

# Supporting Information

## Materials

The chemical reagents and solvents used in the experiments were of analytical grade and did not require any purification.  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99%), urea (99%) and P-benzoquinone (97%) were purchased from Aladdin Industrial Corporation.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99%),  $\text{VO}(\text{acac})_2$  (99%),  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{NH}_4\text{F}$  (99.9%) were purchased from Shanghai Macklin Biochemical Co., Ltd.  $\text{KI}$  (99%),  $\text{KOH}$  (90%),  $\text{Na}_2\text{SO}_3$  (96%),  $\text{Na}_2\text{SO}_4$  (98%),  $\text{HNO}_3$  (69%),  $\text{DMSO}$  (99.5%) and Anhydrous ethanol (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Fluorine-doped tin oxide-coated glass ( $<15 \Omega \text{ sq}^{-1}$ , thickness: 2.2 mm) was purchased from Nippon Sheet Glass Co., Ltd. All experiments in this study used deionized water ( $18.2 \text{ M}\Omega \text{ cm}$ ).

## Preparation of $\text{BiVO}_4$ photoanodes

The  $\text{BiVO}_4$  photoanode was prepared by electrochemical deposition. The detailed procedure is that  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.9701g) dissolved in 0.4 M  $\text{KI}$  solution (50 mL) and the pH adjusted to 1.7. Then 0.23 M p-benzoquinone ethanol solution (20 mL) was added to the above solution, and the electroplating solution was obtained by mixing it evenly. During the electroplating process, the platinum (Pt) sheet is the counter electrode, the FTO is the working electrode, and the  $\text{Ag}/\text{AgCl}$  electrode is the reference electrode. Compared with  $\text{Ag}/\text{AgCl}$ , the electrode potential was set to -0.1 V and the plating time was 8 minutes.  $\text{BiOI}$  compounds were deposited, washed with

deionized water and ethanol in turn, and then dried with nitrogen. Afterwards, 80  $\mu$ L of 0.2 M vanadyl acetylacetonate ( $\text{VO}(\text{acac})_2$ ) DMSO solution was dropped onto BiOI film and annealed at 450 °C for 2 h with a heating rate of 2 °C/min. Finally, the obtained FTO was immersed in 1 M KOH aqueous solution for 1 hour to eliminate  $\text{V}_2\text{O}_5$  on the surface of  $\text{BiVO}_4$  photoanode.

### **Preparation of Nd-BiVO<sub>4</sub> photoanode**

The detailed procedure was as follows:  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  ( 0.9701g ) was dissolved in 0.4 M KI solution (50 mL) and the pH was adjusted to 1.7. Then 0.23 M p-benzoquinone ethanol solution (20 mL) was added to the above solution, and the electroplating solution was obtained by mixing it evenly. Finally, 0.01g  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was directly added to the electroplating solution and stirred. The doped Nd-BiOI product was obtained by electroplating for 8 min, and then 80  $\mu$ L of 0.2 M DMSO solution ( $\text{VO}(\text{acac})_2$ ) was added to the surface of Nd-BiOI film. The temperature was raised to 450 °C at a heating rate of 2 °C / min<sup>-1</sup>, and calcined at 450 °C for 2 h. Then FTO was taken out and immersed in 1 M KOH aqueous solution for 1 hour to remove excess  $\text{V}_2\text{O}_5$  on the surface of Nd-BiVO<sub>4</sub> photoanode. Finally, Nd-BiVO<sub>4</sub> was obtained by washing with distilled water and ethanol in turn and drying with  $\text{N}_2$ .

