

## Contactless Measurement of the Photovoltage in BiVO<sub>4</sub> Photoelectrodes

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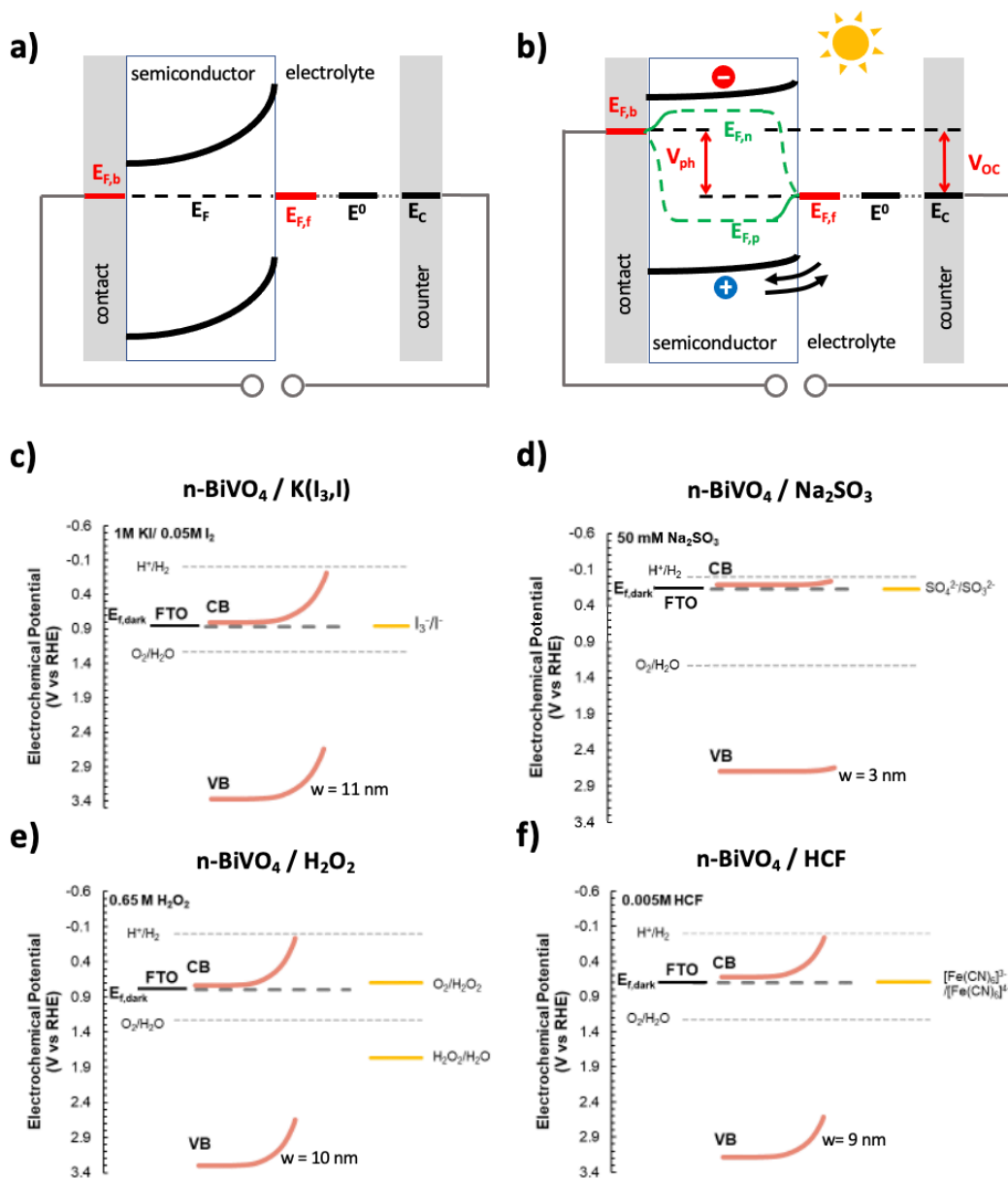
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### ABSTRACT

The power output of photoelectrochemical devices for solar energy-to-fuel conversion is determined by the photovoltage of the junction under illumination. In the presence of fast redox couples, the photovoltage can be obtained directly from current-voltage measurements of the device. However, for slow redox couples ( $H^+/H_2$ ,  $O_2/H_2O$ ) used in solar fuel photoelectrodes, photovoltage measurements are not straightforward, due to the kinetic overpotentials during charge transfer. Here we show that the photovoltage of BiVO<sub>4</sub> electrodes in contact with fast electron donors KI, Na<sub>2</sub>SO<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> or K<sub>4</sub>Fe(CN)<sub>6</sub> can be measured in a contactless way with vibrating Kelvin probe surface photovoltage (SPV) spectroscopy. The photovoltage varies with illumination wavelength and intensity and matches the open circuit potential of the electrodes, obtained separately from electrochemical measurements. Plots of the photovoltage versus irradiance can be used to predict the oxidizing power of each electrode under zero applied bias. Except for K<sub>4</sub>Fe(CN)<sub>6</sub>, which causes shunting in the BiVO<sub>4</sub> electrode, photovoltage values correlate well with the built-in potential of each junction. The ability to obtain photovoltage information through contactless SPV measurements will be useful in the search for solid-liquid junctions with superior energy conversion properties.

## INTRODUCTION

Photoelectrochemical devices for solar energy to fuel conversion, including photoelectrodes and photocatalysts, rely on the reactions of photogenerated charge carriers with redox species in the electrolyte. To drive a reduction or oxidation reaction, the electrochemical potential at the working electrode needs to exceed the standard reduction potentials of the acceptors or donors (e.g. 0.0 V for proton reduction or 1.23 V for water oxidation). Semiconductor electrodes promote these processes by generating a photovoltage  $V_{Ph}$  under illumination. The photovoltage corresponds to the difference of the electrochemical potentials at the back ( $E_{F,b}$ ) and front ( $E_{F,f}$ ) of the illuminated semiconductor – liquid junction, as shown in **Figure 1a** and **b**.<sup>1-5</sup> For a photoelectrode with ideal contacts (no recombination, hole or electron selectivity) the photovoltage  $V_{Ph}$  can approach the quasi-Fermi Level splitting energy (qFLS =  $E_{F,n} - E_{F,p}$ ).<sup>6-8</sup> Here  $E_{F,n}$  and  $E_{F,p}$  are the quasi-Fermi levels of the free electron and hole concentrations of the semiconductor in quasi-equilibrium with the exciting light source.<sup>9-12</sup> However, this situation is rarely approached in real photoelectrodes, where the  $E_{F,n}$  and  $E_{F,p}$  potentials are modified at the interfaces by the selectivity of charge transfer and by electron-hole recombination.<sup>1-3</sup>

