

## Electronic Supplementary Information

### Turning off the “shunt channel” by coating with CoFe layered double hydroxide nanocrystalline for efficient photoelectrocatalytic water splitting

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## Characterizations

UV-Vis absorption measurements were performed on Lambda 750 spectrophotometer (PerkinElmer). X-ray diffraction (XRD) test was performed with Empyrean Panalytical X'Pert Pro X-ray diffractometer. The morphologies of the as-prepared photoanodes and nanoparticles were observed by a field-emission scanning electron microscope (SEM, FEI HELIOS NanoLab 600i), a transmission electron microscope (TEM, TECNAI G2 F30). The transient photovoltage (TPV) measurement was carried out on a home-made instrument. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) data were collected with an PHI 5400 ESCA System.

## Photoelectrochemical measurements

The photoelectrochemical performance of photoelectrodes were investigated in potassium borate buffer solution (0.1 M, pH=9.2) by using a three-electrode system with Ag/AgCl as the reference electrode ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.194 + 0.0591 \times \text{pH}$ ) and a Pt plate as the counter electrode at an electrochemical workstation (CH Instruments, model CHI660E). For photoelectrocatalytic measurement, a Xe lamp with an AM 1.5G filter was used as light source ( $100 \text{ mW cm}^{-2}$ ). Electrochemical impedance spectroscopy (EIS) curves were collected at bias potential of 0.8 V vs. RHE, with the frequency ranging from 100 kHz to 0.1 Hz and the modulation amplitude of 10 mV. The  $J$ - $V$  curves were collected by LSV mode (linear sweeping voltammetry) with a  $10 \text{ mV s}^{-1}$  scan rate .

The relative charge separation efficiency (relative  $\eta_{\text{sep}}$ ) was calculated using with

the equation (1) as below.

$$\eta_{\text{sep}} = J_{\text{Na}_2\text{SO}_3} / J_{\text{abs}} \times 100\% \quad (1)$$

According to the literature [24,27,28], to calculate the  $J_{\text{abs}}$ , AM 1.5G ( $\text{W} \cdot \text{m}^{-2} \cdot \text{nm}^{-1}$ , ASTM G173-03) simulated sunlight irradiance is converted to solar photocurrents vs. wavelength assuming 100% IPCE for photons, according  $\text{IPCE} = (1240 \times J_{\text{solar photocurrent}}) / (\lambda \times P_{\text{in}})$ ,  $\lambda$  is the absorption wavelength, and the  $P_{\text{in}}$  is the incident light intensity. Then the  $J_{\text{solar photocurrent}}$  are multiplied by the light harvesting efficiency (LHE) at each wavelength (from 380nm to 780nm), and the LHE was calculated according to  $\text{LHE} = 1 - 10^{-A(\lambda)}$ , where  $A(\lambda)$  is the absorbance at a specific wavelength in UV-Vis test.

The relative surface holes injection efficiency ( $\eta_{\text{Inj}}$ ) was calculated using the equation (2) as below.

$$\eta_{\text{Inj}} = J_{\text{H}_2\text{O}} / J_{\text{Na}_2\text{SO}_3} \times 100\% \quad (2)$$

Where  $J_{\text{H}_2\text{O}}$  and  $J_{\text{Na}_2\text{SO}_3}$  are the current measure without and with  $\text{Na}_2\text{SO}_3$  as hole scavenger respectively.

The ABPE (applied bias photon-to-current efficiency) was extracted from the J-V data under simulated sunlight illumination using the equation (3) as below, assuming 100% Faradaic efficiency.

$$\text{ABPE (\%)} = (J_{\text{light}} - J_{\text{dark}}) \times (1.23 - \text{RHE}) / P_{\text{light}} \times 100\% \quad (3)$$

Where  $J_{\text{light}}$  and  $J_{\text{dark}}$  are the current measured with and without illumination respectively. RHE is the applied potential vs. a reversible hydrogen electrode, and  $P_{\text{light}}$  is  $100 \text{ mW cm}^{-2}$  (simulated sunlight intensity).

