Electronic Supplementary Information

Boosting the stability and photoelectrochemical activity of a $BiVO_4$ photoanode through a bifunctional polymer coating

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Experimental Section

Synthesis of BVO seed-layer:

The seed layer was deposited on fluorine doped tin oxide (FTO) conductive glass via the spin-coating method. First, an aqueous solution of $Bi(NO_3)_3$ (0.001 mM) was prepared with ethylenediaminetetraacetic acid (EDTA, 0.001 M) as a complexing agent, and the pH was adjusted to 10 by ammonium hydroxide. Then, an aqueous solution of NH_4VO_3 (0.001 mM) was prepared with EDTA (0.001 M) as a complexing agent, and the pH was adjusted to 10 by ammonium hydroxide. Next, these two solutions were mixed uniformity as the precursor solution. Finally, ten drops of the precursor solution were dropped on the FTO conductive glass for spin-coating. After the spin-coating was repeated for three times, the coated glass was annealed at 500 °C.

Synthesis of BVO nanoplate photoanode:

The BVO photoanode was prepared via a hydrothermal process. First, $Bi(NO_3)_3$ (0.001 mol) and EDTA (0.001 mol) were added into water (30 mL). Then, NaOH solution (0.75 mL, 2 M) was added to the former. After the solution was stirred to become transparent, NH_4VO_3 (0.001 mol) was added. Next, the well-mixed solution was transferred into a 50 mL Teflon-lined autoclave. Meanwhile, the FTO conductive glass with BVO seed-layer was put in the autoclave, with the seed-layer side facing down. Finally, the hydrothermal process was

conducted at 180 °C for 3 h, and the as-prepared BVO film was then annealed at 500 °C for 4 h to obtain the BVO photoanode.

Synthesis of PI-coated BVO photoanodes:

The PI-coated BVO photoanodes were prepared via the in-situ thermal polymerization. First, 1,4-diaminobenzene (54 mg) was dissolved in N,N-dimethylformamide (DMF, 30 mL). Then, benzene-1,2,4,5-tetracarboxylic dianhydride (109 mg) was added into the former solution, and the mixed solution was stirred continuously for 12 h. Next, the BVO photoanode was immersed in the pre-polymerized solution for 10s, and the resulted photoanode was placed vertically in air to make it dried. Finally, the photoanode was annealed at 300 °C with N_2 for 8 h in order to make full polymerization. The obtained photoanode was named BPI-1. In addition, the concentration of the precursor solution could be changed to alter the thickness of the polymer film. The concentration was increased to double, triple, and fourfold, and the obtained corresponding photoanodes were named BPI-2, BPI-3 and BPI-4.

Characterizations:

Powder X-ray diffraction (XRD) was conducted by the X-Ray diffractometer (Bruker-D8). Fourier transform infrared (FTIR) spectroscopy was performed on the FT-IR spectrometer (Perkin-Elmer). Scanning electron microscopy (SEM) was carried on a field emission scanning electron scope (Hitachi-S4800). High-resolution transmission electron microscopy (HRTEM) images were collected on a transmission electron microscopy (JEOL-2100F), and the elemental mapping was obtained in STEM mode. A UV-Vis spectrophotometer was used to record the diffuse reflectance ultraviolet-visible (DR UV-Vis) spectra. X-Ray photoelectron spectra were collected on the X-ray photoelectron spectrometer (ESCALab220i-XL). Photoluminescence (PL) spectra and time-resolved transient photoluminescence measurements were performed on a fluorescence lifetime spectrometer (Edinburgh-FLS1000). The surface photovoltage (SPV) was recorded on a surface photovoltage spectrometer (Perfectlight, PL-SPV/IPCE1000).

Electrochemical and photoelectrochemical measurements:

All the measurements were conducted in a three-electrode system with the photoanode as the work electrode, the Pt sheet as the counter electrode, and the saturated calomel electrode as the reference electrode. The electrolyte is potassium phosphate buffer (0.2 M, pH = 7), and the pH is altered by adding KOH. During the testing process, a Xenon light source (Beijing

Prefectlight, PLS-SXE300D) with an AM1.5G light filter provides illumination from the back side of the photoanode, and an electrochemical workstation (Zahner-IM6) was used to record the electrochemical data. The O_2 gas evolved from the PEC system was detected by a gas chromatograph (China, Techcomp GC 7900), and a syringe was used to transfer 50 μL from sealed electrolytic cell to the gas chromatograph instrument every 30 min.

