

## Supporting information for

### Self-adaptive semiconductor-liquid junction for highly active and stable solar water splitting

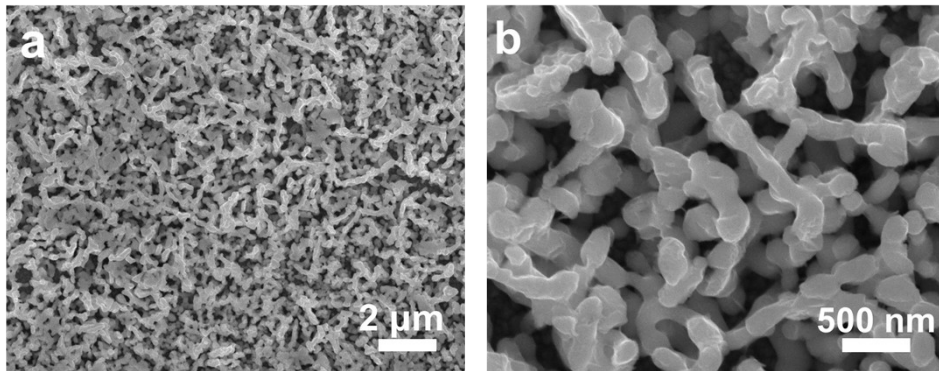
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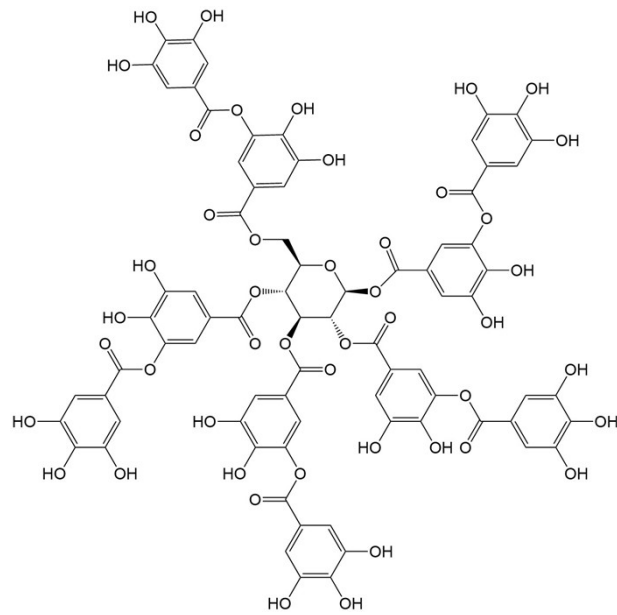
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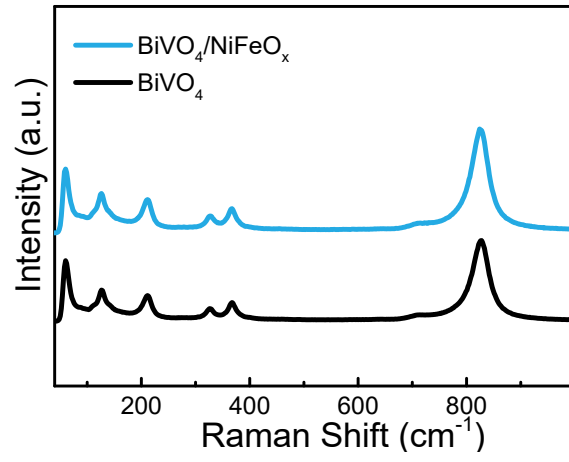
*E-mail addresses:* wangjiangan@nwpu.edu.cn (J.-G. Wang), liyy2019@qhu.edu.cn (Y. Li).