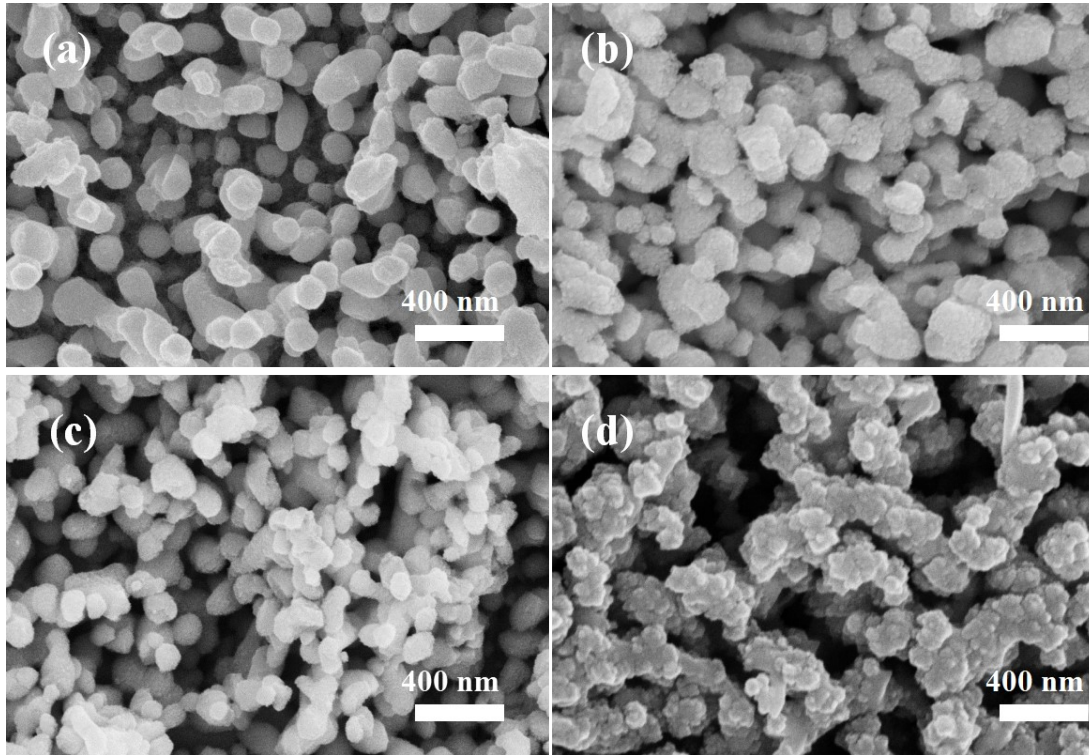
The Faradaic efficiency was calculated using the equation (4) as below.

$$\text{Faradaic efficiency (\%)} = N_{\text{O}_2} / (Q / 4 / 96485) \quad (4)$$

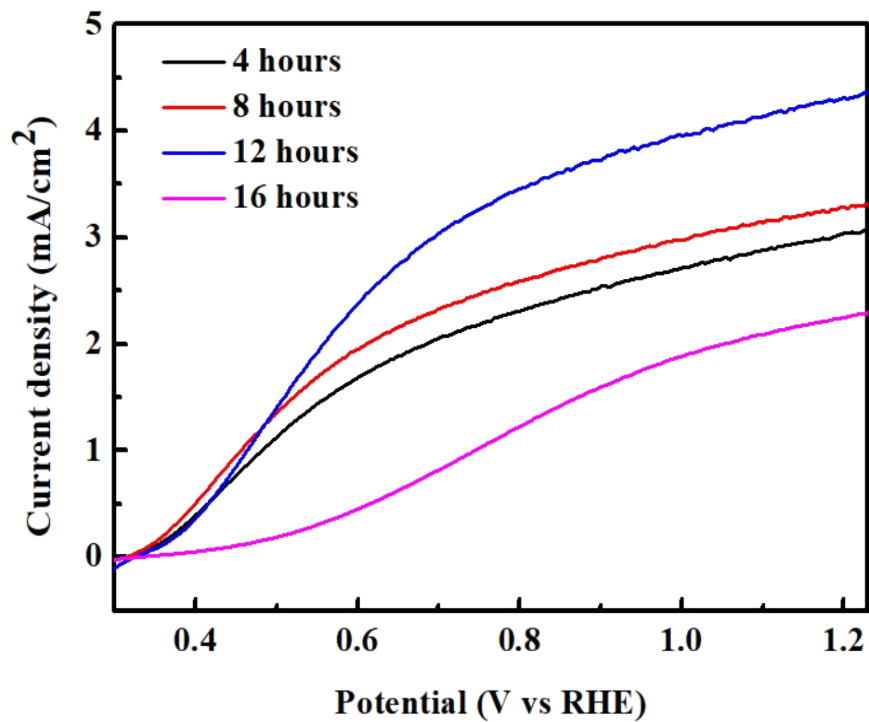
Where  $N_{\text{O}_2}$  is the amount of  $\text{O}_2$  evolved,  $Q$  is the integrated charge passed.

### **Oxygen Evolution**

Controlled potential electrolysis experiments were performed in a 45 mL volume flask with 20 mL potassium borate buffer solution electrolyte (0.1 M, pH=9.2) as electrolyte. The electrode was used as the working electrode. The flask was sealed before experiments. After every 1 h illumination, 0.4 mL gas was taken from flask to injected into a gas chromatography for measuring the evolution of oxygen.

