Unraveling Charge Transfer in CoFe Prussian Blue Modified BiVO₄ Photoanodes

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* Supporting Information

ABSTRACT: Catalyst modification of metal oxide photoanodes can result in markedly improved water oxidation efficiency. However, the reasons for improvement are often subtle and controversial. Upon depositing a CoFe Prussian blue (CoFe-PB) water oxidation catalyst on BiVO₄, a large photocurrent increase and onset potential shift (up to 0.8 V) are observed, resulting in a substantially more efficient system with high stability. To elucidate the origin of this enhancement, we used time-resolved spectroscopies to compare the dynamics of photogenerated holes in modified and unmodified BiVO₄ films. Even in the absence of strong positive bias, a fast (pre-ms), largely irreversible hole transfer from BiVO₄ to CoFe-PB is observed. This process retards recombination, enabling holes to accumulate in the catalyst. Holes in CoFe-PB remain reactive, oxidizing water at a similar rate to holes in pristine BiVO₄. CoFe-PB therefore enhances performance by presenting a favorable interface for efficient hole transfer, combined with the catalytic function necessary to drive water oxidation.

Metal oxides, such as TiO₂, Fe₃O₄, WO₃, and BiVO₄, have been extensively studied as candidate photoanodes for water oxidation (WO). Despite their ideally aligned valence bands, which provide a large driving force for WO, large additional positive applied potentials are still required to access high photon-to-current conversion efficiencies. A common approach to reduce the need for such strong positive potentials is to deposit an electrocatalyst on the surface of the photoanode to act as a co-catalyst. This strategy is often successful, yielding enhanced photocurrents and reduced WO onset potentials. However, improvements in performance are not necessarily linked to improved WO kinetics. Other mechanisms, such as retarding electron–hole recombination within the semiconductor, may dominate. For example, deposition of cobalt phosphate (CoPi) on dense BiVO₄ leads to a 100–250 mV negative shift in the onset potential of WO. Independent studies of CoPi, modified films using electrochemical impedance spectroscopy, intensity modulated photocurrent spectroscopy, and transient absorption spectroscopy (TAS) indicate that this improvement is not related to hole transfer to CoPi (i.e., charge separation) and/or WO catalyzed by CoPi, but rather stems from retarded surface recombination within BiVO₄. Intriguingly, unfavorable interfacial kinetics for hole transfer to CoPi are observed, despite this transfer having a large driving force, with time scales 2–10 times slower than direct WO on the BiVO₄ surface (which has a characteristic time constant of ca. 0.5 s). Although some oxidation of CoPi was observed under WO conditions, this oxidation of CoPi did not contribute significantly to the overall WO flux due to CoPi’s relatively slow WO kinetics. In this study, we examined CoFe-PB as a co-catalyst that acts directly enhancing WO on its active sites. As such, finding a co-catalyst that acts by directly enhancing WO on its active sites remains a key challenge for the development of more efficient photoanodes. While studies have reported indirect evidence for such performance enhancement, we focus herein on a direct kinetic study of a promising candidate system, cobalt iron Prussian blue on BiVO₄.

CoFe-PB exhibits much faster WO kinetics than CoPi (1.4 s⁻¹ for CoFe-PB vs 2 × 10⁻³ s⁻¹ for CoPi, per active site). It has recently been demonstrated that CoFe-PB modification of mesostructured...
Nanostructured BiVO₄ photoanodes produce substantial improvements in both the onset potential and photocurrent, maintaining stability for over 50 h. Preliminary investigations of CoFe-PB modified BiVO₄ using photoelectrochemical impedance and hole scavenger studies, suggest that the origin of this improvement is distinct from the effect of CoPᵢ, i.e., suppression of surface recombination within BiVO₄ and related to more efficient hole transfer to water, presumably via CoFe-PB. These findings are consistent with hybrid density functional theory calculations, which predict the existence of a strong energetic offset (thermodynamic driving force) for hole transfer between the valence band of BiVO₄ and CoFe-PB.

Herein, we present the first study of the effect of CoFe-PB modification of BiVO₄ electrodes on the kinetics of photogenerated holes. Using time-resolved absorption spectroscopy, we demonstrate that BiVO₄ holes quickly and efficiently transfer to CoFe-PB, leading to persistent oxidized CoFe-PB states even at very low bias. This capacity to separate charges at modest applied potential is coupled with effective catalytic functionality as accumulated holes in CoFe-PB form multiply oxidized states, which react with water with similar catalytic WO onset potential (1.6 V_RH, a value similar to that observed for CoFe-PB/FTO electrocatalysis). Taking the voltage required to attain 0.1 mA/cm² as the onset potential for photocurrent under 1 sun irradiation, a negative shift of 0.8 V of the onset potential is achieved upon CoFe-PB deposition (Figure S3), in agreement with previous reports. In order to confirm that the measured current is due to WO, gas chromatography experiments were carried out and a Faradaic efficiency close to 100% was achieved (Figure S4).

