

# Supporting Information

## Photogenerated Charge Separation at BiVO<sub>4</sub> Photoanodes Enhanced by Ag-Modified Porphyrin Polymers Skeleton

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## Experimental Section

### Materials

Fluorine-doped tin oxide (FTO) was purchased from Wuhan Jingge Solar Technology Co. Ltd. Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, KI, p-benzoquinone, HNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, hexachlorocyclotriphosphonitrile (HCCP, 98%), and 4-hydroxybenzaldehyde (95%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Acetonitrile, triethylamine and DMSO were purchased from Tianjin Damao Chemical Reagent Co.,

LTD. Silver nitrate was purchased from Tianjin Best Chemical Co., LTD. Propionic acid was purchased from Jinan Trands Chemical Co. LTD. Pyrrole was purchased from Shanghai Bangcheng Chemical Co., LTD. Ultrapure water was produced by a Milli-Q system.

### **Synthesis of Tetrahydroxyphenyl Porphyrin (THPP)**

The synthesis procedure of THPP is consistent with the literature reported. [1] 4-hydroxybenzaldehyde (6.11 g, 50 mmol) was added to a 100 mL round-bottomed flask, mixed with 250 mL propionic acid, and heated to 145 °C. In addition, 3.5 mL of new steamed pyrrole was dripped into the mixed solution within 2 min, and the reflux was carried out for 2 h. About 150 mL of propionic acid was evaporated when the reaction was completed. After restoring room temperature, the appropriate amount of anhydrous ethanol was added, and cooled overnight a 4 °C. The crude product was then filtered, washed with ethyl acetate and dried in a vacuum oven at 70 °C for 12 h. Finally, the product is recrystallized. Yield, 14.6%. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.95(s, 4H), 8.87(s, 8H), 7.99-8.01(d, *J*= 8 Hz, 8H), 7.20-7.22(d, *J*= 8 Hz, 8H), -2.88(s, 2H).

### **Preparation of THPP-HCCP**

We used hexachlorotricyclophosphazene (HCCP) as the stable structural skeleton unit to react with tetrahydroxyphenyl porphyrin, which was synthesized with a simple polycondensation reaction by one-step ultrasonic method. [2] First, HCCP (20 mg) and THPP (20 mg) were mixed in a 100 mL round-bottomed flask. Then acetonitrile (60 mL) was added and treated with ultrasound for 20 min. After TEA (2.0 mL) was injected into the mixture, the solution was kept at 20 °C. After the reaction was completed, centrifuging, washing and freezing dry to get the final product.

### **Preparation of Ag-THPP-HCCP**

Dissolved THPP-HCCP in 20 mL of DMF containing 50 μL of TEA and slowly added ethanol-dissolved silver nitrate dropwise to a round-bottom flask and reflux. After the reaction and cooled to room temperature, centrifuged to obtain a gray-yellow

precipitate, and washed with ethanol 3 times to obtain Ag-modified porphyrin-phosphazene polymer (Ag-THPP-HCCP). Ag/THPP-HCCP ratio optimization: The mass ratios of Ag and the THPP-HCCP were optimized at 0.5, 1.0 and 1.5, and the other steps were consistent with the above methods. The prepared composites were named Ag-THPP-HCCP-0.5, Ag-THPP-HCCP-1.0, and Ag-THPP-HCCP-1.5.

### **Preparation of BV photoelectrode**

BV film was prepared by electrodeposition and annealing procedure. In particular, the pH of KI solution (20 mmol KI, 50 mL ultrapure water) was adjusted to 1.7 by adding HNO<sub>3</sub>. Then, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.97 g) was added into the solution slowly. Next, p-benzoquinone was dissolved in ethanol (0.23 M, 20 mL), and mixed with the above solution to obtain the final electrolyte solution. Cathodic electrodeposition was carried out potentiostatically at -0.1 V versus Ag/AgCl for 5 min under the three-electrode system. Next, DMSO solution of VO(acac)<sub>2</sub> (0.2 M, 200 μL) was added to the BiOI electrode and annealed at 450 °C for 2 h (2 °C/min). Excess V<sub>2</sub>O<sub>5</sub> on the photoanodes was eliminated through immersing in NaOH solution (1 M). Finally, the photoanodes were rinsed with ultrapure water and dried to obtain BiVO<sub>4</sub>.

### **Preparation of Ag-THPP-HCCP/BV photoelectrode**

0.1 mg/mL of Ag-THPP-HCCP ethanol solution was configured. Taking the optimal volume of Ag-THPP-HCCP dropwise onto the prepared BV to form an Ag-THPP-HCCP/BV composite photoanode.

