

Supporting information

Construction of organic-inorganic hybrid photoanodes with metal phthalocyanine complexes to improve photoelectrochemical water splitting performance

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Experimental section

Materials.

Cobalt Phthalocyanine (CoPc), Iron(II) Phthalocyanine (FePc), N,N-Dimethylformamide (DMF), Bismuth(III) Nitrate Pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), Dimethyl sulfoxide (DMSO) were purchased from Innochem, Nickel Phthalocyanine (NiPc) were purchased from Acros, Zinc Phthalocyanine (ZnPc) were purchased from Alfa, Potassium iodide (KI), p-Benzoquinone, Vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) were purchased from Aladdin. FTO was purchased from Advanced Election Technology Co., Ltd, and rinsed with acetone, ethanol, and DI water before use.

Synthesis of BVO photoanode.

Typically, 3.32 g KI is solved in 50 mL H_2O and stirred in an ice bath with pH adjusted to 1.7 by adding HNO_3 . Then adding 970 mg $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to the above solution and continue stirred 1 h. After that, this solution was mixed with 20 mL absolute ethanol containing 0.23 M p-Benzoquinone and continue stirred for 1 h to form electrolyte. A standard three-electrode cell was used for electrodeposition. A FTO (1 cm \times 2 cm) was used as working electrode, an Ag/AgCl (4 M KCl) was used as reference electrode, and a Pt foil (1 cm \times 1 cm) was used as counter electrode, the deposition area of FTO is controlled at 1 cm \times 1 cm. The electrodeposition process was performed at -0.1 V vs. Ag/AgCl to form the BiOI, and the amount of charge passing through was 0.3 C cm^{-2} . Then, a 75 μL DMSO solution containing 0.2 M $\text{VO}(\text{acac})_2$ was dropped onto the surface of BiOI, and then heated at 450 $^\circ\text{C}$ (heating rate at 2 $^\circ\text{C min}^{-1}$) for 2 h to convert BiOI to BiVO_4 . After cooling down to the room temperature, BiVO_4 was placed in 1 M NaOH for 20 min with gentle stirring, and then rinsed with DI water and dried.

Synthesis of BVO/MPc (M=Ni, Co, Fe, Zn) photoanode.

BiVO₄/MPc photoanode was synthesized by a facile drop-casting method. Typically, 2.5 mM MPc was dissolved in DMF, and then dropped into BiVO₄ surface with different volumes (40 μL, 80 μL, 120 μL, 160 μL, 200 μL). After that, the BiVO₄/MPc photoanode was put in oven at 80 °C for 20 min.

Characterization.

The crystalline structure was carried out by X-ray diffraction analysis (XRD, Rigaku SmartLab). The elemental composition and the chemical state of the materials were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo fisher Scientific K-Alpha+). The C 1s peak with the binding energy of 284.8 eV is employed to correct the binding energy of other elements. The surface morphology and elemental distribution was analyzed by scanning electron microscopy (SEM, Zeiss Sigma300) equipped with an X-ray energy-dispersive spectrometer (EDX). Before SEM measurement, the samples were evaporated with Pt for 60 s. The optical property was analyzed by UV-Vis spectroscopy (UV-Vis, PE lambda950).

Photoelectrochemical measurement.

All the photoelectrochemical measurements were tested in a standard three-electrode cell with an electrochemical workstation (CHI760E, Shanghai Chenhua Instrument Co., Ltd). The photoanode was used as working electrode, an Ag/AgCl (4 M KCl) was used as reference electrode, a Pt foil (1 cm × 1 cm) was used as counter electrode, and 1 M KBi buffer (pH=9) was used as electrolyte. A 300 W Xenon lamp (PLS-SEX300, Beijing Perfectlight Technology Co., Ltd) equipped with an AM 1.5G filter was used as light source and the incident light intensity was calibrated to 100 mW/cm². The linear sweep voltammogram (LSV) was measured at a scan rate of 10 mV s⁻¹. The photoelectrochemical impedance spectroscopy (PEIS) was performed with a frequency range from 100 kHz to 0.1 Hz. Nyquist plots were fitted to the corresponding

equivalent circuits by Z-view software. Mott-Schottky measurements were performed in dark at a frequency of 1 kHz. The flat band potential (V_{fb}) and the carrier densities (N_d) in semiconductors were quantified via equation:

$$1/C^2 = (2/e_0\epsilon\epsilon_0N_d)[(V - V_{fb}) - KT/e]$$

Where C is the capacitance of the space charge region, e_0 is the electron charge (1.602×10^{-19} C), ϵ is the dielectric constant of BVO (68), ϵ_0 is the vacuum permittivity (8.854×10^{-14} F/cm), V is the potential applied at the electrode, K is the Boltzmann constant, T is the absolute temperature. The carrier densities (N_d) were calculated with following equation:

$$N_d = (2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1}$$

The applied bias photon-to-current efficiency (ABPE) can be calculated by the following equation:

$$ABPE = ((1.23 - V_b) \times J/P_{light}) \times 100\%$$

Where V_b represents the applied potential vs. RHE, J is the measured photocurrent current density (mA/cm^2). P_{light} is the light density ($100 \text{ mW}/\text{cm}^2$).

Incident-photon-to-current conversion efficiency (IPCE) was determined based on the equation:

$$IPCE = (1240 \times J) / (\lambda \times P_{light}) \times 100\%$$

Where J is the measured photocurrent density (mA/cm^2) at a specific wavelength, λ is the wavelength (nm) of incident light, and P_{light} is the power intensity (mW/cm^2) at a specific wavelength.

The surface charge separation efficiency ($\eta_{surface}$) was calculated based on the equation:

$$\eta_{surface} = J_{H_2O} / J_{Na_2SO_3}$$

Where $J_{\text{H}_2\text{O}}$ is the photocurrent density for PEC water oxidation, and $J_{\text{Na}_2\text{SO}_3}$ is the photocurrent density using Na_2SO_3 as sacrificial agent.

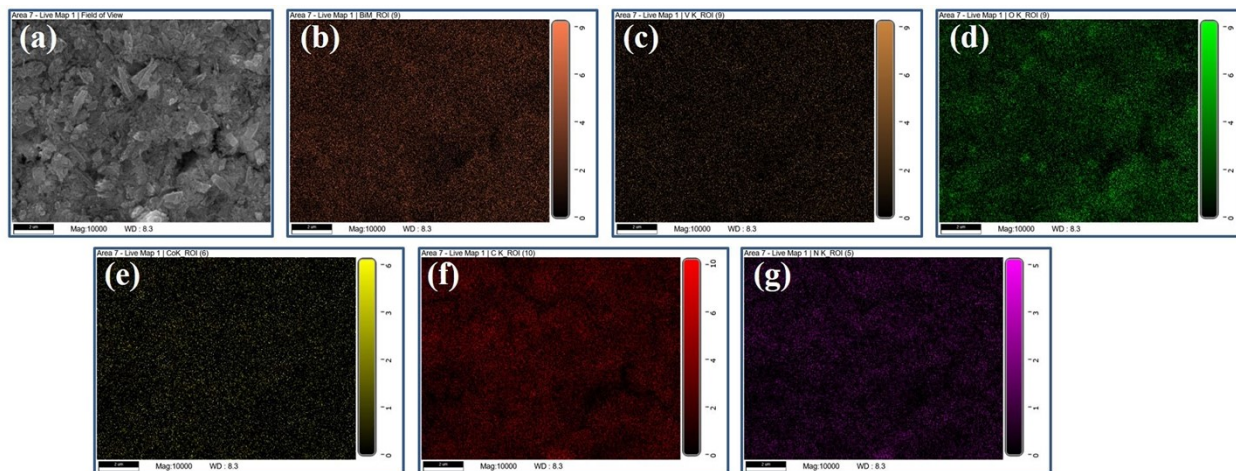


Fig. S1. EDX mapping of BVO/CoPc photoanode: **(a)** Selective area, **(b)** Bi, **(c)** V, **(d)** O, **(e)** Co, **(f)** C, **(g)** N.

