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Rate Law Analysis of Water Oxidation and Hole Scavenging on a BiVO₄ photoanode

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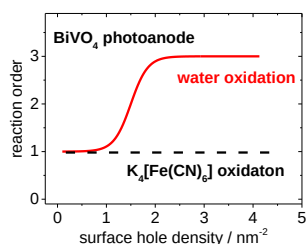
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ABSTRACT Spectroelectrochemical studies employing pulsed LED irradiation are used to investigate the kinetics of water oxidation on undoped dense bismuth vanadate (BiVO_4) photoanodes under conditions of photoelectrochemical water oxidation, and compared to those obtained for oxidation of a simple redox couple. These measurements are employed to determine the quasi steady-state densities of surface accumulated holes, p_s , and correlate these with photocurrent density as a function of light intensity, allowing a rate law analysis of the water oxidation mechanism. The reaction order in surface hole density is found to be first order for $p_s < 1 \text{ nm}^{-2}$, and third order for $p_s > 1 \text{ nm}^{-2}$. The effective turn over frequency of each surface hole is estimated to be 14 s^{-1} at AM 1.5 condition. Using a single-electron redox couple, potassium ferrocyanide, as the hole scavenger, only the first order reaction is observed, with a higher rate constant than for water oxidation. These results are discussed in terms of catalysis by BiVO_4 and implications for material design strategies for efficient water oxidation.

TOC GRAPHICS



Solar-driven water oxidation on metal oxide semiconductors is central to many approaches for solar driven fuel synthesis.¹⁻² Bismuth vanadate, BiVO_4 , is a particularly promising photoanode material for water oxidation.^{1, 3} Employing various optimization strategies, including gradient-doping,⁴ surface modification,⁴⁻⁹ and the use of host-guest scaffolds,¹⁰ onset potentials for

photoelectrochemical (PEC) water oxidation on BiVO_4 as low as 0.2 V vs RHE and photocurrent densities at 1.23 V_{RHE} as high as 4 mAcm^{-2} have been reported.⁷ Several studies on both BiVO_4 and other oxide surfaces have identified the relatively slow (up to seconds) timescale of water oxidation on such oxides as a key limitation to photoanode performance.¹¹⁻¹⁵ However, to date, studies of the kinetics and mechanism of water oxidation on BiVO_4 surfaces have been very limited in the literature.¹ Transient absorption studies have indicated a timescale for water oxidation on metal oxide surfaces, such as BiVO_4 and hematite under short-pulsed laser excitation of 1 s,^{12-13, 16-18} whilst intensity-modulated photocurrent spectroscopic analyses have indicated timescales of 0.1 s for this reaction.^{15, 19-20} Photocurrent density studies employing chemical hole scavengers such as sodium sulfite (Na_2SO_3) have been employed to demonstrate the role of kinetic competition between surface recombination and water oxidation in limiting the performance of BiVO_4 photoanodes.⁷ Herein we report the first direct study of the kinetics of water oxidation on BiVO_4 under conditions of photoelectrochemical water oxidation, and employ a rate law analysis of these data to provide insight into the mechanism of water oxidation on this oxide.

Compared to the binary metal oxides such as TiO_2 and Fe_2O_3 typically employed as photoanodes for water oxidation, it has been suggested that BiVO_4 is unusual in that its valence band edge (VBE) results from the hybridization of $\text{Bi}(6s)$ and $\text{O}(2p)$ orbitals.²¹⁻²² It has also been reported that the photoelectrochemical reactivity of BiVO_4 can be strongly modulated by the exposed crystal facet.²³ We have recently reported a rate law analysis of the kinetics of water oxidation on hematite photoanodes as a function of the density of surface accumulated valence band holes. This study showed a transition from 1st order behavior at low light flux to 3rd order at higher light fluxes. These data suggested the rather surprising conclusion that, under conditions of solar irradiation, the rate determining step for water oxidation on hematite is associated with three valence band

holes. This contrasts with the four hole overall stoichiometry required to oxidize two molecules of water to one molecule of oxygen. However it is unclear from this study if this third order behavior is specific to the particular chemistry of water oxidation on hematite (which has been proposed to be associated with the formation of surface iron-oxo groups²⁴), or is more generally observed on other metal oxide surfaces.²⁵⁻²⁶

Herein, we report the kinetics of water oxidation on undoped, dense BiVO₄ photoanodes under quasi steady-state conditions, as determined by spectroelectrochemical photoinduced absorption (PIA) measurements employing pulsed LED excitation. The reaction kinetics were obtained using the rate law analysis employed previously for hematite photoanodes.¹¹ These data are compared against those obtained using potassium ferrocyanide (K₄[Fe(CN)₆]) as a facile hole scavenger.²⁷⁻²⁸ The results and implications of the reaction kinetics are discussed with regards to optimization of water oxidation on BiVO₄ photoanodes.