Before considering the effect of CoFe-PB modification on the transient absorption of BiVO₄, we first determined the photoelectrochemical WO occurring after 1.6 V_RH, a smaller, semi-reversible redox wave observed before the onset of catalytic current (Figures 1b and S5c). CoFe-PB films are non-stoichiometric, likely containing a mixture of neighboring Co²⁺ and Fe²⁺, Co³⁺ and Fe²⁺ (and possibly Co²⁺ and Fe³⁺) centers, each with different coordination environments and redox potentials. Consequently, this redox wave cannot clearly be assigned uniquely to either a Co²⁺/Co³⁺ or a Fe²⁺/Fe³⁺ couple. For simplicity, we hereafter refer to this oxidized state as “CoFe-PB⁺.” At potentials positive of the electrocatalytic WO onset potential (1.6 V_RH, a smaller, flat difference spectrum with increased amplitude toward blue wavelengths is observed (red line in Figure 1c). This second spectrum exhibits a blue-shifted maximum compared to CoFe-PB. We assign this change in spectral shape to further oxidation of CoFe-PB⁺, which again for simplicity we label “CoFe-PB²⁺.” The appearance of this second spectrum correlates with the onset of WO catalysis (Figure 1b).

Utilizing the spectral fingerprints of oxidized CoFe-PB states to interpret our results, we now turn to TAS (see the SI for details), which we use to assess the effect of CoFe-PB modification on the kinetics of photogenerated holes in BiVO₄.
Figure 2a presents a comparison of the transient absorption spectra (at 10 ms) of CoFe-PB modified and unmodified BiVO₄ films, both at strong positive bias, while Figure 2b,c shows kinetics at selected wavelengths as a function of applied bias. Consistent with previous reports, unmodified BiVO₄ exhibits a transient absorption spectrum peaking at 550 nm and decaying toward the near-IR. This spectrum has previously been assigned to BiVO₄ surface holes. After CoFe-PB modification, the amplitude at 550 nm is lost, and a new peak bearing a strong resemblance to the absorption of CoFe-PB⁺ (~700 nm, decaying more strongly toward shorter wavelengths) is observed. Taken together, these results demonstrate efficient hole transfer from the BiVO₄ surface to CoFe-PB.

An increase in the lifetime of photogenerated charges upon CoFe-PB modification at low applied potentials is clearly visible in the TA kinetics of the electrodes (Figure 2b,c). Concordant with previous transient studies, strong positive bias (1.5 V_RHE) is required to produce persistent (with lifetime \( \tau > 10 \text{ ms} \)) photogenerated holes in unmodified BiVO₄ (Figure 2b). However, after CoFe-PB modification, persistent transient absorption is observed even at low applied potentials (0.25 V_RHE, Figure 2c, see also spectra in Figure S6). Figure 2c also shows that the signal amplitude at early times (10 \( \mu \text{s} \)) remains almost unchanged for tenths of ms. This data indicates that hole transfer from BiVO₄ to CoFe-PB is largely complete by 10 \( \mu \text{s} \). We attribute this increased hole lifetime to fast and efficient hole transfer. This is because hole transfer to CoFe-PB corresponds to a spatial separation of charge, which suppresses recombination even in the absence of a strong applied potential.

To better understand the fate of persistent separated holes in CoFe-PB under operational conditions, we utilize photo-induced absorption spectroscopy (PIAS), employing a 5 s, 365 nm LED pulse to simulate in operando conditions (details can be found in the SI and previous publications). Unmodified BiVO₄ again shows a peak at 550 nm, assigned to the accumulation of BiVO₄ surface holes facilitated by a strong positive applied potential (Figure 3a). Upon CoFe-PB modification, the amplitude at 550 nm decreases and a new peak consistent with oxidized CoFe-PB (~650–750 nm; see the following section for discussion of spectral shape and CoFe-PB oxidation state) is observed (Figure 3a). This change is broadly similar to the spectral change observed in TAS upon CoFe-PB modification, further supporting the conclusion that photogenerated holes transfer to, and accumulate in, CoFe-PB rather than BiVO₄.

The effect of the CoFe-PB layer on the dynamics of accumulated charges can be found by examining the PIA kinetics as a function of applied bias (Figure 3b,c). At lower applied potentials, a negligible PIA signal is observed for unmodified BiVO₄, indicating that only a few holes accumulate (Figure 3b). Under large positive bias, a strong PIA signal is observed, indicative of the accumulation of surface holes under illumination (Figure 3b). After CoFe-PB modification, such strong positive potentials are no longer required to observe large PIA signals (Figure 3c), again consistent with our TAS data (Figure 3c). The decay kinetics of the PIA traces at high anodic bias (where recombination processes are strongly suppressed for both electrodes) gives a clear indication of the WO kinetics under these in operando conditions. In unmodified BiVO₄, an initial rate analysis yields a WO time constant from BiVO₄ surface holes on the order of seconds (Figures 3b and S8a), consistent with our previous reports.