### **Characterization**

Photoelectrochemical performances were measured by Autolab PGSTAT 302 in a typical three-electrode system. The material-grown FTO conductive glass, platinum electrode, and Ag/AgCl served as the working, counter, and reference electrode, respectively. The electrolyte was 0.5 M Na<sub>2</sub>SO<sub>4</sub>. The crystal phase spectra were obtained by X-ray diffraction analysis (XRD, SmartLab 9 KW). UV-visible diffuse reflectance spectroscopy (UV-DRS) was tested by a UV-3600 (Shimadzu)

spectrometer using BaSO<sub>4</sub> as a reference. Scanning electron microscopy (SEM) images were performed with the JSM-6710F instrument (Japan). The morphology and microstructure of the photoelectrode were characterized by energy-dispersive X-ray spectroscopy (EDX). The high-resolution transmission electron microscope (HRTEM) and TEM images were observed by a JEM-3010 instrument. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha model) was used to obtain the chemical state of metallic elements. The intensity-modulated photocurrent spectroscopy (IMPS) test light source is an LED lamp with a wavelength of 470 nm and an applied potential of -0.1 V (vs. Ag/AgCl). Scanning photoelectrochemical microscopy (SPECM) related tests were carried out on the UV-vis/SPECM platform independently built by our research group. The platform includes a 300 W Xe lamp and a CHI 920D SECM bipotentiostat. The light source is a 300 W Xenon lamp with a power of 100 mW/cm<sup>2</sup> and the light source is equipped with a 1.5 G filter.

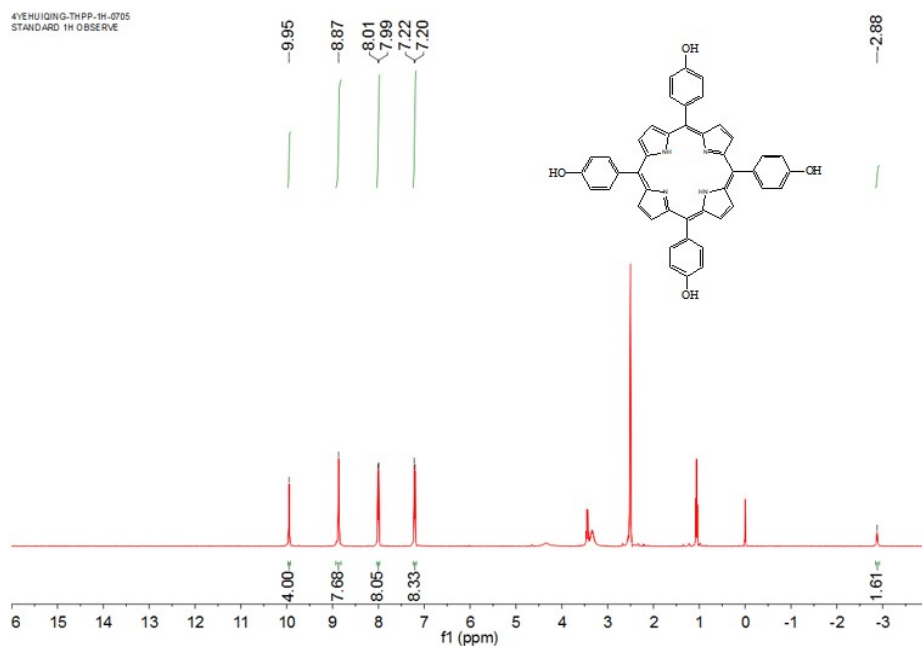


Figure S1.  $^1\text{H-NMR}$  characterization of THPP in  $\text{DMSO-}d_6$ .

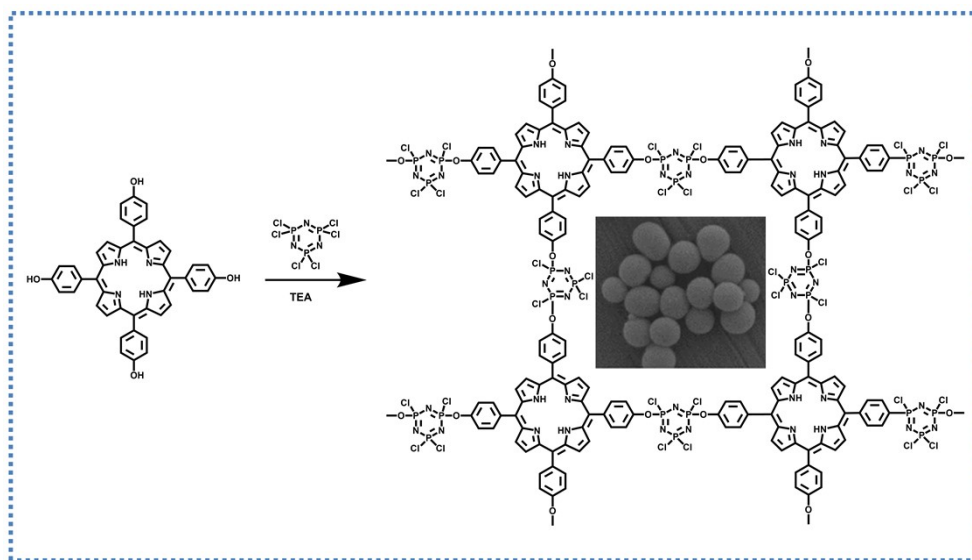


Figure S2. The synthesis process of THPP-HCCP and corresponding SEM image.