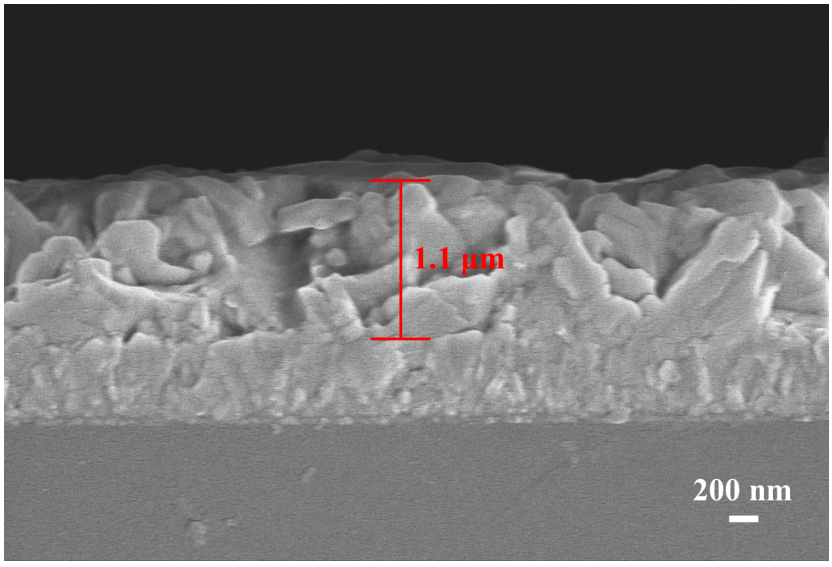

Figure S1. Cross-sections SEM of BVO photoanode.

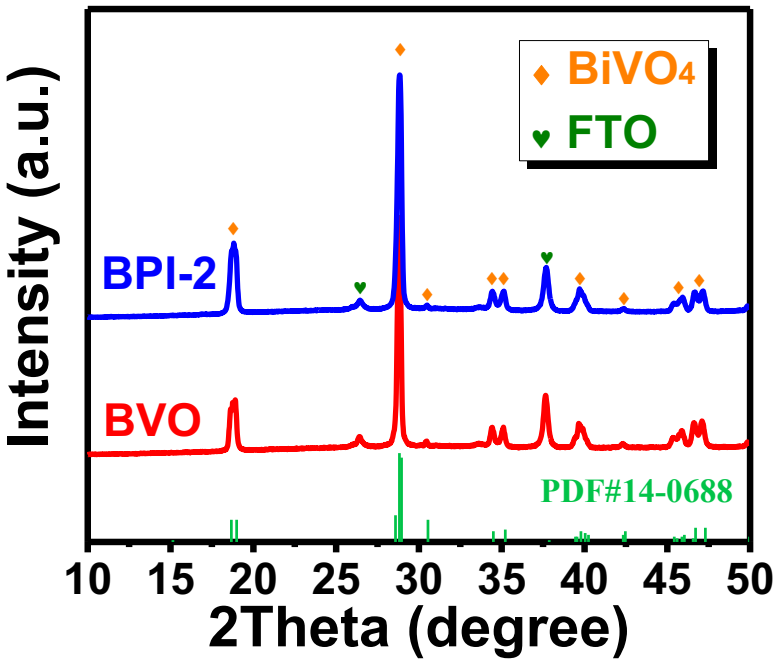

Figure S2. Powder XRD patterns of BVO and BPI-2 photoanodes.

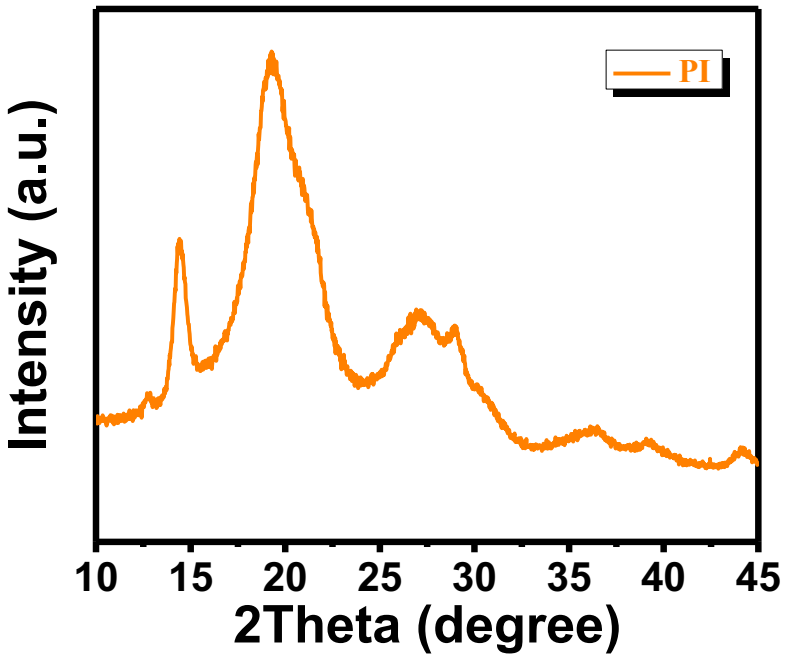

Figure S3. Powder XRD pattern of PI.

