

**Enhanced water oxidation reaction kinetics on BiVO₄
photoanode by the surface modification with Ni₄O₄ cubane**

Bin Gao^a, Tao Wang^{a,*}, Xiaoli Fan^a, Hao Gong^a, Peng Li^a, Yaya Feng^a,
Xianli Huang^a, Jianping He^{a,*}, Jinhua Ye^{b,*}

^a College of Materials Science and Technology, Jiangsu Key Laboratory of Electrochemical Energy Storage Technologies, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China.

^b International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044 (Japan)

*Corresponding authors:

Prof. Tao Wang, Tel: +86 25 52112900; Fax: +86 25 52112626, E-mail:
wangtao0729@nuaa.edu.cn;

Prof. Jianping He, Tel: +86 25 52112900; Fax: +86 25 52112626, E-mail:
jianph@nuaa.edu.cn;

Prof. Jinhua Ye, Tel: +81 29 8592646; Fax: +81 29 8604958, E-mail:

Jinhua.YE@nims.go.jp.

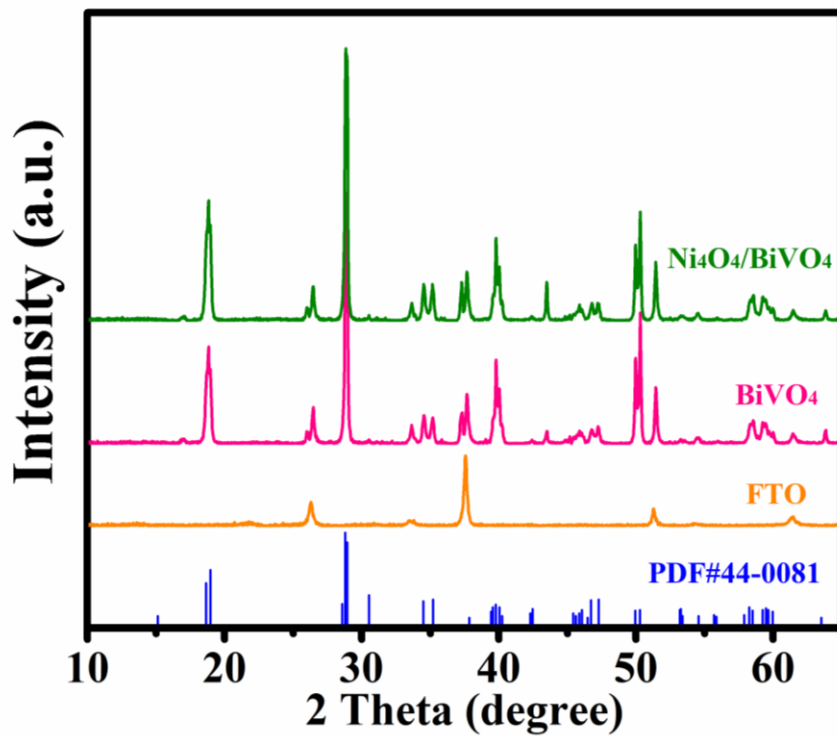


Fig. S1. XRD of Ni₄O₄/BiVO₄ and BiVO₄ photoanodes.

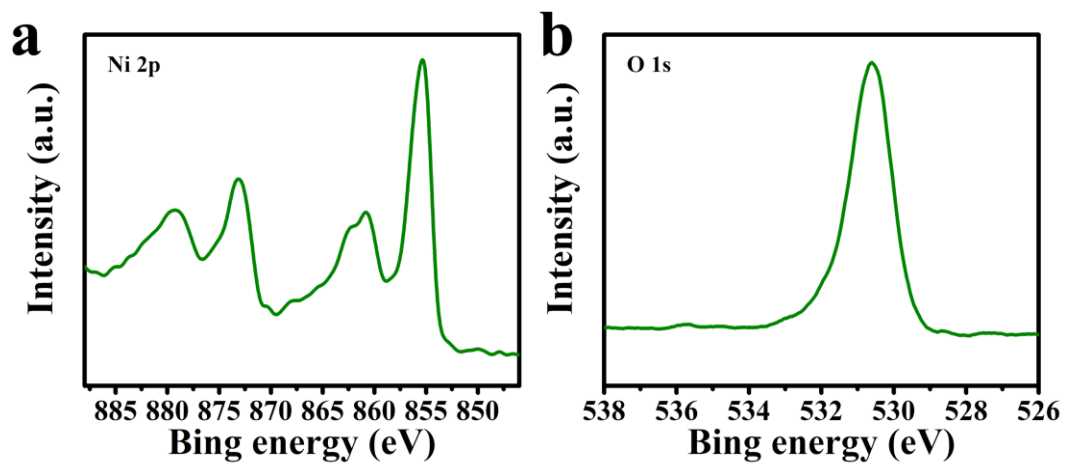


Fig. S2. High-resolution spectrum of Ni 2p (a) and O 1s (b) of Ni(OH)_2 .