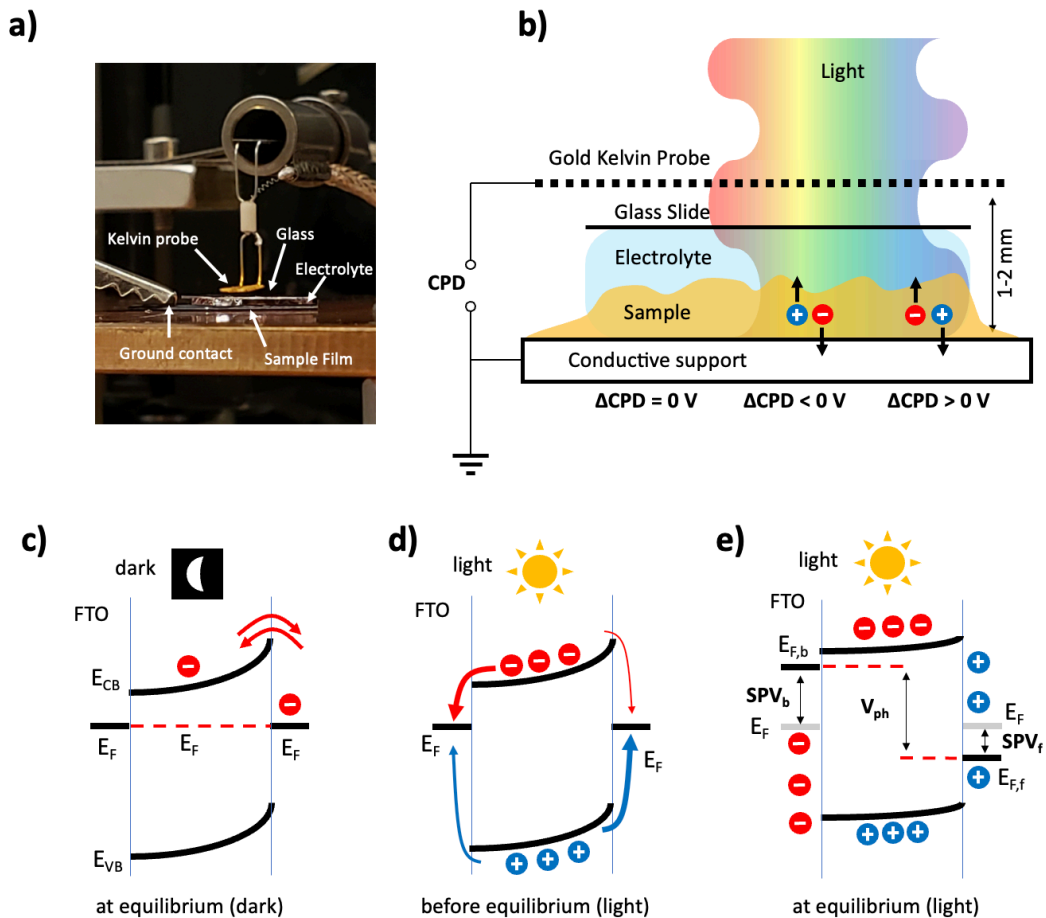


**Figure 1.** Energy diagram for n-semiconductor – liquid photoelectrochemical cell with a fast redox couple. a) In the dark the redox couple is in electrochemical equilibrium with the semiconductor and the counter electrode, so that  $E_{F,b} = E_{F,f} = E^0 = E_C$ . b) Under illumination the Fermi Levels split to produce the photovoltage,  $V_{Ph} = (E_{F,b} - E_{F,f})/e$ , where  $e$  is the electron charge, and  $E_{F,f}$  and  $E_{F,b}$  are the Fermi levels at the front and back of the semiconductor. The quasi-Fermi levels  $E_{F,n}$  and  $E_{F,p}$  are shown also. c-f) Band energy diagrams for BiVO<sub>4</sub> /liquid junctions in the dark. c) n-BiVO<sub>4</sub>/K(I<sub>3</sub>,I), d) BiVO<sub>4</sub>/ Na<sub>2</sub>SO<sub>3</sub>, e) BiVO<sub>4</sub>/ H<sub>2</sub>O<sub>2</sub>, f) BiVO<sub>4</sub>/ HCF (K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub>).  $w$  = calculated space charge layer width. Numerical data in **Table S1**.

In semiconductor photoelectrodes with fast and reversible redox couples,  $V_{Ph}$  can be obtained from open circuit voltage ( $V_{OC}$ ) measurements. This works because such redox couples are in electrochemical equilibrium with  $E_{F,f}$  of the semiconductor (**Figure 1a and 1b**). However, this condition is no longer fulfilled for slow redox couples ( $H^+/H_2$ ,  $H_2O/O_2$ ,  $CO_2/CH_3OH$ ) encountered in photoelectrosynthetic cells for the production of solar fuels. The slow charge transfer kinetics of these redox couples cause kinetic overpotential losses that are difficult to quantify because they depend on the electrode material, the photocurrent and other factors.<sup>3, 13</sup> For example,  $IrO_x$  has a water oxidation overpotential of 0.32 V,<sup>13</sup> whereas for  $Au_2O_3$  it is 0.95 V<sup>14</sup> (both at 10.0 mA cm<sup>-2</sup>). This makes it impossible to obtain the electrochemical potential  $E_{F,f}$  from standard photoelectrochemical measurements. In order to measure  $E_{F,f}$  in these cases, electric contact to the semiconductor-liquid junction is required. For example, Lobato et al.<sup>8</sup> and Zhang et al.,<sup>15</sup> measured the qFELS in dye-sensitized photoanodes after thermally evaporating a Ti foil electrode onto the porous  $TiO_2$  layer. Boettcher and coworkers observed the electrochemical potential of the hematite photoelectrode surface by adding a porous gold film to it.<sup>16, 17</sup> Alternatively, potential-sensing electrochemical atomic force microscopy was employed to measure the electrochemical potential at silicon/nickel/liquid interfaces,<sup>18, 19</sup> and recently at illuminated  $BiVO_4$ /polymer interfaces.<sup>20</sup>

