

*Supplementary Information*

**Tuning Surface Hydrophilicity of BiVO<sub>4</sub> Photoanode through Interface Engineering for Efficient PEC Water Splitting**

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## **1. Experimental section**

### **1.1. Materials**

Nitrate Pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), Cobalt Phthalocyanine (CoPc), Dimethyl sulfoxide (DMSO) were purchased from Aladdin. Vanadyl acetylacetonate ( $\text{VO}(\text{acac})_2$ ), potassium iodide (KI), nitric acid ( $\text{HNO}_3$ ), p-benzoquinone were purchased from Shanghai HanSI CHEMICAL Co. LTD. FTO and sodium hydroxide (NaOH) were obtained from Jiangxi Shengwei Technology Co. LTD. Natrium sulfurosum was purchased from Xi 'an Qiyue Co., LTD. Among them, the FTO glass substrate was ultrasonically cleaned in pure water, acetone and ethanol for 10 minutes before use and then dried.

### **1.2. Synthesis of BVO photoanode**

0.97 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 3.32 g KI were dissolved in 50 mL deionized water to form a brick red solution. Then slowly add concentrated nitric acid, and adjust the pH to 1.7. The solution turned bright red with ice bath stirring for one hour. Then 20 mL p-benzoquinone ethanol solution was added, and sonicated to mix evenly. After stirred in an ice bath for one hour, an electrolyte solution was formed. FTO, Pt electrode and saturated calomel electrode were used for electrodeposition as working electrode, counter electrode and reference electrode, respectively. BiOI/FTO was obtained by constant potential technology with a charge of  $0.3 \text{ C cm}^{-2}$ . The DMSO solution containing vanadium acetylacetonate was dropped onto BiOI/FTO. This electrode was calcined at  $450 \text{ }^\circ\text{C}$  for 2h in a muffle furnace. After cooling to room temperature, it was soaked in 1 mol NaOH solution to remove the excess vanadium

oxide on the surface. BVO/FTO photoanode can be obtained according to above process.

### **1.3. Synthesis of BVO@CoPc-S, BVO@CoPc-I and BVO@CoPc-Dc photoanodes**

20 mg CoPc was dissolved in 20 mL ethanol. After stirred for 30 min and sonicated for 60 min, the mixture was transferred to a 30 mL autoclave with a BVO/FTO (conductive face down) and heated at 120 °C for 6 h. After natural cooling to room temperature, the electrode was washed with ethanol three times. The prepared photoanode noted as BVO@CoPc-S was obtained after dried at 80 °C for 12 h. For comparison, other photoanodes were also prepared with the same precursor solutions. 40  $\mu$ L CoPc solution was drip-coated on the surface of BVO/FTO electrode and BVO@CoPc-Dc photoanode was obtained after dried. BVO@CoPc-I photoanode was prepared with BVO/FTO immersed in the solution for 20 min and dried.

### **1.4. Characterization**

2. X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab diffractometer within the angular range of 10°-70° and the crystal structure was analyzed. Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Nicolet iS 5 spectrometer, with wave numbers ranging from 400  $\text{cm}^{-1}$  to 2000  $\text{cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo Scientific K-Alpha instrument. The microstructure and elemental distribution of the samples were characterized using a scanning electron microscope (SEM, TESCAN MIRA LMS) equipped with energy dispersive X-ray spectroscopy (EDS). Before measurement, the material was evaporated with Pt for 80 s. Reflectance spectra were collected with a

PerkinElmer Lambda950 UV-Vis spectrometer over the range of 300-800 nm. Raman spectra were obtained at room temperature using a Zolix RTS2 Raman spectrometer. High-resolution transmission electron microscopy (HRTEM) images were captured using a JEM-ARM200F microscope.

### **2.1. Photoelectrochemical measurement**

The photoelectrochemical (PEC) performance of BVO, BVO@CoPc-S, BVO@CoPc-I, BVO@CoPc-I photoanodes was evaluated by electrochemical workstation (CHI760E, Shanghai Chenhua Instrument Co., Ltd.). All measurements were performed using a typical three-electrode system in 1 M KBi (PH=9) buffer, with a (1 cm × 1 cm) Pt foil as the counter electrode, Ag/AgCl as the reference electrode, and the photoanode (exposure area at 1 cm<sup>2</sup>) as the working electrode. Linear scanning voltammetry (LSV) was performed at a scan rate of 10 mV s<sup>-1</sup> under simulated sunlight (AM 1.5 G, 100 mW cm<sup>-2</sup>). Electrochemical impedance spectroscopy (EIS) was performed under light and dark conditions in the frequency range of 100 kHz to 0.1 Hz. Mott-Schottky (M-S) measurements were performed in the dark at a frequency of 1 kHz.