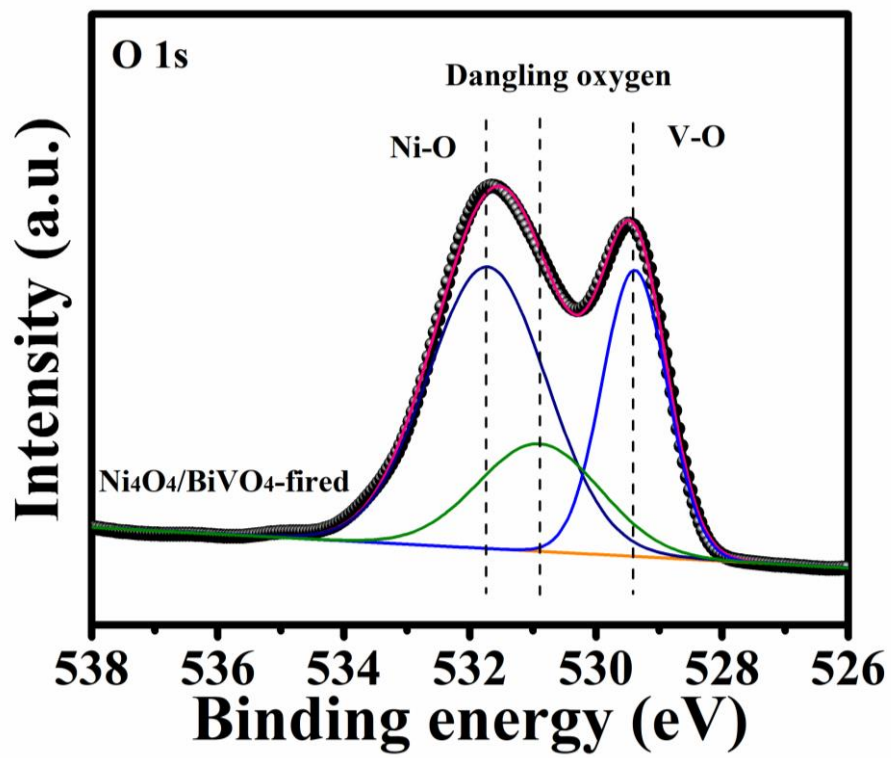


Fig. S3. High-resolution spectrum of O 1s of Ni₄O₄/BiVO₄ photoanode after fired.

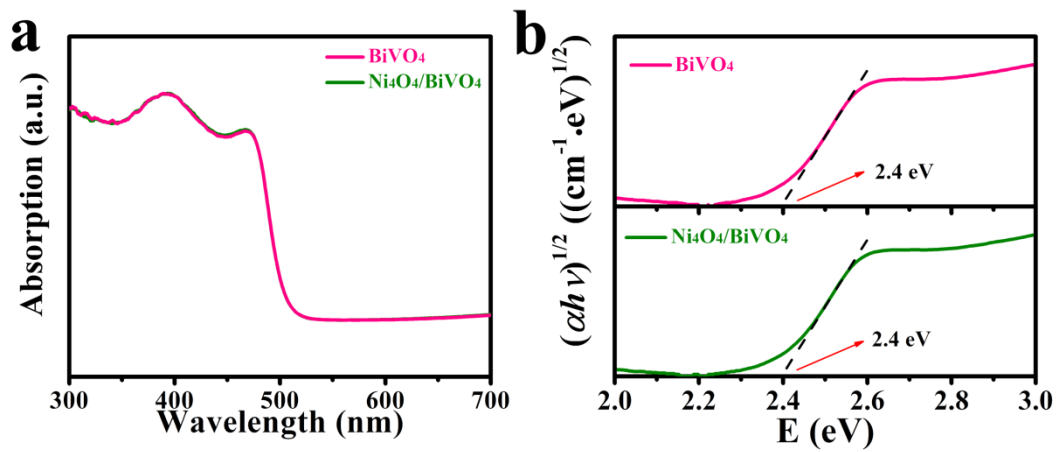


Fig. S4. UV-vis spectra (a) and tauc plots (b) of BiVO₄ and Ni₄O₄/BiVO₄.

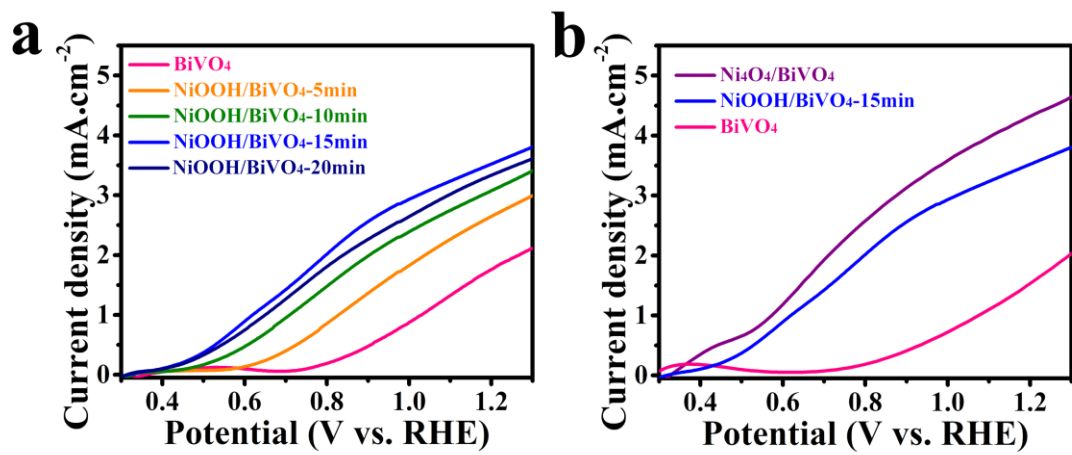


Fig. S5. (a) LSV of NiOOH modified BiVO₄ photoanodes with different deposition time; (b) LSV of Ni₄O₄/BiVO₄ and NiOOH/BiVO₄. Depositional condition: three-electrode system, 0.1 M NiSO₄ solution with pH adjusted to 7 by NaOH and a bias voltage of 1 V (vs. SCE)