### **Material characterization**

The microstructure and surface morphology of all prepared photoanodes were researched by field emission scanning electron microscopy (SEM, Hitachi S-4800, Chiyoda-Ku, Tokyo, Japan). The crystallization was studied by the X-

ray diffraction spectra (XRD), conducted on a Rigaku D/max-2400 diffractometer with the X-ray source of Cu K $\alpha$  radiation, and data were collected in Bragg–Brentano mode with a scan rate of 0.2° s<sup>-1</sup> in the range of 10°–70°. The surface composition of the samples was studied by X-ray photoelectron spectroscopy (XPS) measurements, operated on a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al K $\alpha$  X-ray source, operating at 15 kV and 10 mA and referenced to the C 1s peak (284.6 eV). TEM and high-resolution TEM (HRTEM) images were analyzed on a Tecnai G<sup>2</sup>Tf20 transmission electron microscope operated at 200 kV. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping was investigated using an annular darkfield detector under TEM. The optical properties of the samples were determined by using a Hitachi U-4000 spectrometer with BaSO<sub>4</sub> as reference.

## **Photoelectrochemical test**

Photoelectrochemical chemistry (PEC) measurements were made using a standard three-electrode electrochemical cell and a flat quartz window in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> buffer solution on the CHI760E Electrochemical Workstation (CH instrument). Pt electrode and saturated Ag/AgCl electrode were used as a counter electrode and reference electrode, respectively, and the sample was used as a working electrode. A 300 W xenon arc lamp (Perfect Light solar simulator) with an AM 1.5 G filter was employed as the light source. The light intensity on the electrode surface was adjusted to 100 mW cm<sup>-2</sup> (1 sun

illumination). The photoanode activity area used for testing was  $1 \times 1 \text{ cm}^2$ . Linear sweep voltammetry curve measurements were conducted with a scanning rate of  $5 \text{ mV s}^{-1}$  in a voltage range of 0.4-1.0 V versus the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS) was measured under AM 1.5G illumination at a potential of 1.23 V vs. RHE and a 5mV alternating current (AC) voltage (frequency range 0.1 to  $10^5 \text{ Hz}$ ) was applied. Mott-Schottky (M-S) was tested in the absence of light, with a voltage range of -0.25 to 0.25V vs. RHE, and the parameters were set as increase by 10 mV; frequencies of 500, 750, and 1000 Hz; the amplitude of 0.005 V versus Ag/AgCl.

## Calculations

1. **During the experiment, the electrode potential is converted to reversible hydrogen electrode potential (RHE), and the conversion formula is:**

$$R_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}}^0 \quad \text{equation S1}$$

S1

$$(E_{\text{Ag/AgCl}}^0 = 0.1976\text{V vs. RHE at } 25^\circ\text{C})$$

Where  $E_{\text{RHE}}$  is the potential versus(vs.) RHE,  $E_{\text{Ag/AgCl}}$  is the experimental Potential measured vs. the Ag/AgCl electrode [1].

2. **Calculation of Applied bias photon to current conversion efficiency (ABPE):**

ABPE could be calculated using the following equation:

$$ABPE(\%) = \frac{J \times (1.23 - V_b)}{P_{total}} \times 100\% \quad \text{equation}$$

S2

Among them,  $J$  is the photocurrent density of the electrode without a sacrificial agent ( $\text{mA cm}^{-2}$ ).  $V_b$  is the applied bias voltage (relative to the reversible hydrogen potential), and  $P_{total}$  Is the light intensity of the simulated solar energy (AM 1.5 G,  $100 \text{ mW cm}^{-2}$ ) [2].

### 3. Mott-Schottky (M-S) analysis:

In the M-S plot, the flat band potential and the carrier densities of the photoelectrode are measured according to the following equations:

$$N_D = \frac{2}{e\epsilon\epsilon_0} \times \left( \frac{d\left(\frac{1}{C^2}\right)}{dV_s} \right)^{-1} \quad \text{equation}$$

S3

Where  $e$  is the charge of an electron ( $1.6 \times 10^{-19} \text{C}$ ), The vacuum dielectric constant  $\epsilon_0$  is  $8.86 \times 10^{-12} \text{ F m}^{-1}$ , The relative permittivity  $\epsilon$  of  $\text{BiVO}_4$  is 68,  $C$  ( $\text{F cm}^{-2}$ ) is Space charge capacitance in semiconductors,  $V_s$  (V) is Potential applied when measuring the M-S curve [2].