The PIA signal decays for CoFe-PB modified BiVO₄, assigned to oxidized CoFe-PB states, exhibit broadly similar decay kinetics to BiVO₄ holes, indicative of similar WO oxidation kinetics on both BiVO₄ and CoFe-PB (Figure 3c). However, in contrast to BiVO₄, significant PIA signal is observed for CoFe-PB modified BiVO₄ even at 0.3 V_RHE with the PIA decay kinetics accelerating with increasing applied potential. The signal decaying faster cannot be attributed to recombination being suppressed as this would result in retardation of this decay. This acceleration with increased positive bias coincides with a blue shift of the PIA spectrum.
(Figure 4a). This is analogous to the blue shift observed with increased positive bias in our spectroelectrochemical data for CoFe-PB on FTO (Figures 4b and 1c), assigned to the subsequent generation of CoFe-PB$^{2+}$ states. These data thus indicate that under modest applied potential (0.3 V$_{\text{RHE}}$) hole transfer from BiVO$_4$ to CoFe-PB results primarily in the generation of unreactive (and therefore slowly decaying) CoFe-PB$^+$ states. However, as the applied potential (and photocurrent) increases, irradiation results in the generation of CoFe-PB$^{2+}$ states capable of driving WO. The greater reactivity of these states is consistent with their faster PIA decay kinetics. Fitting the decay of PIA traces gives a time constant for WO by CoFe-PB$^{2+}$ states on the order of seconds (Figure S8b), in agreement with a previously reported time scale for electrocatalytic WO on CoFe-PB.\cite{19}

In summary, and as illustrated in Scheme 1, our kinetic studies indicate that the enhanced photoelectrochemical WO performance of CoFe-PB modified BiVO$_4$ results from fast ($\mu$s or faster) hole transfer from BiVO$_4$ to CoFe-PB. This charge transfer enables the generation of long-lived photogenerated holes (i.e., CoFe-PB$^{1/2+}$ states in CoFe-PB) in the absence of strong anodic bias. WO kinetics are on the order of seconds on both BiVO$_4$ and CoFe-PB, despite the more oxidizing nature of BiVO$_4$ holes. The resultant suppression of recombination losses, without any compromise in WO kinetics, is the origin of the remarkable shift of the WO onset potential following CoFe-PB deposition.

The kinetics that we report herein for CoFe-PB modified BiVO$_4$ differ substantially from those that we have reported previously for CoP$_i$ modified dense BiVO$_4$ films (Scheme 1b). WO on CoP$_i$ is 2$–$3 orders of magnitude slower than WO via the BiVO$_4$ surface or WO via CoFe-PB. This slow catalysis results in the accumulation of large amounts of relatively unreactive charge in CoP$_i$ when used as a co-catalyst, observed as slowly decaying PIA signals with amplitudes 2 orders of magnitude greater than those observed in CoFe-PB, where holes in the catalyst are removed from the catalyst by WO.\cite{14}

However, these large signals arise from a CoP$_i$ layer 10 times thicker than the CoFe-PB layer studied herein (200 vs 20 nm). Consequently, despite larger signals, only singly oxidized (i.e., precatalytic) CoP$_i$ states are observed, corresponding to a lower hole density. This contrasts the multiply oxidized CoFe-PB states observed herein. This is consistent with the concept of enhanced performance following CoP$_i$ deposition resulting from retarded recombination within BiVO$_4$ due to increased band bending, suggested to result from Schottky junction formation\cite{10} (see Scheme 1b). A further difference is that in CoP$_i$/BiVO$_4$ hole transfer to the CoP$_i$ was observed to be relatively slow and inefficient (occurring on order of seconds), despite similar apparent energy offsets for hole transfer (roughly 1 eV), and contributed little to the overall WO kinetics.

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Scheme 1. (a) Photon Conversion Efficiency in Unmodified BiVO$_4$ Limited by the Kinetic Competition between Potential-Dependent Surface Recombination (rec (V)) and WO, (b) CoP$_i$ Modification Reducing the Applied Potential Needed to Effectively Suppress Surface Recombination, Allowing Holes to React via the BiVO$_4$ surface,\textsuperscript{a} and (c) CoFe-PB Enhancing the Efficiency via a Different Mechanism.\textsuperscript{b}

\textsuperscript{a}Hole charge transfer (CT) to CoP$_i$ and WO via CoP$_i$ is slow and does not contribute to photocurrent. \textsuperscript{b}Efficient hole CT to CoFe-PB separates holes from electrons in the BiVO$_4$ surface (thereby suppressing this recombination pathway). This is coupled to effective WO catalysis.
Those covalent linkages can largely decrease the barrier for this di
conclusions of this work, in particular, the e
studied herein are highly textured and interface via a high
semiconductor/co-catalyst interface on the e
catalyst systems.

principles for assessing the compatibility of semiconductor/co-
transfer as well as the factors that control the kinetics of WO,
All authors have given approval to the

favorable surface facets of BiVO4 is signi
between the BiVO4 studied as in our previous study of CoPi/

thick (200 nm) CoPi layer was used.10 The BiVO4 samples

 Asterisk

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ABBREVIATIONS

BiVO4 = bismuth vanadate; CoFe-PB = cobalt iron Prussian
blue (cobalt hexacyanoferrate); WO = water oxidation; SEC =
spectroelectrochemistry; TAS = transient absorption spectro-
scopy; PIAS = photoinduced absorption spectroscopy

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Notes

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