

Supplementary Information

**Tailoring the Electronic Structure of Cobalt Phthalocyanine on
BiVO₄ via Substituent Effects for Enhanced Photoelectrochemical
Water Splitting**

Zhehui Xiao^{a†}, Shuangwei Yu^{a†}, Zihan Bian^a, Qianqian Dong^a, Haohao Yuan^{a*}, Xue Gong^a,
Xiong He^{a*}, Daochuan Jiang^b, Zijun Sun^{a*}

^aSchool of Electronic Engineering, Guangxi Key Laboratory of Multidimensional
Information Fusion for Intelligent Vehicles, Guangxi University of Science and Technology,
Liuzhou 545006, China.

^bSchool of Materials Science and Engineering, Anhui University, Hefei 230601, China.

[†]These authors contributed equally to this work.

*Corresponding authors.

E-mail: yuanhao_1027@gxust.edu.cn; hexiong@gxust.edu.cn; sunzijun@gxust.edu.cn.

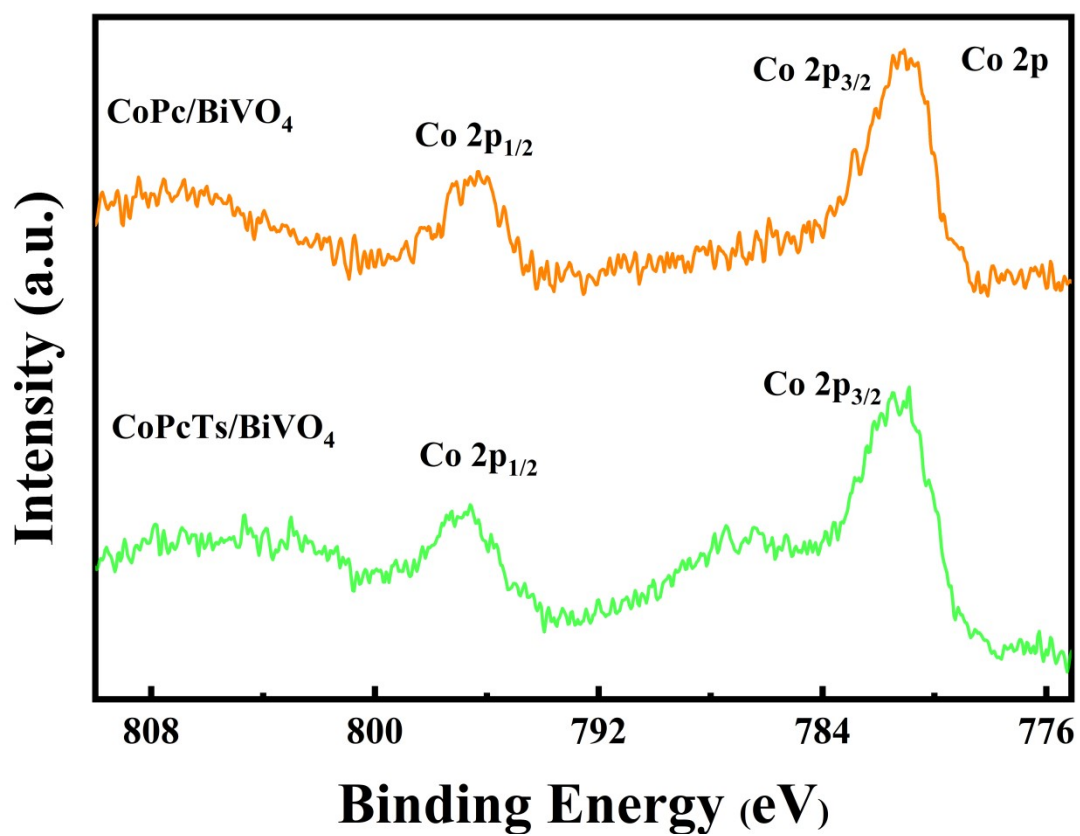


Fig. S1 The high-resolution Co 2p XPS spectrum of CoPc/BiVO₄ and CoPcTs/BiVO₄.