BiVO₄ photoanodes were fabricated using metal-organic deposition,¹² yielding dense films with a relatively flat surface (roughness factor ~ 1). Experimental details are given in Supporting Information. Figure 1 shows the typical current-voltage responses of these BiVO₄ photoanodes measured in potassium phosphate buffer (KPi, 0.1 M, pH 6.7) with, and without, the addition of K₄[Fe(CN)₆] (0.2 M) as a hole scavenger. In the KPi buffer, the onset potentials for dark- and photo- water oxidation currents occur at $>2.0 V_{RHE}$ and $\sim 0.8 V_{RHE}$, respectively. These results are consistent with previous reports of such BiVO₄ photoanodes.^{12, 16} In contrast, K₄[Fe(CN)₆] oxidation dark current onset is $1.0 V_{RHE}$, approximately 1 V cathodic of the dark onset in KPi. Under 365 nm LED irradiation, the onset potential for K₄[Fe(CN)₆] oxidation is $0.55 V_{RHE}$, ~ 250 mV cathodic of the water oxidation onset potential. Such cathodic shift of current onset is consistent with previous reports of BiVO₄ in the presence of hole scavengers.^{5, 7, 9}

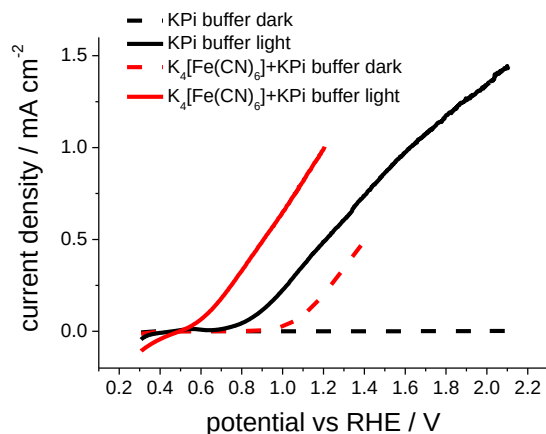


Figure 1. Current-voltage response of BiVO₄ measured in 0.1 M KPi buffer with (red) and without (black) 0.2 M K₄[Fe(CN)₆] hole scavenger. The dark currents are shown in dashed lines. Scan rate: 10 mV s⁻¹. Light intensity: 365 nm illumination equivalent to 100% AM1.5.

In order to investigate the kinetics of water oxidation by photogenerated holes in BiVO₄ under quasi steady-state conditions, we carried out spectroelectrochemical PIA measurements in 0.1 M KPi buffer monitoring the photoinduced absorption changes (ΔOD) and photocurrent densities (J) induced by pulsed (5 s) 365 nm LED excitation. Data were collected as a function of LED excitation intensity at a fixed applied potential at 1.7 V_{RHE} to ensure effective suppression of surface electron/hole recombination.^{12, 16} Under these conditions BiVO₄ holes exhibit a maximum absorption change at 550 nm (Figure S2), in agreement with our previous studies of analogous films under pulsed laser excitation.^{12, 29} As we have previously reported, these quasi-steady conditions result in the observation of long-lived holes accumulated at the photoelectrode surface, and thus, measuring the absorption change at 550 nm provides an assay of their reaction kinetics. Bulk BiVO₄ holes are not monitored in these experiments due to their relatively short (< ns) lifetime.³⁰