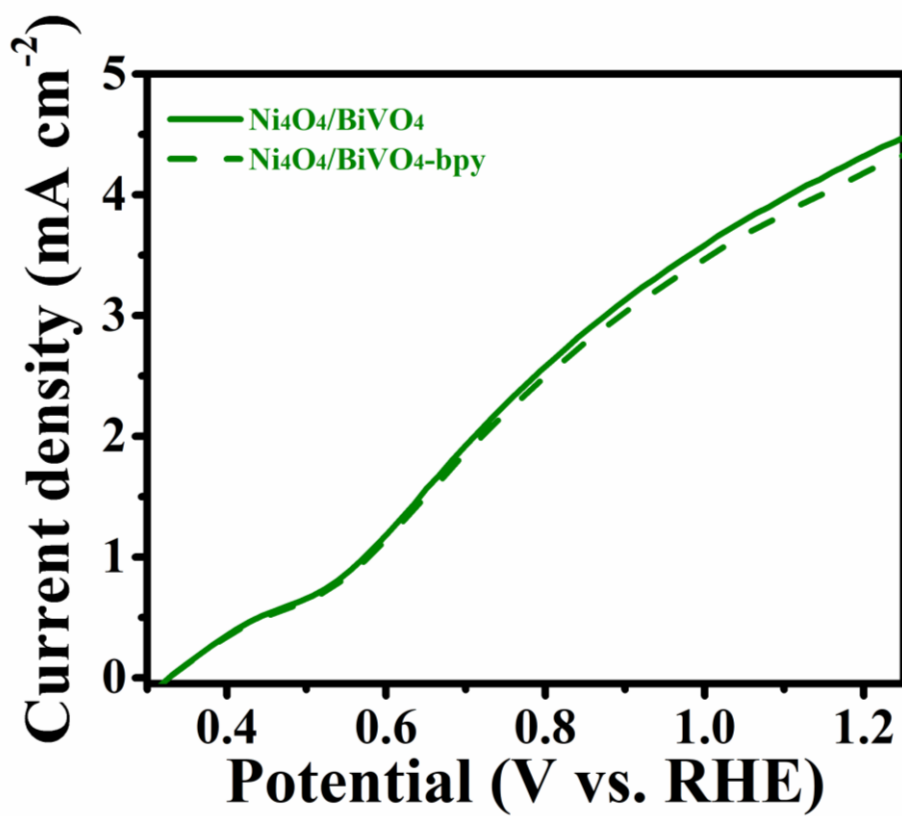


Fig. S6. LSV curves of Ni₄O₄/BiVO₄ in phosphate buffer electrolyte (pH=7) with 80 μ M bpy and without bpy.

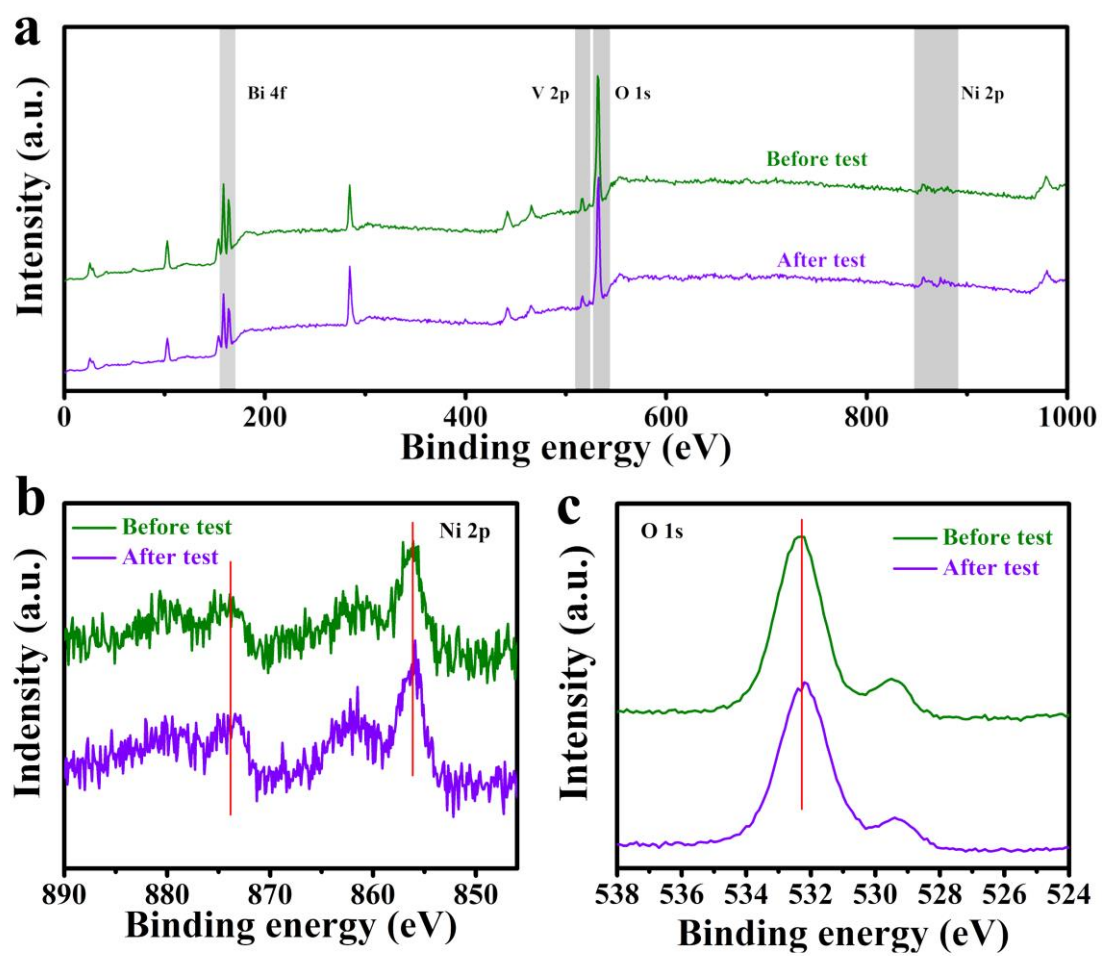


Fig. S7. XPS survey spectrum (a) and high-resolution spectra of Ni 2p (b), O 1s (c) of $\text{Ni}_4\text{O}_4/\text{BiVO}_4$ before and after testing.