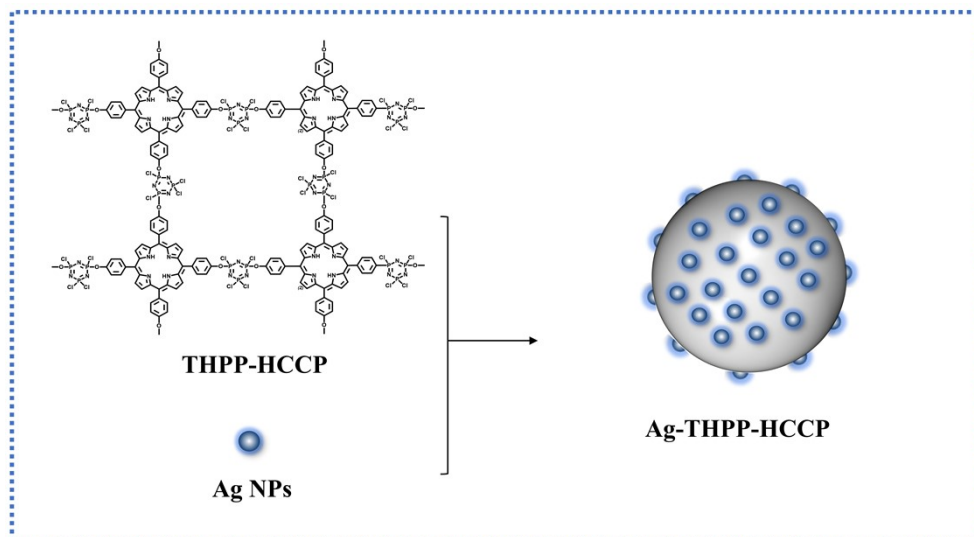


Figure S3. The preparation process of Ag-THPP-HCCP.

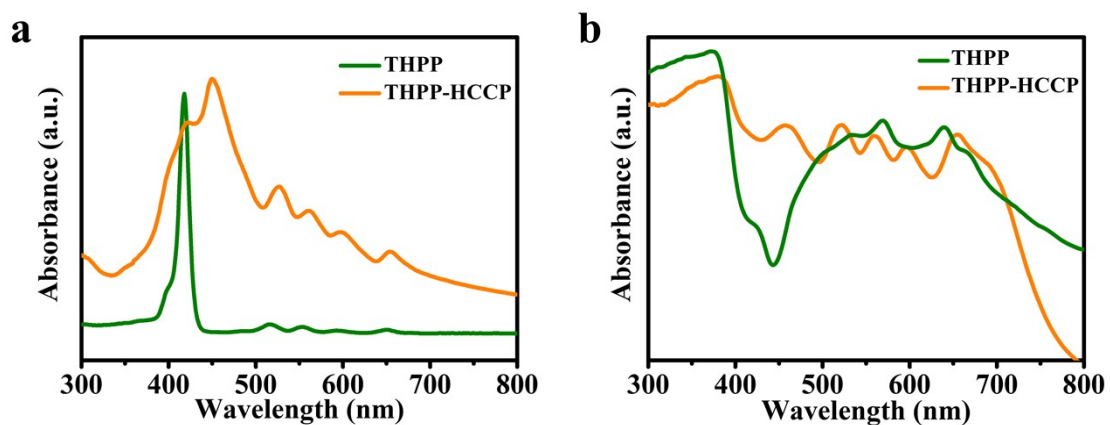


Figure S4. a) UV-vis spectra of THPP and THPP-HCCP in  $\text{CH}_3\text{CN}$  solution; b) Solid UV-vis diffuse reflectance pattern of THPP and THPP-HCCP.