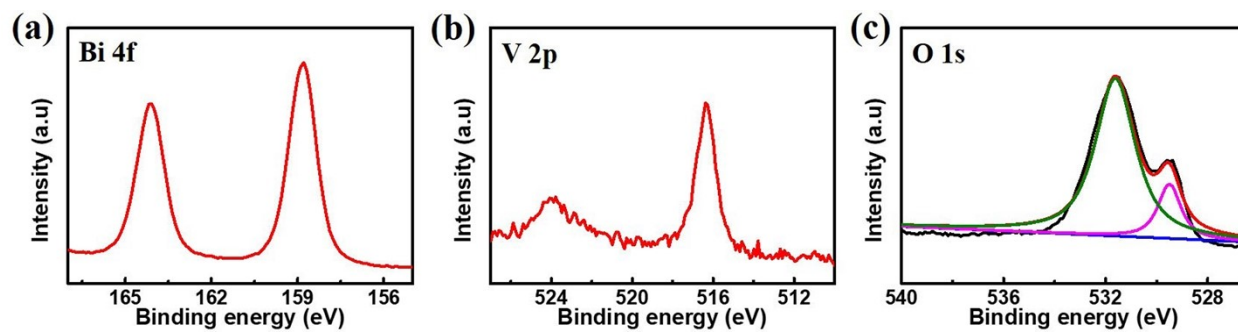


Fig. S2. High-resolution XPS spectrum of (a) Bi 4f, (b) V 2p, and (c) O 1s of the BVO.

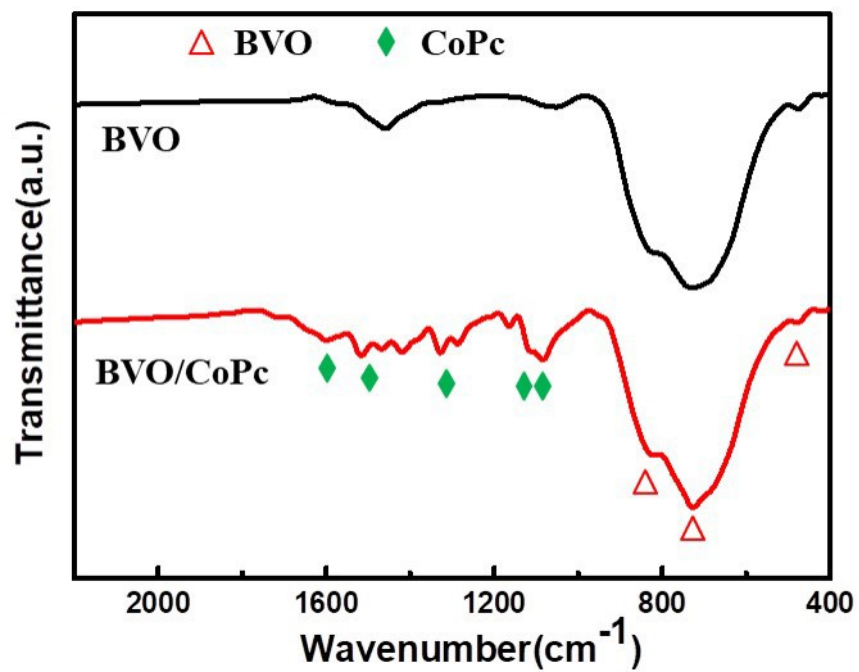


Fig. S3. FT-IR spectrum of the BVO and BVO/CoPc photoanodes.

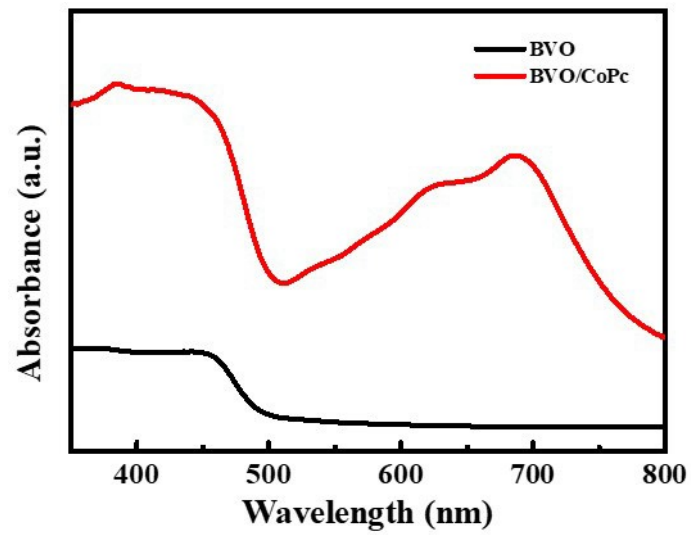


Fig. S4. UV-Vis spectrum of the BVO and BVO/CoPc photoanodes.