### 4. Light-harvesting efficiency (LHE):

LHE is defined as the fraction of photons absorbed per photons impinging on the sample, which could be calculated using the following equation:

$$LHE = 1 - 10^{-A(\lambda)} \quad \text{equation}$$

S4

$A(\lambda)$  is the absorbance at a specific wavelength [3].

#### 5. Theoretical maximum photocurrent density ( $J_{abs}$ ):

Theoretical maximum photocurrent density ( $J_{abs}$ ) is the photocurrent density assuming that all absorbed photons can be converted into current (i.e., APCE = IPCE/LHE = 100%); it is a constant with the AM 1.5 G spectrum and the light-harvesting efficiency of the fixed photoelectrode. In the case of  $J_{abs}$ , it can be calculated according to the following equation:

$$J_{abs} = \int_{\lambda_1}^{\lambda_2} \frac{\lambda \times LHE(\lambda) \times P(\lambda)}{1240} d(\lambda) \quad \text{equation}$$

S5

Where  $\lambda$  and  $P(\lambda)$  are the light wavelength (nm) and the corresponding power density ( $mW cm^{-2} nm^{-1}$ ) For the standard solar spectrum AM 1.5G (ASTMG-173-03), respectively [3].

#### 6. The surface charge injection efficiency ( $\eta_{surface}$ ) and bulk charge separation efficiency ( $\eta_{bulk}$ ):

The surface charge injection efficiency and bulk charge separation efficiency of the as-obtained photoanodes can be calculated using the following equations:

$\eta_{bulk}$  is the yield of photo-induced holes which have migrated to the semiconductor/electrolyte interfaces and  $\eta_{surface}$  is the yield of holes that are involved in the water oxidation reaction. In this

work, we chose the widely used  $\text{Na}_2\text{SO}_3$  as the hole scavenger. Moreover,  $\eta_{bulk}$  and  $\eta_{surface}$  were calculated according to the equations, respectively:

$$\eta_{bulk} = \frac{J_{\text{Na}_2\text{SO}_3}}{J_{abs}} \quad \text{equation}$$

S6

$$J_{surface} = \frac{J_{\text{H}_2\text{O}}}{J_{\text{Na}_2\text{SO}_3}} \quad \text{equation}$$

S7

$J_{\text{H}_2\text{O}}$  and  $J_{\text{Na}_2\text{SO}_3}$  are the photocurrent densities obtained in 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte without and with 0.2 M  $\text{Na}_2\text{SO}_3$ , respectively [3].

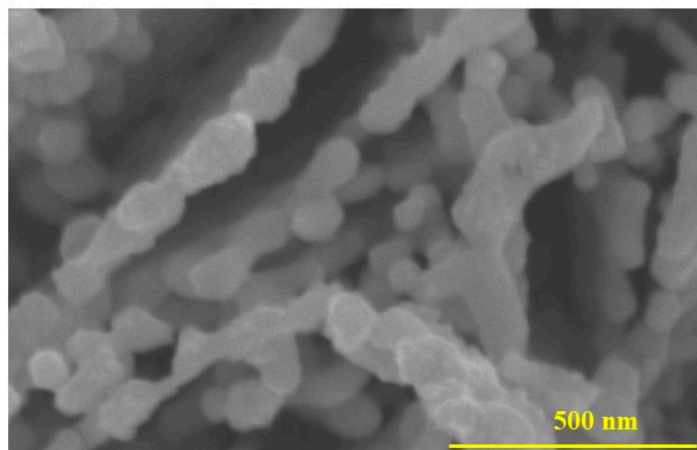
## 7. Tauc-plot calculated the band gap energy ( $E_g$ ):

According to the UV-vis absorption spectra, after the plotting  $(\alpha h\nu)^2$  vs.  $h\nu$ , the optical band gap energy could be easily evaluated using the following equation:

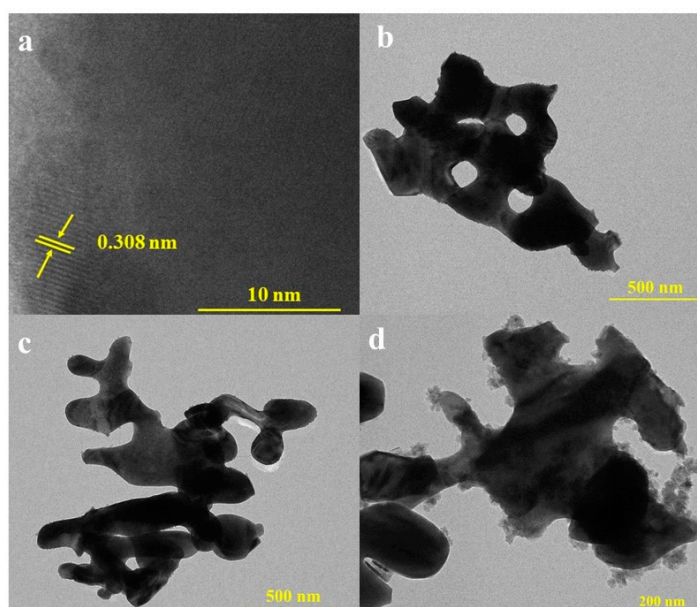
$$\alpha h\nu = A(h\nu - E_g)^{\frac{n}{2}} \quad \text{equation}$$

S8

where  $\alpha$ ,  $h$ ,  $\nu$ ,  $A$  and  $E_g$  are the optical absorption coefficient, Planck constant, light frequency, optical absorbance and band gap energy, respectively. The value of  $n$  depends on the nature of the type of optical transition in the semiconductor [4].

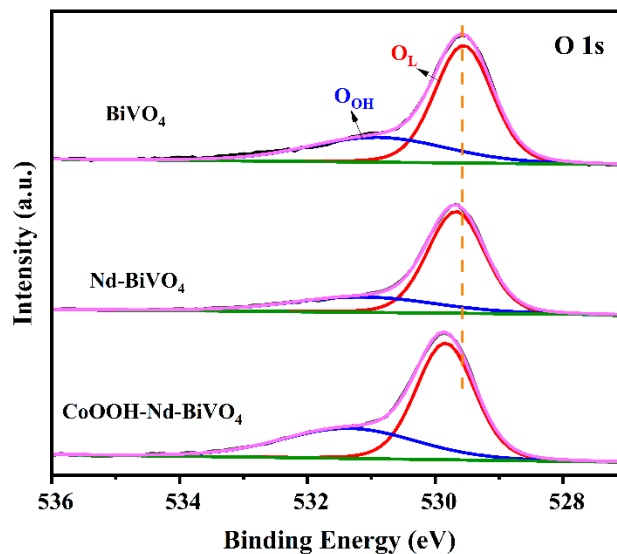


**Figure S1.** SEM of CoOOH-Nd-BiVO<sub>4</sub>.

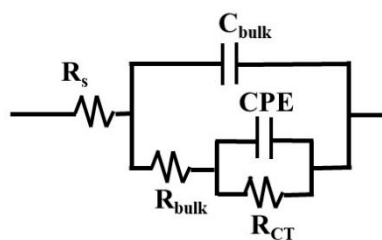


**Figure S2.** (a) HR-TEM of BiVO<sub>4</sub>, TEM of (b) BiVO<sub>4</sub>, (c)Nd- BiVO<sub>4</sub> and (d)CoOOH-Nd-BiVO<sub>4</sub>, respectively.