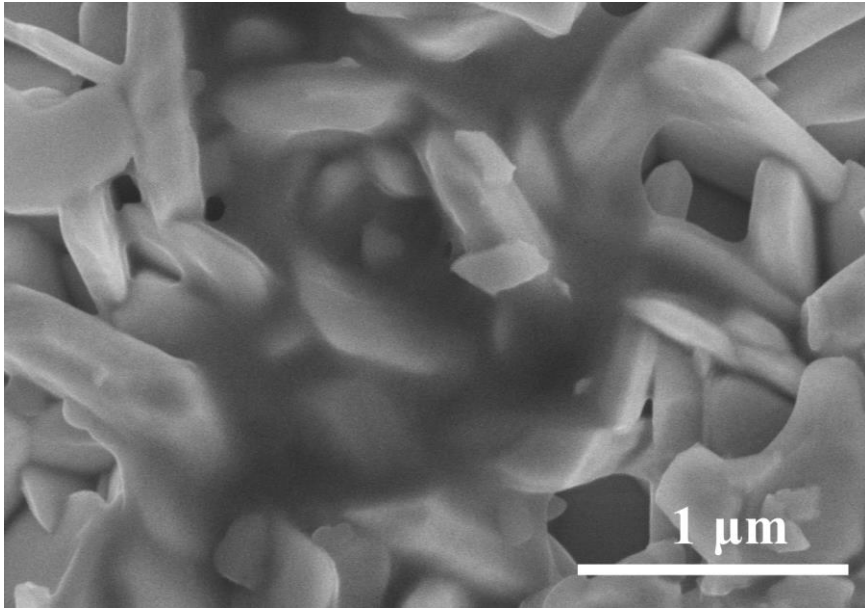


Fig. S8. The SEM image of Ni₄O₄/BiVO₄ photoanode after tested.

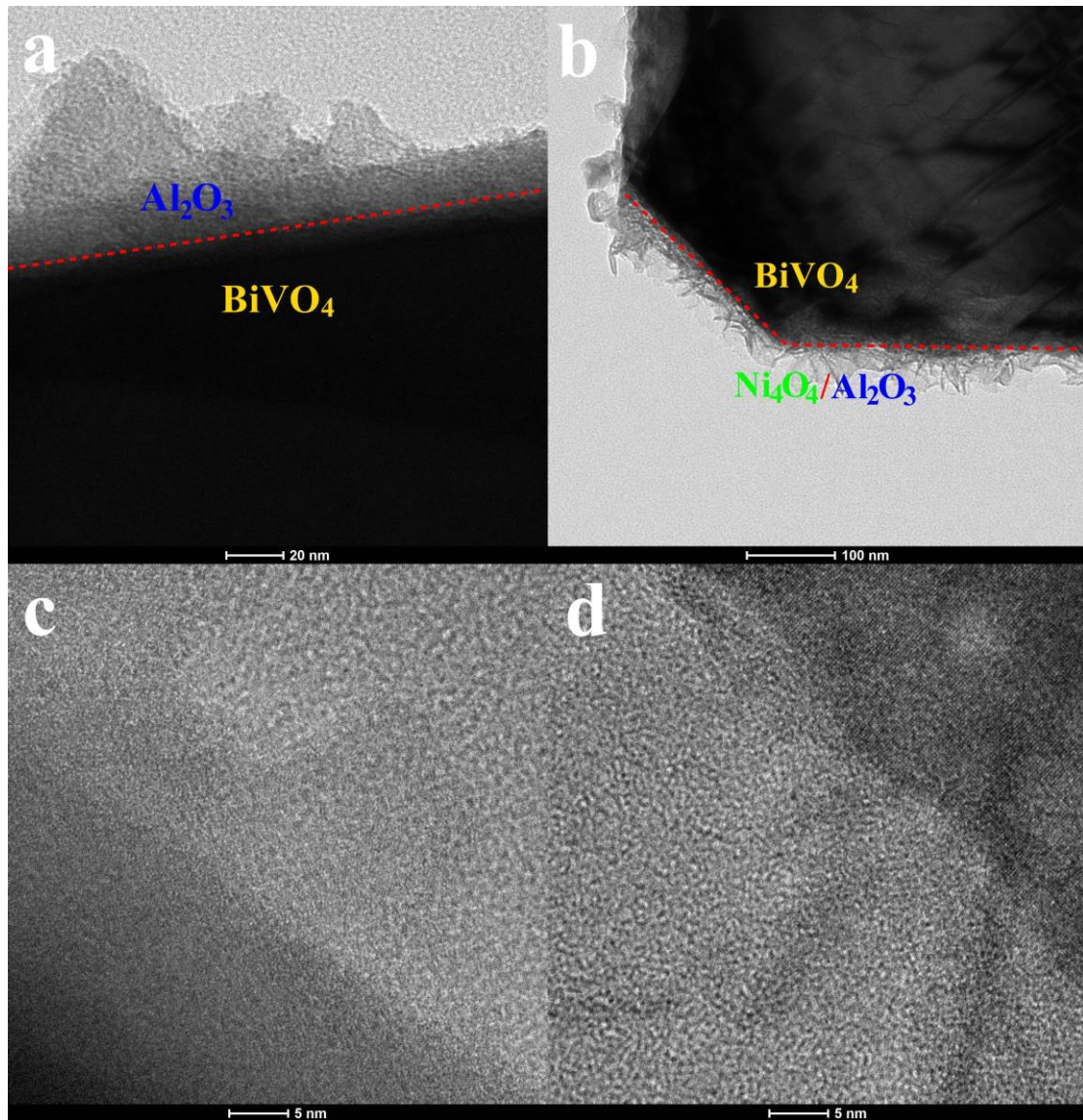


Fig. S9. The TEM and HRTEM images of $\text{Al}_2\text{O}_3/\text{BiVO}_4$ (a, c) and $\text{Ni}_4\text{O}_4/\text{Al}_2\text{O}_3/\text{BiVO}_4$ (b, d) nanoplating.