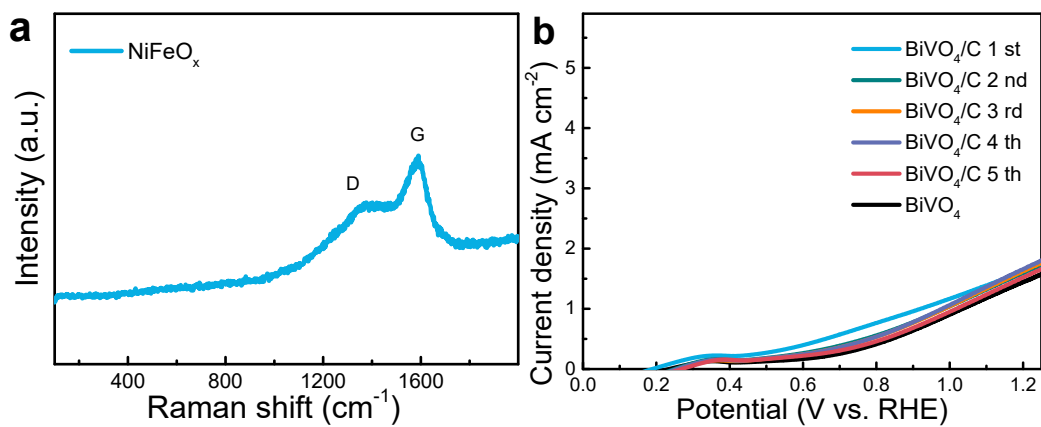
**Fig. S1** SEM image of the  $\text{BiVO}_4$  decorated by NiFe-TA complex.



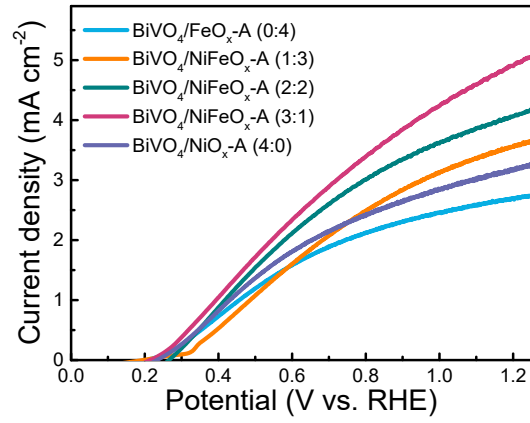
**Fig. S2** The constitutional formula of TA molecule.



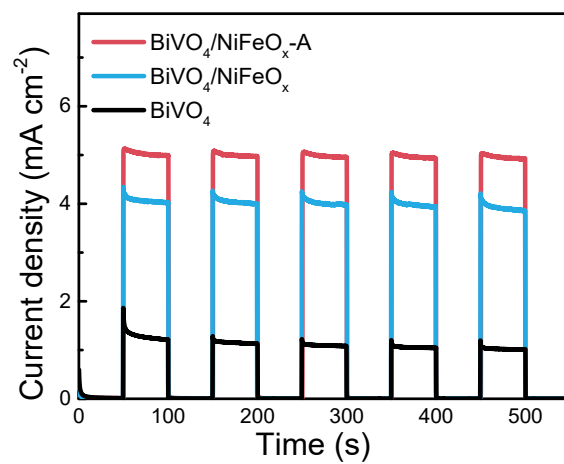
**Fig. S3** Raman shift of bare BiVO<sub>4</sub> and BiVO<sub>4</sub>/NiFeO<sub>x</sub> film.



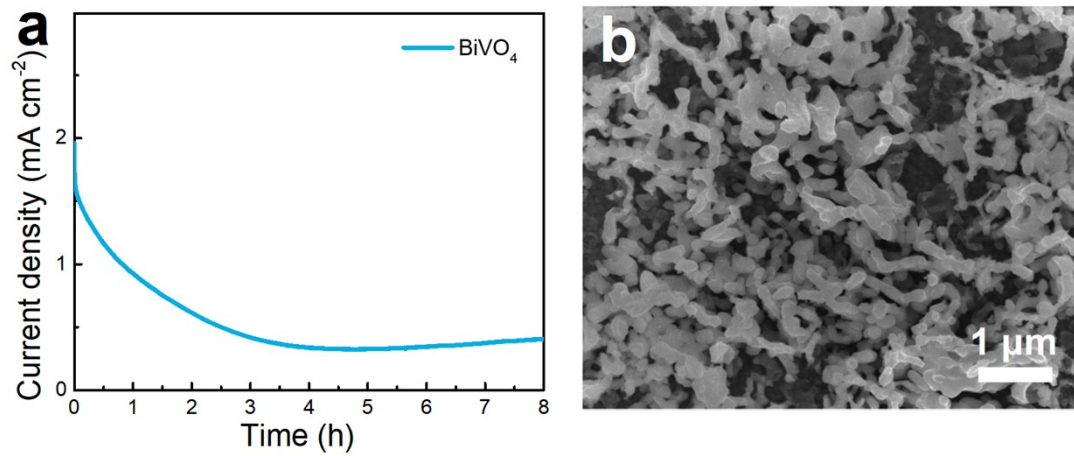
**Fig. S4** (a) Raman shift of the NiFeO<sub>x</sub> powder. (b) LSV curves of BiVO<sub>4</sub>/C photoanode.