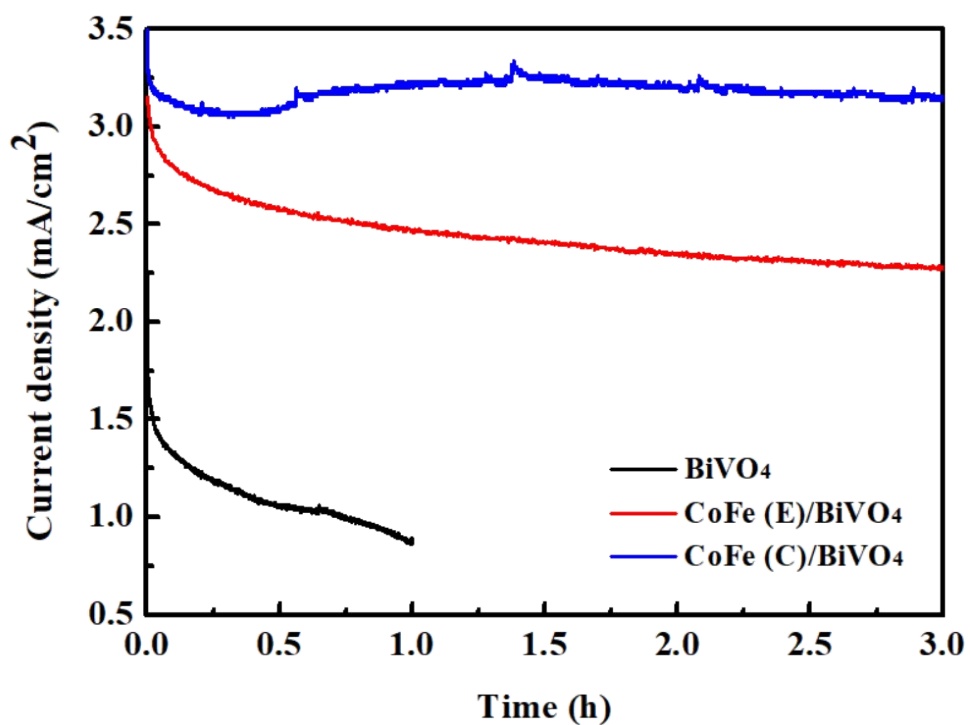


**Fig S1.** SEM image of CoFe(C)/BiVO<sub>4</sub> photoanodes under 4-16 h deposition time (a-d)

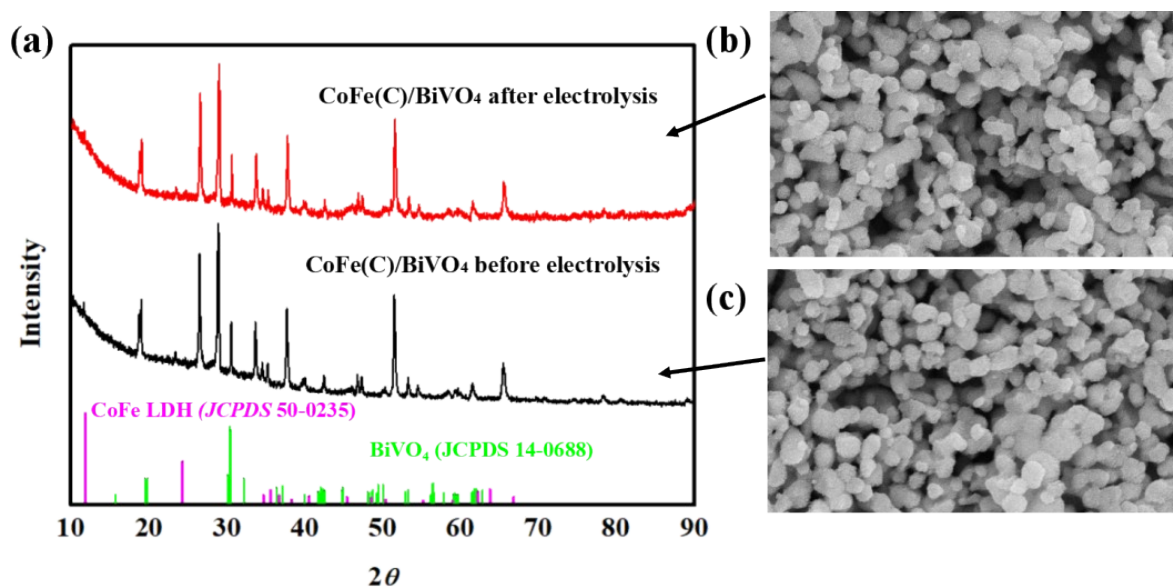


**Fig S2.** *J-V* of CoFe(C)/BiVO<sub>4</sub> photoanodes under different deposition time in 0.1 M

potassium borate buffer solution



**Fig S3.** The  $J$ - $t$  plot of CoFe(C)/BiVO<sub>4</sub> photoanode for water oxidation at 0.7 V vs. RHE in 0.1 M potassium borate buffer solution under AM 1.5G illumination



**Fig S4.** XRD patterns of (a) as-prepared CoFe(C)/BiVO<sub>4</sub> electrode before and after reaction for 3 hours. Corresponding SEM images are shown on the right (b,c).