## **Supplementary Information for**

## Accelerating Water Oxidation on BiVO<sub>4</sub> Photoanodes via Surface Modification with Co Dopants

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## **Experimental Methods**

**Preparation of the photoanodes:** BiVO<sub>4</sub> photoanodes were prepared by electrodeposition of bismuth oxyiodide (BiOI) film followed by dripping vanadium source and heat treatment <sup>1</sup>. BiOI electrodeposition solution was prepared by dissolving 1.49 g of sodium iodide (NaI) in 25 mL of DI water (pH adjusted to 1.8 using nitric acid) and the addition of 480 mg of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O. Then, 240 mg of p-benzoquinone was dissolved in 10 mL ethanol and stirred for 15 minutes. Two solutions were mixed up and stirred for 30 min. The electrodeposition of the BiOI film was done by applying -0.1 V vs. Ag/AgCl electrode for 2 min. The remaining solution was removed from the surface of the film by washing with DI water followed by drying in air. 2 µl of 0.4 M solution of VO(acac)<sub>2</sub> in dimethyl sulfoxide (DMSO)was dropped on BiOI films with a 1 cm<sup>2</sup> area. After 5 min wait time for penetration of the solution into porous BiOI film, the extra solution was removed by gentle touching of the edge of the glass substrate on a filter paper. The films were annealed at 450 °C for 2 h (ramping rate of 2 °C/min) in air. After cooling down the photoanodes, extra vanadium oxide was removed from the photoanodes by soaking them in 1 M NaOH solution for 30 min while gently stirring. For preparing Co-doped BiVO<sub>4</sub>, the CoO<sub>x</sub> layer was deposited on BiVO<sub>4</sub> photoanodes by atomic

layer deposition (ALD) using Cambridge Nanotechnology Savannah 200 system. Cobaltocene  $(Co(C_5H_5)_2)$  was used as the reactant precursor. The temperature of the precursor was 85 °C and the reactor temperature was set to 150 °C during deposition. Each ALD cycle consisted of a 3 s pulse of cobaltocene, a 10 s purge in N<sub>2</sub> at 20 sccm, and a 0.01 s O<sub>3</sub> pulse followed by a 15 s purge on N<sub>2</sub> again. This process was repeated for 5, 10, 15, 20, and 25 cycles and the optimum amount of deposition was obtained. The photoanode after deposition of CoO<sub>x</sub> is named BiVO<sub>4</sub>/CoO<sub>x</sub>. In order to make surface doped photoanode, Co-BiVO<sub>4</sub>, a mild thermal treatment at 200 °C for 2 h was done on BiVO<sub>4</sub>/CoO<sub>x</sub> films under O<sub>2</sub> flow. CoO<sub>x</sub> was deposited on BiVO<sub>4</sub> using a different number of ALD cycles and the highest photocurrent density was achieved for 20 ALD cycles. Current-voltage behavior for BiVO<sub>4</sub> films with 10, 20, and 25 CoO<sub>x</sub> ALD cycles before and after heat treatment are shown in Fig. S1.

**Structural and surface characterizations:** Raman spectroscopy investigations were done via Renishaw Invia Raman Microscope using a 532 nm excitation laser source. UV-visible spectra were collected (via Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer) in diffuse reflection mode and converted to absorption spectra by Kubelka-Munk transformation. EPR measurements were performed with the spectrometer of Bruker EMX Nano with an integrated referencing for g-factor calculation and also integrated spin counting units. The microwave frequency of the resonator was 9.63 GHz (X-band) and all spectra were measured at room temperature with 1 G modulation amplitude, 10 mW microwave power, and 50 scans. Each scan has a sweep time and time constant of 120 s and 81.92 ms, respectively. Samples were inserted into spin-free 25 cm long quartz tubes (Qsil, Germany).

XPS analysis was carried out by utilizing a Thermo K-alpha laboratory XPS system equipped with a monochromatized Al K- $\alpha$  X-ray source. For angle-resolved XPS, an emission angle of 67° was used and the ratio of Bi/Co is obtained from Bi 4f and Co 2p peak areas and compared with the normal electron emission measurement with the angle of 0°. The ratios of Bi/Co were determined by using the integrated area of Bi 4f and Co 2p XPS peaks and sensitivity factors according to the below equation:

$$\frac{n_{Bi}}{n_{Co}} = \frac{I_{Bi} S_{Co}}{I_{Co} S_{Bi}}$$

where n is the number of atoms per  $\text{cm}^3$ , I is the area under the peak, and S is the elemental sensitivity factor. The sensitivity factor of Bi 4f and Co 2p were 38.3 and 18.24, respectively.