**Fig. S5** LSV curves of BiVO<sub>4</sub>/NiFeO<sub>x</sub> photoanode with different Ni/Fe ratio.

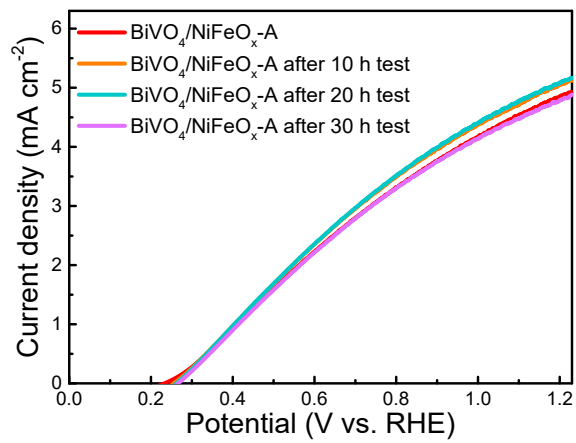


**Fig. S6** Chopped light current-time curves of BiVO<sub>4</sub>, BiVO<sub>4</sub>/NiFeO<sub>x</sub>, and BiVO<sub>4</sub>/NiFeO<sub>x</sub>-A at 1.23 V vs.RHE.

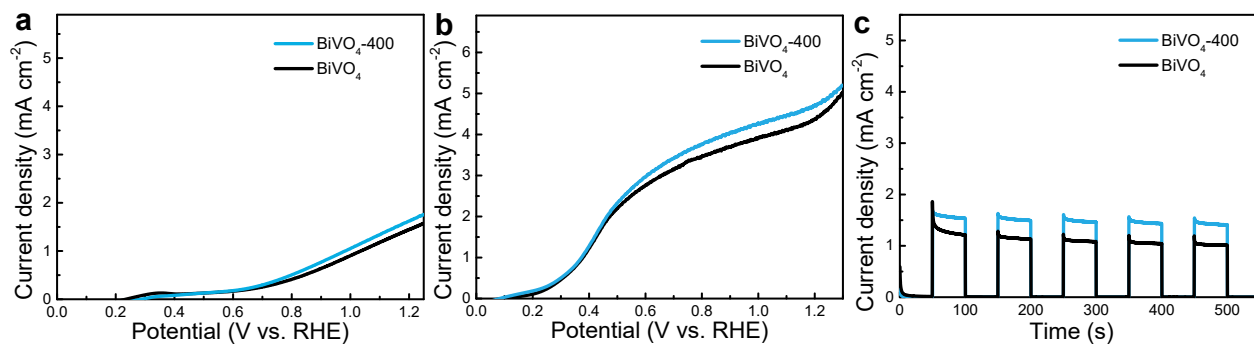


**Fig. S7** (a) PEC stability of bare BiVO<sub>4</sub> photoanode at 1.23 V vs.RHE and (b) SEM image of the BiVO<sub>4</sub> photoanode after stability test.

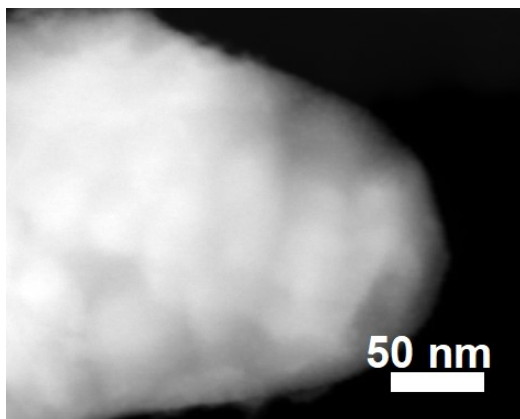




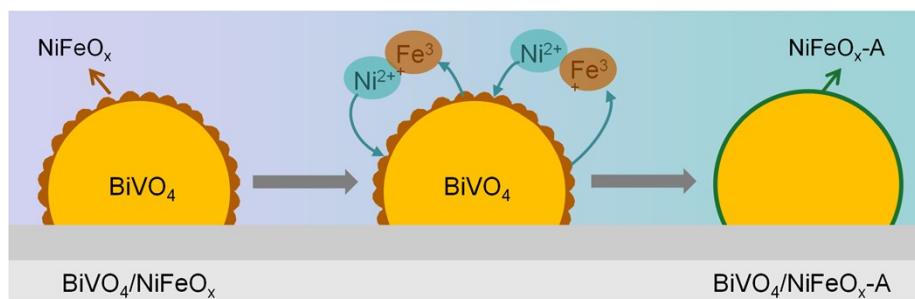
**Fig. S8** LSV curves of BiVO<sub>4</sub>/NiFeO<sub>x</sub>-A photoanode after stability test.



