This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Bismuth vanadate photoanodes surface-modified with cobalt phosphate catalysts are studied using transient absorption spectroscopy and transient photocurrent methods. The cathodic shift of onset potential is due to efficient suppression of back electron/recombination on the timescale of seconds.
1. Introduction

Surface modification of n-type semiconductor photoanodes is an effective method to promote photo-assisted water oxidation. Such surface modifications include the deposition of both catalytic (e.g. cobalt oxides) and non-catalytic layers (e.g. Al$_2$O$_3$) on photoanodes such as hematite (α-Fe$_2$O$_3$) and bismuth vanadate (BiVO$_4$). However, the mechanism by which such surface modifications enhance photoanode function remains unclear. In particular it is unclear whether the electrocatalytic properties of the surface layer with respect to water oxidation are functionally important.Whilst several studies have suggested that enhancements in photoanode performance are associated with the catalytic properties of the surface modification layer, others have reported evidence that, at least for cobalt phosphate (CoPi) modified hematite, the enhancement in photoanode performance results primarily from a retardation of recombination kinetics. These studies indicated that the kinetics of water oxidation on hematite are unchanged by CoPi modification.

Bismuth vanadate (BiVO$_4$) is a promising photoanode material for photoelectrochemical (PEC) water splitting, where surface modifications can be particularly effective in shifting the photocurrent onset close to the flat-band potential. Surface modification with CoPi electrocatalysts has resulted in a shift of the onset potential for photocurrent generation from ~ 0.8 V$_{RHE}$ to 0.4 V$_{RHE}$. Additionally, a NiOOH/FeOOH dual layer surface modified BiVO$_4$ has been reported with the onset potential (0.2 V$_{RHE}$) close to the flat-band potential (0.1 V$_{RHE}$). These reports clearly demonstrate the importance of surface modification using electrocatalysts if high energy conversion efficiencies are to be achieved at low applied potentials.

In the study reported herein, we employ transient absorption and transient photocurrent measurements to investigate the origin of such cathodic shifts of photocurrent onset potential, employing undoped BiVO$_4$ photoanodes with and without CoPi surface modification.

Recently, we investigated the charge carrier dynamics of photogenerated holes in flat, dense, undoped BiVO$_4$ photoanodes using transient absorption spectroscopy and photoelectrochemical methods. We observed that the yield of long-lived photogenerated holes increased with increasing space charge layer depth. However, the efficiency of water oxidation was found to be severely limited by recombination between these long-lived holes accumulated at the BiVO$_4$ surface and electrons in the BiVO$_4$ bulk. Due to the rather slow rate constant for water oxidation (~ 1 s$^{-1}$), there is significant kinetic competition between this back electron/hole recombination and water oxidation at moderate applied bias potential. Consequently, approximately 600 mV additional...
anodic potential is required for photocurrent generation, due to this slow surface recombination. It is therefore of particular interest to consider whether surface treatments impact upon this kinetic competition by retarding back electron/hole recombination and/or by accelerating water oxidation.

CoPi was first reported as an efficient water oxidation electrocatalyst by Kanan and Nocera, significantly reducing the overpotential for water oxidation.21 X-ray absorption studies indicate that the structure of CoPi composite is amorphous, forming a cubane-like CoO₂ reaction center with phosphate ligands.22-24 CoPi is also widely reported to reduce the photocurrent onset potential and increase the photocurrent of photo-assisted water oxidation on BiVO₄.6,11 and α-Fe₂O₃.4,7 It was initially suggested that photo-driven water oxidation in these systems occurred via oxidation of the CoPi catalyst by photogenerated holes from the semiconductor. This CoPi oxidation process also implies a charge separation at the semiconductor surface, which could mitigate electron/hole recombination thought to occur via an intra-band gap state at the surface.8,14,25 This conclusion of enhanced charge separation due to hole transfer has been supported by studies comparing water oxidation photocurrents for photoanodes with and without CoPi modification in a hole scavenger solution.8,10 However, our recent optical studies of CoPi-modified α-Fe₂O₃ indicated that the most significant effect of CoPi is to reduce the anodic potential required to retard recombination losses within the α-Fe₂O₃. This reduces the bias potential required to generate the long-lived holes required for water oxidation.4,8 Whilst steady-state CoPi oxidation was observed, it was suggested that this oxidation was not the primary reason for the cathodic shift of the photocurrent onset potential.4 A similar conclusion was also obtained from frequency domain photoelectrochemical analyses.15 It is not clear, however, whether this observation is specific to the CoPi surface modified α-Fe₂O₃ system, or a general effect for n-type semiconductors surface-modified by CoPi. In addition, our previous studies of CoPi-modified α-Fe₂O₃ did not distinguish between the impact of CoPi upon bulk recombination losses (which limit hole transfer to the surface) and upon back electron/hole recombination. This latter (slower) recombination pathway is particularly important in limiting the onset potential for undoped BiVO₄ photoanodes.