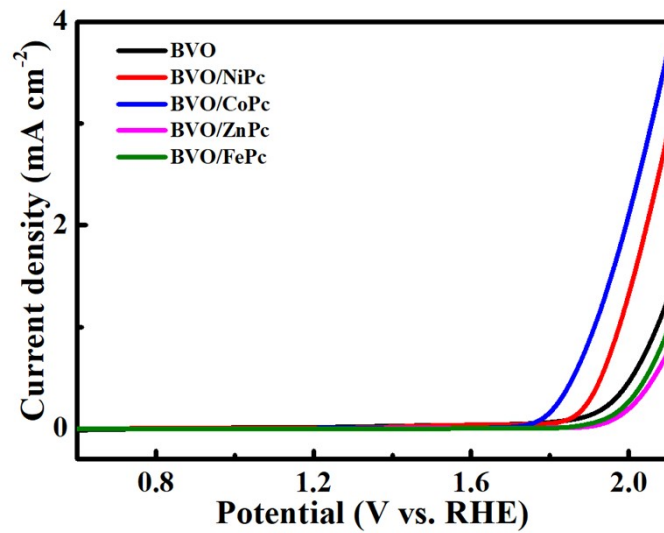


Fig. S5. LSV curves of BVO and BVO/MPc photoanodes without light irradiation.

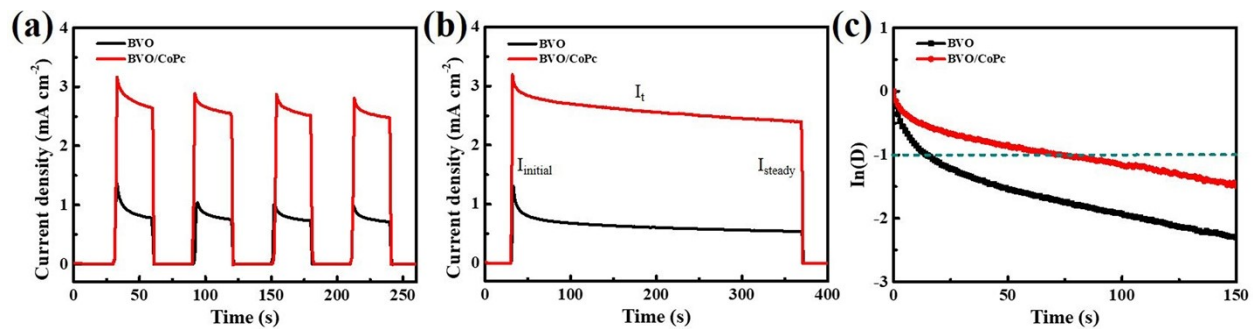


Fig. S6. (a) Photocurrent density of BVO and BVO/CoPc photoanodes at 1.23 V_{RHE} under chopped-light irradiation. (b) Transient photocurrent curves of BVO and BVO/CoPc photoanodes. (c) Normalized plots of $\ln(D)$ as a function of time (t).