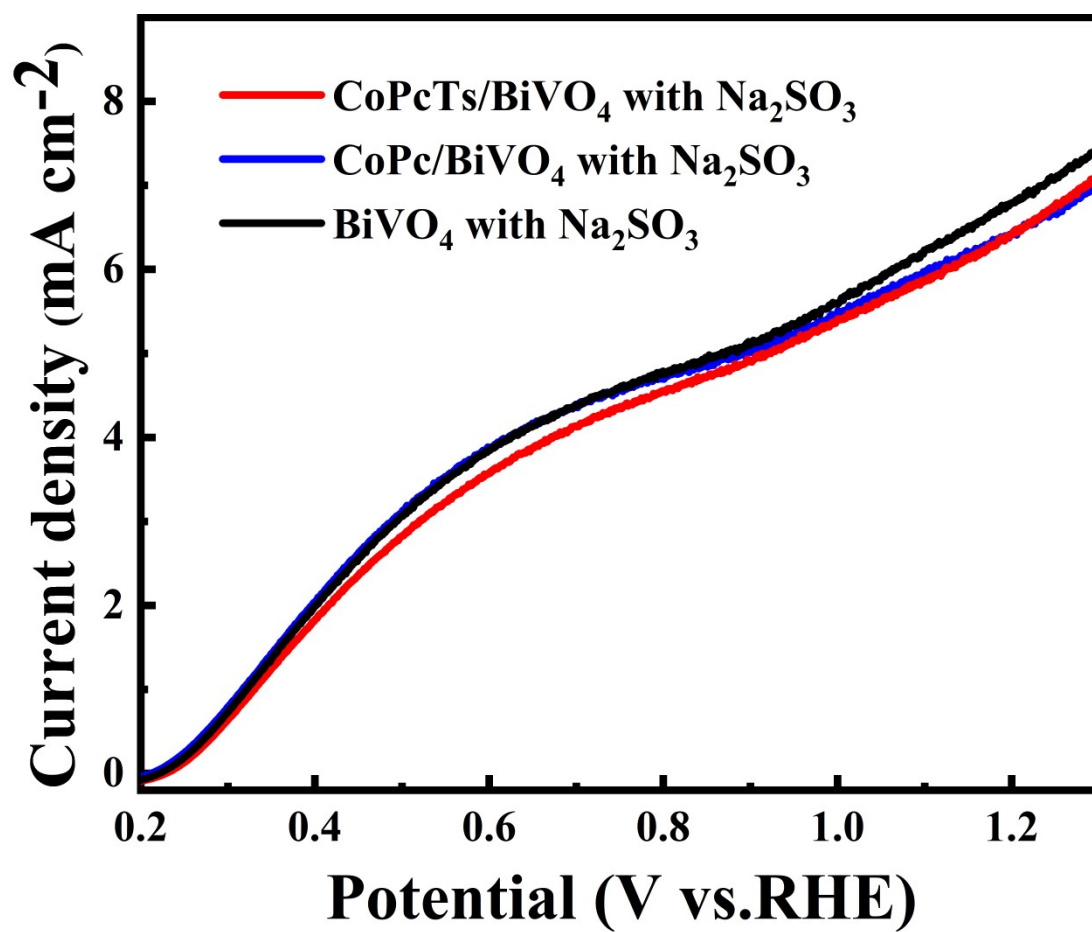


Fig. S2 LSV curves of BiVO₄, CoPc/BiVO₄ and CoPcTs/BiVO₄ with Na₂SO₃.