Here we demonstrate an alternative, contact-less, non-invasive, and simple method for the determination of  $V_{Ph}$  and  $E_{F,f}$  in illuminated photoelectrodes. The approach employs Vibrating Kelvin Probe Surface Photovoltage Spectroscopy (VKP-SPS) as a highly sensitive technique (**Figure 2**) to observe photochemical charge separation in semiconductor thin films.<sup>21-23</sup> In VKP-SPS the contact potential difference (CPD) of a light-responsive material is measured with a

commercially available (*Besocke Delta Phi*) semitransparent gold Kelvin probe placed 1.0 - 2.0 mm above the sample. Illumination changes the charge carrier distribution to produce a surface photovoltage,  $SPV = CPD(light) - CPD(dark)$ . The wavelength dependence of the SPV signal, its size, sign, and reversibility, contain information about the sample band gap, the majority carrier type, the depletion layer, and defects.<sup>24-28</sup> The method is complementary to Kelvin Probe Force Microscopy (KPFM), which measures the surface photovoltage signal with an Atomic Force Microscopy (AFM) tip.<sup>22</sup>



**Figure 2.** a) Vibrating Kelvin Probe Surface Photovoltage (VKP-SPV) Spectroscopy in liquids (Photo.) b) Schematic of the measurement configuration. Sample illumination occurs through the 60% semi-transparent KP, placed 1-2 mm above the sample, and through the electrolyte, enclosed by a microscopy glass cover slide. A water-saturated gas environment serves to prevent drying out of the electrolyte. The Contact Potential Difference (CPD) change under

illumination equals the surface photovoltage signal  $SPV = CPD(\text{light}) - CPD(\text{dark})$ . c) Energetics and charge carrier dynamics of a n-semiconductor-liquid junction at equilibrium in the dark, d) upon illumination, e) at quasi-equilibrium under illumination. The scheme assumes that other contributions to the SPV signal (intra-molecular charge separation, photoinduced molecular adsorption / desorption, etc.) can be neglected. <sup>21</sup>

Inspired by Bastide et al's work in 1999 <sup>29</sup> we constructed the measurement configuration in **Figure 2a** to measure SPV for *semiconductor-liquid* contacts. Here, the electrically grounded light-sensitive sample is covered by a drop of the liquid electrolyte and a microscopy cover glass slide. The Kelvin probe is then positioned about 1.0 mm over the glass surface, and the sample is illuminated through the Kelvin probe. Under these conditions, the SPV signal is generated by charge carrier separation at the semiconductor-solution interface (**Figure 2b**) and directly corresponds to the photovoltage of the semiconductor-liquid junction. <sup>21-23</sup> The formation of the SPV signal can be quantitatively understood with the energy schemes in **Figure 2c-e**. In the dark, the Fermi level of the semiconductor is in electrochemical equilibrium with its interfaces at the back contact and the electrolyte. Illumination disrupts this equilibrium through production of photogenerated carriers. Transfer of the charge carriers to the back and front contacts is driven thermodynamically by the electrochemical potential gradients in the semiconductor and at its interfaces (**Figure 2d**). This produces the SPV signal with components  $SPV_b$  and  $SPV_f$  at the back and front, respectively, as defined in **equations 1** and **2**.

$$SPV_b = -(CPD_{b,fin} - CPD_{b,ini}) = -\frac{E_{F,b} - E_F}{e} \quad (\text{Eq. 1})$$

$$SPV_f = CPD_{f,fin} - CPD_{f,ini} = \frac{E_{F,f} - E_F}{e} \quad (\text{Eq. 2})$$

$$SPV = SPV_b + SPV_f = \frac{E_{F,f} - E_{F,b}}{e} = V_{Ph} \quad (\text{Eq. 3})$$

At quasi-equilibrium (**Figure 2e**) the electrochemical potentials of the back contact and the semiconductor-liquid interface equal  $E_{F,b}$  and  $E_{F,f}$ , respectively, and the SPV signal corresponds to  $V_{Ph}$  (**equation 3**).

In order to verify **equation 3** experimentally, we performed SPV and  $V_{OC}$  measurements for n-BiVO<sub>4</sub> photoelectrodes immersed in solutions of various fast redox couples. For these fast redox couples, the open circuit potential  $V_{OC}$  is expected to equal the photovoltage  $V_{Ph}$  of each junction (See **Figure 1b**). Thus, a comparison of the SPV signal to  $V_{OC}$  allows us to test **equation 3**. Full details on the outcome of the measurements are presented in the following.

