

Electronic Supplementary Material

Citric acid-driven interface engineering of BiVO₄ photoanodes for enhanced photoelectrochemical performance

Xingsheng Hu^{1*}, Bing-Hao Wang^{1*}, Xiong Wang¹, Chao Peng¹, Sheng Tian¹, Huijuan Wang¹, Mingming Yin¹, Yang Li¹, Yuyun Liu¹, Yutong Dai¹, Weifan Shao¹, Lang Chen (✉)¹, Shuang-Feng Yin^{1,2}

1 Advanced Catalytic Engineering Research Center of the Ministry of Education, State Key Laboratory of Chemo and Biosensing, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

2 College of Chemistry and Chemical Engineering, Central South University of Forestry and Technology, Changsha 410004, China

E-mail: huagong042c1@163.com

* These authors contributed equally to the work.

Experimental Procedures

Materials

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), potassium iodide (KI), sodium sulfate (Na₂SO₄), sodium sulfite (Na₂SO₃), sodium hydroxide (NaOH), potassium hydroxide (KOH), ethanol absolute (EtOH), dimethyl sulfoxide (DMSO) are purchased from Sinopharm Chemical Reagent Co., Ltd. *p*-benzoquinone (C₆H₄O₂), vanadyl acetylacetonate (VO(acac)₂) are purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. All reagents are used as received without further purification. Ultra-pure water (18.2 MΩ/cm) is homemade using UPT-II-10T supplied by Ulupure. Fluorine-doped tin oxide (FTO) coated glass substrates were purchased from Wuhan Jinglat Solar Technology Co., Ltd. (~14 Ω/cm²) and cleaned in ultra-pure water, ethanol and acetone by ultrasonic bath before use.

Table S1. Comparison of our work with the recent reported BiVO₄-based photoanodes for PEC water oxidation under AM 1.5 G (100 mW/cm²) illumination

Samples	Electrolyte	LSV at 1.23V vs. RHE (mA/cm ²)	Ref.
Bi _{1-x} VO ₄ /Co-Bi	KBi, pH=9.5	4.5	1

2-BVO-1.5h/FeOOH/NiOOH	KBi, pH=9.5	5.87	2
C-BiVO ₄ /CQD	KBi, pH=9.5	4.83	3
NiOOH/Co ₃ O ₄ /BiVO ₄	KBi, pH=9.5	6.4	4
AuCo(OH) _x /BiVO ₄	KBi, pH=9.5	6.2	5
CoFe _{1.5} Cr _{0.5} S ₃ O/COFs//BiVO ₄	KBi, pH=9.5	5.1	6
H-BiVO ₄ /MgO/FeCo ₂ O ₄	Na ₂ SO ₄ , pH=7.3	4.3	7
H-CoAl-LDH/BiVO ₄	Na ₂ SO ₄ , pH=7.3	3.5	8
NiFe/CA/Fe-BiVO ₄	KBi, pH=9.5	6.2	9
Au/BVO-SMSI	KBi, pH=9.3	6.25	10
FeNiOOH/Fe-N-BVO	KBi, pH=9.5	7.01	11
BiVO ₄	Na ₂ SO ₄ , pH=7.3	6.8	This work

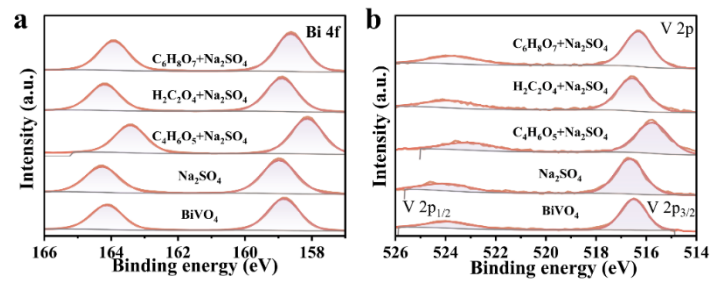


Fig. S1. XPS data of Bi 4f of prepared samples (a); XPS spectra of V 2p.

