upon 500 nm excitation parallels that previously observed for trapped holes in the same coupled system (Figure S8). This confirms the key role played by WO$_3$ in increasing the lifetime of both photogenerated charge carriers. Consequently, the electron lifetime in the WO$_3$/BiVO$_4$ electrode excited at 500 nm is expected to extend beyond our fs TA window (~5 ns). Therefore, flash photolysis experiments up to the microsecond time scale, with a 2050 cm$^{-1}$ probe, were performed to measure the actual lifetimes of the photopromoted electrons (Figure 3).

Since free electrons photopromoted in BiVO$_4$ decay within 1 ns, the absorption observed in flash photolysis experiments is generated exclusively by longer living electrons in WO$_3$. Indeed, WO$_3$ containing electrodes clearly show a long-lived IR signal (Figure 3). Also selective excitation of BiVO$_4$ at 500 nm in WO$_3$/BiVO$_4$ generates a long-lived IR signal, which provides uncontroversial evidence that electrons photopromoted in BiVO$_4$ CB promptly move to the WO$_3$ CB. Thus, very long-lived electrons in the heterojunction film are photoproduced under visible light excitation, and are here detected for the first time by mid-IR spectroscopy.

![Scheme 1](image)

**Scheme 1.** The excitation wavelength dependent electronic interactions in WO$_3$/BiVO$_4$ under (A) selective excitation of BiVO$_4$ and (B) simultaneous excitation of both oxides (500 and 410 nm pump, respectively).

In conclusion, photopromoted electrons live much longer in WO$_3$ than in BiVO$_4$, in line with the far better electron conductivity of the former oxide. The main electron transfer pathways occurring between the two oxides in the heterojunction system are illustrated in Scheme 1. Free electrons photoxcited under visible light in the BiVO$_4$ CB can avoid trapping and recombination in BiVO$_4$ by flowing into WO$_3$ where they live longer (path A in Scheme 1A). Thus, WO$_3$ has a key role in elongating the electron lifetime in the WO$_3$/BiVO$_4$ heterojunction under visible light excitation. On the other hand, a recombination channel between electrons photopromoted in WO$_3$ and holes in the BiVO$_4$ VB is active upon simultaneous excitation of both oxides (path B in Scheme 1B). Therefore, in optimized heterojunctions, care should be taken to avoid this parasitic process.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website. Experimental section; IR spectra of reduced WO$_3$ and BiVO$_4$; steady-state UV-Vis absorption spectra, IPCE measurements; complementary time-resolved IR experiments and data; power and wavelength dependent excitation of BiVO$_4$ hole vs. electron TA dynamics (PDF).

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Notes
The authors declare no competing financial interests.

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