+Supporting Information

Cobalt doped BiVO$_4$ with rich oxygen vacancies for efficient

photoelectrochemical water oxidation

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Experiment section

Chemical reagents and Instruments

Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, ≥ 98.0%), Vanadium(IV)oxy Acetylacetonate (VO(acac)$_2$, 98%), were purchased from Aladdin. p-Benzoquinone (≥ 98.0%) and Cobaltous chloride (CoCl$_2$, 99.5%) was supplied by Sinopharm Chemical Reagent Co., Ltd. Potassium iodide (KI, ≥ 98.5%) was purchased from Tianjin Guangfu Development Co., LTD. High purity water (18.2 MΩ/cm) supplied by a Milli-Q system (Millipore, Direct-Q 3 UV) was used in all experiments. FTO substrates were purchased from Dalian Heptachroma SolarTech Co., Ltd. (thickness of ~2.2 mm, transmittance of > 90%, resistance < 15 Ω/cm^2). Before using, the FTO substrates were ultrasonically cleaned in deionized water, ethanol, and acetone, respectively. All other reagents were commercially available and used as received.

UV-vis diffuse reflectance spectrum (DRS) of the sample was measured using a Shimadzu UV-2000 spectrophotometer. Electrochemical measurements were taken with a CHI760E electrochemical potentiostat (Shanghai Chenhua, China). X-ray Diffraction (XRD) was collected with a SmartLab 9KW diffractometer using Cu Kα radiation (154.1 nm). Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) mapping of the electrodes were conducted with a Hitachi SU8220 instrument with an accelerating voltage of 5.0 kV. Transmission Electron Microscope (TEM) was carried out by Thermo Scientific TF30 instrument X-ray photoelectron

spectroscopy (XPS) measurement was performed on a Thermo ESCALAB XI+ instrument using 150 W Kα radiate.

Preparation of BiVO$_4$ and Co-BiVO$_4$ photoanode

BiVO$_4$ and Co-BiVO$_4$ films were prepared by electrodeposition.[1] First, the 2 mmol of Bi(NO$_3$)$_3$ was dissolved in 50 mL of a pH 1.7 HNO$_3$ solution. After the mixture was stirred for 5 min, 20 mmol of KI was added to the solution at room temperature and the mixture was stirred for another 5 min. This solution was mixed with 20 mL of absolute ethanol containing 4.6 mmol of *p*-benzoquinone and was vigorously stirred for a few minutes. Then cobaltous chloride dissolved in the solution forms a (0, 2.5, 5, 7.5, 10, 12.5mg/ml) Co^{2+} precursor solution. A typical three-electrode cell containing a fluorine-doped tin oxide (FTO) working electrode, a saturated Ag/AgCl reference electrode, and a Pt wire counter electrode were used for electrodeposition. Electrodeposition was carried out at constant potential -0.1 V vs. Ag/AgCl for 3 min to obtain the BiOI and Co-BiOI electrode, which was rinsed with deionized water and dried in ambient air. The BiVO$_4$ and Co-doped BiVO$_4$ film were prepared by placing 30 μL dimethyl sulfoxide (DMSO) solution containing 0.2 M vanadyl acetylacetonate (VO(acac)$_2$) on the BiOI electrodes, followed by heating in a muffle furnace at 450 °C (ramping rate 2 °C/ min) for 2 h. After they cooled to room temperature, the electrodes were soaked in 1 M NaOH solution for 30 min to remove the excess V$_2$O$_5$. The obtained pure BiVO$_4$, 2.5Co-BiVO$_4$, 5Co-BiVO$_4$, 7.5Co-BiVO$_4$, 10Co-BiVO$_4$ and 12.5Co-BiVO$_4$ electrodes were rinsed with deionized water and dried in air.