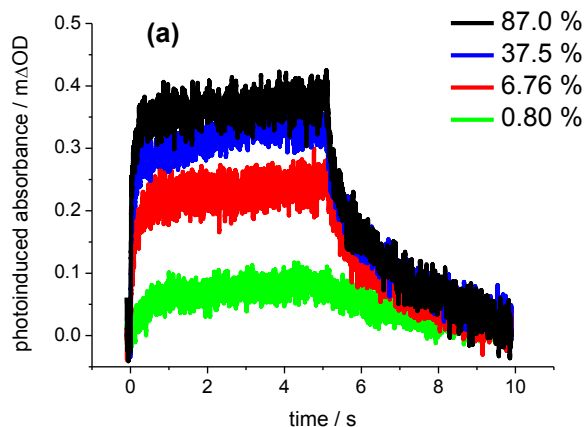
The photoinduced absorbance (milli- Δ OD, m Δ OD) and photocurrent (J) transients results from 5 s pulsed LED excitation are shown in Figures 2 a and b. All Δ OD signals increased from zero to an approximate plateau over a 1 s period from light-on, assigned to surface hole accumulation at the BiVO₄/electrolyte interface. In contrast, the transient photocurrent rises within the time resolution of the measurement (0.4 ms), then rapidly decays within a few hundred milliseconds after LED turn on before also plateauing. The initial photocurrent decay most probably derives from a decrease in band bending due to hole accumulation, reducing the photoanode charge separation efficiency, as discussed previously.¹¹ When the excitation light is switched off, the Δ OD signal decays to zero on the seconds timescale, with the slow timescale of this decay being assigned primarily to slow water oxidation by these surface holes, as discussed further below. In contrast, the current decreases to zero rapidly with no negative current transients, indicative of negligible losses from surface back electron/hole recombination under the strongly anodic bias conditions employed.

The plateaued photocurrent density, measured between 1 s and 5 s after light-on, was observed to increase linearly with LED intensity, whereas the Δ OD signal increased sub-linearly (Supporting Information Figure S3). This is qualitatively similar to results from Si-doped α -Fe₂O₃, reported previously.¹¹

Figure 2c shows the photocurrent density vs Δ OD measured in 0.1 M KPi buffer (red dots) on a log-log scale. Previously we have determined the molar extinction coefficient of photogenerated holes in BiVO₄ photoanodes ($420 \text{ M}^{-1} \text{ cm}^{-1}$),²⁹ allowing us to convert the Δ OD signal amplitude into a surface hole density (p_s : holes nm^{-2}) for this plot. From Figure 2c, it is apparent that this plot of J versus p_s exhibits two distinct phases: a lower gradient for $p_s < 1 \text{ hole nm}^{-2}$, and a significantly larger gradient at higher surface hole densities. This indicates that the kinetics of

water oxidation on BiVO₄ are intensity-dependent, showing qualitatively different dependencies on surface hole density at low and high densities.

Analogous data to those shown in Figures 2a and 2b were collected in the presence of the hole scavenger K₄[Fe(CN)₆] (see Figure S4). The applied potential was fixed at 0.7 V_{RHE} to eliminate any contribution from water oxidation; under these conditions the photocurrent can be assigned entirely to K₄[Fe(CN)₆] oxidation. The resulting plot of J versus p_s is also shown in Figure 2c. We note that due to the different electrolyte compositions, and likely changes in surface charge, flat-band potential etc, the absolute magnitudes of the J versus p_s cannot be compared with/without K₄[Fe(CN)₆]. In any case, it is apparent from Figure 2c that the data with K₄[Fe(CN)₆] shows only one linear region across the light intensity employed, as discussed further below.