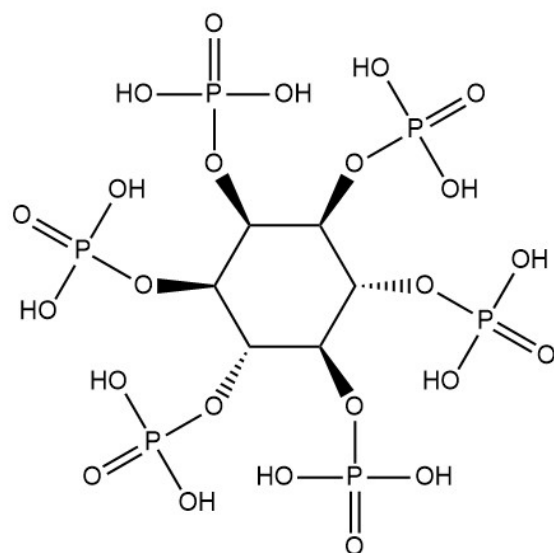
**Fig. S9** (a) LSV curves for water oxidation, (b) LSV curves for sulfite oxidation, and (c) chopped light current-time curves of BiVO<sub>4</sub> and BiVO<sub>4</sub> calcined at 400 °C for 2 h.



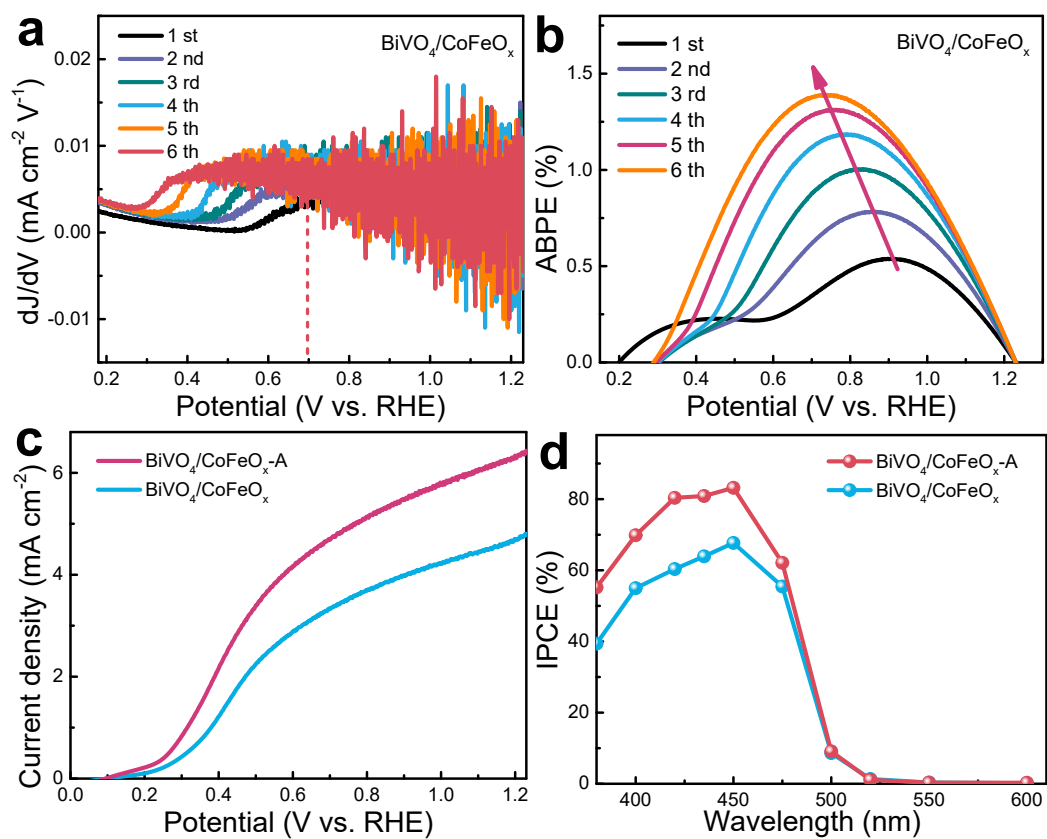
**Fig. S10** HAADF image of the  $\text{BiVO}_4/\text{NiFeO}_x\text{-A}$ .