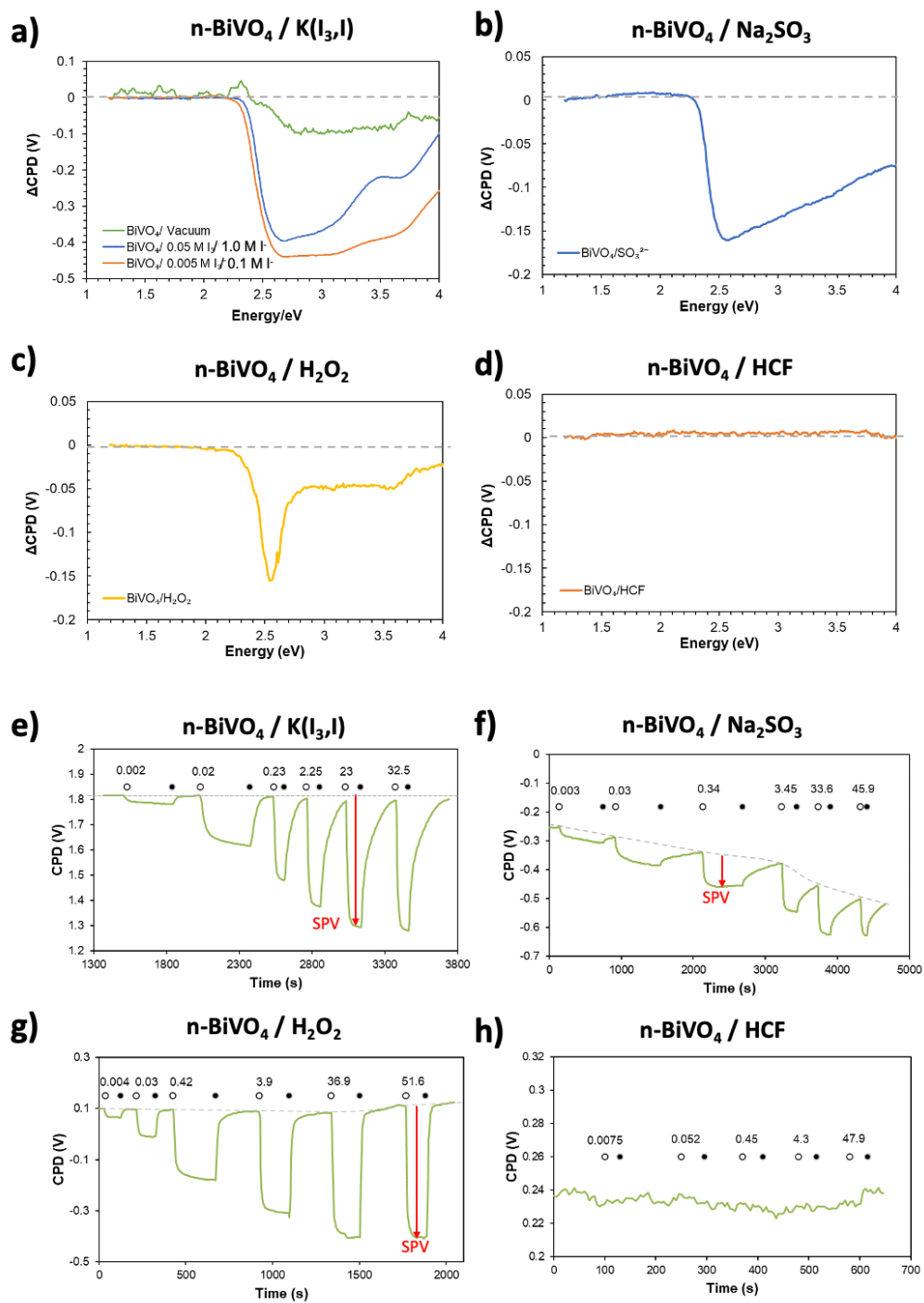
## RESULTS AND DISCUSSION

Based on their electronic properties (**Table S1**) n-BiVO<sub>4</sub> electrodes are expected to form a depletion layer when in contact with aqueous redox couples with standard reduction potentials oxidizing relative to the n-BiVO<sub>4</sub> flatband potential. The resulting band energy schemes are shown in **Figure 1c-f** for BiVO<sub>4</sub> in contact with aqueous solutions of K(I<sub>3</sub>,I), Na<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and iron hexacyanoferrate (II and III) (HCF). Built-in potentials vary between 0.17 V for the SO<sub>4</sub><sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> redox couple, to 0.89 V for the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> couple and depletion layers between 3 and 11 nm, respectively. Based on these energy diagrams, all BiVO<sub>4</sub> electrodes are expected to function as a photoanode under illumination.

SPV spectra acquired for a FTO deposited n-BiVO<sub>4</sub> film exposed to vacuum or aqueous KI/KI<sub>3</sub> solution are presented in **Figure 3a**. A negative surface photovoltage (SPV) signal forms when the photon energy approaches the band gap of BiVO<sub>4</sub> (2.40 eV), in agreement with the energy scheme

in **Figure 2c-e**. In vacuum (**Figure 2a**) the SPV spectrum is noisy and the SPV signal is small (-0.10 V) because the depletion layer is not yet fully formed. The addition of the KI/KI<sub>3</sub> electrolyte increases the SPV to values of -0.40 to -0.44, depending on the concentration. This is due to improved photohole transfer at the solid-liquid junction in **Figure 1c**. Strong SPV signals above the BiVO<sub>4</sub> band gap are also seen with aqueous Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> solutions electron donors, but not with K<sub>3/4</sub>[Fe(CN)<sub>6</sub>](aq), due to reasons discussed further below.





**Figure 3.** Surface photovoltage (SPV) spectra of a) BiVO<sub>4</sub> film on FTO in vacuum, or in contact with aqueous solutions of KI/KI<sub>3</sub>, b) Na<sub>2</sub>SO<sub>3</sub>, c) H<sub>2</sub>O<sub>2</sub>, or d) K<sub>3</sub>/4[Fe(CN)<sub>6</sub>] (HCF). e-h) Surface photovoltage data under monochromatic illumination of variable irradiance (mW cm<sup>-2</sup>). BiVO<sub>4</sub> film on FTO in contact with aqueous solutions of e) KI/KI<sub>3</sub> (470 nm), f) Na<sub>2</sub>SO<sub>3</sub> (400 nm), g) H<sub>2</sub>O<sub>2</sub> (400 nm), or h) K<sub>3</sub>/4[Fe(CN)<sub>6</sub>] (HCF) (400 nm). Empty circles are

light and filled circles are dark periods.  $SPV = CPD(\text{light}) - CPD(\text{dark})$ . Baseline drift is attributed to charge trapping at the solid-liquid interface. Repeat measurements and statistics are shown in **Figure S3** and **Table S4**.

The shape of the spectra is modulated by the intensity output of the Xe lamp,<sup>28</sup> which causes a decay of the SPV signal above 3.6 eV, and, in the case of **Figure 3b** by the irreversible redox oxidation of sulfite, as discussed further below. Changes in the SPV spectra for the two  $K(I_3, I)$  solutions are a result of competing light absorption (shading) by the  $I_3^-$  ion, which absorbs light at  $\lambda < 450$  nm.<sup>30</sup>