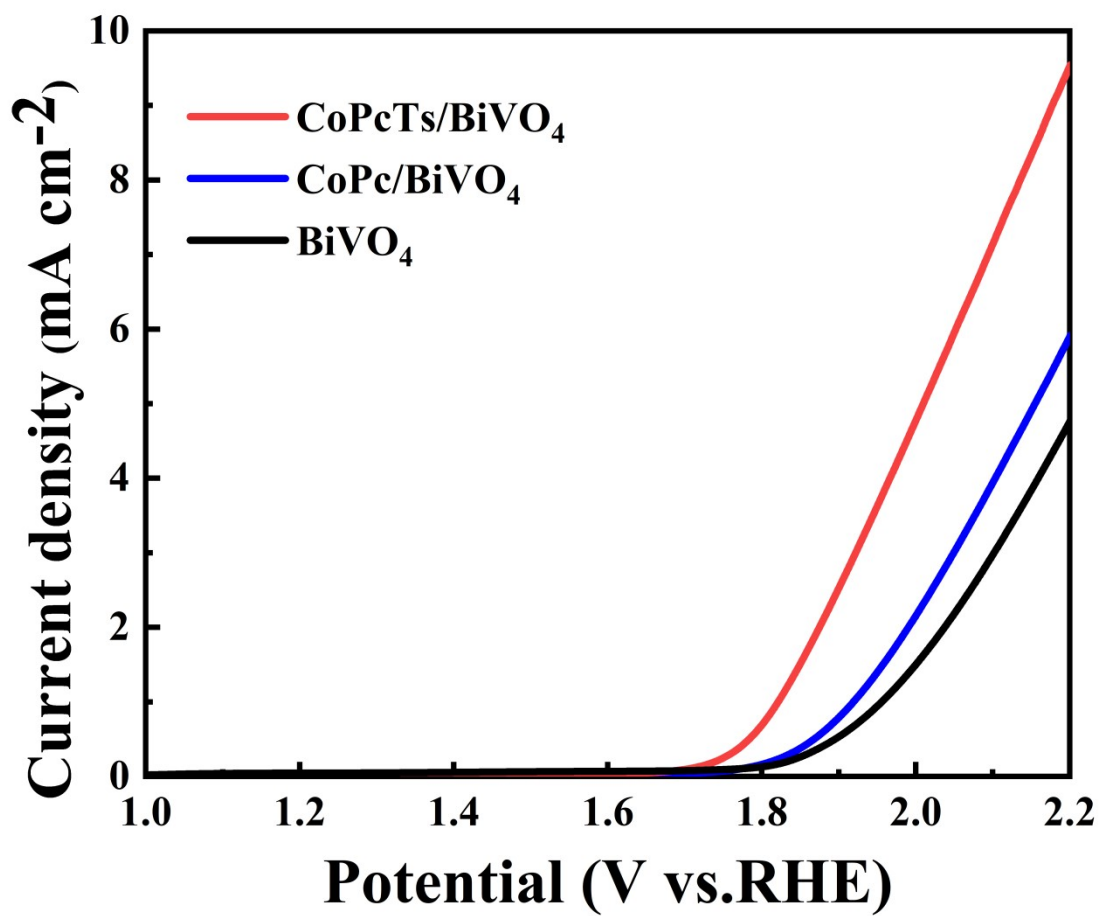


Fig. S3 LSV curves of BiVO_4 , CoPc/BiVO_4 and CoPcTs/BiVO_4 under dark condition.