(a)

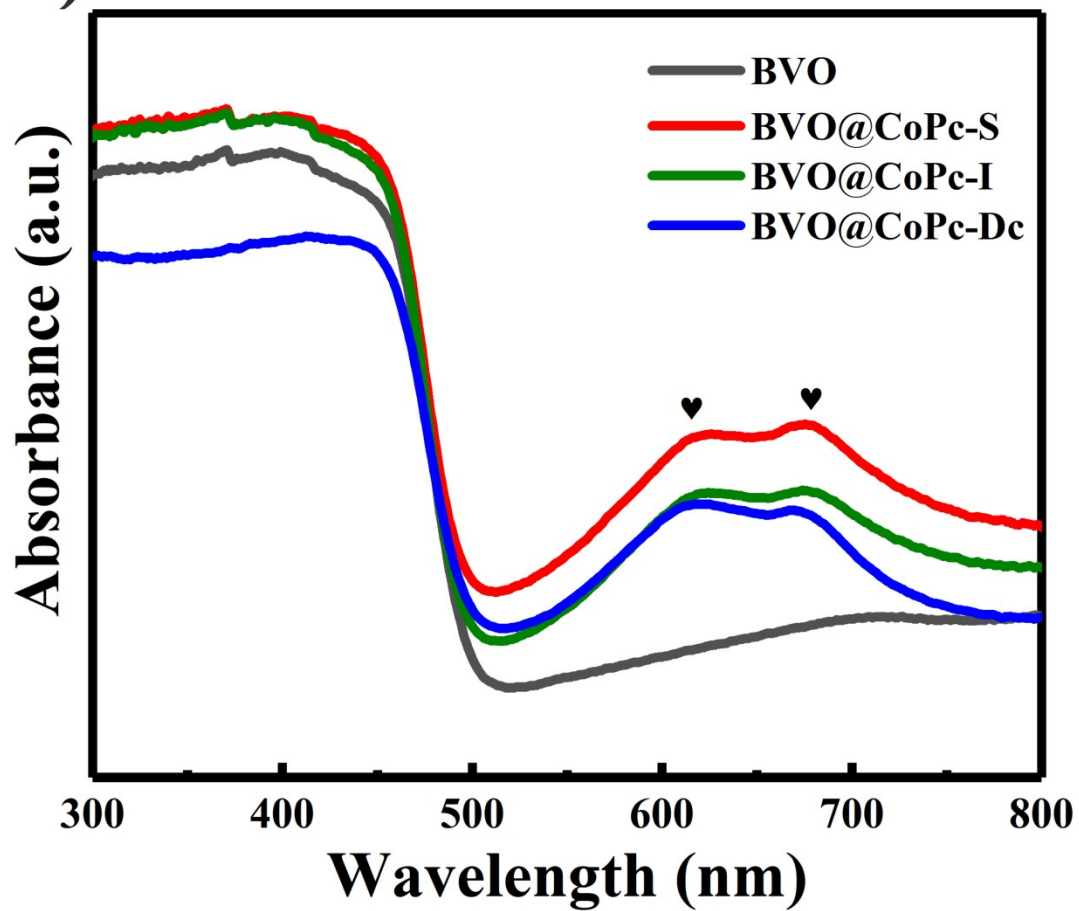
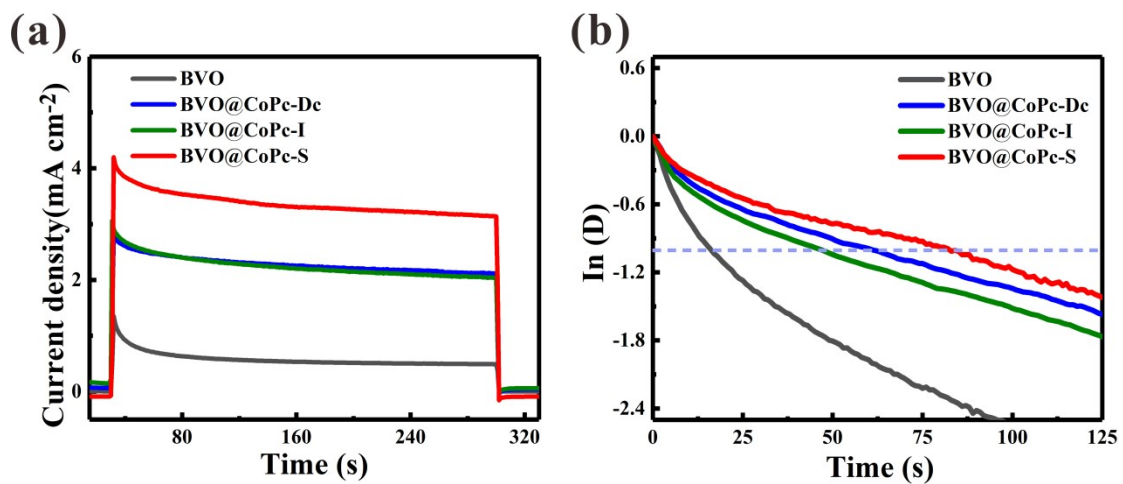


Fig. S1. UV-vis spectra of the prepared photoanodes.

**Table S1** The ratios of C=O, O<sub>Ad</sub> and O<sub>L</sub> in these photoanodes calculated from the XPS

Photoanodes	C=O area ration (%)	O <sub>Ad</sub> area ration (%)	O <sub>L</sub> area ration (%)
BVO		31.99	68.01
BVO@CoPc-Dc	4.53	64.31	31.16
BVO@CoPc-I	4.50	72.39	23.11
BVO@CoPc-S	6.95	80.26	12.79



**Fig. S2.** (a) Transient photocurrent responses curves and (b) normalized plots of the current- time dependence of these prepared photoanodes.