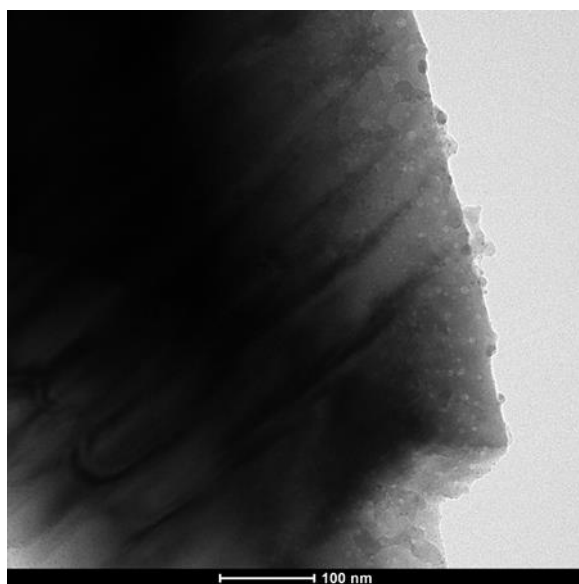


Fig. S10. The TEM image of BiVO₄ crystal.

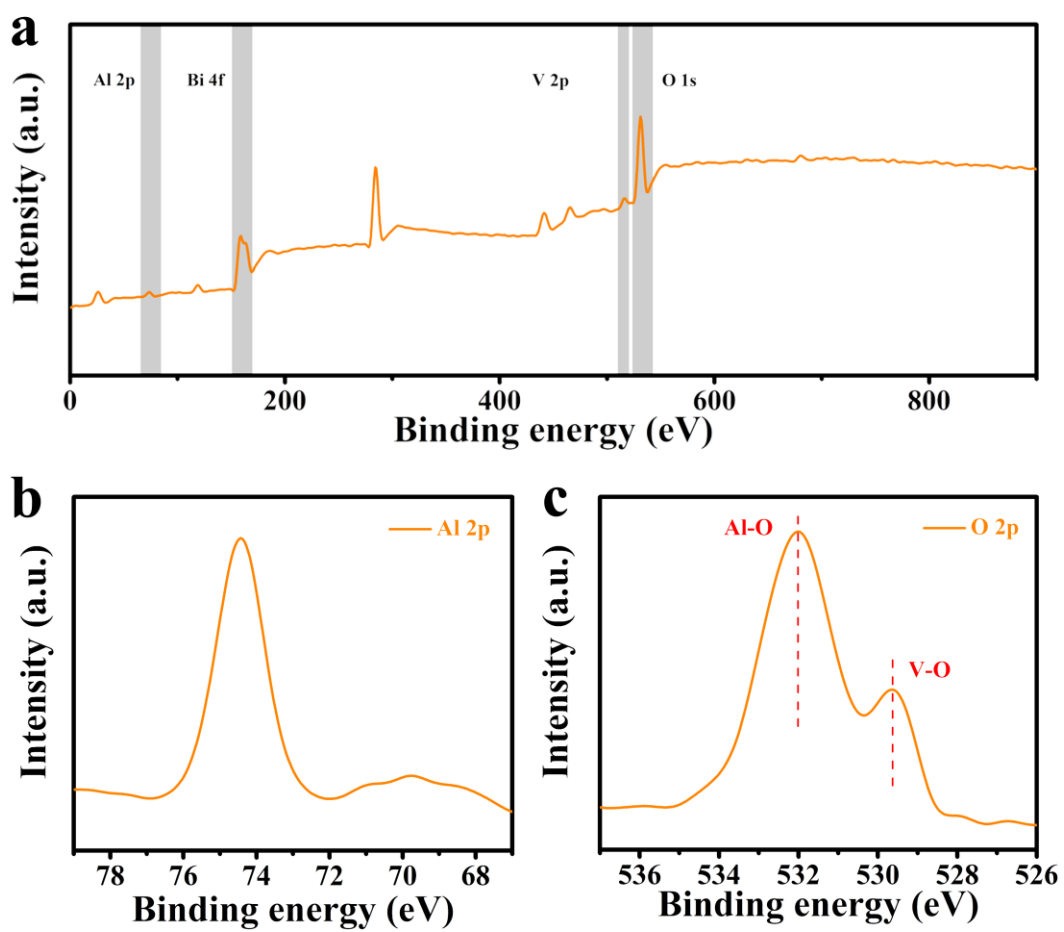


Fig. S11. XPS survey spectrum (a) and high resolution Al 2p (b) and O 2p (c) XPS spectra of $\text{Al}_2\text{O}_3/\text{BiVO}_4$ photoanode.

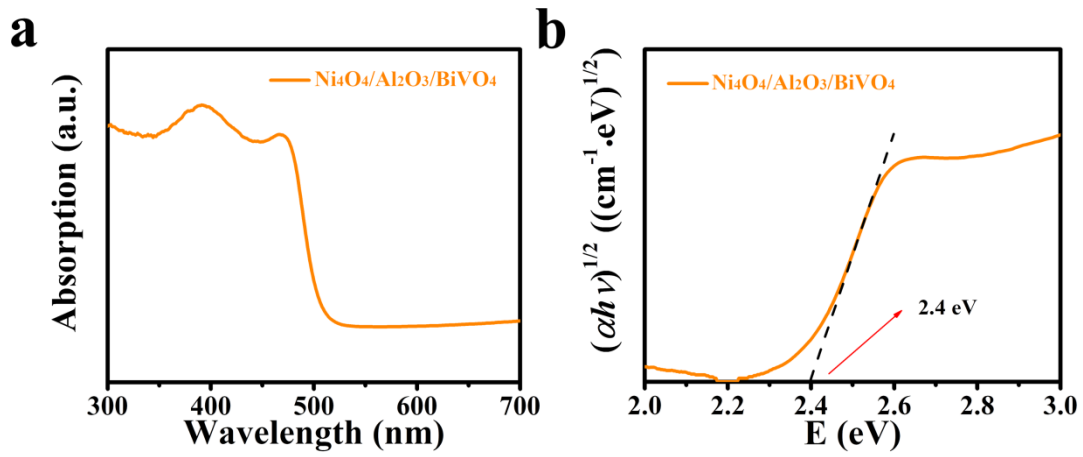


Fig. S12. UV-vis spectra (a) and tauc plots (b) of $\text{Al}_2\text{O}_3/\text{BiVO}_4$.