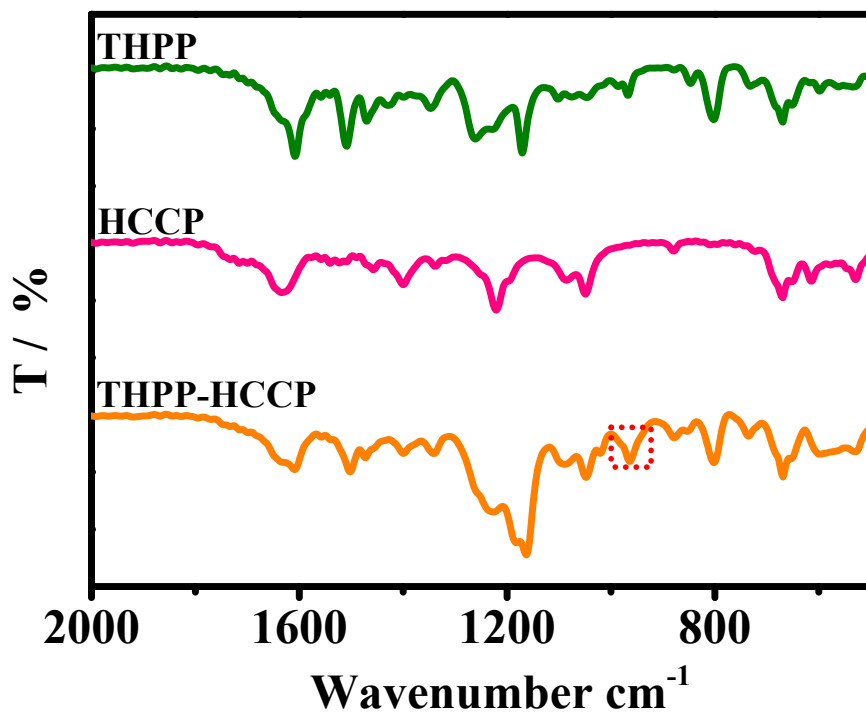


Figure S5. FTIR spectra of THPP, HCCP and THPP-HCCP.

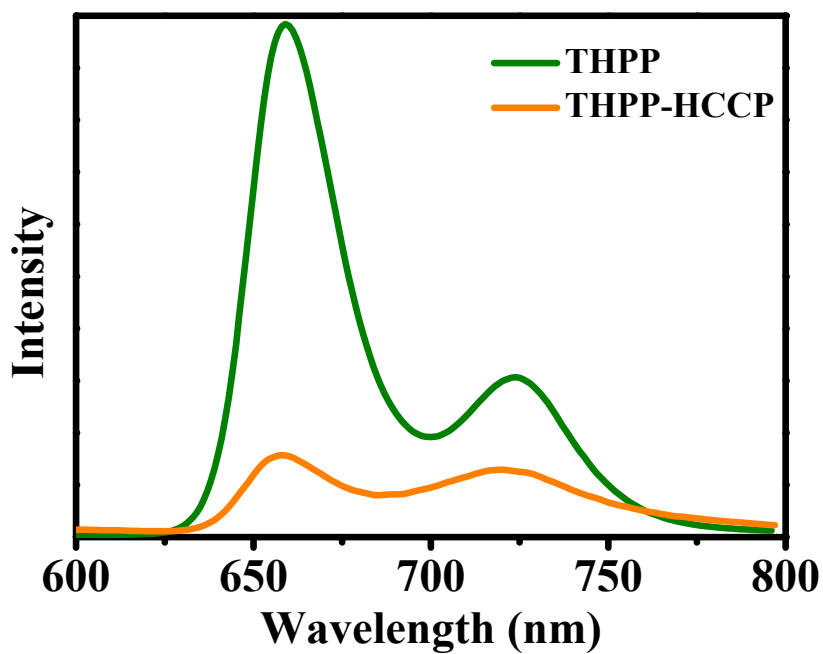


Figure S6. Fluorescence intensity of THPP and THPP-HCCP.