In the study reported herein, we employ transient absorption spectroscopy (TAS) and transient photocurrent (TPC) measurements to investigate the time-resolved behavior of photogenerated holes on CoPi-modified BiVO₄ photoanodes. Transient absorption spectroscopy allows us to directly monitor photogenerated holes. The recombination and water oxidation kinetics occurring on CoPi-modified BiVO₄ were studied as a function of applied potential. The origin of the improvement of photocurrent onset resulting from CoPi treatment is shown to be primarily due to a retardation of back electron/hole recombination across the space charge layer; no evidence of catalytic water oxidation via CoPi was observed.

2. Experimental Section

2.1 Materials

All chemicals used in this paper were purchased from Sigma-Aldrich in the highest purity available, unless otherwise stated. The electrolyte was used with de-ionized Milli-Q water (Millipore Corp., 18.2 MΩ cm at 298 K).

2.2 Fabrication of Undoped BiVO₄ photoanodes

Undoped BiVO₄ photoanodes were fabricated using a modified metal-organic deposition method, as previously described.20,26 Briefly, the precursor was prepared by mixing 0.2 M bismuth nitrate pentahydrate dissolved in acetic acid (99%, BDH) and 0.2 M vanadyl acetylacetonate in acetylacetone (Merck) for 1 hour at room temperature. The BiVO₄ photoanodes were deposited using the precursor on FTO substrates (TEC 15, Hartford Glass Co.) by the spin-coating method (1000 rpm, 20 s). After spin-coating each layer, the substrates were calcined at 450 °C for 15 min. The total number of layers was 15 for each BiVO₄ photoanode and the films were calcined at 450 °C for 5 hours.

2.3 Photoelectrodeposition of CoPi on Undoped BiVO₄ photoanodes

Photoelectrodeposition of CoPi on undoped BiVO₄ photoanodes were carried out following the method developed by Nocera27 and modified by Gamelin.7,8 A three-electrode configuration was used, including the undoped BiVO₄ photoanode as the working electrode, a Ag/AgCl/saturated KCl as the reference electrode and a platinum mesh counter electrode. The deposition solution was prepared with 0.1 mM cobalt nitrate hexahydrate in 0.1 M KPi buffer (50 mL, pH 6.7). The deposition was carried out at 1.2 V_RHE applied potential by an Autolab potentiostat (PGSTAT101, Metrohm) and under illumination from a Xe lamp coupled with a KG3 filter for 10 minutes; intensity calibrated with a Si photodiode corresponding to 100 % of the AM 1.5 solar spectrum in terms of photo flux below 650 nm (with a short pass filter, 650 nm, Edmund Optics).

2.4 Characterization

X-ray diffraction (XRD) was conducted with a modified Bruker-Axs D8 diffractometer with parallel beam optics equipped with a PSD Linx-Eye silicon strip detector. A Cu source generated X-rays; with Cu Ka1 and Cu Ka2 radiation of λ = 1.54056 and 1.54439 Å, respectively, emitted with an intensity ratio of 2:1 at an applied potential of 40 kV and 30mA of current. The incident beam was kept at 1° and the angular range of the patterns collected was 10° < 2θ < 66° with a step size of 0.025°.

Scanning electron microscopy (SEM) measurements were carried out using a ZEISS FEG-SEM microscope (LEO 1525 equipped with GEMINI field emission column) with
acceleration voltage of 5 kV. Samples prepared for SEM measurements were coated with 10 nm chromium particles to enhance conductivity of BiVO4 films.

2.5 Photoelectrochemical Characterization

All original applied potentials are recorded versus Ag/AgCl/sat’d KCl reference electrode (0.197 V vs. RHE at 298 K; Metrohm). These potentials are then converted to be versus reversible hydrogen electrode using Nernst equation:

\[ V_{\text{RHE}}(V) = V_{\text{Ag}/\text{AgCl}}(V) + 0.0591 \times pH + 0.197 \text{ (V)} \]

where \( V_{\text{RHE}} \) is the applied potential versus RHE; \( V_{\text{Ag}/\text{AgCl}}(V) \) is the applied potential versus Ag/AgCl/sat’d KCl reference electrode during measurements; \( V_{\text{Ag}/\text{AgCl}}^0 \) is the standard potential of the Ag/AgCl reference electrode.