Electrochemical and photoelectrochemical Measurements

Photoelectrochemical and electrochemical performances of as-prepared anodes ($BiVO_4$, $Co-BiVO_4$) were collected in a standard three-electrode system, with the anodes as the working electrodes, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode controlled by a CHI 760E potentiostat. The simulated solar illumination was obtained by passing light from a 300 W xenon lamp equipped with an AM 1.5 filter, and the power intensity of the incident light was calibrated to 100 mW/cm^2 using a THORLABS PM100D S121C photodetector. The 0.5 M sodium borate buffer solution (pH 9.3) was used as the electrolyte, which is obtained by dissolving 0.5 mol of H_3BO_3 in 1L deionized water, followed by adding NaOH to adjust the pH to 9.3. The photocurrent was measured by linear sweep voltammetry with a scan rate of 10 mV/s. The recorded potential versus Ag/AgCl ($E_{Ag/AgCl}$) was converted against RHE using the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059$ pH). The data were collected by back illumination.

Electrochemical impedance spectroscopy (EIS) of the as-prepared film electrodes was measured at 1.23 V vs. RHE in a frequency range of 0.1-100000 Hz with an amplitude of 5 mV in 0.5 M sodium borate buffer solution (pH 9.3) under 100mW/cm^2 irradiation. The measured EIS spectra were fitted by Zview software using the proposed equivalent circuit model. The incident photon-to-current conversion efficiency (IPCE) of as-prepared films was measured at 1.23 V vs. RHE in 0.5 M sodium borate buffer solution (pH 9.3) under irradiation of monochromatic light. Incident light power was

measured using a THORLABS PM100D S120VC photodetector. The IPCE at each

wavelength was calculated by the following equation:

$$IPCE\ (\%) = \frac{1240 \times (J_{light} - J_{dark})}{\lambda \times P_{light}} \times 100\%$$

Where J is the photocurrent density (mA/cm^2), P_{light} is the incident light power

density (mW/cm^2), and λ is the wavelength (nm) of the incident light.

The applied bias photon-to-current efficiency (ABPE) was calculated by the

following equation:

$$ABPE(\%) = \frac{(J_{light} - J_{dark}) \times (1.23 - V_{bias})}{P_{light}} \times 100\%$$

where J is the photocurrent density, V_{bias} is the applied potential, P_{light} is the

incident light power density (mW/cm^2).

The donor densities and flat band potential of BiVO$_4$ and Co-doped BiVO$_4$ films

were investigated using the Mott-Schottky measurement at a frequency of 1 kHz in

dark. The donor densities was determined using the following equation:

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_d} [(V - V_f) - \frac{KT}{e}]$$

$$N_d = \frac{2}{e\varepsilon\varepsilon_0} [\frac{d\left(\frac{1}{C^2}\right)}{d_V}]^{-1}$$

where C is the differential capacitance of the space-charge region, ε is the relative

dielectric constant of sample, ε_0 is the permittivity of vacuum, A is the surface area of sample, N_d is the concentration of charge carriers, V is the applied potential, V_f is the flat band potential, K is Boltzmann constant, T is temperature and e is the elemental charge.

The surface charge separation sufficiency ($\eta_{surface}$) was calculated using the equation:

$$\eta_{surface}(100\%) = \frac{J_{water}}{J_{sulfite}} \times 100\%$$

Calculations on the formation energies (E_f) of oxygen vacancy and the energy of adsorption of H_2O molecule

The formation energies of oxygen vacancy in $BiVO_4$ and $Co\text{-}BiVO_4$ (200) have been studied by means of periodic density functional calculations were conducted using the "Vienna *ab initio* simulation package" (VASP 5.4.1), applying the generalized gradient correlation functional, which were calculated as:
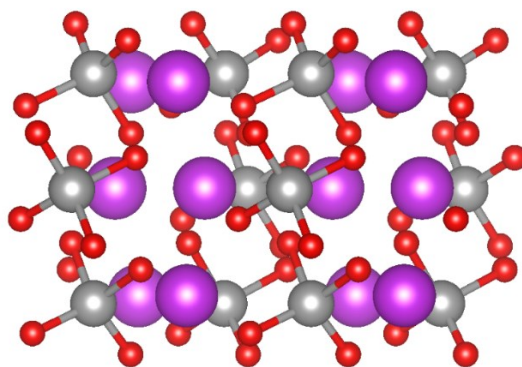
The total energy of $BiVO_4$ structure :