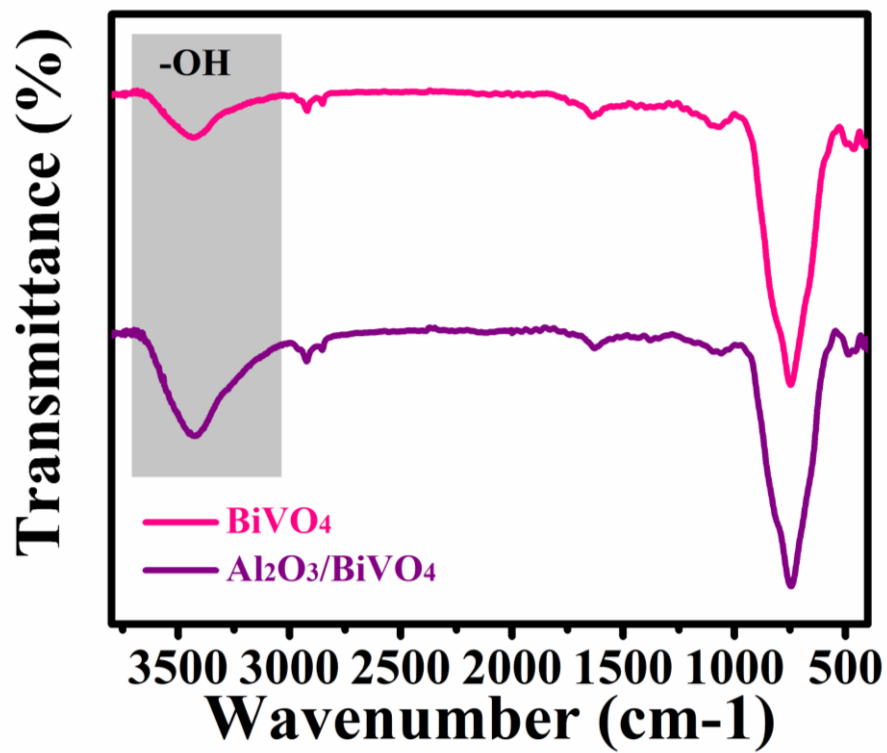


Fig. S13. FTIR of BiVO₄ and Al₂O₃/BiVO₄.

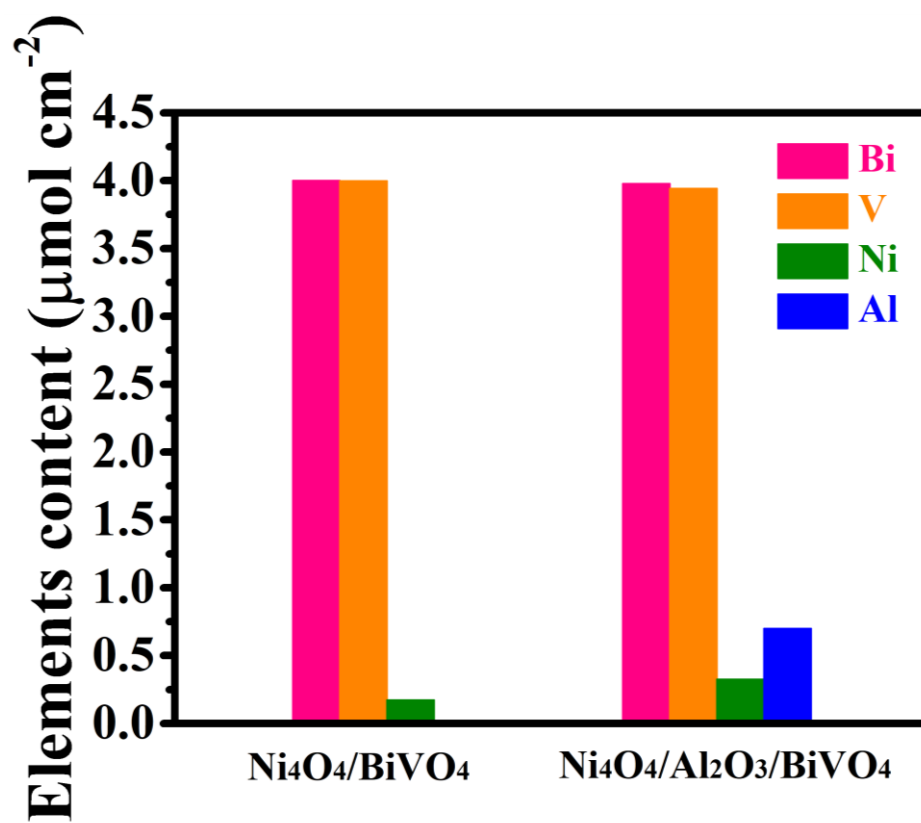


Fig. S14. ICP of $\text{Ni}_4\text{O}_4/\text{BiVO}_4$ and $\text{Ni}_4\text{O}_4/\text{Al}_2\text{O}_3/\text{BiVO}_4$.