Photoelectrochemical measurements were carried out in a home-made PTFE cell with quartz windows in the front and back of the cell. The same three-electrode setup was used as described in the CoPi deposition section. All PEC experiments were carried out through back-side illumination (FTO-BiVO4) in order to avoid the parasitic absorption by CoPi. An Autolab potentiostat (PGSTAT 12) was used to control the applied potential. Potassium phosphate buffer solution (0.1 M KPi) and 0.1 M K2HPO4 was prepared as the electrolyte for PEC and transient absorption measurements.

Transient photocurrent measurements were carried out with the same photoelectrochemical cell as for PEC measurements. A constant anodic potential was applied to the BiVO4 working electrode and the current response was measured under chopped light illumination from a 365 nm LED (LZ1-10U600, LedEngin Inc.). The LED intensity was adjusted to be 20 % of chopped light illumination from a 365 nm LED (LZ1-10U600, LedEngin Inc.). The chopped light was controlled by a chopper (LedEngin Inc.). The LED intensity was adjusted to be 20 % of chopped light illumination from a 365 nm LED (LZ1-10U600, LedEngin Inc.). The LED intensity was adjusted to be 20 % of chopped light illumination from a 365 nm LED (LZ1-10U600, LedEngin Inc.).

In order to achieve small perturbation excitation, a continuous bias light was employed using an array of 12 white LEDs (Philips Lumileds, Model white star LXHL-NW8) with \( \sim 100 \% \) of AM 1.5 intensity below 650 nm, calibrated with the thickness of the CoPi overlayer \( \sim 100 \text{ nm} \) being selected to give optimum performance enhancement (ESI Fig. S1). The flat BiVO4 photoanodes requires thicker CoPi overlayers than reported 30 nm for porous BiVO4 photoanodes. This result is similar to a previous report of CoPi-modified α-Fe2O3 nanstructured/flat photoanodes.6 X-ray diffraction characterization in Fig. S1 indicates that the CoPi deposited on BiVO4 is amorphous, consistent with previous reports of CoPi overlayers prepared via electrochemical methods.21-23

Fig. 1 compares the chopped light current-voltage of BiVO4 photoanodes before and after CoPi modification, measured in potassium phosphate buffer (KPi, pH 6.7). For the unmodified BiVO4 photoanodes, the onset potentials (versus reversible hydrogen electrode, RHE) for water oxidation in light and dark are \( 0.7 \text{ V vs. RHE} \) and \( 1.9 \text{ V vs. RHE} \), respectively, consistent with our previous studies20 and literature data.21-23 A cathodic shift of 200–300 mV for the onset potentials of both dark and light current generation is observed for the CoPi-modified BiVO4 photoanode, similar to previous reports.8, 11, 27 The more cathodic dark onset obtained with the CoPi overlayer is consistent with its electrocatalytic properties.21, 23

2.6 Transient Absorption Spectroscopy

The setup of transient absorption spectrometer (μs-s) has been described previously. Briefly, a Nd:YAG laser (Big Sky Laser Technologies, Ultra CFR Nd:YAG laser system) was used as the excitation source (355 nm, 3rd harmonic, pulsed laser, 6 ns band width). The laser flash rate was 0.33 Hz; The laser excitation intensity was set at 100 μJ cm−2, unless otherwise stated; the probe light source was a 100 W Bentham IL1 tungsten lamp equipped with a monochromator (OBB-2001, Photon Technology International); the transmitted light was filtered using long pass filters and a band pass filter (Comar Optics) to block the scattered laser light into the detector (Si photodiode, Hamamatsu S3071). The signal collected by the detector was sent to an amplifier (Costronics) and recorded by an oscilloscope (Tektronics TDS 2012c) on μs-ms timescales and a DAQ card (National Instruments, NI USB-6211) on ms-s timescales. Each decay was averaged by 300-500 times. All data were acquired by home-programmed software based on the LabVIEW software.
Fig. 2 Transient photocurrent measured at 0.6 $V_{	ext{RHE}}$ for unmodified (black) and CoPi-modified (red) BiVO$_4$ photoanodes under white light bias illumination with a 5 s small-perturbation 365 nm pulse. The background currents due to bias light have been corrected to zero.

Transient photocurrent (TPC) measurements (using white light bias and a 5 s small-perturbation 365 nm LED pulse) were conducted as an initial study of charge carrier dynamics. Fig. 2 presents typical TPC results for unmodified (black) and CoPi-modified (red) BiVO$_4$ photoanodes under modest applied anodic potential (0.6 $V_{	ext{RHE}}$), just anodic of the photocurrent onset. We are particularly interested in the negative transient current peaks observed after light off, assigned to back electron/hole recombination.\textsuperscript{20, 29, 30} This negative transient is reduced in amplitude and retarded in recovery time in the presence of the CoPi overlayer, indicative of suppression of back electron/hole recombination,\textsuperscript{30} discussed further below.