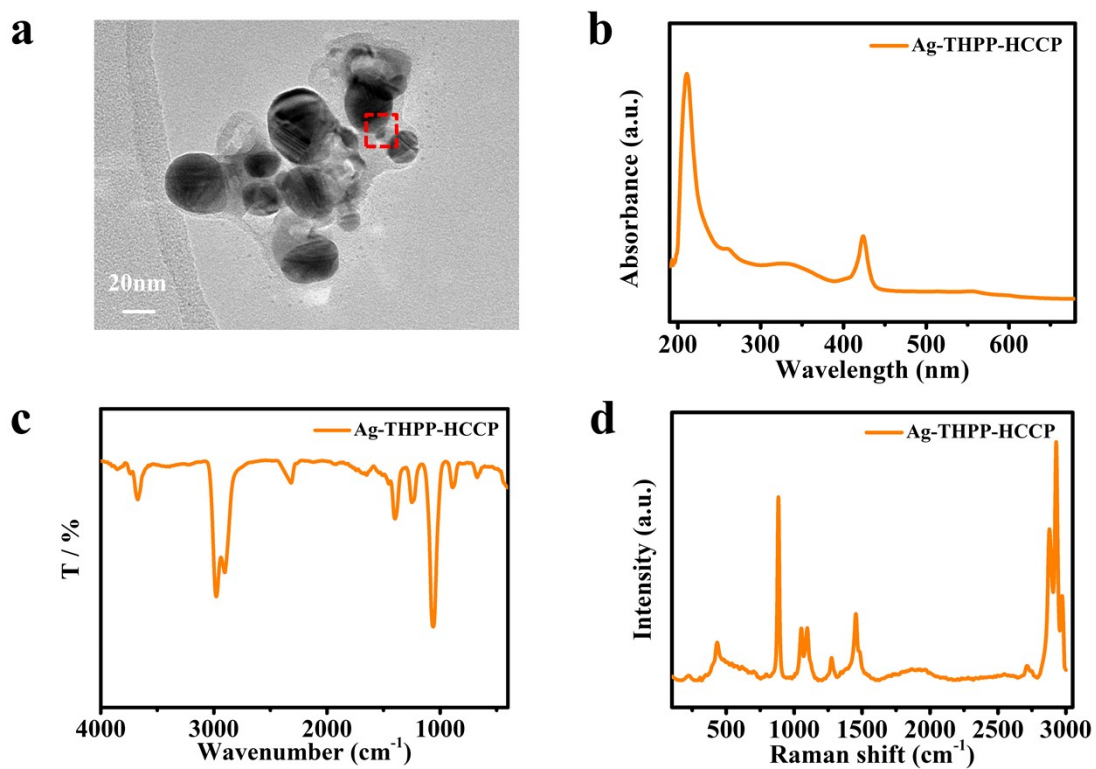


Figure S7. The TEM (a), UV-vis absorption (b), FTIR (c) and Raman measurement of Ag partials modified THPP-HCCP polymer.

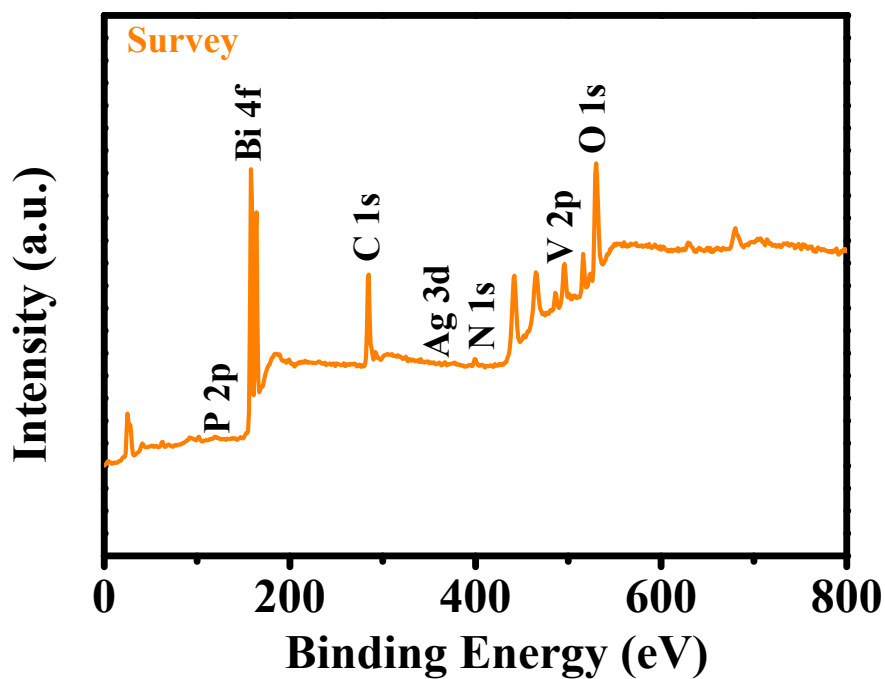


Figure S8. The survey XPS spectrum of the integrated Ag-THPP-HCCP/BV photoanode.