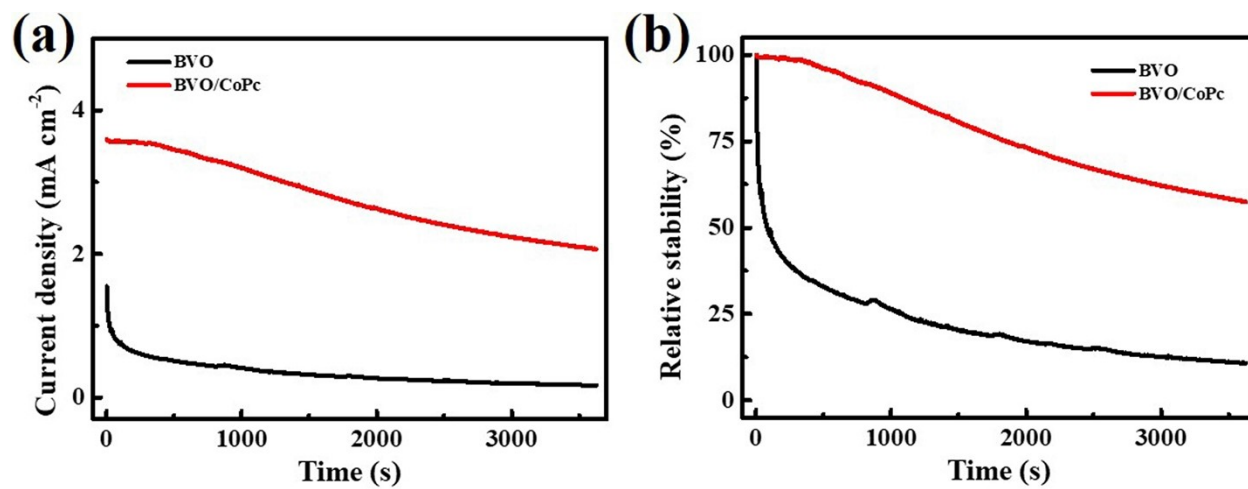


Fig. S7. (a) Long-term stability test of BVO and BVO/CoPc photoanodes at 1.23 V_{RHE} . **(b)** On the basis of the data in (a), the calculated relative stability of the BVO and BVO/CoPc photoanodes.

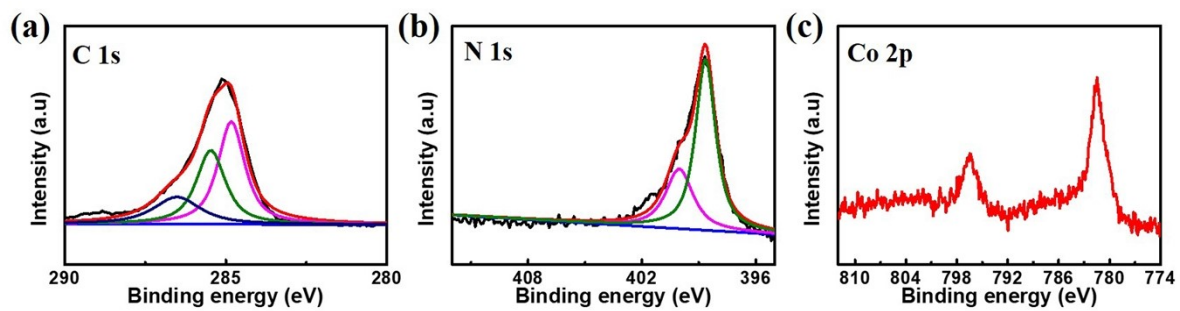


Fig. S8. High-resolution XPS spectrum of (a) C 1s, (b) N 1s, and (c) Co 2p of the BVO/CoPc photoanode after long-term stability test.

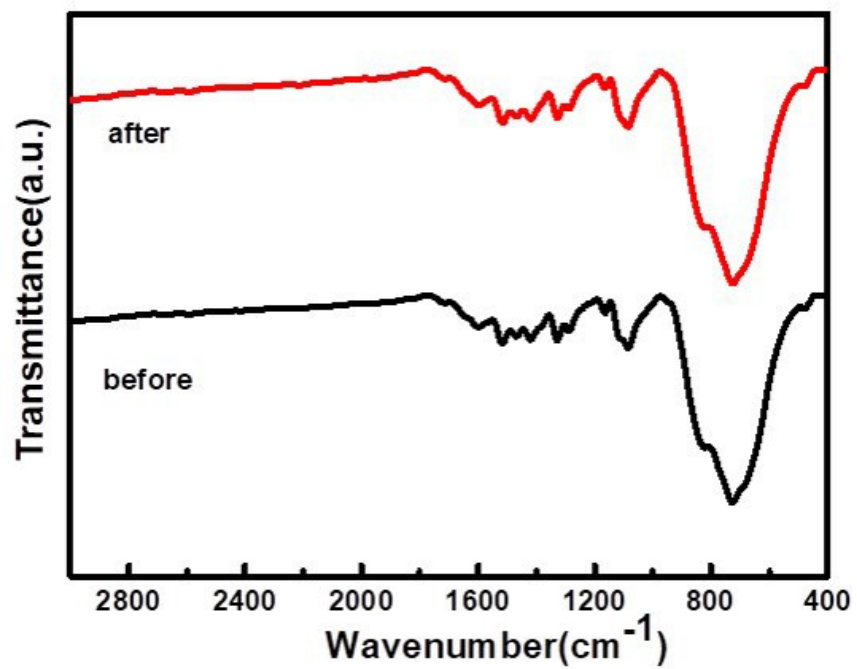


Fig. S9. FT-IR spectrum of the BVO/CoPc photoanode before and after long-term test.