Translucent absorption spectroscopy was employed to investigate the dynamics of photogenerated holes in CoPi-modified BiVO$_4$ water oxidation photoanodes. Previously we have shown that the transient absorption spectrum of photogenerated holes in unmodified BiVO$_4$ photoanodes comprises a broad absorption across the visible and near-IR, with a maximum at 550 nm, which was also reported by other groups.\textsuperscript{31, 32} Under anodic bias, the decay dynamics of this photoinduced absorption for an unmodified undoped BiVO$_4$ photoanode were observed to be biphasic. A “fast” power law phase, assigned to electron/hole recombination competing with hole accumulation on the BiVO$_4$ surface, is observed on $\mu$s–ms timescales. This is followed by a “slow” exponential decay phase (ms–s) assigned to water oxidation in kinetic competition with back electron/hole recombination.\textsuperscript{20}

We first compare the transient absorption spectra of unmodified BiVO$_4$ and CoPi-modified BiVO$_4$ from microsecond to second timescales, at 1.2 $V_{	ext{RHE}}$. Fig. 3a shows the transient absorption spectra of unmodified BiVO$_4$ at 1.2 $V_{	ext{RHE}}$ applied potential. A broad transient absorption feature was observed between the timescale of microseconds and seconds, from 500 nm to 900 nm, peaking at 550 nm, consistent with our previous transient absorption results of unmodified BiVO$_4$ with applied potential. These transient absorption spectra have been assigned to photogenerated holes in unmodified BiVO$_4$, as determined using electron/hole scavengers and applied potentials.\textsuperscript{20} We have previously shown that the shape of the transient absorption spectrum of photogenerated holes in BiVO$_4$ is independent of applied potential.\textsuperscript{20} Fig. 3b shows that CoPi surface modification does not significantly change the shape or the amplitude of the transient absorption spectra; both photoanodes exhibit broad spectra peaking at 550 nm with initial amplitudes of $\Delta \text{OD} \sim 5.5 – 6 \times 10^{-5}$. We note that CoPi oxidation results in a broad increase of the steady-state absorption in the visible region, particularly at wavelengths < 550 nm.\textsuperscript{4} This is clearly different from the transient absorption spectra (Fig. 3). Therefore we assign the transient absorption signals for both the CoPi-modified and unmodified BiVO$_4$ primarily to photogenerated BiVO$_4$ holes.

Fig. 4 shows typical transient absorption decay kinetics of photogenerated holes measured at 550 nm for both unmodified and CoPi-modified BiVO$_4$ photoanodes under modest (0.6 $V_{	ext{RHE}}$) and strong (1.4 $V_{	ext{RHE}}$) anodic potentials. As previously,\textsuperscript{20, 33, 34} these decays were fitted by a combination of power law (for the “fast” decay phase) and single-exponential (for the “slow” decay phase) functions,

$$ \Delta \text{OD} = at^b + \phi_{\text{PSV}_2} e^{-t/\tau_{\text{PSV}_2}} $$  \hspace{1cm} (2)
where $a$ and $b$ define the power law function, $\phi_{TAS2}$ is the amplitude of the exponential decay phase and $\tau_{TAS2}$ is its decay time constant. The power law represents a bimolecular recombination process on sub-milliseconds timescales, as determined by transient absorption studies of unmodified BiVO$_4$ as a function of laser excitation intensity. As previously demonstrated for unmodified BiVO$_4$, both water oxidation and back electron/hole recombination occur on timescales of milliseconds to seconds, fitted by the single exponential function in Equation 2.

It is apparent from Fig. 4a and 4b that, under the low applied potential, the lifetime of the exponential decay is increased by up to one order of magnitude after CoPi-modification. Similar results were obtained from our transient absorption studies of CoPi surface-modified $\alpha$-Fe$_2$O$_3$ photoanodes. Considering both the transient absorption spectra (Fig. 3) and the kinetics (Fig. 4), there is no evidence for hole transfer from BiVO$_4$ to CoPi under these pulsed laser measurements. If hole transfer...
was occurring from BiVO\(_4\) to CoPi (as would be expected if water oxidation occurs via CoPi), this would result in changes to the spectrum and faster decay kinetics. Neither of these phenomena are observed. These results suggest that, for the films studied herein, water oxidation does not primarily occur via hole transfer from BiVO\(_4\) to CoPi, in contrast to the conclusion of previous photoelectrochemical studies.\(^8\), \(^10\)

Instead, the primary effect of CoPi overlayers is to slow down electron/hole recombination within the BiVO\(_4\), as demonstrated below.