E_{per} = -0.53425014E+03= -534.25 eV
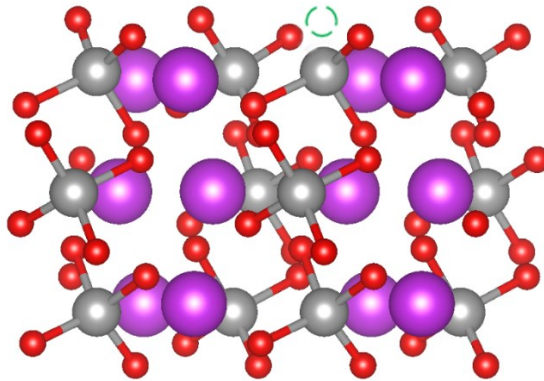
The energy of BiVO$_4$ with oxygen vacancy :

E_{tot} = -0.52648191E+03= -526.48 eV

The energy of the O atom:

$$E_O = \frac{1}{2} \times (\text{-8.84 eV}) = \text{-4.42 eV}$$

The formation energy of oxygen vacancy:

$$E_f = E_{tot} - E_{per} + E_o = \text{-526.48 eV} - (\text{-534.25 eV}) + \frac{1}{2} \times (\text{-8.84 eV})$$

$$= 3.35 \text{ eV}$$
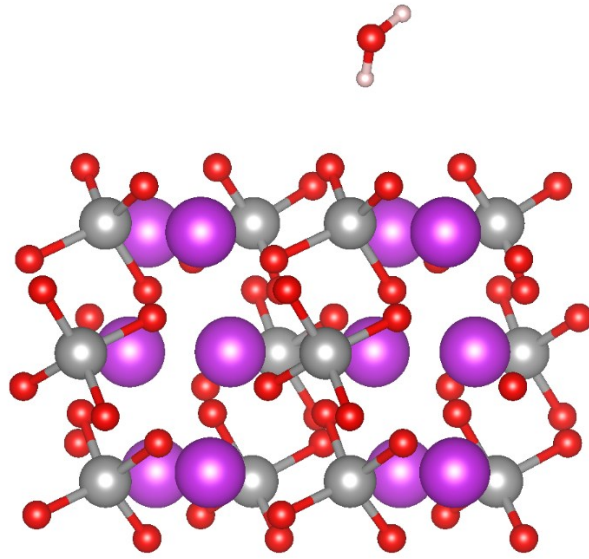
The energy of H$_2$O molecule：

E$_{H2O}$ = -0.14224670E+02 = -14.22 eV

The total energy of BiVO$_4$ after adsorption of H$_2$O molecule：

E$_{tot}$ = -0.54875740E+03 = -548.75 eV

The energy of adsorption of H$_2$O molecule onto the BiVO$_4$ structure：

E$_{ads}$ = -548.75 eV – (-534.25 eV -14.22 eV) = -0.28 eV
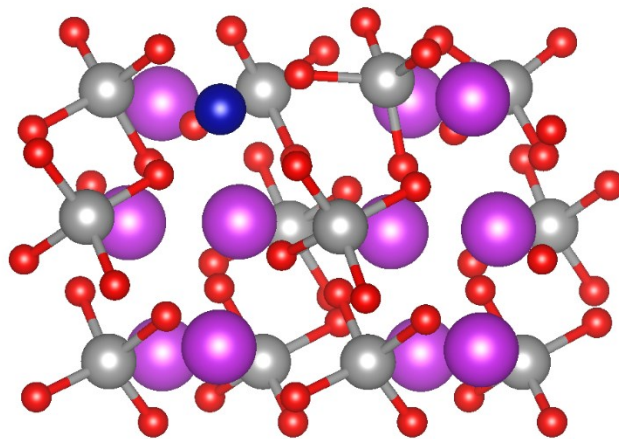
The energy of Co-doped $BiVO_4$:

E_{per} = -0.53398119E+03 = -533.98 eV
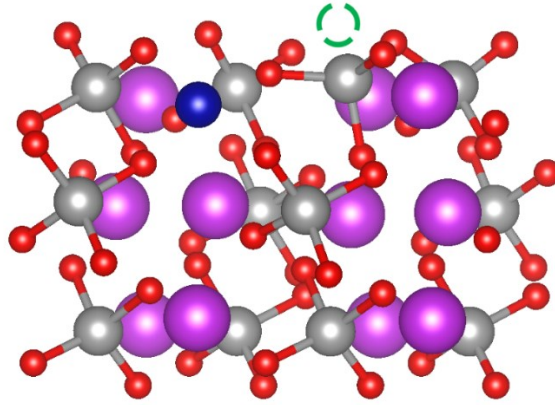
The energy of Co-doped $BiVO_4$ with oxygen vacancy :

E_{tot} = -0.52816242E+03 = -528.16 eV

The formation energy of oxygen vacancy :

$$E_f = E_{tot} - E_{per} + E_o = -528.16 \text{ eV} - (-533.98 \text{ eV}) + \frac{1}{2} \times (-8.84 \text{ eV})$$
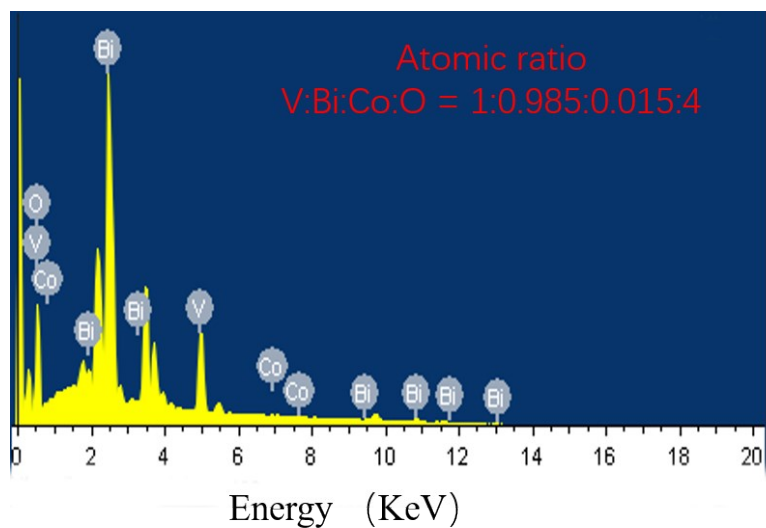
$$= 1.4 \text{ eV}$$
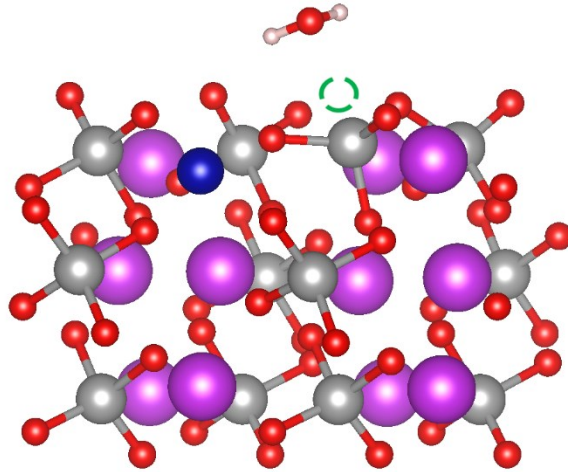
The energy of H_2O molecule :