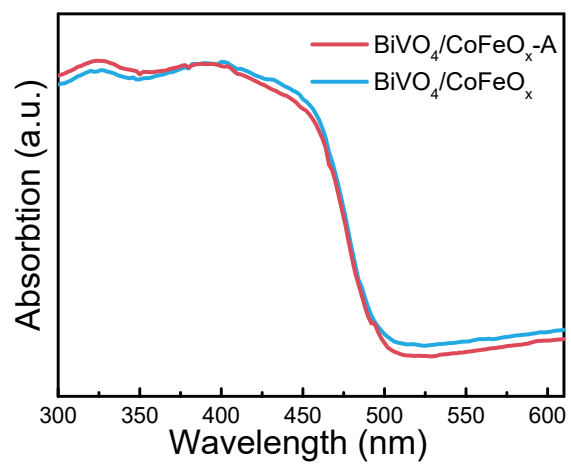
**Fig. S11** Schematic illustration of the surface reconstruction process.



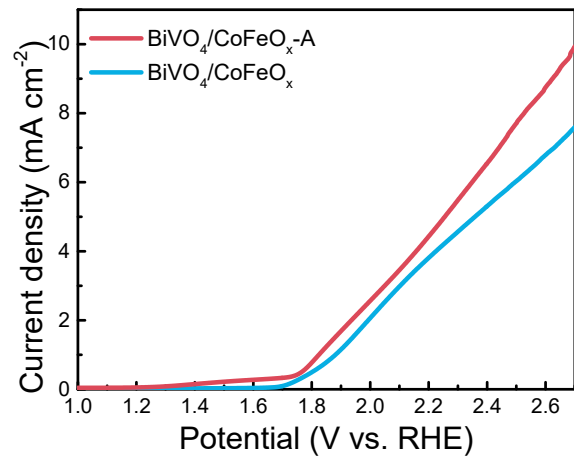
**Fig. S12** The constitutional formula of PA molecule.



**Fig. S13** (a) The first derivatives of photocurrent densities versus voltages and (b) ABPE plots of BiVO<sub>4</sub>/CoFeO<sub>x</sub> photoanode. (c) LSV curves and (d) (IPCE) plots of BiVO<sub>4</sub>/CoFeO<sub>x</sub> and BiVO<sub>4</sub>/CoFeO<sub>x</sub>-A photoanodes.

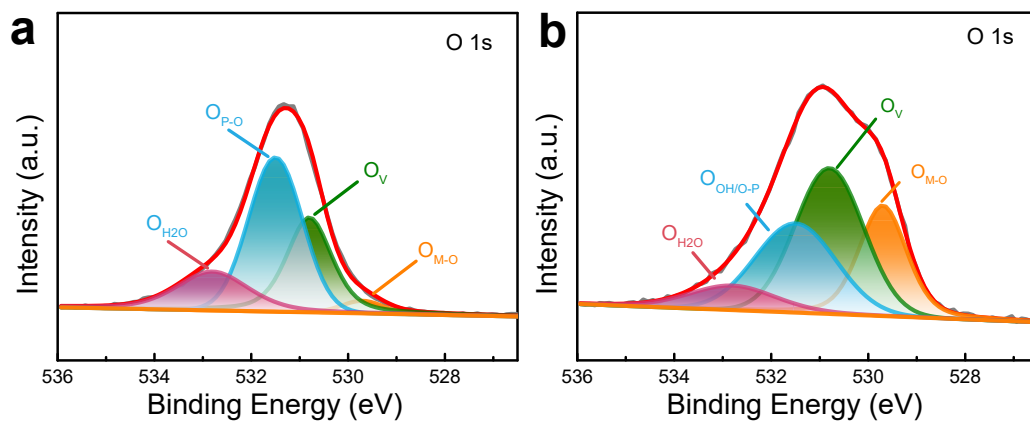


**Fig. S14** UV-vis diffuse reflectance spectra of BiVO<sub>4</sub>/CoFeO<sub>x</sub> and BiVO<sub>4</sub>/CoFeO<sub>x</sub>-A.