Fig. 4c and d show the lifetimes and amplitudes of the slow exponential decay phase in unmodified and CoPi-modified BiVO\(_4\) as a function of applied anodic potential, determined from fits of the data to Equation 2. The decay time constants and amplitudes increase with increasing anodic potential in both photoanodes. It is apparent that CoPi deposition does not significantly change the amplitude of the exponential decay phase, \(\phi_{\text{TAS2}}\) for its dependence upon applied potential (Fig. 4d). In contrast, the potential dependence of the lifetime of this decay phase (\(\tau_{\text{TAS2}}\)) is substantially different after CoPi deposition (Fig. 4c). For unmodified BiVO\(_4\), \(\tau_{\text{TAS2}}\) increases gradually across the potential range studied, from \(~10\) ms at 0.2 V\(_{\text{RHE}}\) to \(~1.4\) s at 1.6 V\(_{\text{RHE}}\). In contrast, for the CoPi-modified photoanode, \(\tau_{\text{TAS2}}\) increases in lifetime much more sharply with applied potential, saturating at 1.6 s for potentials \(\geq 1.0\) V\(_{\text{RHE}}\). We have previously assigned the potential dependence of \(\tau_{\text{TAS2}}\) for unmodified BiVO\(_4\) to retardation of back electron/hole recombination.\(^20\) The significant increase in lifetime of the ms-exponential phase under modest applied potentials following CoPi deposition suggests that this back electron/hole recombination is retarded by CoPi deposition, as we discuss in more detail below.

To provide further evidence of retardation of back electron/hole recombination on BiVO\(_4\) by CoPi deposition, transient photocurrent data such as that shown in Fig. 2 were collected as a function of applied potential from 0.1 to 1.6 V\(_{\text{RHE}}\). The positive and negative current transients immediately after light on/off are associated with recombination of surface accumulated holes and bulk electrons. In addition, there is a contribution from water oxidation to the negative transient after light off. These transients are well fitted by a single exponential function.\(^2\), \(^20\), \(^29\), \(^30\) In this paper, we are particularly interested in the negative current transients after light off. The background current due to the bias light was subtracted, and the negative transient peaks were fitted by a single exponential function:

\[
I(t) = I_0 e^{-t / \tau_{\text{TPC}}} \tag{3}
\]

where \(I(t)\) is the transient current measured under applied potential; \(I_0\) is the amplitude of negative transient peak, and \(\tau_{\text{TPC}}\) is the time constant of the negative transient recovery. We and others have previously assigned this negative current transient to back electron/hole recombination, in kinetic competition with water oxidation.\(^20\), \(^30\) The TPC time constants \(\tau_{\text{TPC}}\) are shown in Fig. 4c as a function of applied potential, overlaid with the transient absorption time constants \(\tau_{\text{TAS2}}\). There is a good agreement between \(\tau_{\text{TPC}}\) and \(\tau_{\text{TAS2}}\) for both the unmodified and CoPi-modified BiVO\(_4\) photoanodes, suggesting that both \(\tau_{\text{TPC}}\) and \(\tau_{\text{TAS2}}\) are monitoring the same process, consistent with our previous results for unmodified BiVO\(_4\) photoanodes.\(^20\)

Quantification of the total charge lost to back electron/hole recombination following light-off in our TPC measurement can be obtained by integrating the negative TPC transient. Fig. 5 shows this integrated charge (broken and solid lines) as a function of applied potential for unmodified and CoPi-modified BiVO\(_4\) photoanodes. The amount of charge (i.e. surface accumulated holes) lost due to this back electron/hole recombination is strongly potential-dependent, being maximal at 0.5–0.6 V\(_{\text{RHE}}\). It is also apparent that deposition of CoPi results in a substantial cathodic shift in the potential required to turn off these back electron/hole recombination losses. The disappearance of negative current transients in CoPi-modified BiVO\(_4\) has also been reported previously.\(^31\) This cathodic shift of the potential required to turn off back electron/hole recombination is also consistent with our transient absorption data, and likely to be a key reason for the cathodic shift of photocurrent onset potential following CoPi deposition, discussed in detail below.