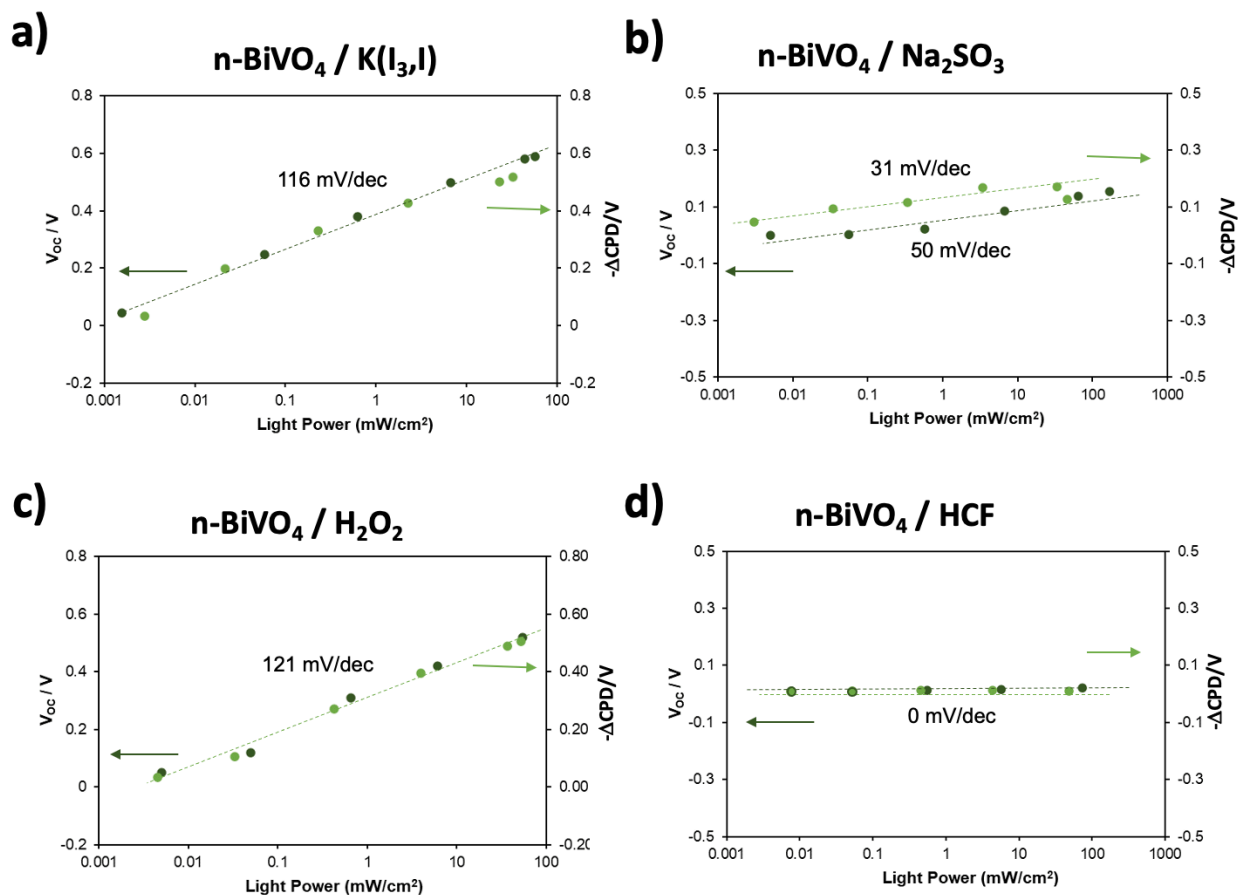
According to the Shockley diode equation (below), the open-circuit voltage of an illuminated diode increases with the logarithm of the absorbed light intensity.<sup>1, 3</sup> Therefore, to quantitatively correlate the SPV signal with the photoelectrochemical properties of each junction, SPV measurements on the  $BiVO_4$  liquid electrolyte configurations were repeated under 400 nm LED illumination with varied intensity (**Figure 3e-h**). For the n- $BiVO_4$ /  $K(I_3, I)$  system (**Figure 3e**), a 470 nm LED was used to minimize the effect of shading by the  $I_3^-$  ion. For this system, SPV signals under  $32.5 \text{ mW cm}^{-2}$  illumination form within seconds of light exposure ( $\tau_{\text{on}} = 10$  s) and decay back to baseline over the course of minutes ( $\tau_{\text{off}} = 61$  s) when the light is turned off. The slower  $\tau_{\text{off}}$  is due to charge transfer occurring by diffusion whereas charge separation ( $\tau_{\text{on}}$ ) occurs by drift in the electric field in the depletion layer. The return to baseline shows that photochemical charge separation in this system is reversible without notable charge trapping.

A different behavior is seen for the n- $BiVO_4$  film in contact with  $Na_2SO_3(aq)$ . Here the SPV signal is smaller, less reversible, and the baseline drifts to more oxidizing CPD values over the course of the experiment. This smaller SPV signal is due to the smaller built-in potential of the junction (0.07 V in **Table S1**), whereas the low reversibility and the baseline drift to more oxidizing values indicate the accumulation of photoholes near the  $BiVO_4$ /liquid interface. This is a result of the

irreversibility of sulfite oxidation under these conditions.<sup>31</sup> Larger and more reversible SPV signals are seen with H<sub>2</sub>O<sub>2</sub>, due to the larger built-in voltage of the n-BiVO<sub>4</sub> /H<sub>2</sub>O<sub>2</sub> junction and because of the fast electron transfer to O<sub>2</sub> (from H<sub>2</sub>O<sub>2</sub> oxidation). No SPV signal is observed for the n-BiVO<sub>4</sub> /HCF system, even at the highest light intensities. This is attributed to the fast reaction kinetics of the [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> redox couple, which promote back electron transfer from BiVO<sub>4</sub> or the FTO substrate to the oxidized [Fe(CN)<sub>6</sub>]<sup>3-</sup> ion. Shunting of metal oxide photoelectrodes with hexacyanoferrate has been previously observed with BiVO<sub>4</sub><sup>32</sup> and with Fe<sub>2</sub>O<sub>3</sub> photoelectrodes.<sup>33</sup> and is promoted by pinholes in the porous BiVO<sub>4</sub> film. Based on repeat measurements in **Figure S3** the SPV data is reproducible with a 6% standard deviation at the highest intensities. Standard deviations reach up to 67% for the BiVO<sub>4</sub>/Na<sub>2</sub>SO<sub>3</sub> system (**Figure S3 and Table S4**), as a result of baseline shifts associated with the irreversible charge transfer properties of the SO<sub>4</sub><sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> redox couple.

According to the diagram in **Figure 1b**, for these fast redox reagents, the photovoltage V<sub>Ph</sub> equals the open circuit potential (OCP) for semiconductor-liquid junctions. To verify that, OCP measurements were conducted for the four junctions in the dark and under variable light intensity (**Figure S5**). In the dark, the Fermi levels of all electrodes equal the electrochemical potential of the redox couples, in agreement with the band energy diagrams in **Figure 1**. For the BiVO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> electrode, E<sub>F</sub> (0.80 V RHE) is found 0.105 V positive of the H<sub>2</sub>O<sub>2</sub> oxidation potential (0.695 V RHE). This shows that E<sub>F</sub> is controlled in part by the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (1.78 V RHE) and O<sub>2</sub>/H<sub>2</sub>O (1.23 V RHE) redox couples, whose standard reduction potentials are much more positive. Under illumination, all photoanodes generate cathodic Fermi level shifts from the transfer of

photoelectrons toward the FTO/BiVO<sub>4</sub> interface. The largest potential changes (>0.60 V) are seen for BiVO<sub>4</sub>/K(I<sub>3</sub>,I) and the smallest (<0.04 V) for BiVO<sub>4</sub>/HCF.