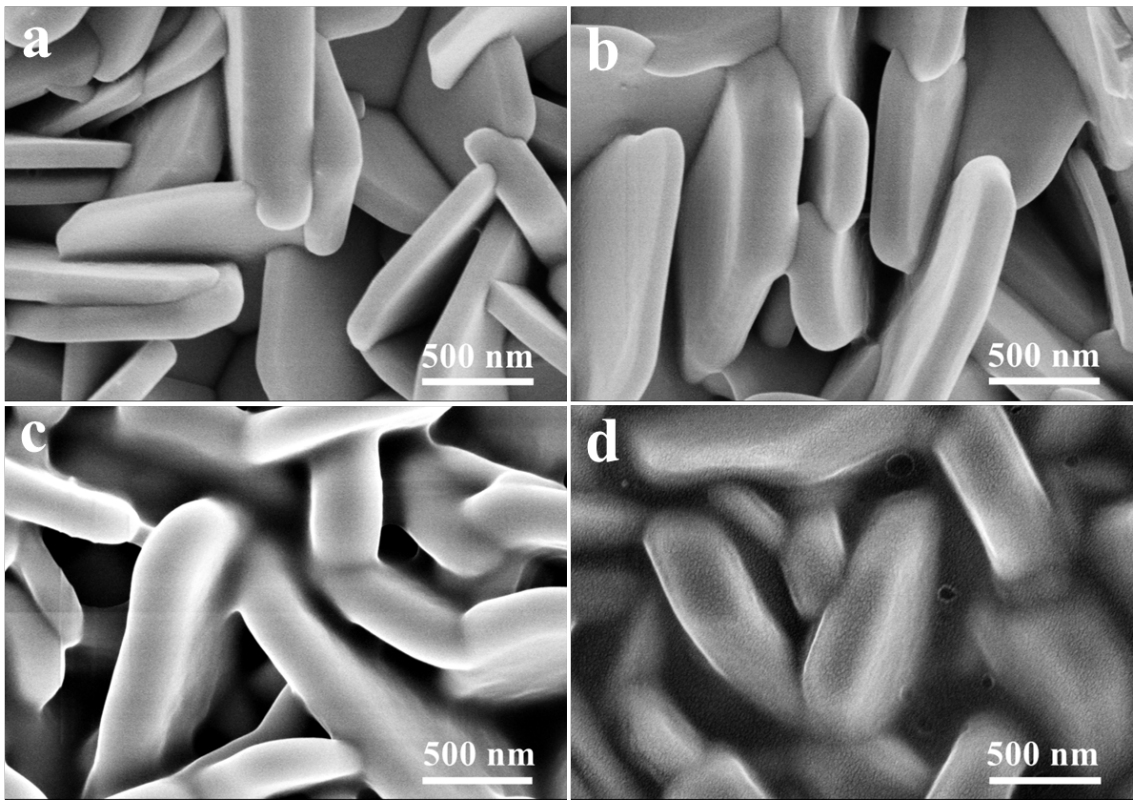

Figure S4. SEM images of PI-coated BVO photoanodes: (a) BPI-1, (b) BPI-2, (c) BPI-3 and (d) BPI-4.