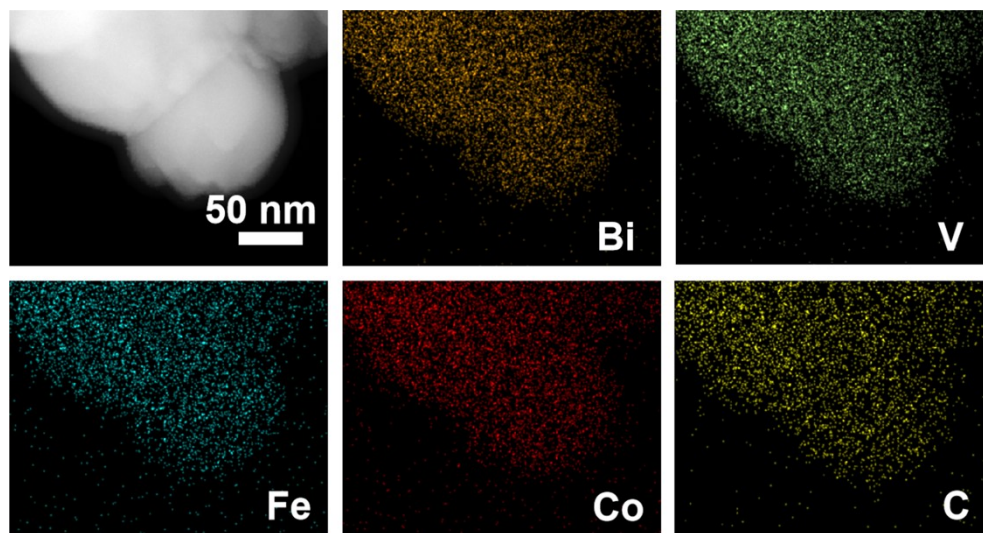


**Fig. S15** LSV curves in dark of BiVO<sub>4</sub>/CoFeO<sub>x</sub> and BiVO<sub>4</sub>/CoFeO<sub>x</sub>-A.

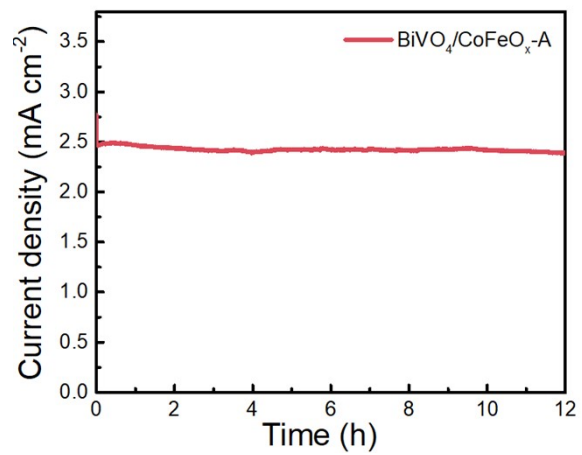




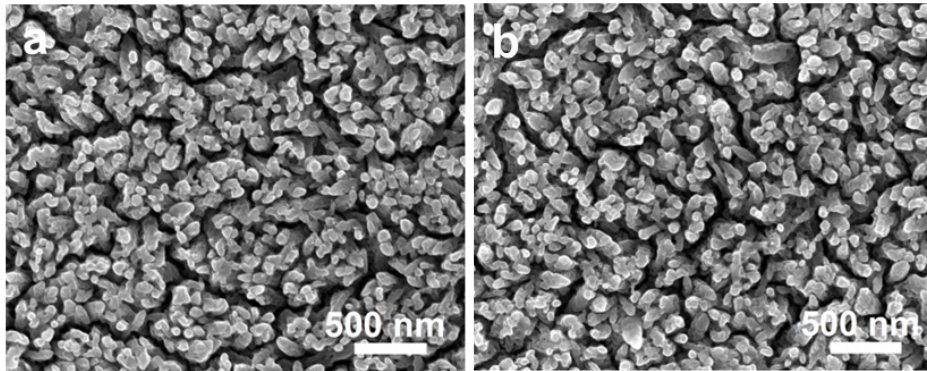
**Fig. S16** O 1s XPS spectra of the (a) BiVO<sub>4</sub>/CoFeO<sub>x</sub> and (b) BiVO<sub>4</sub>/CoFeO<sub>x</sub>-A.