**Figure 4.** Open circuit potentials ( $V_{oc}$ ) and  $-\Delta CPD$  values versus logarithmic irradiance ( $mW cm^{-2}$ ).  $V_{oc}$  values were calculated from the data in **Figure 3** and **S5** using **equation 4**.

From the  $E_{F,b}$  and  $E_F$  values in **Figure S5**, the open circuit voltage  $V_{oc}$  of each electrode can be calculated with **equation 4**.

$$V_{oc} = E_{F,b} - E_F (\text{dark}) \quad (\text{Eq. 4})$$

**Figure 4** plots the  $V_{OC}$  data and the SPV data versus the logarithm of the irradiance. With  $K(I_3, I)$ ,  $H_2O_2$ , and HCF electrolytes,  $V_{OC}$  values and SPV values are nearly identical over the entire irradiance range. This is an important confirmation of **equation 3**. For  $Na_2SO_3$ , SPV values are found to be  $\sim 100$  mV larger than  $V_{OC}$  values. This discrepancy arises because of the irreversible redox chemistry of the  $SO_4^{2-}/SO_3^{2-}$  redox couple under the measurement conditions. Because  $SO_4^{2-}$  cannot accept electrons from  $BiVO_4$ , positive charge (protons from  $2 h^+ + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2 H^+$ ) builds up at the  $BiVO_4$ /electrolyte interface. This shifts the  $E_F$  level to more oxidizing values after each illumination cycle as can be seen in the SPV baseline shift (0.25 V) in **Figure 3f** and in the OCP baseline shift (0.07 V) in **Figure S5b**. **Equation 4** does not capture this  $E_F$  variation and therefore underestimates the  $V_{OC}$  values by 0.07-0.25 V. As a result, the SPV values in **Figure 8b** are a more reliable descriptor of the open-circuit voltage of the  $BiVO_4/Na_2SO_3$  contact.

The Shockley diode equation (**equation 5**)<sup>34-36</sup> predicts a linear increase of SPV and  $V_{OC}$  values versus the logarithmic irradiance.\* The data in **Figure 4** mostly conforms to the equation. Deviations from linearity at higher light intensity for the  $V_{OC}$  with  $Na_2SO_3$  are attributed to the irreversibility of sulfite oxidation, as discussed above.

$$V_{OC} = n \frac{kT}{e} \ln \left( \frac{j_{phot}}{j_0} + 1 \right) \quad (\text{Eq. 5})$$

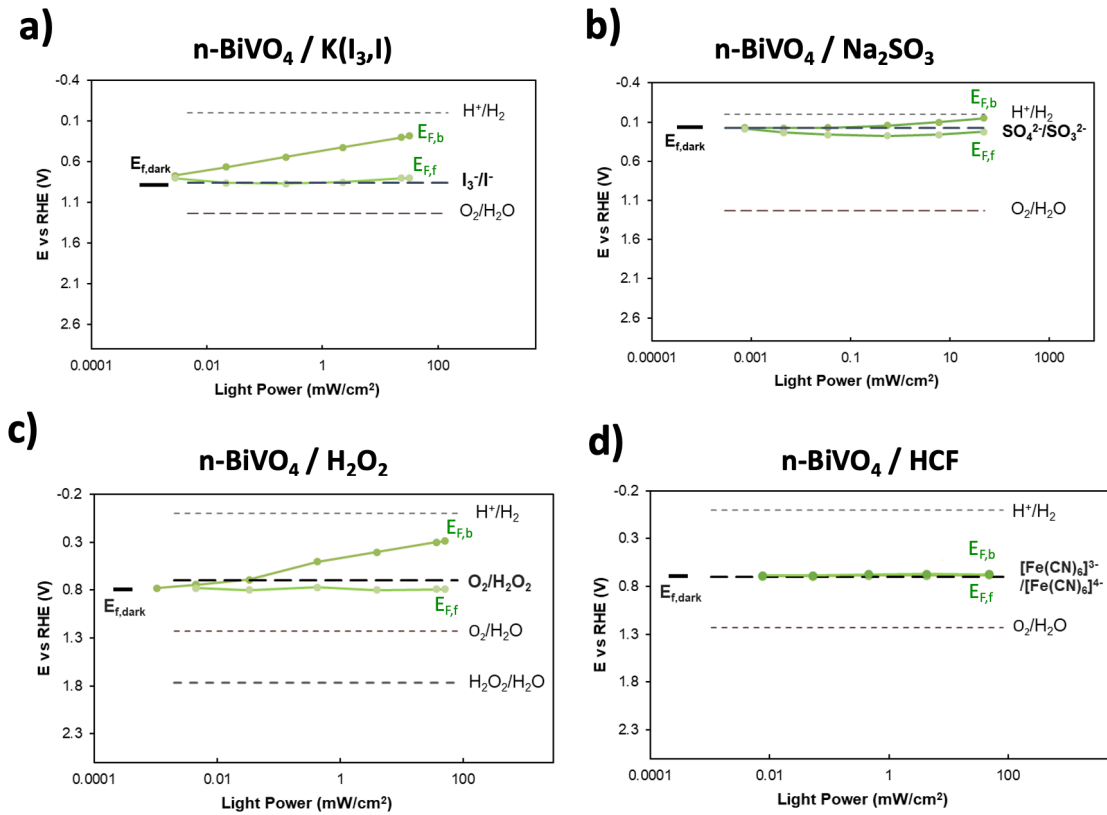
For ideal junctions, the open-circuit voltage increases by 59 mV for every decadic increase of the irradiance, corresponding to a diode ideality factor  $n=1$ . However, solid-liquid junctions in photoelectrochemical cells are rarely ideal because the built-in potential changes with the chemical

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\* In the equation,  $k, T$  and  $e$  have their usual meanings, and  $j_{phot}$  and  $j_0$  are the photocurrent density and reverse bias current density of the junction

composition and oxidation state of the interface.<sup>16, 37</sup> Indeed, experimental slopes for KI and H<sub>2</sub>O<sub>2</sub> are 116 - 121 mV dec<sup>-1</sup>, corresponding to ideality factors of 2.0 - 2.1, while the small slope of 31 mV dec<sup>-1</sup> for Na<sub>2</sub>SO<sub>3</sub> corresponds to  $n = 0.5$ . These deviations from ideality are due to the irreversibility of the SO<sub>4</sub><sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> redox couple under these conditions<sup>38</sup> and due to the multi-electron redox chemistry of H<sub>2</sub>O<sub>2</sub> and iodide oxidation.