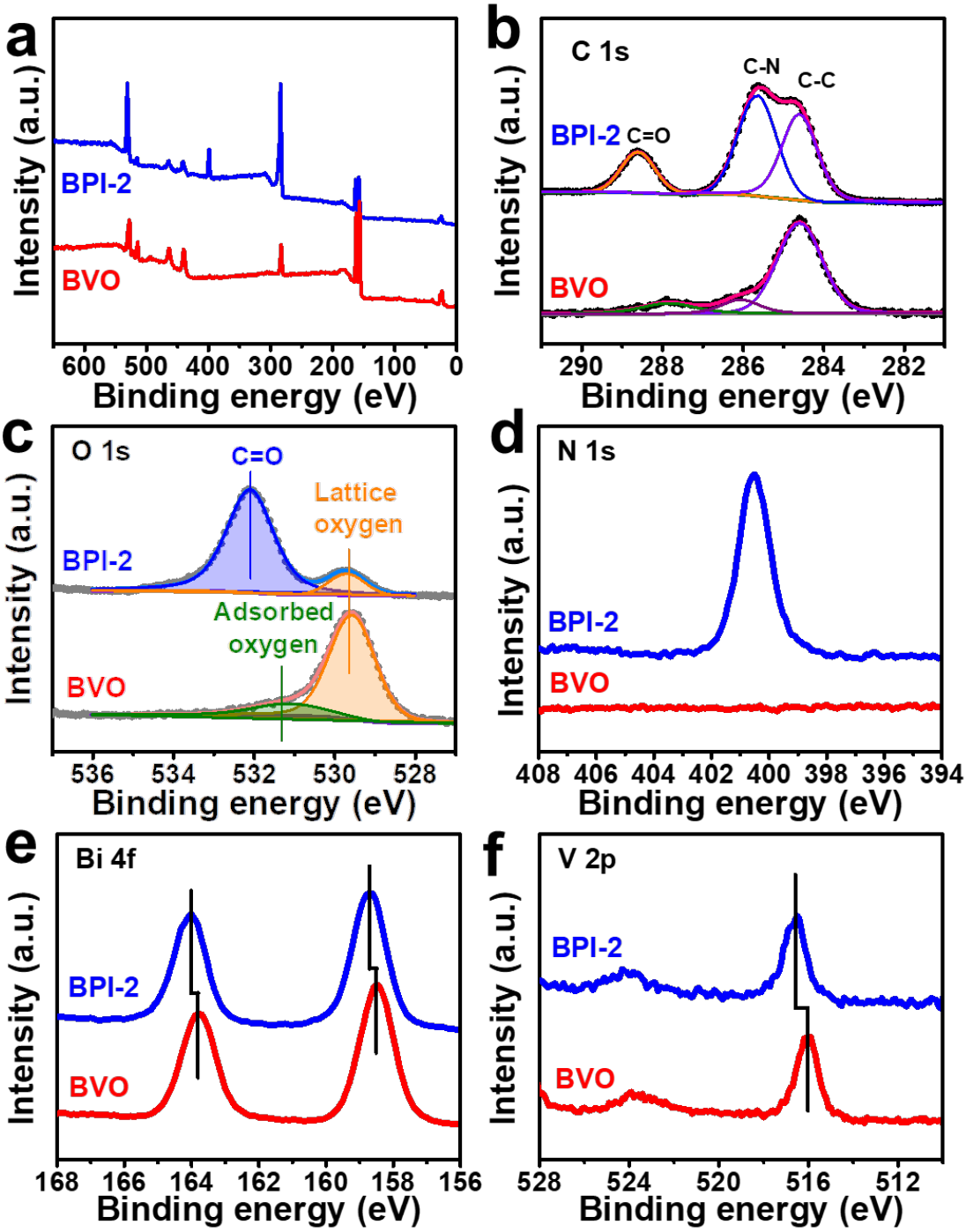

Figure S5. (a) XPS survey, and (b) C 1s, (c) O 1s, (d) N 1s, (e) Bi 4f and (f) V 2p spectra of BVO and BPI-2.

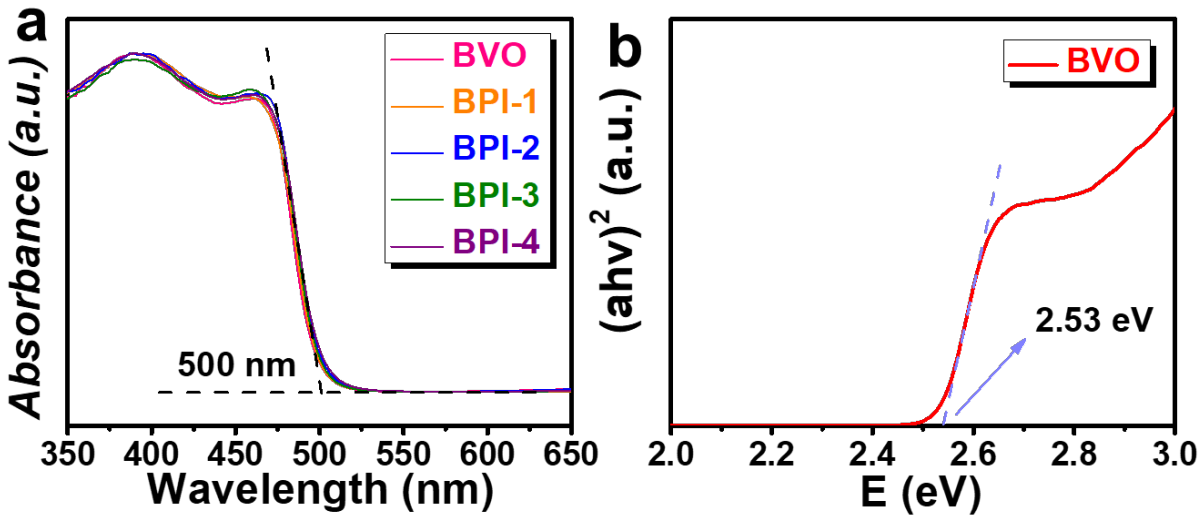

Figure S6. UV-Vis absorption spectra of (a) BVO, BPI-1, BPI-2, BPI-3, and BPI-4 photoanodes and (b) Tauc plot of BVO photoanode.