E_{H_2O} = -0.14224670E+02 = -14.22 eV

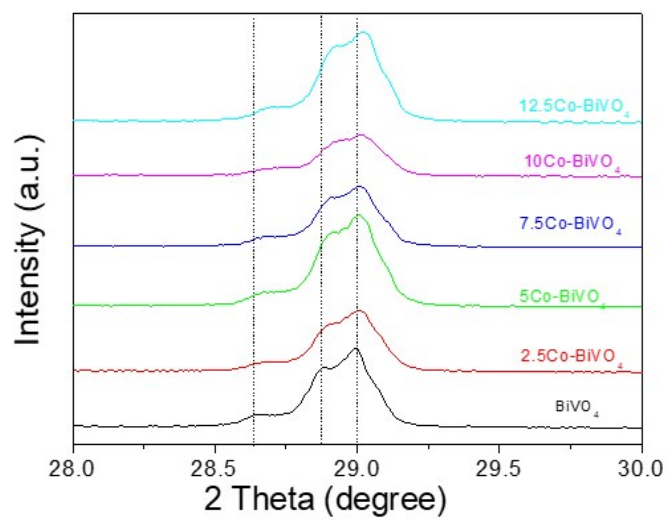The total energy of Co-doped $BiVO_4$ with oxygen vacancy after adsorption of H_2O

molecule :

E_{tot} = -0.54281575E+03 = -542.81 eV

The energy of adsorption of H_2O molecule onto the Co-doped $BiVO_4$ with oxygen
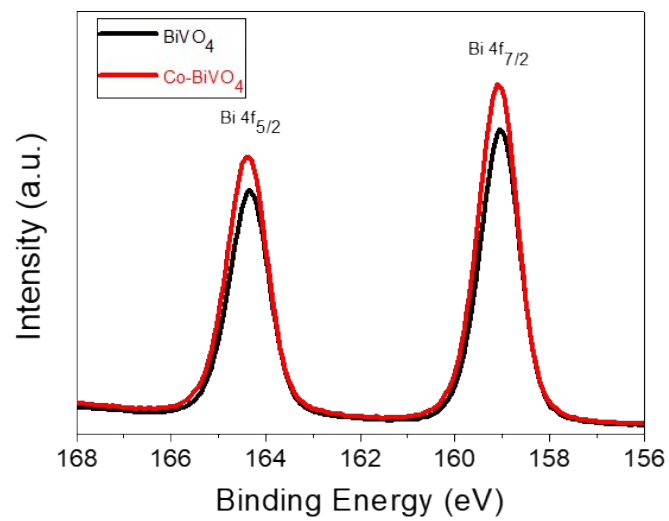
vacancy structure :