Using the intensity-dependent  $V_{Ph}$  and  $E_{F,b}$  data, the absolute electrochemical potential  $E_{F,f}$  at the semiconductor-liquid interface can be calculated from **equation 3**. All  $E_F$  values are plotted versus the logarithmic irradiance in **Figure 5**.



**Figure 5.** Plots of Fermi Levels  $E_{F,b}$  and  $E_{F,f}$  versus logarithm of irradiance.  $E_{F,b}$  values are from open circuit potential measurements in **Figure S5** and  $E_{F,f}$  values were calculated from SPV data using **equation 3**.

In the dark, the  $E_{F,f}$  values of all electrodes are controlled by the electrochemical potentials of the redox couples. Illumination with increasing light intensity moves  $E_{F,b}$  to reducing potentials, whereas  $E_{F,f}$  values remain near the  $E^0$  solution potential. This confirms that the position of  $E_{F,f}$  is controlled by the electrochemical potential of the redox couples, as expected for these fast hole acceptors.<sup>38, 39</sup>  $E_{F,f}$  for  $\text{SO}_4^{2-}/\text{SO}_3^{2-}$  is  $\sim 0.1$  V more oxidizing than the  $E^0$  value for this redox couple. This is a result of the irreversible redox chemistry of sulfite, which leads to positive charge accumulation at the  $\text{BiVO}_4/\text{liquid}$  interface, and a corresponding shift of  $E_{F,f}$  to more oxidizing values. Comparing  $E_{F,f}-E_{F,b}$  differences at equal irradiance of  $15 \text{ mW cm}^{-2}$ ,  $\text{K}(\text{I}_3,\text{I})$  enables the largest open-circuit voltage (0.50 V), followed by  $\text{O}_2/\text{H}_2\text{O}_2$  (0.44 V), and  $\text{SO}_4^{2-}/\text{SO}_3$  (0.17 V). This trend follows the relative sizes of built-in potentials with KI (0.79 V),  $\text{H}_2\text{O}_2$  (0.7 V),  $\text{Na}_2\text{SO}_3$  (0.07 V) (**Table S1** and **Figure 4**). Larger built-in potentials enable better hole selectivity and lower electron-hole recombination. Despite the large band bending ( $V_{\text{bi}}=0.60$  V, see **Table S1**), the  $\text{BiVO}_4/\text{HCF}$  system does not produce a photovoltage because of back electron transfer via the  $\text{BiVO}_4$  conduction band or the FTO back contact.

Based on the Fermi level plots in **Figure 5**,  $\text{BiVO}_4$  photoanodes should be able to oxidize  $\text{Na}_2\text{SO}_3$ ,  $\text{H}_2\text{O}_2$ , and KI without applied bias, but not HCF. To test this prediction, short circuit current measurements with a Pt counter electrode were conducted. The results in **Figure S6** show that indeed, large short-circuit current ( $I_{\text{SC}}$ ) of  $>0.90 \text{ mA cm}^{-2}$  for the  $\text{BiVO}_4/\text{K}(\text{I}_3,\text{I})$  system and of  $2.5 \text{ mA cm}^{-2}$  for the  $\text{BiVO}_4/\text{H}_2\text{O}_2$  junction can be obtained. For the latter,  $\text{O}_2$  gas evolution is observed at the  $\text{BiVO}_4$  electrode (**Figure S1c**), confirming that the current is from  $\text{H}_2\text{O}_2$  oxidation. Similar gas bubbles are also seen at the end of the SPV experiment (**Figure S1b**). The relatively small short-circuit current ( $I_{\text{SC}}$ ) of  $\sim 32 \text{ } \mu\text{A cm}^{-2}$  for the  $\text{BiVO}_4/\text{Na}_2\text{SO}_3$  system is a result of the small open-circuit voltage of this junction. As expected, no photocurrent is seen with HCF because of

shunting. Overall, the photocurrent data confirms the validity of the quasi-Fermi Level plots in **Figure 5**.

## CONCLUSION

In summary these first Vibrating Kelvin Probe Surface Photovoltage (VK-SPV) measurements on BiVO<sub>4</sub> in contact with liquid electrolytes show that the SPV signal equals the photovoltage ( $V_{Ph}$ ) of each electrode.  $V_{Ph}$  values depend on illumination wavelength and irradiance, as predicted by the Diode equation. By combining the  $V_{Ph}$  data with open circuit potential measurements, the electrochemical potentials  $E_{F,f}$  at the front of the photoelectrodes can be estimated. We find that  $E_{F,f}$  values are ‘pinned’ to the electrochemical potential of the respective redox couples because of rapid hole transfer from BiVO<sub>4</sub>. Except for  $[Fe(CN)_6]^{3-/4-}$ , which causes shunting, the  $V_{Ph}$  values correlate well with the built-in voltage  $V_{bi}$  of each system. This confirms  $V_{bi}$  as an important predictor of the energy conversion efficiency of BiVO<sub>4</sub> photoelectrodes. Because the VKP-SPV technique is non-destructive and non-invasive, it should be of significant value in the search for new photoelectrodes and photocatalysts for the conversion of solar energy into fuels and electricity.

## CONFLICTS OF INTEREST

There are no conflicts of interest to declare.