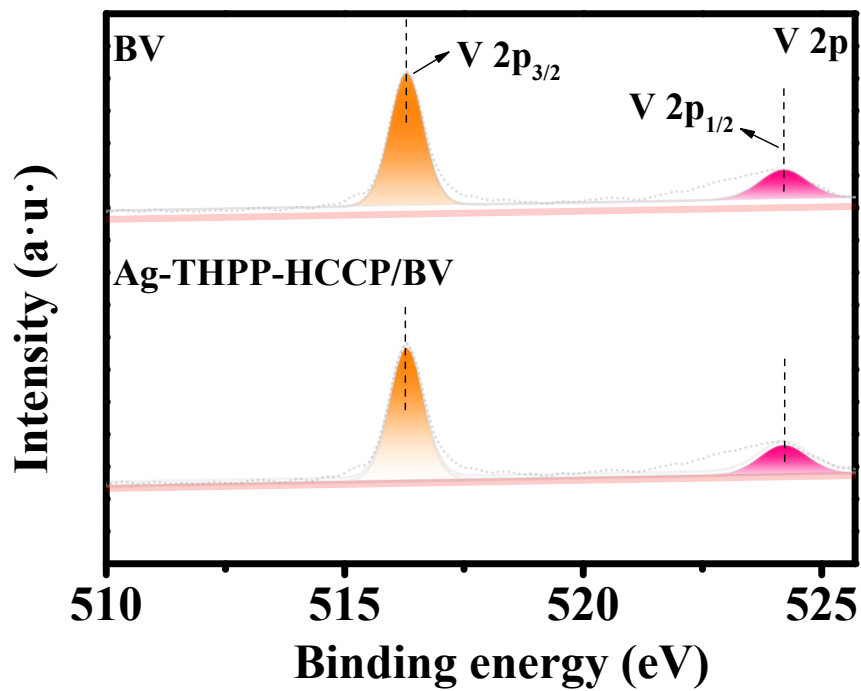


Figure S9. V<sub>2p</sub> high-resolution XPS spectroscopy of BV and Ag-THPP-HCCP/BV photoanode.

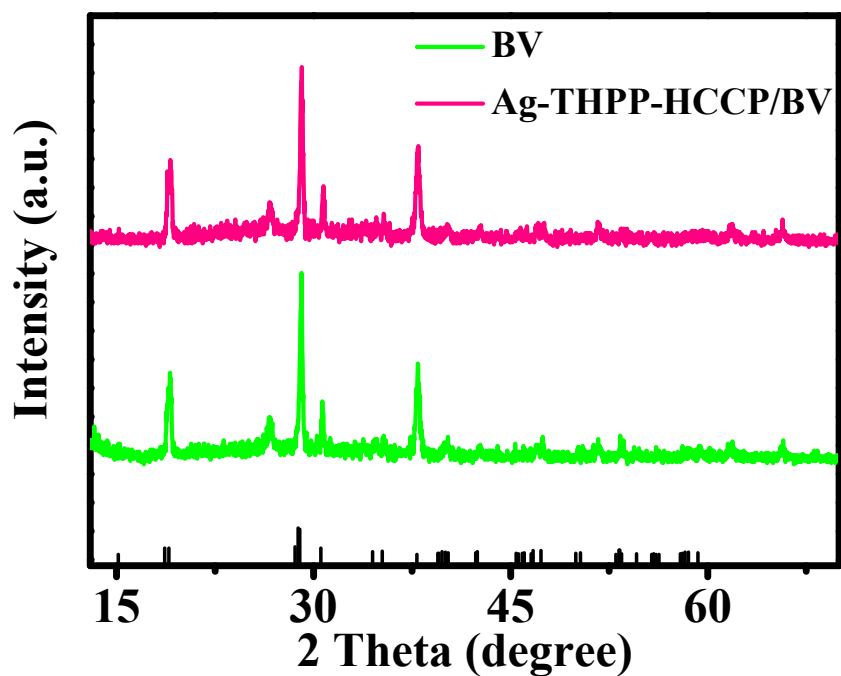


Figure S10. XRD patterns of different photoanodes.

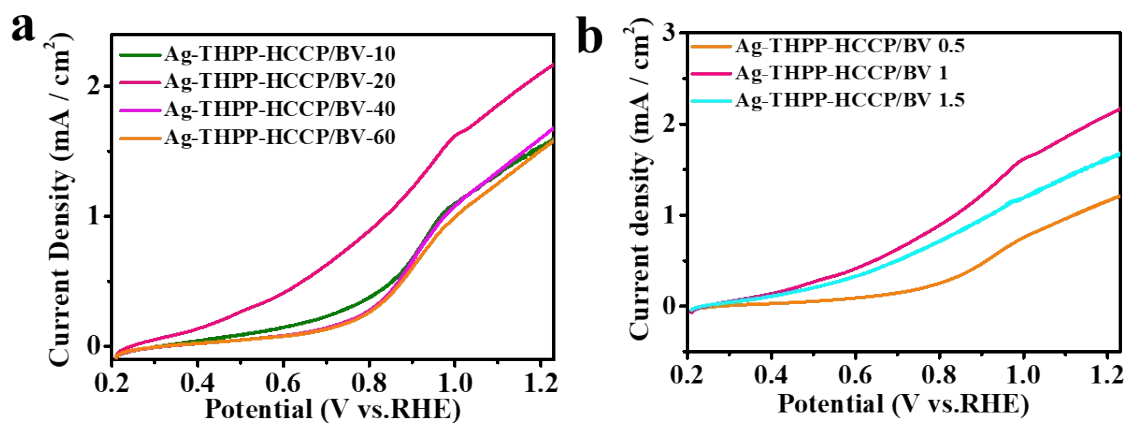


Figure S11. a) Optimization drip-coating amount of Ag-THPP-HCCP in different volumes (10, 20, 40 and 60  $\mu\text{L}$ ). b) Optimization of the mass ratio of Ag to THPP-HCCP.