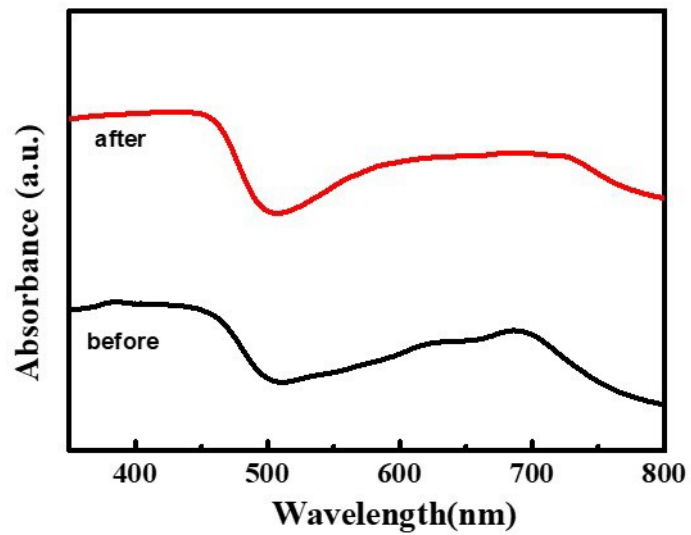


Fig. S10. UV-Vis spectrum of the of the BVO/CoPc photoanode before and after long-term test.

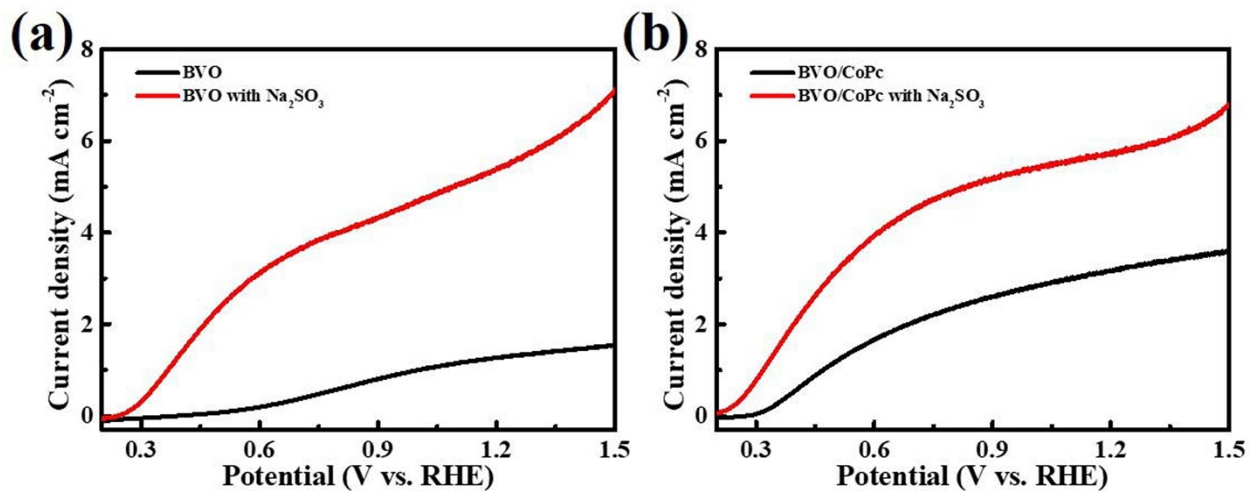


Fig. S11. LSV curves of (a) BVO, and (b) BVO/CoPc photoanodes performed in the absence/presence of Na₂SO₃.

Table S1. Resistance and CPE values of BVO and BVO/CoPc photoanodes.

R/CPE (Ω/F)	R_s	R_{ct}	CPE-T	CPE-P
BVO	26.69	436.6	6.3×10^{-4}	0.58
BVO/CoPc	21.68	180.8	1.7×10^{-4}	0.73

Table S2. The V_{fb} and N_d of BVO and BVO/CoPc photoanodes.

	BVO	BVO/CoPc
V_{fb} (V vs. RHE)	0.77	0.73
$N_d \times 10^{17}$ (cm ⁻³)	7.12	11.27