**Photoelectrochemical (PEC) measurements:** Photoelectrochemical measurements were performed in a quartz cell with a three-electrode configuration, using a platinum counter electrode, Ag/AgCl (Sat. KCl) reference electrode, and prepared photoanodes as the working electrode. An LCS-100 solar simulator with 1.0 Sun AM 1.5G output from a 100 W Xenon Lamp and a VSP-300 BioLogic potentiostat were utilized for the photoelectrochemical activity measurements in dark and under illumination. Nernst equation was used to convert the measured potential from V vs. Ag/AgCl to V vs. RHE (reversible hydrogen electrode):

 $V(V) = V_{Ag/AgCl}(V) + 0.059 \times pH + V_{Ag/AgCl}^{0}(V)$ 

where V is the applied potential versus RHE;  $V_{Ag/AgCl}$  (V) is the applied potential versus Ag/AgCl reference electrode during measurements;  $V_{Ag/AgCl}^0$  (V) is the standard potential of the reference electrode (0.197 V). All the potentials mentioned are vs. RHE.

Water oxidation measurements were carried out in 0.1 M potassium phosphate (KPi) buffer electrolyte with pH=7.5. Sulfite oxidation measurements were performed in the presence of 0.5 M sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) as a hole scavenger. Transient photocurrent densities (j) versus time were measured under chopped light by a homemade light chopper. Linear sweep voltammetry (LSV) measurements were performed with a scan rate of 50 mV/s.

Flat band potential ( $V_{FB}$ ) and carrier densities ( $N_d$ ) were obtained by utilizing the Mott-Schottky equation (Equation 1). The details can be found in the literature <sup>2</sup>. The MS analysis was performed in 0.1 M KPi buffer electrolyte (pH 7.5) containing 0.5 M Na<sub>2</sub>SO<sub>3</sub> in the dark at the frequency of 1 kHz.

Carrier density is calculated from the slopes of the MS equation below:

$$\frac{1}{C^2} = \left(\frac{2}{\varepsilon_r \varepsilon_0 A^2 e N_d}\right) (V - V_{fb} - \frac{kT}{e})$$
Equation 1

Herein,  $\varepsilon_r$  is the relative permittivity of the media (~ 68 for BiVO<sub>4</sub> <sup>3</sup>),  $\varepsilon_0$  is permittivity in the vacuum (8.85 × 10<sup>-12</sup> F/m), A is the surface area, e is the charge of an electron (1.6×10<sup>-19</sup> C), N<sub>d</sub> is the free carrier density, E<sub>fb</sub> is the flat band potential, k is the Boltzmann constant (1.380649 × 10<sup>-23</sup> m<sup>2</sup>.kg/(s<sup>2</sup>K)), and T is the temperature (K) <sup>2</sup>.

The slope is inversely proportional to carrier density (N<sub>d</sub>) according to Equation 2:

Slope = 
$$\frac{2}{\epsilon_r \epsilon_0 A^2 e N_d}$$
 Equation 2

Charge injection efficiency  $(\eta_{inj})$  was calculated from  $j_{water}/j_{sulfite}$  ratio where  $j_{sulfite}$  is the photocurrent density for sulfite oxidation and  $j_{water}$  is the photocurrent density for water oxidation in the absence of Na<sub>2</sub>SO<sub>3</sub><sup>4</sup>.

Incident photon conversion efficiency (IPCE) was measured using the same three-electrode cell and electrolyte via a Newport monochromator coupled to a 300 W Xenon Lamp. IPCE values were calculated by the following ratio:

IPCE =  $[j (mA/cm^2) \times 1239.8 (V.nm)] / [P_{\lambda} (mW/cm^2) \times \lambda (nm)]$ 

where j is the photocurrent density under illumination at a wavelength  $\lambda$  of the incident light,  $P_{\lambda}$  is the power of light at each wavelength. All PEC measurements under illumination were performed in front illumination mode.

Electrochemical surface area (ECSA) comparisons for the photoanodes were performed by capacitance measurements. Cyclic voltammetry was recorded in dark in 0.1 M KPi electrolyte using different scan rates: 25, 50. 100, 200, 300, and 400 mV/s. Current density differences in cathodic and anodic cycles were plotted against the potential scan rates and the slope of this plot was used to compare the ESCA.

**Transient photocurrent (TPC) measurements with pulsed LED light:** TPC measurements were performed using white-LED light pulses with 50.0 ms, pulse widths under different anodic potentials. The photocurrent response was measured at every 400.0  $\mu$ s. The power of the white LED was measured to be 15.0 mW/cm<sup>2</sup>.

**Transient absorption spectroscopy (TAS) measurements:** TAS measurements were performed with a pump-probe spectrometer. A commercial Ti:sapphire regenerative amplifier (MKS Spectra-Physics, Spitfire Ace) operating at 800 nm and producing <150 fs pulses at a repetition rate of 1 kHz was used to generate pump pulses at 320 nm in an optical parametric amplifier (Light Conversion, TOPAS). The probe beam (between 360 and 900 nm) obtained via supercontinuum generation in a photonic crystal fiber had a sub-nanosecond pulse duration (EOS, Ultrafast Systems). The delay between the pump and probe beams was controlled electronically. The change  $\Delta A$  in the nonlinear absorbance spectrum was then

measured as a function of the probe delay by using a fiber-coupled spectrograph. Here,  $\Delta A$  corresponds to the difference in the absorbance of the pumped and unpumped sample.