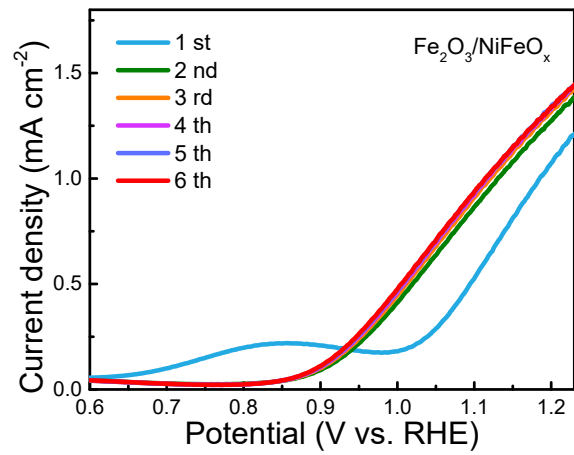
**Fig. S17** HAADF image and corresponding EDX mapping of the  $\text{BiVO}_4/\text{CoFeO}_x\text{-A}$ .



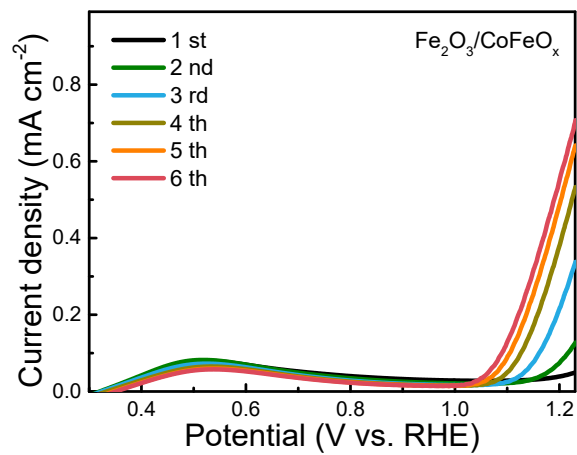
**Fig. S18** Long-term stability test of the BiVO<sub>4</sub>/CoFeO<sub>x</sub>-A at 0.7 V vs.RHE.



**Fig. S19** SEM image of (a)  $\text{Fe}_2\text{O}_3$  and (b)  $\text{Fe}_2\text{O}_3/\text{NiFeO}_x$  films.



**Fig. S20** Self-adaptive reconstruction of Fe<sub>2</sub>O<sub>3</sub>/NiFeO<sub>x</sub> photoanode.



**Fig. S21** Self-adaptive reconstruction of Fe<sub>2</sub>O<sub>3</sub>/CoFeO<sub>x</sub> photoanode.

**Table S1** Comparison of the PEC performance for BiVO<sub>4</sub>/cocatalyst photoanodes.

Simple	J (mA cm <sup>-2</sup> ) @1.23 V <sub>RHE</sub>	Stability	Electrolyte (pH)	Ref.
Ov-BiVO <sub>4</sub> @NiFe-MOFs	5.3	10 h@0.7 V <sub>RHE</sub>	1 M KBi + V <sup>5+</sup>	1
NiOOH/FeOOH/BiVO <sub>4</sub>	4.7	500 h@0.6 V <sub>RHE</sub>	1 M KBi + V <sup>5+</sup>	2
NiFe-OEC/Mo: BiVO <sub>4</sub>	2.6@0.6 V <sub>RHE</sub>	1100 h@0.6 V <sub>RHE</sub>	1 M KBi + Fe <sup>2+</sup>	3
NiFe-OEC/BVO	4.0@0.8 V <sub>RHE</sub>	200 h@0.8 V <sub>RHE</sub>	1 M KBi + Fe <sup>2+</sup>	4
BVO/NiFe-H	3.65	2.5 h@1.23 V <sub>RHE</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	5
BiVO <sub>4</sub> /Fe <sub>x</sub> Ni <sub>1-x</sub> OOH	5.8	3 h@1.23 V <sub>RHE</sub>	0.5 M KBi	6
Urea-NiFeOOH/BiVO <sub>4</sub>	4.85	40 h@0.7 V <sub>RHE</sub>	1 M KBi	7
F-BiVO <sub>4</sub> @NiFe-LDH	3.26	60 min@1.23 V <sub>RHE</sub>	1 M KBi	8
A-CoMoO <sub>4-x</sub> /BVO	3.5	8 h@1.23 V <sub>RHE</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	9
NiFeY LDH/BiVO <sub>4</sub>	5.2	25 h@0.8 V <sub>RHE</sub>	1 M KBi	10
FeCoO <sub>x</sub> /BiVO <sub>4</sub>	4.82	10@1.23 V <sub>RHE</sub>	1 M KBi	11
NiCo <sub>2</sub> O <sub>4</sub> /Mo: BiVO <sub>4</sub>	4.5	1 h@1.23 V <sub>RHE</sub>	1 M KPi	12
β-FeOOH/BiVO <sub>4</sub>	4.3	2 h@1.23 V <sub>RHE</sub>	0.2 M Na <sub>2</sub> SO <sub>4</sub>	13
BiVO <sub>4</sub> /O <sub>v</sub> /FeO <sub>x</sub>	3.13	2 h@1.23 V <sub>RHE</sub>	0.1 M KPi	14
<b>BiVO<sub>4</sub>/NiFeO<sub>x</sub>-A</b>	<b>5.1</b>	<b>30 h@1.23 V<sub>RHE</sub></b>	<b>0.5 M NaBi</b>	<b>This work</b>