## EXPERIMENTAL SECTION

Bismuth(III) nitrate pentahydrate (99.999 %, Acros Organics), Nitric acid (70.0 %, Sigma-Aldrich), Vanadyl acetylacetonate (99%; Acros Organics), Dimethyl sulfoxide ( $\geq 99.9\%$ ; Sigma-Aldrich), P-benzoquinone ( $\geq 98\%$ ; Sigma-Aldrich), Potassium iodide (99.0%; Merk), Iodine ( $\geq 99.8\%$ ; Sigma-Aldrich), Sodium sulfate ( $\geq 99.0\%$ ; Sigma-Aldrich), Potassium hexacyanoferrate(II) trihydrate (98.5-102.0%; Sigma-Aldrich), Potassium ferricyanide (99.2%; Sigma-Aldrich), Sodium sulfite ( $\geq 98\%$ ; Sigma-Aldrich), Sodium sulfite ( $\geq 98\%$ ; Sigma-Aldrich), Potassium phosphate monobasic (98%; Sigma-Aldrich), Hydrogen peroxide (30% aqueous solution, by weight; Sigma-Aldrich), Sodium hydroxide ( $\geq 97\%$ ; Sigma-Aldrich), were used as-received.

n-BiVO<sub>4</sub> films were prepared on fluorine doped tin oxide (FTO) by electrochemical deposition of BiOI followed by reaction with VO(acac)<sub>2</sub> at 450 °C according to Kyoung-Shin Choi's method and etching in 1.0 M NaOH solution.<sup>39</sup>

Surface photovoltage (SPV) data was obtained with the vibrating Kelvin probe technique, using a semi-transparent (60%) 3.0 mm diameter gold Kelvin probe (*Kelvin Probe S, Delta PHI Besocke*) and a *Besocke Kelvin Control*. Measurements were conducted in a custom-made chamber under vacuum ( $\leq 2 \times 10^{-4}$  mbar) or in H<sub>2</sub>O-saturated N<sub>2</sub> gas. Samples were coated with 10-15  $\mu$ L of liquid electrolytes using a micropipette and covered with a glass cover slip (Fisher Scientific, 0.17 to 0.25 mm thickness). For the acquisition of full spectra, samples were illuminated through the Kelvin probe using light from a 300 W Ce lamp filtered through an Oriel Cornerstone 130 monochromator (1-10 mW cm<sup>-2</sup>). Scans were performed from 9600 cm<sup>-1</sup> to 40000 cm<sup>-1</sup> by stepping

the photon energy by 0.0124 eV every 5 s and by measuring the contact potential difference (CPD) value at each step. The light exiting the monochromator had a FWHM (full-width/half-maximum) of 8 nm–15 nm, depending on the wavelength, and an average intensity of 50  $\mu\text{W}/\text{cm}^2$  in the 2.0 eV–3.6 eV interval. The contact potential difference (CPD) data were corrected for drift effects by subtracting a fitted logarithmic curve of a dark scan from the spectral scan.

Intensity-dependent measurements were performed with air-cooled 400 nm or 470 nm LED arrays connected to a DC power supply. The voltage was regulated to produce irradiances of  $5 \times 10^{-4}$  – 60  $\text{mW}/\text{cm}^2$  at the sample surface, as measured by a photometer equipped with a GaAsP UV-Vis detector (International Light Technologies, Inc), and after correction using a 60% transmission value for the Kelvin probe.

Open circuit potential (OCP) measurements were conducted with a Gamry Reference 600 potentiostat in a two-electrode system consisting of the sample as working electrode and a calomel electrode (3.5 M KCl) as counter electrode. All electrolytes were purged with  $\text{N}_2$  for 20 min before and during the measurements, except for  $\text{H}_2\text{O}_2$  solutions, which were left open to air. The cell was calibrated using the standard reduction of potential of hexacyanoferrate (0.358 V vs NHE) and potentials were then adjusted to the RHE scale using the formula  $V_{\text{RHE}} = V_{\text{NHE}} + 0.0592 \times \text{pH}$ . Illumination was provided by 400 nm or 470 nm LEDs.

Chronoamperometry scans were performed in a 2-electrode set-up, with the sample as the working electrode and a Pt wire as both the counter and reference electrode. For  $\text{H}_2\text{O}_2$  short circuit photocurrent measurement, a graphite electrode was used as both the counter and reference electrode to avoid  $\text{H}_2\text{O}_2$  disproportionation. A 0 V bias was applied and a 400 nm or 470 nm LED was used as the light source.

Electrolytes were prepared as follows: 1.0 M phosphate buffer stock solution (PBS) at pH 6.66 was prepared by dissolving 3.40 g  $\text{KH}_2\text{PO}_4$  in 250 mL of water, followed by adjusting the pH to 6.66 with 2M KOH solution. 0.05 M PBS was prepared by diluting the stock solution and by adjusting the pH further with 2.0 M KOH to 6.66. pH was measured with a pH meter (Fisher Scientific *Accumet* AE150). 0.05 M  $\text{Na}_2\text{SO}_3$  in 0.1M  $\text{Na}_2\text{SO}_4$  was prepared by adding 0.630 g  $\text{Na}_2\text{SO}_3$  to 100 mL of 0.1M  $\text{Na}_2\text{SO}_4$  (0.05 M  $\text{Na}_2\text{SO}_3$  pH=9.58). 5 mM HCF in 0.1M  $\text{Na}_2\text{SO}_4$  was prepared by adding 0.0739 g of  $\text{K}_4\text{Fe}(\text{CN})_6$  and 0.0576 g of  $\text{K}_3\text{Fe}(\text{CN})_6$  to 35 mL of 0.1 M  $\text{Na}_2\text{SO}_4$  (5 mM HCF pH=5.6). 0.65 M  $\text{H}_2\text{O}_2$  in 0.1M  $\text{Na}_2\text{SO}_4$  was prepared by adding 2.0 mL of a 30% aqueous  $\text{H}_2\text{O}_2$  to 28 mL of 0.1 M  $\text{Na}_2\text{SO}_4$  (0.65 M  $\text{H}_2\text{O}_2$  pH=4.21). 0.05 M triiodide solution in 0.05 M PBS was prepared by making a 95%/5% molar ratio between KI and  $\text{I}_2$  solutions. For that, 1.0 M KI/0.05 M  $\text{I}_2$  was prepared by adding 1.66 g of KI and 0.128 g of  $\text{I}_2$  to 0.05 M PBS. 10 times diluted solution was prepared by preparing 0.1M KI/5 mM  $\text{I}_2$  through adding 0.166 g of KI and 0.0128 g of  $\text{I}_2$  to 0.05 M PBS.

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## AUTHOR CONTRIBUTIONS

The experiments were designed by F.E.O and S.D. and conducted by S.D. The manuscript was written by F.E.O and S.D. with contributions by A.K, K.B., and P.C. All authors have given approval to the final version of the manuscript.

## SUPPORTING INFORMATION

The following supporting information is available: Selected Semiconductor Data, Photos of the Photoelectrodes, Open Circuit Potential Data, Short Circuit Photocurrent Data.

## DATA AVAILABILITY

Data will be made available at the UC Davis University Repository at <https://datadryad.org> and can be downloaded using the following link: <https://doi.org/10.25338/B83H0K>

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