4. Discussion

4.1 Correlating Long-Lived Holes with Photocurrent Density

Water oxidation on metal oxide photoanodes appears to be kinetically rather a slow process.\(^35\) We have previously reported rate constants for water oxidation under pulsed laser excitation of 0.7 s\(^{-1}\) and 5 s\(^{-1}\) for hematite\(^27\) and titania\(^33\) photoanodes respectively. Similarly slow rate constants have also been reported from electrochemical analyses of hematite photoelectrodes.\(^15\) For unmodified BiVO\(_4\), we have reported a rate constant for water oxidation of \(\textit{circa} 1\) s\(^{-1}\).\(^20\) This rate
constant was determined from the time constant of the slow decay phase observed by transient absorption under strong anodic bias, where back electron/hole recombination is turned off. This rate constant is consistent with the data reported herein (~0.7 s⁻¹) for our unmodified films at > 1.6 V_RHE. Due to these slow rate constants, long-lived holes accumulate at the photoanode surface. Determining the yields and lifetimes of these surface holes is therefore central to understanding the efficiency of water oxidation by such photoanodes.

Our studies herein are focused upon the effect of a photoelectrodepositied surface layer of CoPi electrocatalyst on undoped BiVO₄ photoanodes. We first consider the impact of CoPi surface modification on the yield of long-lived holes, as assayed by the amplitude $\phi_{\text{TAS2}}$ of the exponential slow phase observed in our transient absorption studies. This yield is a measure of the efficiency of hole transport to the photoanode surface, and is therefore a measure of the efficiency of charge separation, driven primarily by the space charge layer. Fig. 6 (open symbols) shows $\phi_{\text{TAS2}}$ for unmodified and CoPi-modified BiVO₄ photoanodes as a function of applied potential, overlaid with the photocurrent density. It is apparent that for both photoanodes, there is an offset between the appearance of long-lived photogenerated holes and the photocurrent onset. This difference in the potential dependence of $\phi_{\text{TAS2}}$ and photocurrent is much smaller following CoPi deposition. For unmodified BiVO₄, we have previously assigned this difference in the potential dependence of $\phi_{\text{TAS2}}$ and photocurrent to back electron/hole recombination across the space charge barrier on ms–s timescales, in kinetic competition with water oxidation. This loss necessitates the additional application of a 600–700 mV anodic potential for photocurrent (water oxidation) generation (see Fig. 6a). This implies that for unmodified BiVO₄ photoanodes, a strongly anodic potential, resulting in a wide space charge layer and strong band bending, is required to provide a sufficient barrier to prevent back electron/hole recombination.²⁰ For the CoPi-modified BiVO₄ photoanode, the significantly smaller difference between the potential dependence of $\phi_{\text{TAS2}}$ (i.e. charge separation yield) and photocurrent implies that back electron/hole recombination losses are less severe. We note that the potential for the onset of long-lived holes in unmodified and CoPi-modified BiVO₄ are similar (both ~ 0.2 V_RHE), suggesting that the flat-band potential is largely unaffected by CoPi deposition. This is consistent with studies of cobalt-modified BiVO₄ and α-Fe₂O₃ photoanodes by other groups. Additionally, the amplitude of the long-lived holes is only slightly increased by CoPi (Fig. 4d) indicative of only minor retardation of sub-ms electron/hole recombination and indicating that the yield of hole transfer to the photoanode surface is largely independent of CoPi surface modification. These results suggest that the main effect of CoPi on BiVO₄ photoanodes is to significantly reduce recombination of bulk electrons with surface accumulated holes.

4.2 Kinetic model for photoanode function

We now consider a simple kinetic model for water oxidation focused on the kinetic competition between water oxidation and back electron/hole recombination, as shown in Scheme 1. We have previously applied this kinetic model to unmodified BiVO₄ and α-Fe₂O₃ photoanodes.²⁰,²⁹ Assuming 100% Faradaic efficiency of water oxidation during the transient absorption measurements, the relative water oxidation yield, $\phi_{\text{WO}}(V)$, and back electron/hole recombination yield, $\phi_{\text{REC}}(V)$, can be calculated from:

$$\phi_{\text{WO}}(V) = \phi_{\text{TAS2}}(V) \times \frac{k_{\text{WO}}}{k_{\text{WO}} + k_{\text{REC}}(V)}$$

(4)

$$\phi_{\text{REC}}(V) = \phi_{\text{TAS2}}(V) \times \frac{k_{\text{REC}}(V)}{k_{\text{WO}} + k_{\text{REC}}(V)}$$

(5)

$$k_{\text{WO}} + k_{\text{REC}}(V) = \frac{1}{\tau_{\text{TAS2}}(V)}$$

(6)
where $\phi_{TAS2}(V)$ and $\tau_{TAS2}$ are the amplitudes and lifetimes of the slow transient absorption decay phase, and therefore proportional to the yield and lifetimes of holes transferred to the photoanode surface, as shown in Fig. 4d; $k_{WO}$ and $k_{SC2}(V)$ are the water oxidation and back electron/hole recombination rate constants, respectively. The water oxidation rate constant is assumed, as previously, as to be potential independent, and is determined directly from $\tau_{TAS2}$ in the limit of strong anodic bias, where back electron/hole recombination does not occur.