E_{ads} = -542.81 eV - (-528.16 eV-14.22 eV) = -0.43 eV

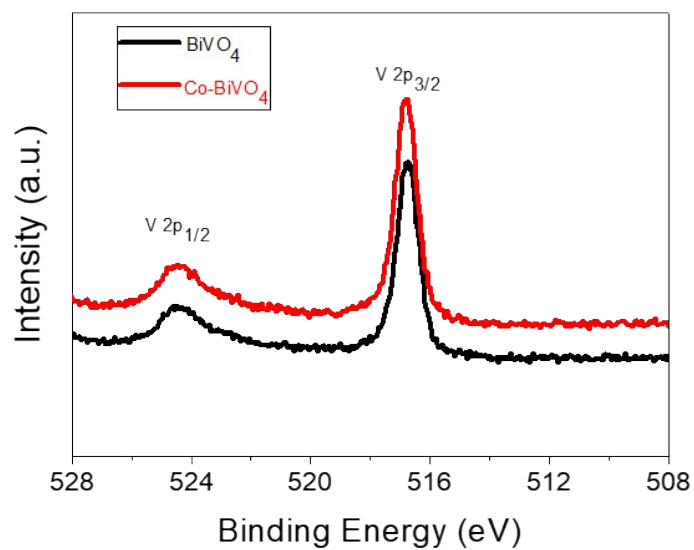Atomic ratio
V:Bi:Co:O = 1:0.985:0.015:4

Energy （KeV）

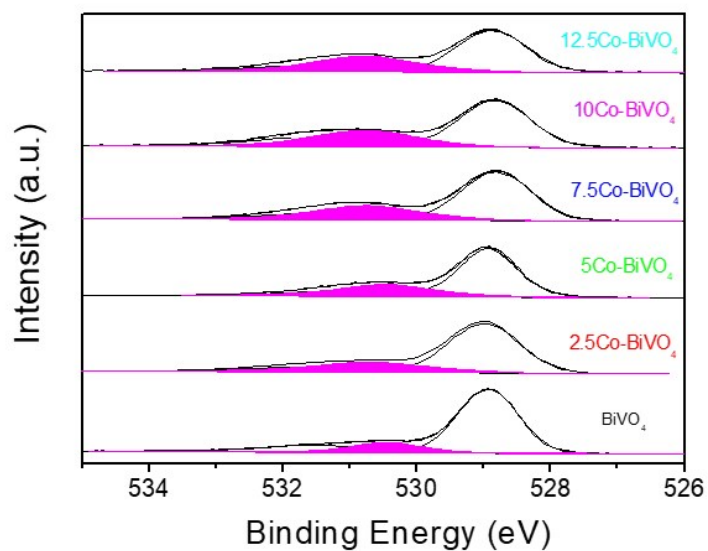**Figure S1**. EDS data of 10Co-BiVO$_4$ photoanode.

Figure S2. The magnified analysis of the XRD pattern of different Co-doped BiVO$_4$
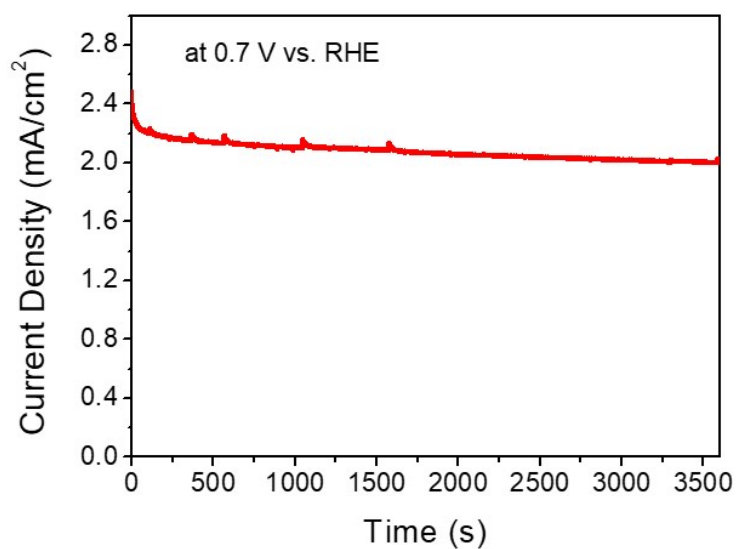
photoanodes.

**Figure S3**. High-resolution XPS spectra of Bi 4f for pure BiVO₄ and Co-BiVO₄ electrode.

**Figure S4**. High-resolution XPS spectra of V 2p for pure BiVO₄ and Co-BiVO₄ electrode.

Figure S5. High-resolution XPS spectra of O 2p for pure $BiVO_4$ and Co-doped $BiVO_4$

photoanodes varied with the cobalt concentration.