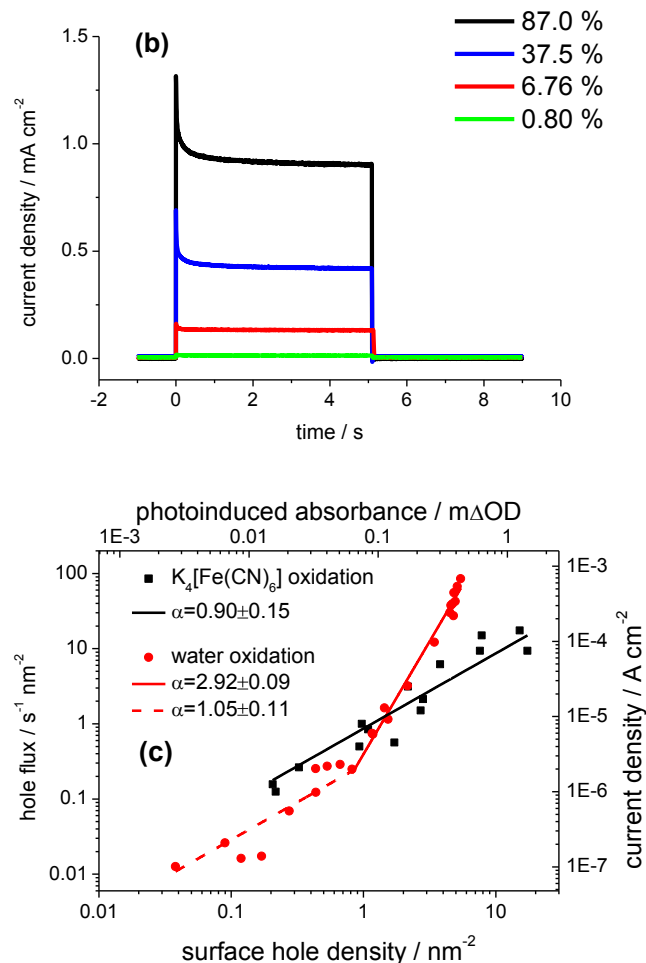


Figure 2. Photo-induced absorption (a) and transient photocurrent density (b) from a BiVO₄ photoanode in 0.1 M KPi buffer as a function of light intensity compared to one sun condition. (c) Relationship of PIA amplitude and quasi steady-state photocurrent density for water oxidation (red dots) and K₄[Fe(CN)₆] oxidation (black squares).

We employ a simple kinetic model to interpret these spectroelectrochemical results, as previously used for Si-doped α -Fe₂O₃,¹¹ and shown as a schematic representation in Scheme 1. We assume the Faraday efficiency is unity on the dense BiVO₄ photoanodes employed in these studies.³¹ No impurities, such as trace of Fe or Ni on the electrode surface from the electrolyte, were deposited as catalysts,³²⁻³⁵ according to our previous X-ray photoelectron spectroscopy

result.²⁹ Therefore, the results shown herein represent water oxidation by photogenerated holes in BiVO₄. Under 1.7 V_{RHE} anodic potential, we considered a model for surface-accumulated holes at the semiconductor-electrolyte interface as follows:

$$(1) \frac{dp_s}{dt} = J_{hole} - k \times p_s^\alpha$$

where p_s is the hole density at the BiVO₄ surface, J_{hole} is the hole flux to the surface during irradiation, k is the rate constant of reaction of holes with water/potassium ferrocyanide and α is the reaction order in surface hole density.

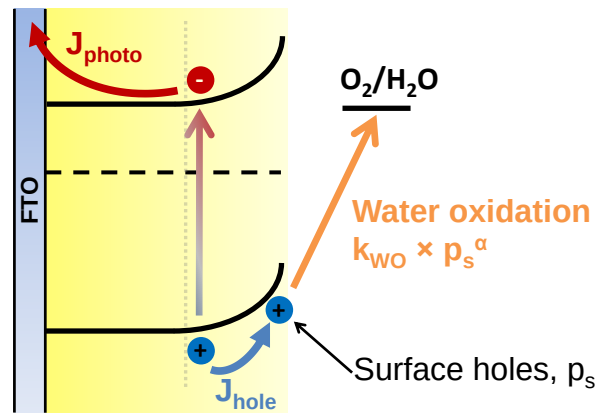
At steady state (i.e.: after 5 s irradiation), the rate of change in surface hole density is zero, therefore Equation 1 can be written as:

$$(2) \frac{dp_s}{dt} = J_{hole} - k \times p_s^\alpha = 0$$

$$(3) J_{hole} = k \times p_s^\alpha; J_{photo} = J_{hole}$$

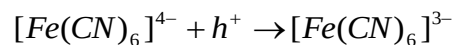
$$(4) \log(J_{photo}) = \log k + \alpha \times \log p_s$$

where J_{photo} is the steady-state photocurrent density measured at 5 s after light-on (Figure 2b).



Scheme 1. Schematic representation of surface accumulated holes in the BiVO₄ photoanodes oxidizing water. The dashed horizontal line is the dark Fermi level of the photoanode determined by the applied potential.

Following equation 4, the photocurrent density J should, on a log-log scale, increase linearly with increasing surface hole density p_s , with the gradient corresponding to the reaction order α . Figure 2c shows the rate of oxidation of K₄[Fe(CN)₆] increases linearly with hole density, corresponding to first order kinetics ($\alpha=0.90\pm0.15$ and $k=0.8\text{ s}^{-1}$) in surface hole density over the light intensity range employed in this study (0.8 to 81 % of AM 1.5). The first order reaction determined from our rate law analysis indicates that the oxidation of K₄[Fe(CN)₆] involves a single electron redox process, consistent with the redox reaction of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ shown below.