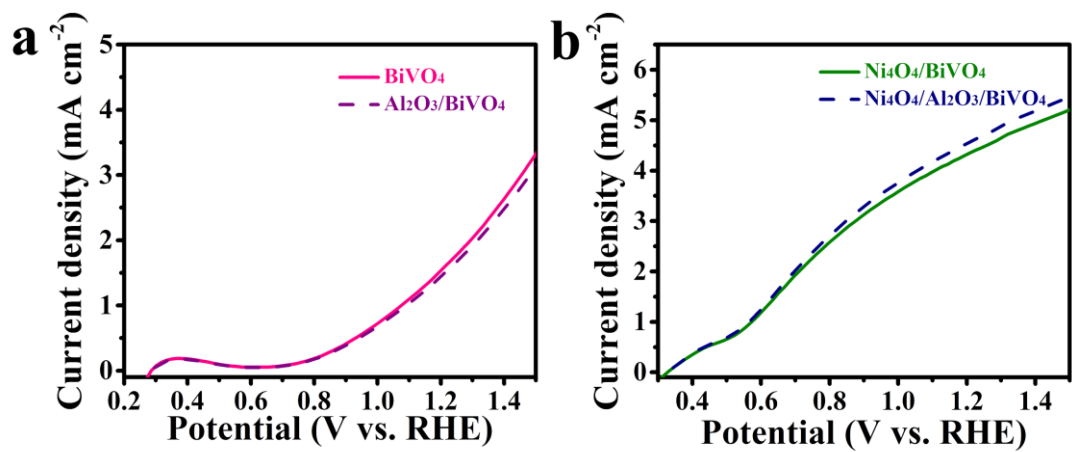


Fig. S15. The LSV curves of BiVO₄ and Al₂O₃/BiVO₄ (a) and Ni₄O₄/BiVO₄ and Ni₄O₄/Al₂O₃/BiVO₄ (b).

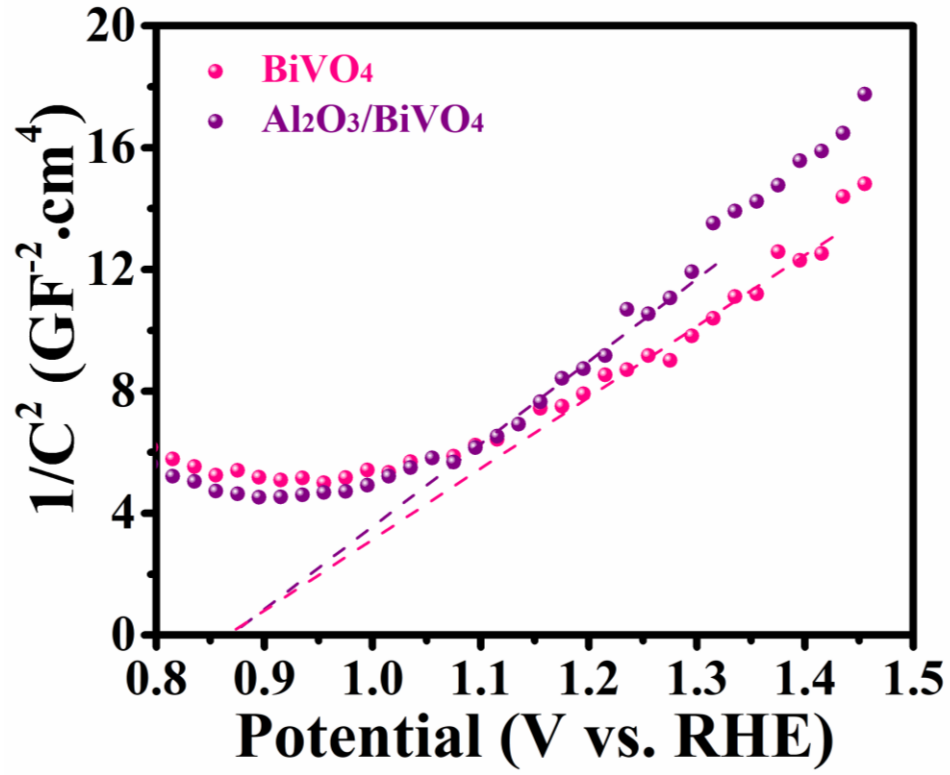


Fig. S16. Mott-schottky plots of BiVO_4 and $\text{Al}_2\text{O}_3/\text{BiVO}_4$ photoanode.

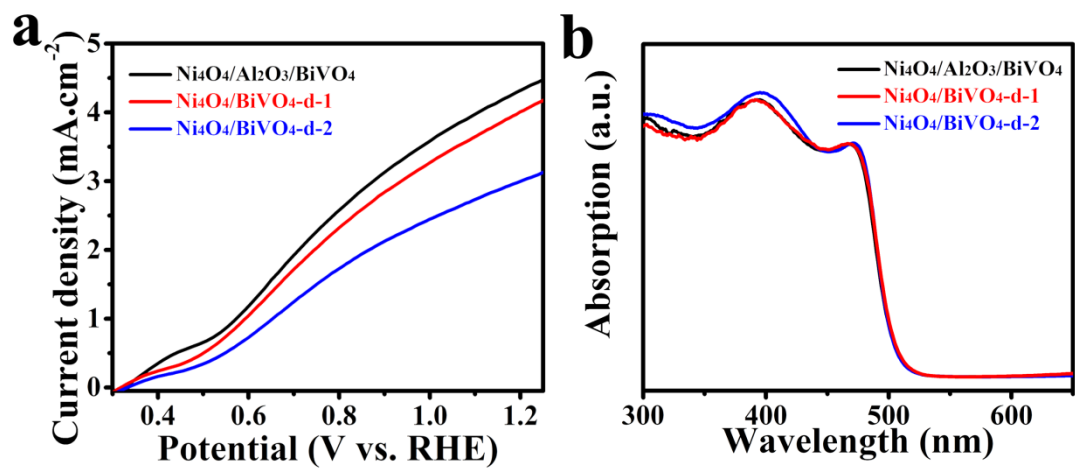


Fig. S17. (a) LSV and (b) UV-vis spectra of Ni₄O₄/Al₂O₃/BiVO₄, Ni₄O₄/BiVO₄-d-1 and Ni₄O₄/BiVO₄-d-2.