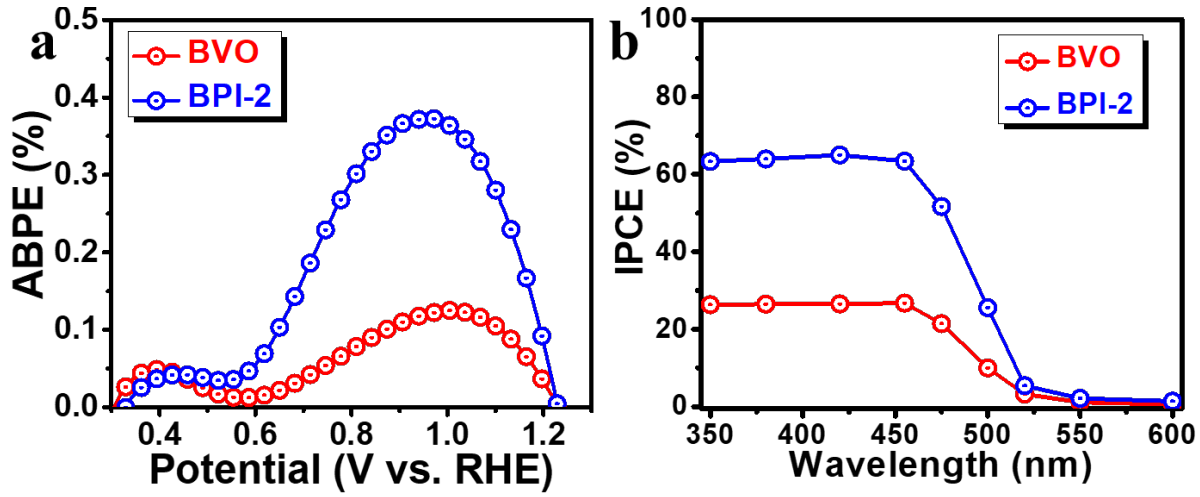

Figure S7. (a) ABPE and (b) IPCE curves of BVO and BPI-2 photoanodes.

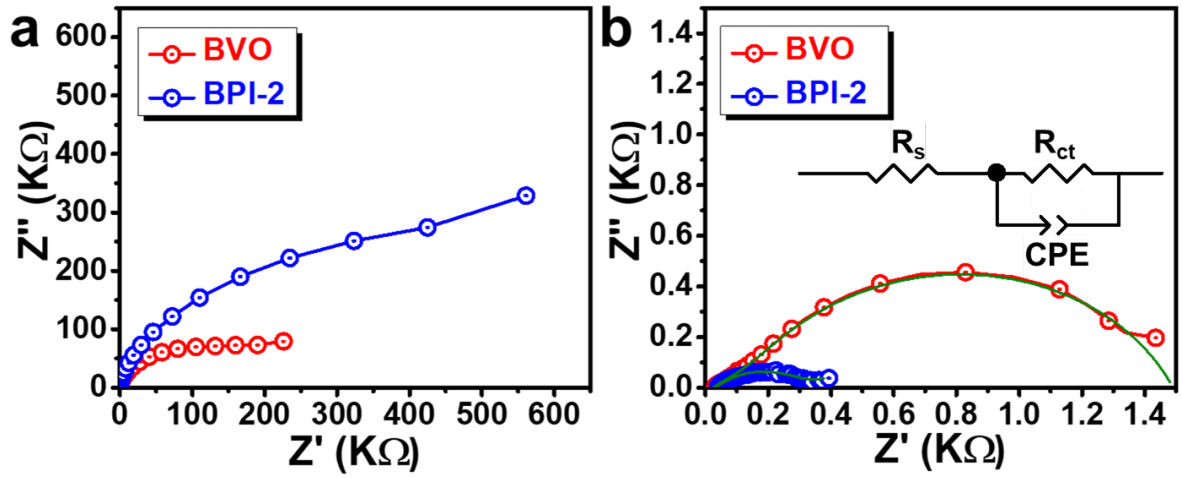

Figure S8. EIS curves of BVO and BPI-2 photoanodes (a) without and (b) with light illumination (Frequency: 100000 Hz-0.01 Hz; Potential: 1.23 V (vs. RHE)).