The water oxidation yield $\phi_{WO}(V)$ calculated from Equation 4 using the data shown in Fig. 4 is shown in Fig. 6 (filled circles/squares). For both the unmodified and CoPi-modified BiVO$_4$ photoanodes, the calculated water oxidation yield is in agreement with the measured photocurrent density, demonstrating the effectiveness of this simple kinetic model.

The yield of back electron/hole recombination $\phi_{REC}(V)$, as quantified from Equation 5 from our transient absorption data, is shown in Fig. 5 (red symbols). This is overlaid with the charge lost through back electron/hole recombination as determined from integration of photocurrent transients (black lines). For both photoanodes, there is an excellent agreement between our transient absorption and transient photocurrent assays of the losses due to back electron/hole recombination, providing further support for the validity of our analyses. Also clear from Fig. 5, the losses of charges due to back electron/hole recombination are greatest around the photocurrent onset potential, i.e. 0.4 V $V_{RHE}$ for CoPi-modified BiVO$_4$ and 0.7 V $V_{RHE}$ for unmodified BiVO$_4$. This has previously been observed for $\alpha$-Fe$_2$O$_3$ and undoped BiVO$_4$ photoanodes.$^{30,20}$ With increasing anodic potential, the width of the space charge layer increases, so more photogenerated holes reach the photoanode surface, where they accumulate.$^{20}$ However at modest anodic bias the band bending associated with this space charge layer is insufficient to prevent back recombination of these surface holes with bulk electrons. As such, prior to the photocurrent onset, losses due to back electron/hole recombination increase with increasing anodic bias. At larger anodic potentials, the band bending becomes large enough so that the kinetics of this back recombination are slower than water oxidation, resulting in a reduction in back electron/hole recombination losses and the concomitant onset of water oxidation photocurrent. The time constants of back electron/hole recombination and water oxidation underlying this behavior, determined using the model above, are shown in Fig. S3, which result in the observed peak of losses due to back electron/hole recombination at the photocurrent onset potential, as shown in Fig. 5. Our analysis shows the origin of the cathodic shift of the photocurrent onset potential following CoPi deposition on BiVO$_4$. It appears that CoPi deposition does not substantially change the potential dependence or efficiency of hole transport to the BiVO$_4$ surface. For both photoanodes, the onset potential for the generation of long-lived (ms-s) holes is ~ 0.2 V $V_{RHE}$, close to the flat band potential for BiVO$_4$. However CoPi deposition does reduce the additional potential required to turn off back electron/hole recombination, resulting in the observed cathodic shift in photocurrent generation.

Under sufficiently strong anodic bias, back electron/hole recombination is suppressed for both unmodified and CoPi modified photoanodes; under these conditions $\tau_{TAS2}$ corresponds directly to the time constant for water oxidation. It is apparent from the data in Fig. 4 that this time constant is similar for both photoanodes (1.4 s and 1.6 s without and with CoPi deposition). It can thus be concluded that the rate constant for water oxidation by BiVO$_4$ holes is independent of CoPi. This time constant was also found to be independent of laser excitation density (see ES1 Fig. S4 and S5). It is therefore apparent that CoPi does not accelerate water oxidation on BiVO$_4$ photoanodes. This is consistent with our previous transient absorption studies of CoPi-modified $\alpha$-Fe$_2$O$_3$ and also an intensity-modulated photocurrent spectroscopy study which concluded that cobalt species do not increase the reaction rate of water oxidation on a cobalt-treated $\alpha$-Fe$_2$O$_3$ photoanode.$^{25}$ If anything, CoPi deposition appears to result in a small retardation of water oxidation (from 1.4 to 1.6 s), most probably due to the reduced accessibility of water to the BiVO$_4$ surface following CoPi deposition. We note that these data do not mean that CoPi is not oxidized under steady-state irradiation at anodic bias (resulting for example from a low quantum yield of hole transfer from BiVO$_4$ to CoPi) but only that such oxidation, if present, is relatively unimportant in explaining the cathodic shift in photocurrent onset potential following CoPi deposition. A detailed study of this issue, employing continuous illumination, is ongoing and will be reported elsewhere. We also note that it has been suggested that on $\alpha$-Fe$_2$O$_3$ photoanodes, thicker than optimum CoPi layers may result in a higher proportion of water oxidation proceeding from oxidized CoPi.$^6$ The study herein employed the thickness found to give optimum performance. Notwithstanding these caveats, the data reported herein imply that, for the optimized CoPi layer thickness employed, any such oxidized CoPi, if present, does not contribute strongly to the enhanced water oxidation photocurrent. Instead, for BiVO$_4$ modified by a CoPi overlayer, the improved photocurrent
onset potential and higher photocurrent density can be explained by efficient suppression of back electron/hole recombination.