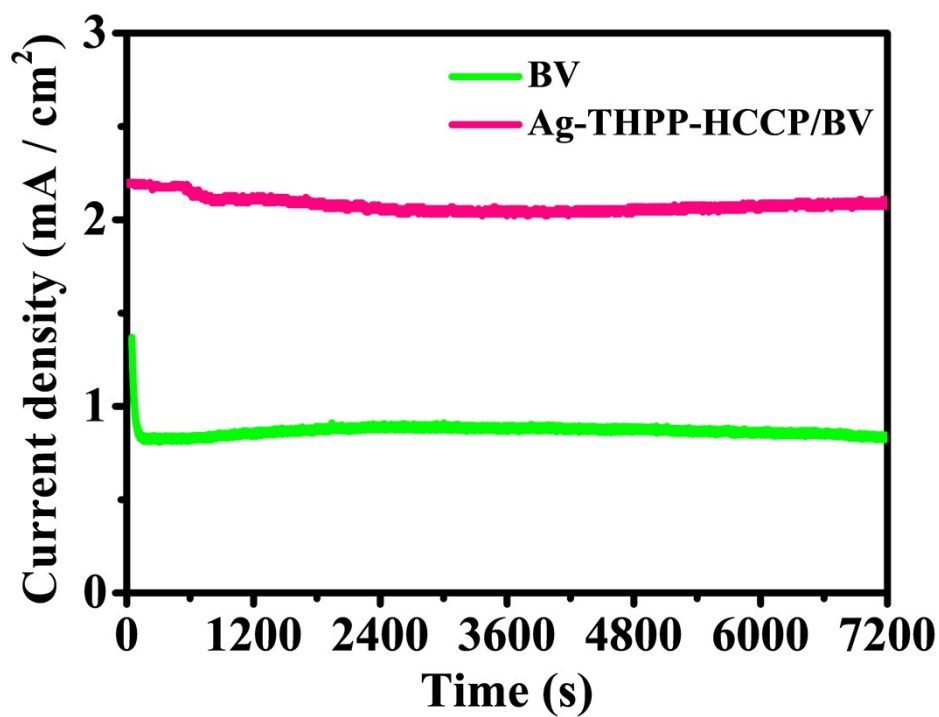


Figure S12. Stability test results of BV and Ag-THPP-HCCP/BV photoanodes.

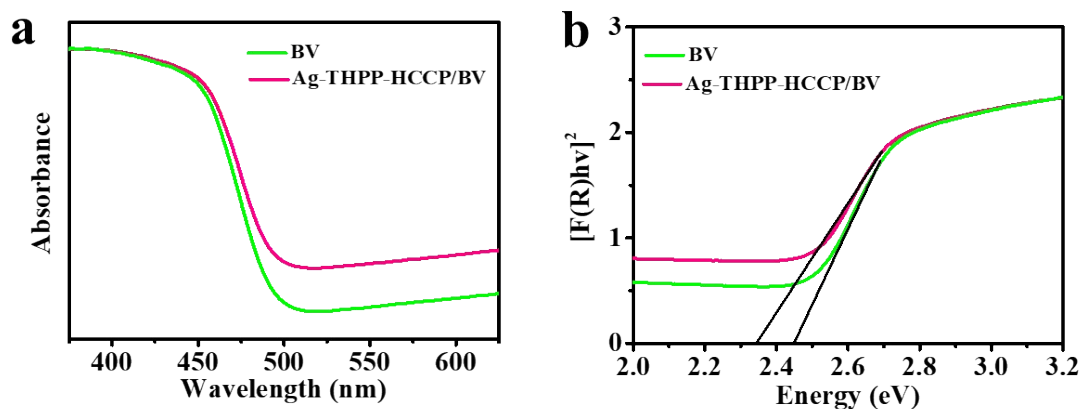


Figure S13. a) UV-vis diffuse reflectance spectra of different photoanodes. b) Band gap values of different photoanodes.