**Figure S6**. Photocurrent density as a function of time course for $BiVO_4$ and Co-$BiVO_4$

at 0.7 V versus RHE under AM 1.5 G illumination.
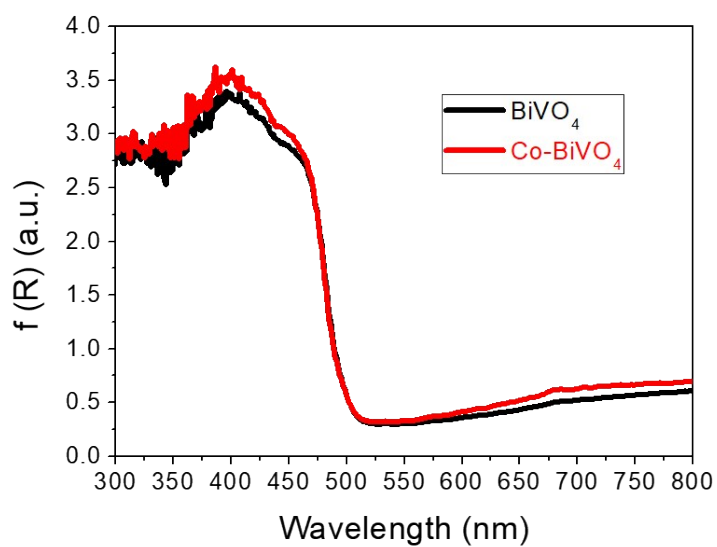
Figure S7. UV-vis absorption spectra of $BiVO_4$ and Co-$BiVO_4$ photoanodes.
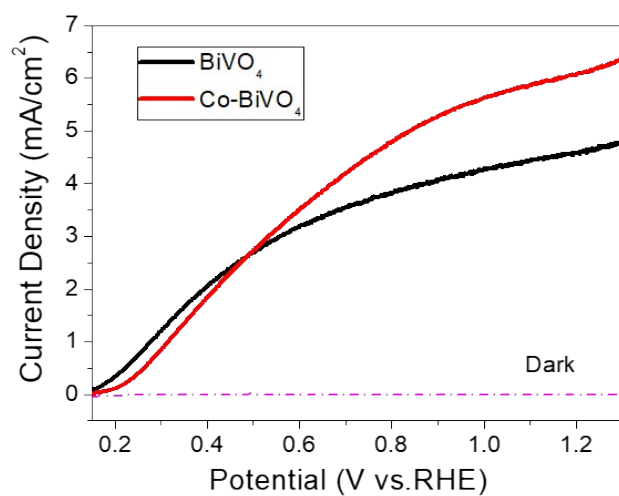
Figure S8. Photocurrent density versus applied potential curves. The PEC performances were measured in a 0.5 M sodium borate electrolyte in the presence of 0.2 M Na_2SO_3 (pH 9.3).
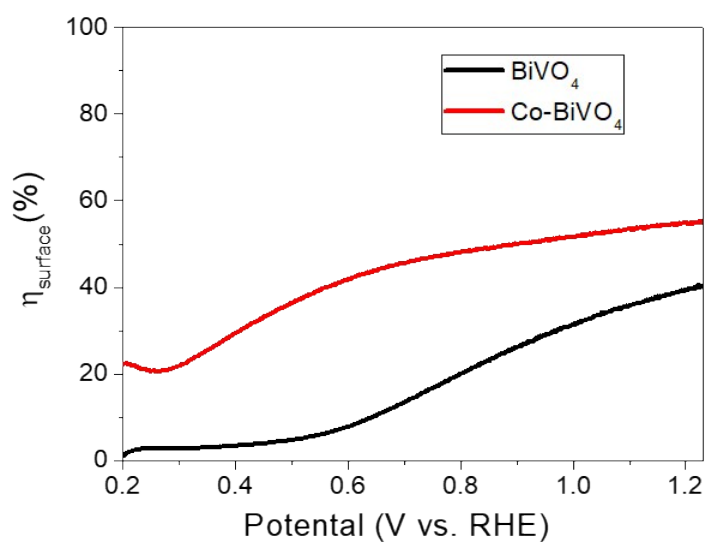
Figure S9. The surface charge separation efficiency of $BiVO_4$ and $Co\text{-}BiVO_4$.
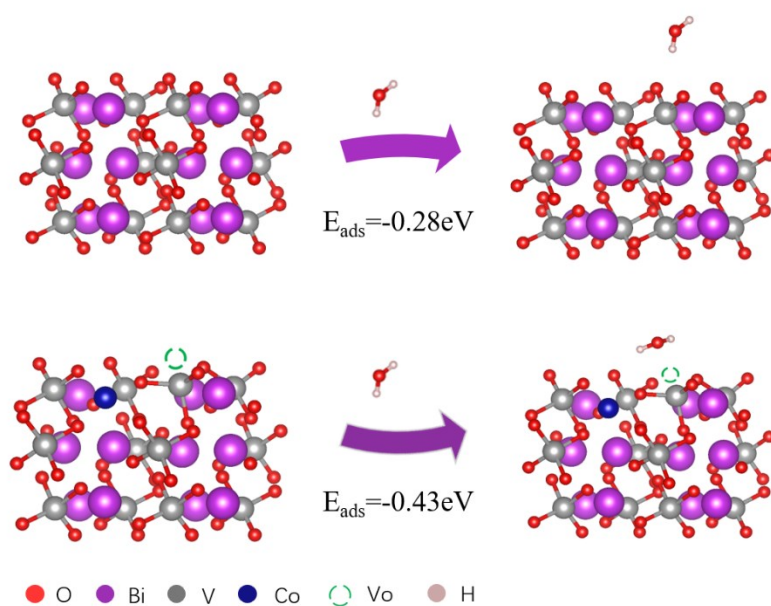
Figure S10. Schematic illustration of the adsorption of water molecular onto the surface