Previously we have observed significant retardation of electron/hole recombination following CoPi-modification of α-Fe$_2$O$_3$ photoanodes. These previous studies did not distinguish between the impact of CoPi deposition on bulk electron/hole recombination (i.e. the efficiency of hole transport to the surface) or on back electron/hole recombination. We also note that back electron/hole recombination losses were less prominent for these hematite photoelectrodes compared to the BiVO$_4$ photoanodes reported herein. This is most probably associated with the higher doping density and faster bulk recombination losses in the hematite photoanodes. Nevertheless, our previous results are consistent with the results presented herein, namely that the primary effect of CoPi deposition is the retardation of recombination losses rather than acceleration of water oxidation.

Our transient absorption study reported herein indicates that the charge separation (i.e. fraction of holes reaching the BiVO$_4$ surface) is not significantly improved in the presence of CoPi overlay, as evidenced by the little improved initial amplitude of long-lived holes (milliseconds to seconds) in BiVO$_4$ photoanodes following CoPi modification. Rather our results demonstrate that the primary function of CoPi overlayers is retardation of recombination. This is in broad agreement with previous PEC studies that indicated that recombination within the space charge layer is reduced in CoPi-modified BiVO$_4$ photoanodes. More specifically, and in contrast to these PEC studies, our results from CoPi-modified BiVO$_4$ indicate that such lower recombination losses result primarily from an inhibition of back electron/hole recombination within the BiVO$_4$ photoelectrode, rather than across the BiVO$_4$ / CoPi interface.

The mechanism of how CoPi deposition reduces the losses due to back electron/hole recombination within the BiVO$_4$ is not clear. Previously we suggested that reduced recombination losses in CoPi modified α-Fe$_2$O$_3$ photoanodes may result from enhanced band bending and space charge layer formation induced by CoPi. We note that the space layer depth in these doped α-Fe$_2$O$_3$ photoanodes is substantially narrower than in the undoped BiVO$_4$ studied herein (≈ 8 nm at 1.23 V$_{RHE}$) is substantially narrower than in the undoped BiVO$_4$ studied herein (≈ 90 nm at 1.23 V$_{RHE}$). The small increase in the long-lived hole amplitude (Fig 4d) and photocurrent (Fig 1 and Fig S2 in the ESI) in CoPi-modified BiVO$_4$ suggests that the width of the space charge layer is marginally increased in the presence of CoPi overlayers. Instead, the significant reduction of back electron/hole recombination may be caused by increased electric field strength associated with the electrostatics of the BiVO$_4$/CoPi interface, although detailed understanding of this point is beyond the scope of this study.

5. Conclusion

Transient absorption spectroscopy and transient photocurrent measurements were employed to characterize the dynamics of photogenerated holes in CoPi-modified BiVO$_4$ photoanodes. The competition between water oxidation and electron/hole recombination was quantified using a simple kinetic model. The photoelectrochemical results confirm that the water oxidation performance of BiVO$_4$ photoanodes can be improved by CoPi deposition, resulting in a cathodic shift in the photocurrent onset potential. However, transient absorption measurements, which allow direct monitoring of photogenerated holes, and transient photocurrent studies indicate that this improvement is not primarily due to the catalytic function of CoPi on the BiVO$_4$ surface, under the measurement conditions employed. Rather, the cathodic shift in onset potential results from suppression of recombination of surface-accumulated holes with bulk electrons (back electron/hole recombination). This allows more holes to contribute to water oxidation. These results emphasize the key role of recombination losses in limiting photoanode performance, and how these losses can be reduced by surface modification.

Acknowledgements

Y.M., F.L.F., A.K., S.R.P. and J.R.D. thank the European Research Council (project Intersolar 291482) for funding. F.L.F. thanks the Swiss National Science Foundation (project: 140709). A.K. thanks the Ramsay Memorial Fellowships Trust. The authors also thank Dr Xiaoe Li for help with SEM measurements.

References