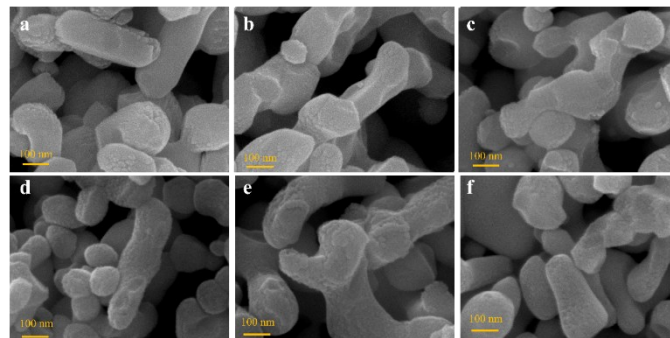


Fig. S2. High-resolution SEM images of (a) bare BiVO₄, and BiVO₄ after reaction in electrolytes of Na₂SO₄ (b), Na₂SO₄ + Na₂SO₃ (c), Na₂SO₄ + C₄H₆O₅ (d), Na₂SO₄ + H₂C₂O₄ (e) and Na₂SO₄ + C₆H₈O₇ (f).



C6H8O7.mp4

Video 1. Contact angle of $\text{Na}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$.

Table S2. The electrolyte resistance (R_s) and charge transfer resistance (R_{ct}) in electrolytes of $\text{C}_4\text{H}_6\text{O}_5$, $\text{H}_2\text{C}_2\text{O}_4$ and $\text{C}_6\text{H}_8\text{O}_7$

electrolyte	R_s (Ω)	R_{ct} (Ω)
Na_2SO_4	12.43	469
$\text{C}_4\text{H}_6\text{O}_5$	14.96	296.6
$\text{H}_2\text{C}_2\text{O}_4$	21.41	281.1
$\text{C}_6\text{H}_8\text{O}_7$	17.85	323.0

Table S3. The electrolyte resistance (R_s) and charge transfer resistance (R_{ct}) in electrolytes of $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_3$, $\text{Na}_2\text{SO}_4 + \text{C}_4\text{H}_6\text{O}_5$, $\text{Na}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4$ and $\text{Na}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$

electrolyte	R_s (Ω)	R_{ct} (Ω)
$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_3$	13.12	420.7
$\text{Na}_2\text{SO}_4 + \text{C}_4\text{H}_6\text{O}_5$	14.24	209.8
$\text{Na}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4$	17.27	220.7
$\text{Na}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$	16.43	169.6

Table S4. Fitting results of TRPL spectra.

samples	A_1	A_2	τ_1 (ns)	τ_2 (ns)
$\text{Na}_2\text{SO}_4 + \text{C}_4\text{H}_6\text{O}_5$	8510.01	30.26	0.31	8.37
$\text{Na}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4$	124.27	15.92	1.10	8.14
$\text{Na}_2\text{SO}_4 + \text{C}_6\text{H}_8\text{O}_7$	41.95	2.74	3.43	78.99

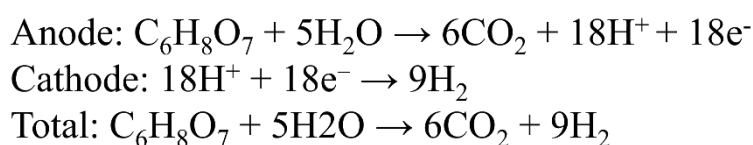
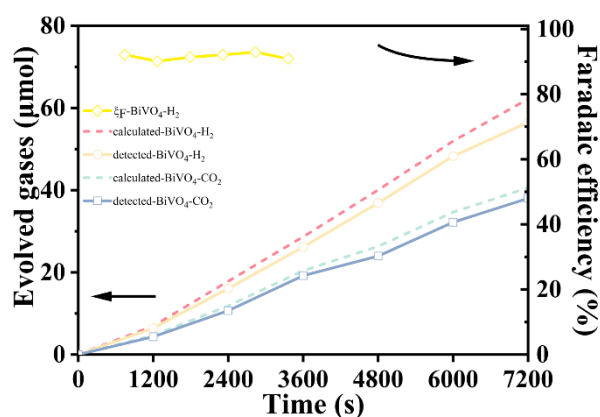


Fig. S3. H₂ and CO₂ evolution in C₆H₈O₇ electrolytes at 1.23 V vs RHE under AM 1.5 G illumination.

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