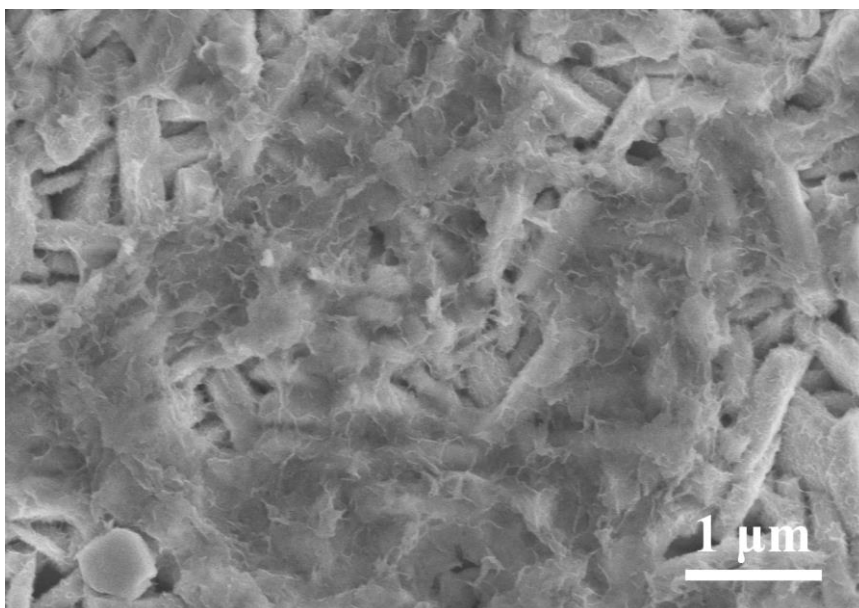


Fig. S18. The SEM image of Ni₄O₄/Al₂O₃/BiVO₄ photoanode after tested.

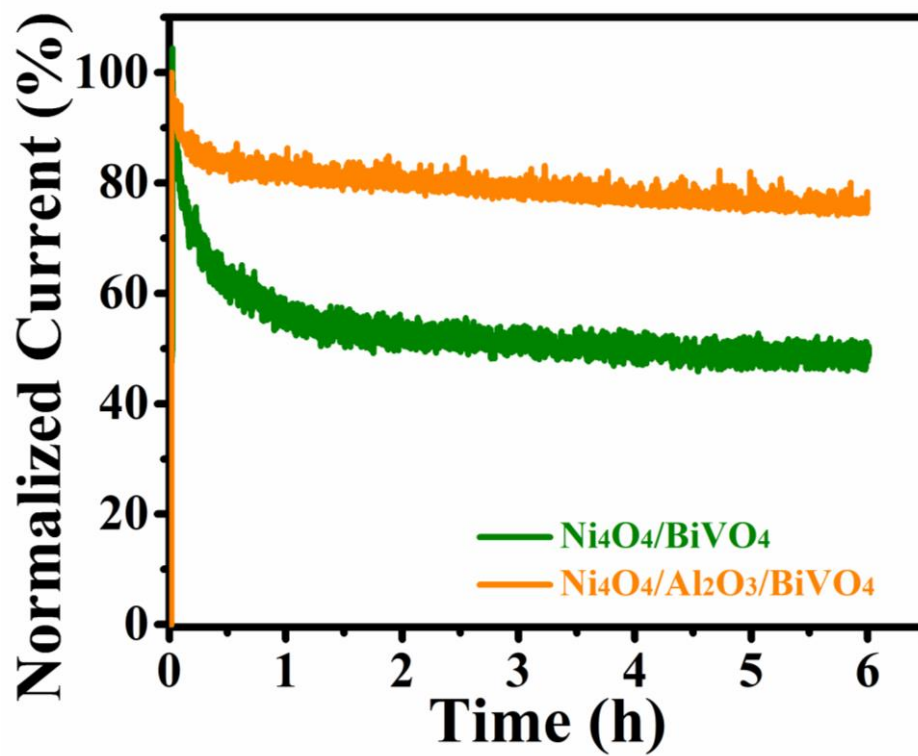


Fig. S19. I-t curve of Ni₄O₄/BiVO₄ and Ni₄O₄/Al₂O₃/BiVO₄ photoanodes for 6 h.

Table S1. Summary of the water oxidation properties of high performing OER catalysts for BiVO₄ based photoanodes.

Photoanode	Light source	Electrolyte	Onset potential with cocatalyst (V)	Onset potential without cocatalyst (V)	Photocurrent density with cocatalyst (mA/cm ² , 1.23 VRHE)	Photocurrent density without cocatalyst (mA/cm ² , 1.23 VRHE)	Ref.
Ni ₄ O ₄ /BiVO ₄	AM 1.5G	0.5 M KPi* (pH=7)	0.35	0.7	3.9	1.5	This work
FeOOH/NiOOH /BiVO ₄	AM 1.5G	0.5 M KPi (pH=7)	0.23	0.43	4.2	1.8	1
NiO/CoO _x /BiVO ₄	AM 1.5G	0.1 M KPi (pH=7)	0.35	0.55†	3.5	1.05†	2
CoFe-H/BiVO ₄	AM 1.5G	0.5 M KPi (pH=7)	0.23	0.68	2.48	0.78	3
β-FeOOH/BiVO ₄	AM 1.5G	0.2 M Na ₂ SO ₄	0.45†	0.65†	4.3	1.45†	4
NiB/BiVO ₄	AM 1.5G	0.5 M KB** (pH=9.2)	0.25	0.35	3.47	1.56	5
Co ₃ O ₄ /BiVO ₄	AM 1.5G	1 M KB (pH=9.5)	0.55	Unconspicuous	2.71	0.71	6
CoPi/BiVO ₄	365 nm LEDs (AM 1.5G)	0.1 M KPi (pH=6.7)	0.5	0.9	2	0.9	7

* KPi: Potassium phosphate buffer

** KB: Potassium borate buffer

† Estimated from figures in reference, unless denoted otherwise

Tab. S2. Calculated and measured gas evolution rates obtained from Fig. 8 (data during the first hour).

	O ₂ evolution rate (μmol h ⁻¹)	Photocurrent density (mA cm ⁻²)	Faradaic efficiency (%)
Actual	31.2	3.34	96.3
Theoretical	32.4	3.47	100

References

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