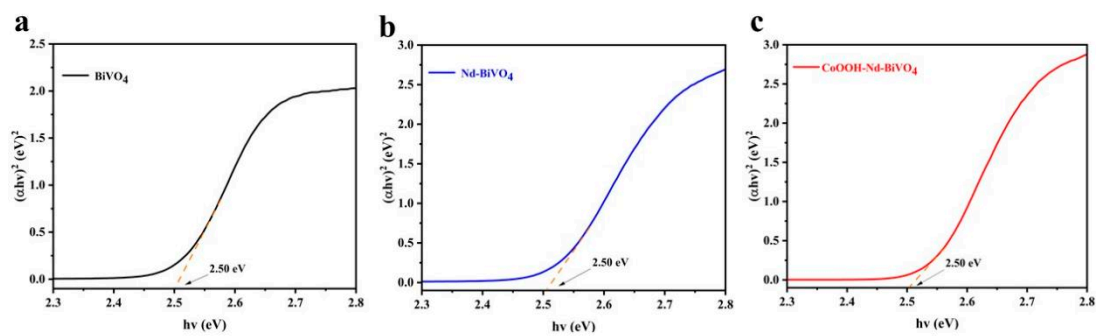


**Figure S3.** XPS patterns of O 1s in  $\text{BiVO}_4$ ,  $\text{Nd-BiVO}_4$  and  $\text{CoOOH-Nd-BiVO}_4$  photoanodes.

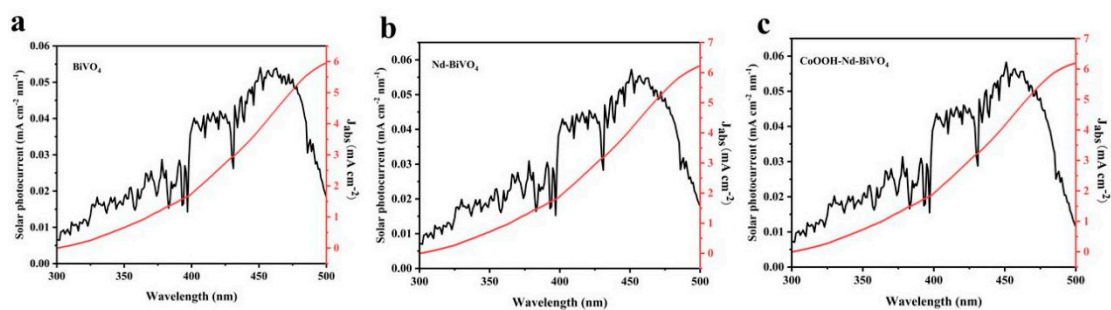


**Figure S4.** Equivalent electric circuit fitting from EIS curve.

Herein,  $R_s$  refers to the series resistance between FTO and the semiconductors.  $R_{\text{bulk}}$  and  $C_{\text{bulk}}$  correspond to the charge transport resistance and space-charge layer capacitance within the bulk semiconductor.  $R_{\text{ct}}$  and CPE relate to charge transfer resistance across the interface and surface states capacitance, respectively.



**Figure S5.** Tauc plots of (a)  $\text{BiVO}_4$ , (b)  $\text{Nd-BiVO}_4$  and (c)  $\text{CoOOH-Nd-BiVO}_4$  photoanodes.



**Figure S6.** Calculated Jabs values of (a)  $\text{BiVO}_4$ , (b)  $\text{Nd-BiVO}_4$  and (c)  $\text{CoOOH-Nd-BiVO}_4$  photoanodes. The calculated values are  $5.96 \text{ mA cm}^{-2}$ ,  $6.22 \text{ mA cm}^{-2}$  and  $6.19 \text{ mA cm}^{-2}$ , respectively.

## References

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3. Lin, C.; Dong, C.; Kim, S.; Lu, Y.; Wang, Y.; Yu, Z.; Gu, Y.; Gu, Z.; Lee, D. K.; Zhang, K.; Park, J. H., Photo-Electrochemical Glycerol Conversion over a Mie Scattering Effect Enhanced Porous BiVO<sub>4</sub> Photoanode. *Adv. Mater.* **2023**, e2209955.
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