Under irradiation, one [Fe(CN)₆]⁴⁻ complex receives one photogenerated hole from BiVO₄, forming one [Fe(CN)₆]³⁻. The redox potential of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ is 0.36 V_{RHE}. Therefore, the BiVO₄ valence band edge (2.6 V_{RHE}) can provide significantly more driving force for the oxidation of [Fe(CN)₆]⁴⁻ than for single-hole water oxidation (2.8 V_{RHE}).³⁶ Thus, the thermodynamic driving force is more favorable for BiVO₄ surface holes to oxidize K₄[Fe(CN)₆] than water.

In contrast to the first order reaction of K₄[Fe(CN)₆] oxidation as a function of surface hole density, Figure 2c also shows that there are two regimes of linearity for water oxidation. Under low surface hole density ($p_s < 1\text{ hole nm}^{-2}$), water oxidation proceeds with first-order (in holes) reaction kinetics ($\alpha=1.05\pm0.11$); at surface hole densities higher than 1 nm^{-2} , the reaction order of water oxidation (in holes) becomes third order ($\alpha=2.92\pm0.09$). In order to provide further support for this change in reaction order, different rate law analyses were carried out: differentiation of the

gradient of one complete PIA decay after light-off; an initial slopes analysis of several PIA decays under different excitation intensities (details are shown in Supporting Information Figure S5); and kinetic analysis of transient absorption spectroscopic (TAS) data previously recorded, showing a mono-exponential decay of surface hole as a function of time for water oxidation.¹² The results of these analyses are shown in Figure 3. It is apparent that these different analyses are in excellent agreement with each other – indicating a change in reaction order from 1st to third order at $p_s \sim 1$ hole nm⁻².

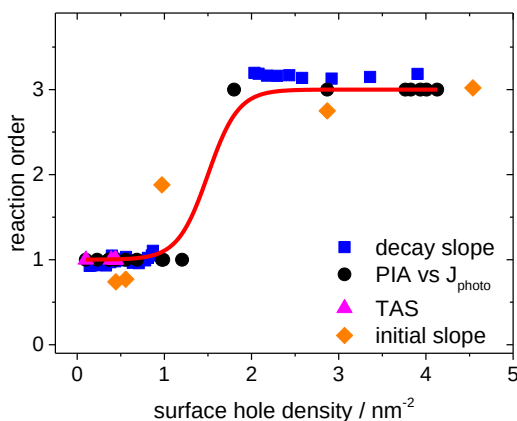


Figure 3. Change in reaction order as a function of surface hole density, determined from four independent methods of analysis. Red line: a guide for the eye (not fit to a model).

The rate constants for both the first and third order water oxidation on BiVO₄ reactions can be calculated from the fit of Figure 2c using Equation 4. For the first order of water oxidation in holes, the rate constant is 0.5 s⁻¹; for the third order reaction, the rate constant is 0.8 s⁻¹ hole⁻² nm⁴. These rate constants are both faster than the corresponding rate constants determined for hematite, 0.2 s⁻¹ and 0.5 s⁻¹ hole⁻² nm⁴, respectively,¹¹ particularly for the 3rd order reaction. The faster rate constants observed on BiVO₄ could be associated with the deeper valence band edge for BiVO₄ (2.6 eV) compared to Si-doped α-Fe₂O₃ (2.4 eV) providing a large energy offset driving water

oxidation, although we note that other factors may also be important (e.g.: electrolyte pH, valence band structure, surface facet etc).