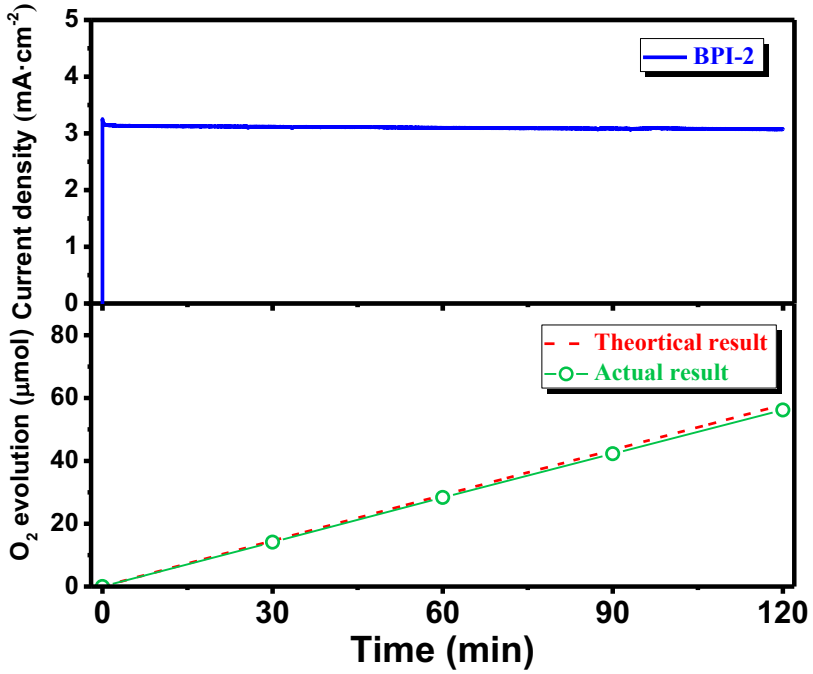

Figure S9. O_2 evolution of BPI-2 at 1.23 V (vs. RHE) in phosphate buffer solution (pH = 7). The dashed line indicates the theoretical result from measured photocurrent.

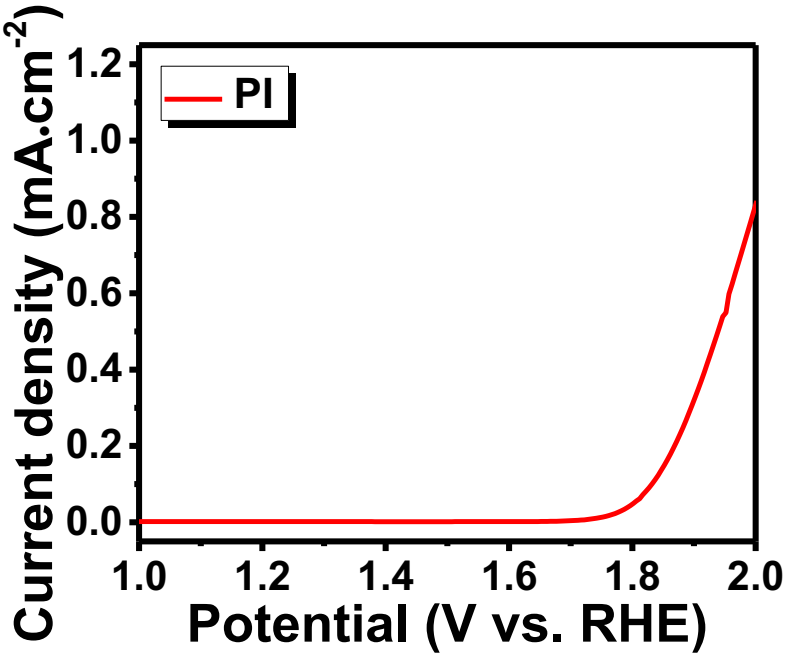

Figure S10. OER curve of PI.

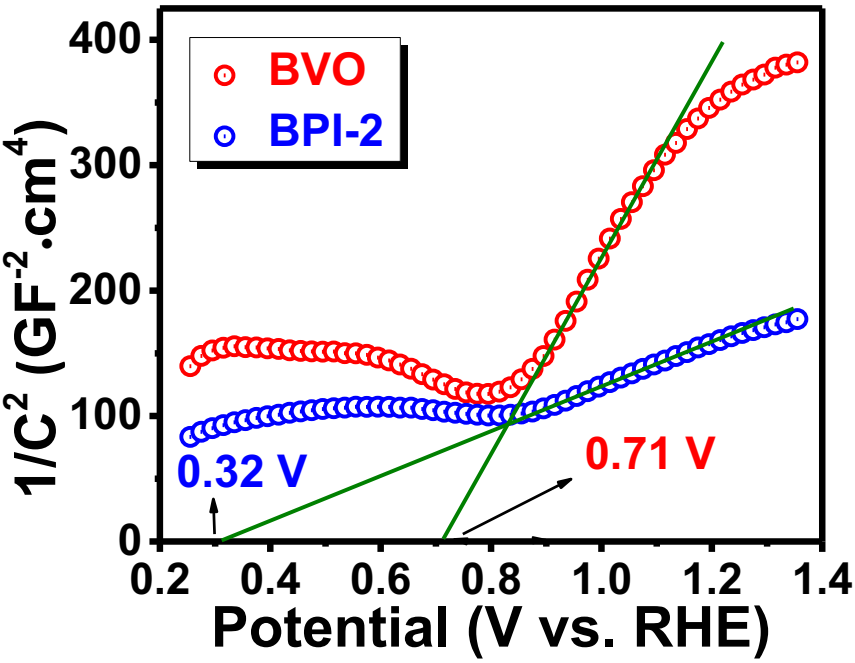

Figure S11. M-S curves of BVO and BPI-2 photoanodes (Frequency: 1000 Hz).