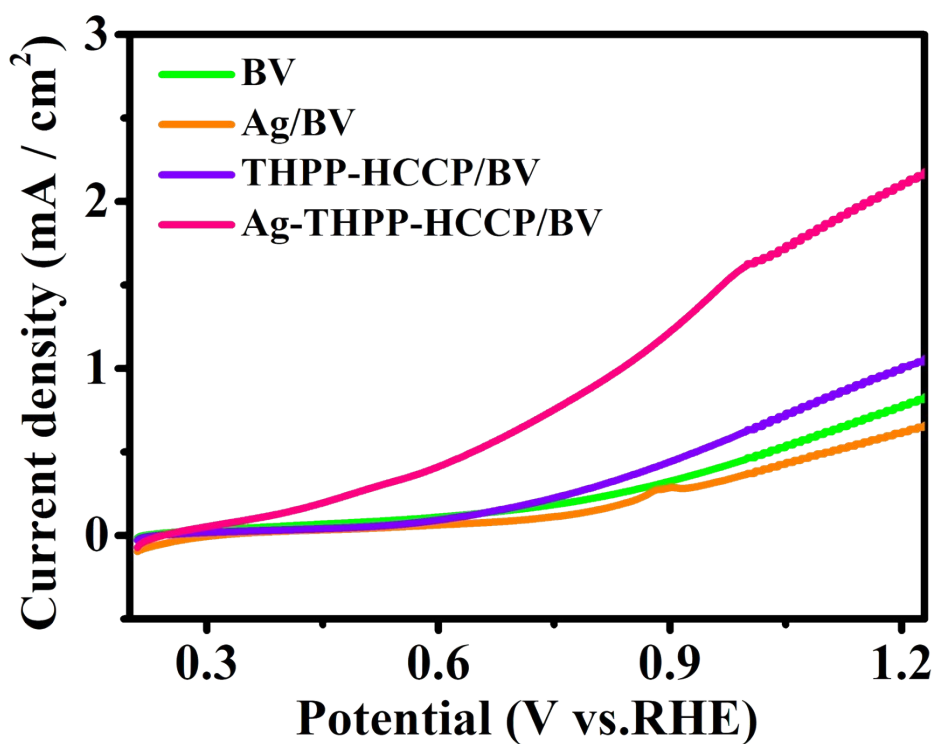


Figure S14. LSV comparison of BV photoanodes modified by Ag, THPP-HCCP, and Ag-THPP-HCCP

Table S1. Comparison of different organic-inorganic hybrid modified BV photoanode PEC performance (AM 1.5G)

<b>Photoanodes</b>	<b>Photocurrent at 1.23 V<sub>RHE</sub></b>	<b>Electrolyte</b>	<b>Reference</b>
<b>BV-C/N-Ag</b> <sup>[3]</sup>	2.42 mA/cm <sup>2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 7.3)	Chem. Eng. J. 2019, 358: 658-665
<b>BV/ZnPtP-CP</b> <sup>[4]</sup>	-	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 7.0)	Adv. Energy Mater. 2021, 11(7): 2003575
<b>BV/Ni<sub>3</sub>B</b> <sup>[5]</sup>	1.47 mA/cm <sup>2</sup>	0.1 M Na <sub>2</sub> SO <sub>4</sub> (pH 7.0)	Nano Res. 2022: 1-7.
<b>Ag/NH<sub>2</sub>-MIL-125/TiO<sub>2</sub></b> <sup>[6]</sup>	1.0 mA/cm <sup>2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 7.0)	Chem. Eng. J. 2020, 388: 124206.
<b>BV/Cu<sub>2</sub>L</b> <sup>[7]</sup>	2.6 mA/cm <sup>2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 7.0)	Chem. Eng. J. 2021, 422: 130092
<b>Ag-Pi/BV</b> <sup>[8]</sup>	2.3 mA/cm <sup>2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	J. of Colloid and Interf. Sci. 2020, 579: 619-627
<b>Ag-THPP-HCCP/BV</b>	<b>2.2 mA/cm<sup>2</sup></b>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	<b>Present Work</b>

## Reference

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- [2] Wei X, Chen H, Tham H P, et al. Combined photodynamic and photothermal therapy using cross-linked polyphosphazene nanospheres decorated with gold nanoparticles. *ACS Applied Nano Materials*, **2018**, 1(7): 3663-3672.
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- [7] Ma Y X, Gao B, He J, et al. Hydrogen bonded metal–organic supramolecule functionalized BiVO<sub>4</sub> photoanode for enhanced water oxidation efficiency. *Chemical Engineering Journal*, **2021**, 422: 130092.
- [8] Gao Y, Li X, Hu J, et al. Ag-Pi/BiVO<sub>4</sub> heterojunction with efficient interface carrier transport for photoelectrochemical water splitting. *Journal of Colloid and Interface Science*, **2020**, 579: 619-627.