**Table S2** The fitted values of Nyquist plots according to the equivalent circuit in Fig. 3h.

Samples	$R_s$ ( $\Omega \text{ cm}^{-2}$ )	$R_{ct}$ ( $\Omega \text{ cm}^{-2}$ )
BiVO <sub>4</sub>	43.1	3895
BiVO <sub>4</sub> /NiFeO <sub>x</sub>	44.9	415.9
BiVO <sub>4</sub> /NiFeO <sub>x</sub> -A	43.6	146.5



## Reference

1. J.-B. Pan, B.-H. Wang, J.-B. Wang, H.-Z. Ding, W. Zhou, X. Liu, J.-R. Zhang, S. Shen, J.-K. Guo, L. Chen, C.-T. Au, L.-L. Jiang and S.-F. Yin, *Angew. Chem. Int. Ed.*, 2020, **59**, 2-10.
2. D. K. Lee and K.-S. Choi, *Nat. Energy*, 2017, **3**, 53-60.
3. Y. Kuang, Q. Jia, G. Ma, T. Hisatomi, T. Minegishi, H. Nishiyama, M. Nakabayashi, N. Shibata, T. Yamada, A. Kudo and K. Domen, *Nat. Energy*, 2017, **2**, 16191.
4. R. T. Gao, D. He, L. Wu, K. Hu, X. Liu, Y. Su and L. Wang, *Angew. Chem. Int. Ed.*, 2020, **59**, 6213-6218.
5. X. Ning, P. Du, Z. Han, J. Chen and X. Lu, *Angew. Chem. Int. Ed.*, 2020, **60**, 3504-3509.
6. B. Zhang, X. Huang, Y. Zhang, G. Lu, L. Chou and Y. Bi, *Angew. Chem. Int. Ed.*, 2020, **59**, 18990-18995.
7. M. Sun, C. Yuan, R.-T. Gao, R. Zhang, X. Liu, T. Nakajima, X. Zhang, Y. Su and L. Wang, *Chem. Eng. J.*, 2021, **426**, 131062.
8. H. Chen, S. Wang, J. Wu, X. Zhang, J. Zhang, M. Lyu, B. Luo, G. Qian and L. Wang, *J. Mater. Chem. A*, 2020, **8**, 13231-13240.
9. S. Ren, M. Sun, X. Guo, X. Liu, X. Zhang and L. Wang, *ACS Catal.*, 2022, **12**, 1686-1696.
10. D. He, R.-T. Gao, S. Liu, M. Sun, X. Liu, K. Hu, Y. Su and L. Wang, *ACS Catal.*, 2020, **10**, 10570-10576.
11. S. Wang, T. He, J.-H. Yun, Y. Hu, M. Xiao, A. Du and L. Wang, *Adv. Funct. Mater.*,

- 2018, **28**, 1802685.
12. C. Feng, Q. Zhou, B. Zheng, X. Cheng, Y. Zhang and Y. Bi, *J. Mater. Chem. A*, 2019, **7**, 22274-22278.
  13. B. Zhang, L. Wang, Y. Zhang, Y. Ding and Y. Bi, *Angew. Chem. Int. Ed.*, 2018, **57**, 2248-2252.
  14. Y. Zhang, J. Bai, J. Wang, S. Chen, H. Zhu, J. Li, L. Li, T. Zhou and B. Zhou, *Chem. Eng. J.*, 2020, **401**, 126134.