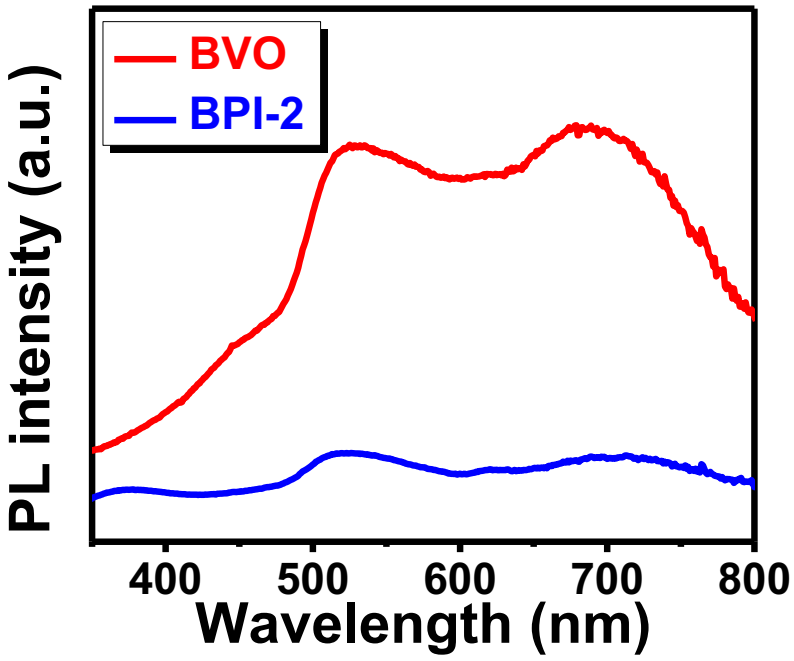

Figure S12. Photoluminescence spectra of BVO and BPI-2 photoanodes.

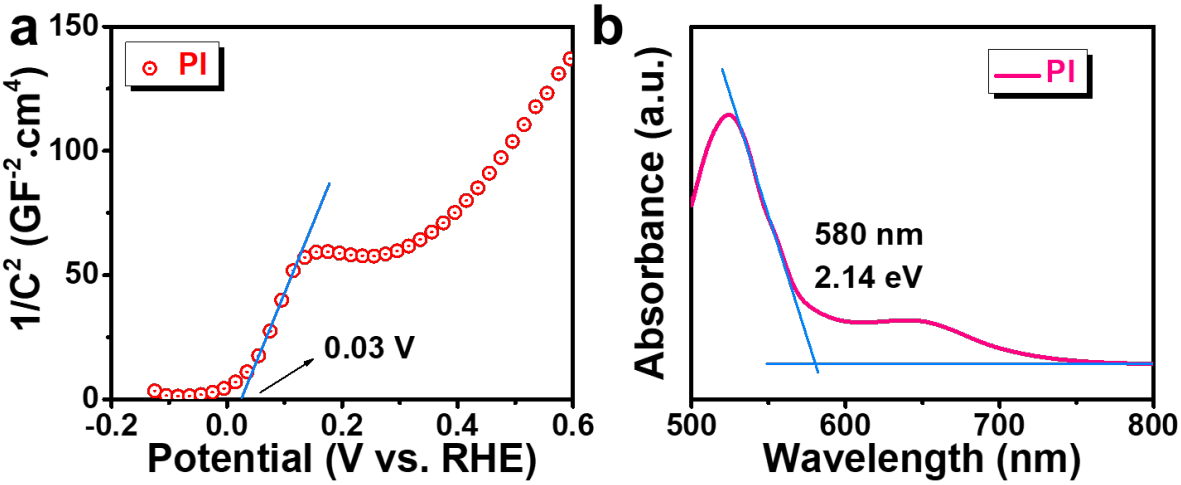

Figure S13. (a) M-S curve and (b) UV-Vis spectrum of PI.

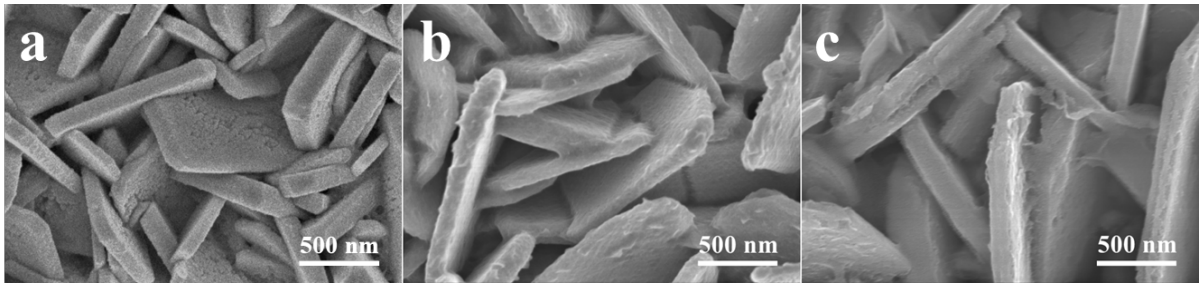

Figure S14. SEM images of (a) BVO, (b) BPI-2 and (c) BPI-4 photoanodes after 6 hours of test in PBS (pH 7).