The transition of BiVO₄'s water oxidation kinetics from first to third in surface hole density (p_s) as p_s is increased is strikingly similar to the behavior we have reported previously for Fe₂O₃.¹¹ The first order behavior at low surface hole densities indicates that the rate-limiting step in water oxidation only involves one surface hole; •OH formation has been suggested as the key intermediate for the single hole oxidation of water, likely to lead to both H₂O₂ and O₂ formation.³⁶ The third order reaction kinetics under high surface hole densities is consistent with, for example, a mechanism involving the formation of an O-O bridging bond between two reaction sites, which consumes three surface accumulated holes. Such mechanisms have been suggested for water oxidation on some metal oxide materials, including Co₃O₄²⁵ and α -Fe₂O₃^{11, 24}, from either detecting the time-resolved IR response during the formation of rate-limiting intermediates on Co₃O₄, or employing a rate law analysis to determine the reaction order. We are aware that studies of the mechanism of water oxidation are still limited due to the difficulties in probing the intermediates involved. However, our observation of remarkably similar 1st/3rd behavior on BiVO₄ to that we have observed for Fe₂O₃ is striking as these oxides present predominantly different surface facets ((121) for the BiVO₄ studied herein versus (110) for the Si-doped Fe₂O₃ reported previously^{11, 37}) and difference valence band hole natures (hybridized O(2p) and Bi(6s) for BiVO₄ and hybridized Fe(3d) and O(2p) for α -Fe₂O₃). It suggests the mechanisms of water oxidation on these two oxides may exhibit close similarities, which has important implications for the development of mechanistic models of water oxidation on this oxide photoanodes.

The slow kinetics of water oxidation on metal oxide surfaces is a key challenge for photoelectrochemical water oxidation on such materials. Such slow kinetics have been reported

by a various spectroscopic techniques, including transient absorption spectroscopy,^{12-13, 17-18, 38-40} impedance spectroscopy⁴¹ and intensity-modulated photocurrent spectroscopy.^{15, 19-20} Such slow kinetics result in a requirement for the accumulation of large hole densities at the photoanode surface to drive the required water oxidation current densities, with a resulting increase in surface recombination losses.^{12, 14, 17} The super-linear increase in the rate of water oxidation as the surface hole density is increased is likely to be a key factor behind the efficient photoelectrochemical water oxidation reported to date for several metal oxide photoanodes. For the BiVO₄ studied herein, the effective turn over frequency (TOF) of each surface hole increases from 0.3 s⁻¹ at 0.1 hole nm⁻² to 14 s⁻¹ at 5 holes nm⁻² (corresponding to ~ one sun irradiation conditions). The faster TOF's for BiVO₄ compared to hematite (5 s⁻¹ at 5 holes nm⁻²)¹¹ may result from its deeper valence band energetics, or from other factors such as lateral surface hole mobilities. In any case, the faster TOF is likely to be one factor behind the less anodic applied biases required to drive efficient water oxidation on BiVO₄ compared to hematite photoanodes.

We note that the water oxidation kinetics we report herein on BiVO₄ are faster in terms of TOF per surface hole/catalytic site compared to those reported for widely used water oxidation electrocatalysts. For example, TOF's for the cobalt phosphate (CoPi) electrocatalyst have been reported to be in the range 0.01-0.001 s⁻¹.⁴² The faster kinetics on BiVO₄ can be attributed to its deep valence band energy providing a large overpotential for water oxidation (with this large overpotential of course being undesirable in terms of energy conversion efficiency). As such, several studies have indicated that following CoPi deposition on BiVO₄, water oxidation primarily proceeds directly from BiVO₄ holes rather than via CoPi oxidation, with enhanced performance in the presence of CoPi being primarily assigned to reduced recombination losses due enhanced space charge layer formation induced by the BiVO₄/CoPi junction, similar to studies of α -Fe₂O₃/CoPi

junctions.^{19, 43-45} We have reported previously PIA and transient absorption spectroscopies of CoPi-modified BiVO₄ photoanodes and have observed that CoPi overlayers did not contribute to significant PEC water oxidation under both pulsed laser and continuous wave LED conditions for the electrodes employed in these studies.^{16, 29} Surface functionalization by co-catalysts is a widely used strategy to enhance the performance of water oxidation photoanodes. Our observation herein of TOF as high as 14 s⁻¹ per surface hole on BiVO₄ provides a clear kinetic challenge for this approach, i.e. that water oxidation by the co-catalyst should be faster than that on BiVO₄ alone, and emphasizes that such strategies must consider both the kinetics of water oxidation on both semiconductor and co-catalyst surfaces as well as the impact of co-catalyst deposition upon recombination losses in the photoelectrode.

ASSOCIATED CONTENT

Supporting Information.

Material preparation, description of photoelectrochemistry and spectroelectrochemistry, PIA spectrum of BiVO₄ photogenerated holes, steady-state PIA amplitude and photocurrent as a function of light intensity, PIA and transient photocurrent signals of photogenerated holes in a BiVO₄ photoanode for ferrocyanide oxidation measured under 5 s LED irradiation, rate law analyses.

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Notes

The authors declare no competing financial interests.

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