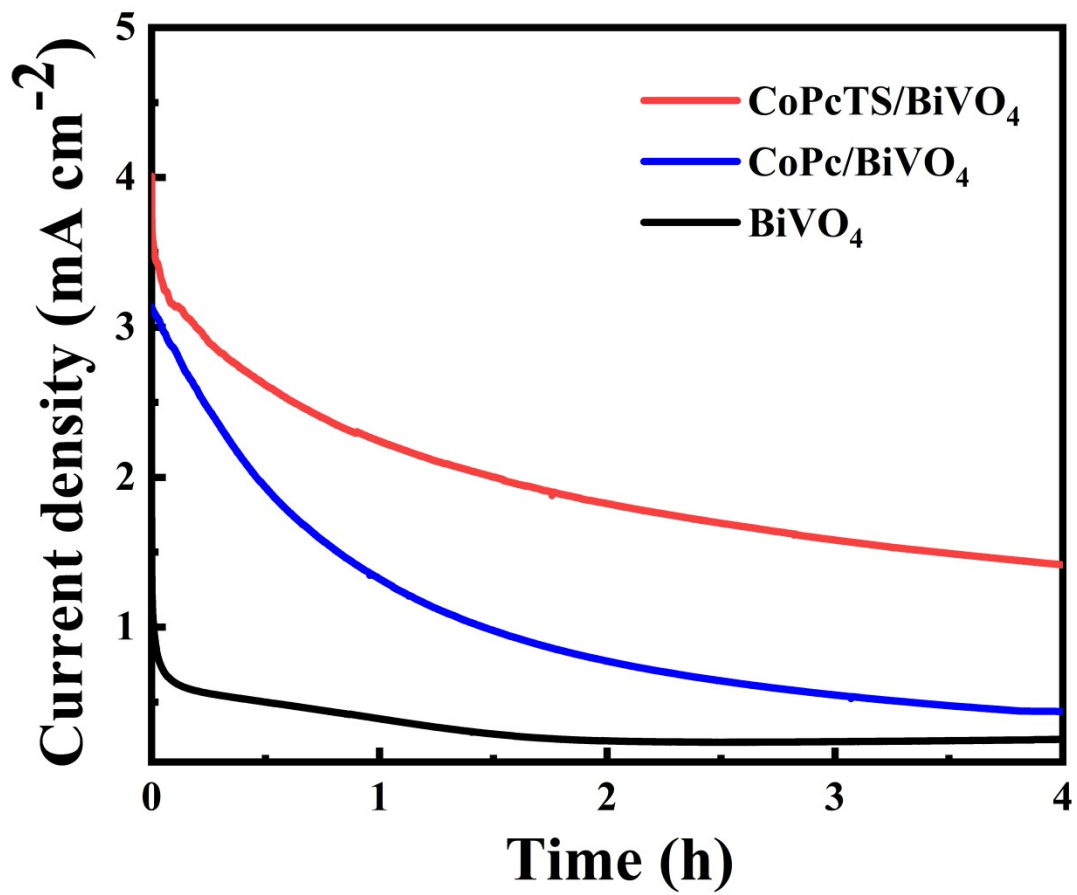


Fig. S4 Long-term PEC performance of BiVO₄, CoPc/BiVO₄ and CoPcTs/BiVO₄ photoanodes.

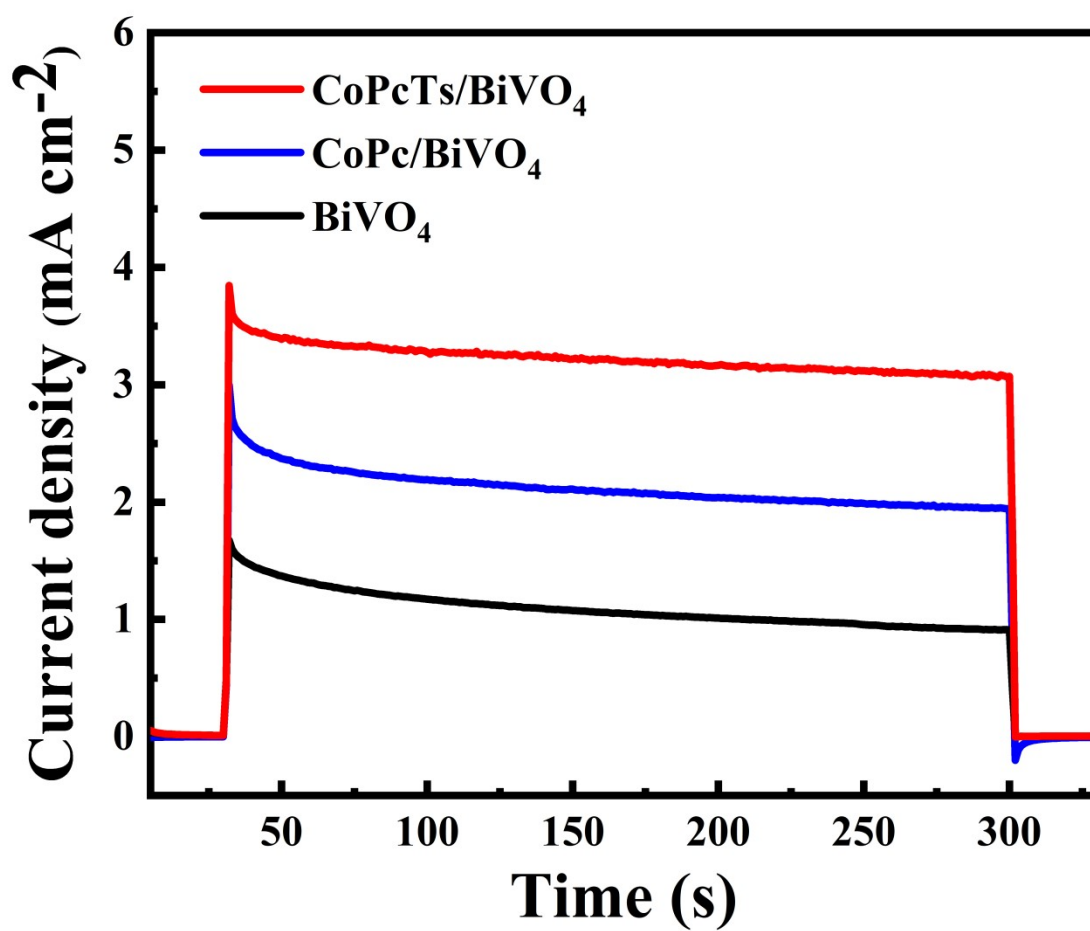
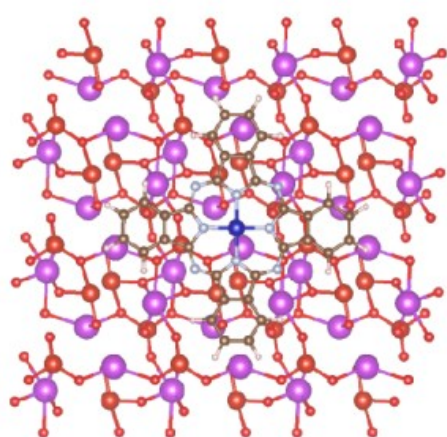
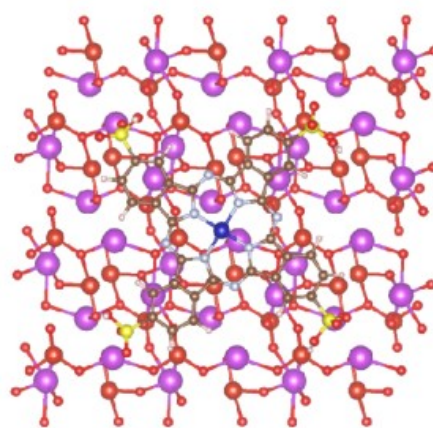