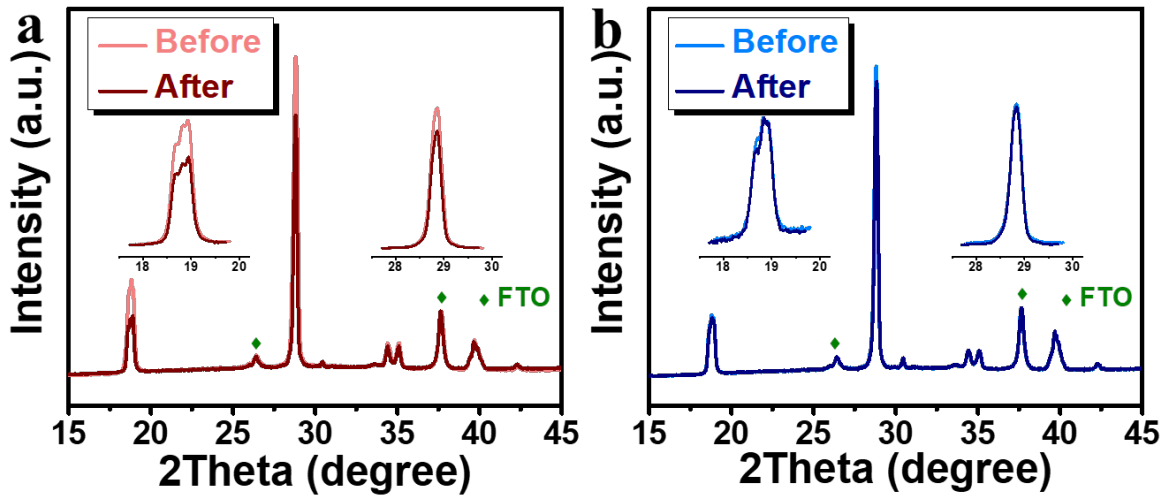

Figure S15. Powder XRD patterns of (a) BVO and (b) BPI-2 photoanodes before and after 6 hours of test in PBS (pH 7).

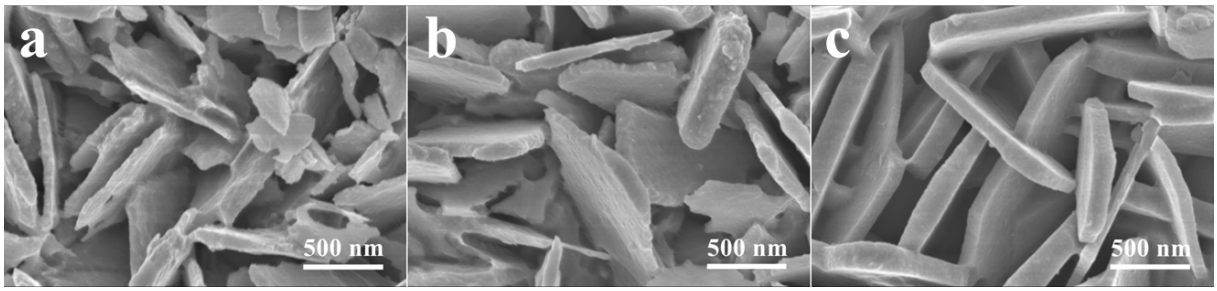

Figure S16. SEM images of (a) BVO, (b) BPI-2 and (c) BPI-4 photoanodes after 6 hours of test in PBS (pH 12).

Table S1. Fitting results of EIS with light illumination.

	R_s (ohm)	R_{ct} (ohm)	C (μF)
BVO	23.5	1292	550
BPI-2	23.5	235.6	54

Table S2. Summary for the stability tests of BVO-based photoanodes in alkaline electrolytes.

Photoanode	Synthetic method	Electrolyte	Test time (current change)	Ref.
BVO/TiO_2/Ni	Atomic-layer deposition and magnetron sputtering	0.1 M KOH (pH = 13)	2h (no change)	1
BVO/$ZnFe_2O_4$	Photodeposition and drop casting	0.1 M KOH (pH = 13)	3000s (60%)	2
BVO/TiO_2	Electrodeposition	0.1 M phosphate buffer (pH = 12)	3h (almost 5%)	3
BVO/PI	In situ thermal polymerization	0.1 M phosphate buffer (pH = 12)	4h (80%); 6h (70%)	This work

References

[1] M. T. McDowell, M. F. Lichterman, J. M. Spurgeon, S. Hu, I. D. Sharp, B. S. Brunschwig and N. S. Lewis, *J. Phys. Chem. C,* 2014, **118**, 19618–19624.

[2] T. W. Kim and K. S. Choi, *J. Phys. Chem. Lett.,* 2016, **7**, 447–451.

[3] D. Lee, A. Kvit and K. S. Choi, *Chem. Mater.,* 2018, **30**, 4704–4712.