**DFT calculations:** DFT calculations were carried out using the Gaussian Plane Waves method as implemented in the CP2K code, using Goedecker-Teter-Hutter pseudopotentials to describe core-valence interactions <sup>5–8</sup>. Wavefunctions were expanded in double- $\zeta$  polarized MOLOPT basis sets as well as an auxiliary plane-wave basis defined up to an energy of 600 Ry <sup>9</sup>. The hybrid exchange-correlation functional PBE0-TC-LRC with 22 % exact exchange was used along with the auxiliary density matrix method <sup>10–13</sup>. The Brillouin zone was sampled at the  $\Gamma$  point. Atomic positions were relaxed until all residual forces were less than 10 meV/Å. The details of defect formation energy calculations may be found for instance in Refs. 47 and 48. The spurious interactions between charges in the repeated slab model are handled using the correction scheme of Freysholdt and Neugebauer <sup>16</sup>.



**Figure S1.** LSV curves of BiVO<sub>4</sub> photoanodes with  $CoO_x$  deposited by various ALD cycles: (a) before heat treatment (BiVO<sub>4</sub>/CoO<sub>x</sub>) and (b) after heat treatment at 200 °C for 2 h (Co-BiVO<sub>4</sub>). Measurements were performed in 0.1 M KPi electrolyte. The highest PEC activity was obtained for 20 cycles of CoO<sub>x</sub> deposition.



Figure S2. SEM images of (a) BiVO<sub>4</sub>, (b) BiVO<sub>4</sub>/CoO<sub>x</sub>, and (c) Co-BiVO<sub>4</sub>.



**Figure S3.** GiXRD patterns of the photoanodes after  $CoO_x$  deposition before and after heat treatment. FTO peaks are shown by asterisk signs. (Smaller FTO peaks in the red pattern are due to the alignment of the sample in GiXRD setup).



Figure S4. UV-visible absorption spectra and Tauc plots (inset) calculated from the absorption data of each photoanode.

The optical properties were studied by UV-visible spectroscopy, which showed that all photoanodes have absorption edges in the visible region (Fig. S4). The bandgap of 2.5 eV was obtained from a Tauc analysis which is the specific bandgap for monoclinic  $BiVO_4$ <sup>17</sup>. No significant change in bandgap energy either after  $CoO_x$  deposition or by Co doping into the surface has been observed. This suggests that the bulk of  $BiVO_4$  remained unchanged after the deposition of  $CoO_x$  and heat treatment.

Table S1. Bi/Co ratio obtained from Bi 4f and Co 2p XPS measurements.

Emission angle	CoO <sub>x</sub> /BiVO <sub>4</sub>	Co-BiVO <sub>4</sub>
0°	28	32.5



**Figure S5.** Bi 4f and Co 2p XPS spectra for  $BiVO_4/CoO_x$  (a) and (b) and for Co- $BiVO_4$  (c) and (d) at different measurement angles.



**Figure S6.** Defect formation energies for surface cobalt incorporation under (a) O-rich, Bi-poor conditions, and (b) O-, moderate, Bi-moderate conditions. The chemical potentials are taken from a previous theoretical study by Österbacka *et al.* <sup>18</sup>



**Figure S7.** The geometry of a singly ionized oxygen vacancy at the surface with the excess electron, shown by the blue isosurface, localized at (a) the subsurface site of the vacancy and (b) far away from the vacancy. The localization site in (a) is stabler by  $\sim$ 230 meV. The structure is presented by red (O), gray (V), and coral (Bi) atoms.



**Figure S8.** The geometry of a singly ionized cobalt-oxygen vacancy complex at the surface with the excess electron, shown by the blue isosurface, localized at (a) the surface site of the vacancy and (b) far away from the vacancy in the subsurface. The localization site in (b) is stabler by  $\sim$ 150 meV. The structure is presented by red (O), gray (V), and coral (Bi) atoms.



**Figure S9.** (a) Current density (i) vs. scan rate obtained by the capacitive measurement shown in (b) to (d) at different scan rates from 25 mV/s to 400 mV/s.



Figure S10. Tafel plots obtained from LSV measurements in dark. The slopes of lines are 998 mV/dec for  $BiVO_4$ , 575 mV/dec for  $CoO_x/BiVO_4$ , and 360 mV/dec for  $Co-BiVO_4$ .



Figure S11. The stability of the photoanodes at 1.23 V in 0.1 M KPi buffer.



Figure S12. Mott-Schottky plots at 1 kHz measured in KPi electrolyte with 0.5 M Na<sub>2</sub>SO<sub>3</sub>.

	$\tau_1$ (µs) at 480 nm	$\tau_1$ (µs) at 600 nm
BiVO <sub>4</sub>	$0.181 \pm 0.002$	$0.110 \pm 0.006$
BiVO <sub>4</sub> /CoO <sub>x</sub>	$0.145 \pm 0.002$	$0.255 \pm 0.017$
Co-BiVO <sub>4</sub>	$0.386 \pm 0.012$	$0.456\pm0.028$

Table S2. The lifetime of the excited state charge carriers at 480 and 600 nm.

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