of $BiVO_4$ and $Co\text{-}BiVO_4$ with rich oxygen vacancies.

Table S1. Comparison of the performance of doped-BiVO$_4$ photoelectrodes under simulated sunlight.

Year	Photoanode	Fabrication method	[a] Electrolyte (pH)	[b] Photocurrent density (1.23 V vs. RHE)	Reference.
2016	Fe/W-BiVO$_4$	drop-casting	0.1M Na$_2$SO$_4$	1.50 mA/cm^2	2
2018	In-BiVO$_4$	drop-casting	0.1 M Na$_2$SO$_4$	1.56 mA/cm^2	3
2018	Mo-BiVO$_4$	dropping	0.5 M KBi (8.5)	2.89±0.05 mA /cm^2	4
2018	Zr-BiVO$_4$	electrodeposition	0.1 M PBS (7.5)	0.32 mA/cm^2	5
2019	Zn-BiVO$_4$	electrodeposition	0.1 M KPi (7.0)	3.06mA/cm^2	6
2018	Mo-BiVO$_4$	pulsed laser deposition	0.5 M KPi (7.0)	1.70 mA/cm^2	7
2018	Zn-BiVO$_4$	drop-casting	0.1 M KBi (8.5)	1.07 mA/cm^2	8
	Cu-BiVO$_4$			0.94 mA/cm^2	
	Ni-BiVO$_4$			0.82 mA/cm^2	
	Co-BiVO$_4$			1.01 mA/cm^2	
	Co-BiVO$_4$	**electrodeposition**	**0.5 M NaBi (9.3)**	**3.50 mA/cm^2**	**This work**

a. KPi: potassium phosphate, KBi: potassium borate, NaBi: sodium borate.

b. The light source of all results (AM 1.5G, 100 mW/cm^2).

Table S2. The carrier densities (N_d) of $BiVO_4$ and $Co-BiVO_4$.

	$N_d/10^{18}$ cm^{-3}
$BiVO_4$	1.7014
$Co-BiVO_4$	3.3232

References

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