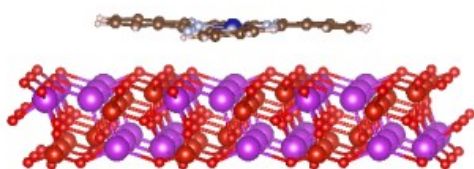
Fig. S5 Transient photocurrent responses curves of BiVO₄, CoPc/BiVO₄ and CoPcTs/BiVO₄ photoanodes.



Top view

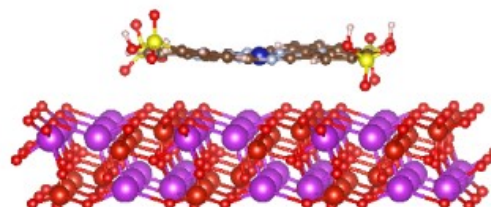


Top view



Side view

CoPc



Side view

CoPcTs

Fig. S6 The geometric models of CoPc/BiVO₄ and CoPcTs/BiVO₄, with top and side views.

Table S1. Comparison of the photocurrent density of modified BiVO₄ photoanodes against other state-of-the-art technologies.

Photoanode	Photocurrent Density (mA cm ⁻²)	Electrolyte	Ref.
CoPcTs/BiVO ₄	3.9	1 M KBi	This work
CoPc(NH ₂)/BiVO ₄	3.0	0.1 M KBi	Appl. Surf. Sci., 2021, 564: 150463.
BiVO ₄ /CoPc	3.23	1 M KBi	New J. Chem., 2022, 46, 9111-9118.
CoOx/C/BiVO ₄	1.47	0.1M NaPi	Catal. Sci. Technol., 2023, 13, 5776–5784.
FeOOH/Ni-BiVO ₄	2.5	1 M PBS	J. Colloid Interface Sci., 2023, 640 162-169.
NiFeOx/BiVO ₄	3.57	0.5 M PBS	Chem. Eng. Sci., 2025, 303 120965.
BiVO ₄ /ZnCoMOF	3.08	0.5 M Na ₂ SO ₄	Int. J. Hydrogen Energy, 2023, 48101-112.
Ni ₂ P ₂ O ₇ -Nd-BiVO ₄	3.6	0.5 M Na ₂ SO ₄	J. Colloid Interface Sci.2023, 644 124-133.
Bi-MOF/BiVO ₄	3.2	0.5 M Na ₂ SO ₄	Appl. Surf. Sci., 2021, 563 150357.

Photoanode	Photocurrent Density (mA cm ⁻²)	Electrolyte	Ref.
CoFeOOH/Mo-BiVO ₄	2.45	0.5 M Na ₂ SO ₄	J. Alloys Compd., 2023, 932 167633.
BiVO ₄ /Vo- MnOx/CoFe	3.53	0.5 M Na ₂ SO ₄	J. Colloid Interface Sci., 2025, 687 531-539.

Table S2. Resistance and CPE values of the pristine BiVO₄, CoPc/BiVO₄ and CoPcTs/BiVO₄.

	R _S	R _{CT}	CPE
BiVO ₄	31.72	597	2.6×10^{-4}
CoPc/BiVO ₄	23.78	268	3.4×10^{-4}
CoPcTs/BiVO	21.89	140	6.5×10^{-4}
4			