Supporting Information

Azide molecule mediated electrolyte engineering for selective photoelectrochemical azo coupling and efficient and stable water splitting

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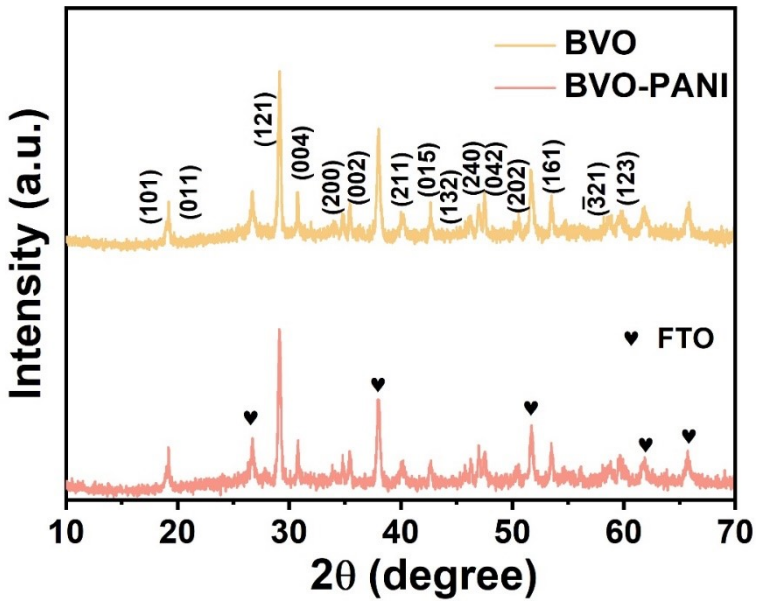

Figure S1. XRD pattern of BVO and BVO-PANI.

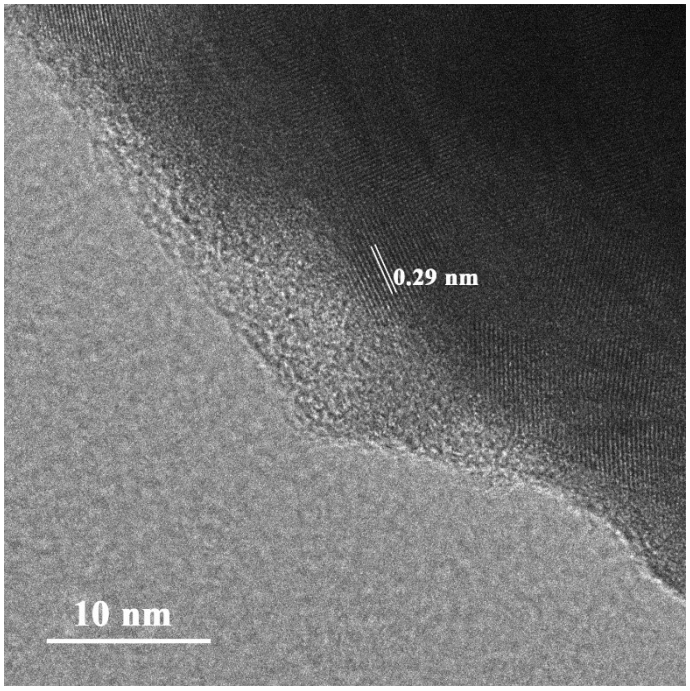

Figure S2. HRTEM image of BVO-PANI

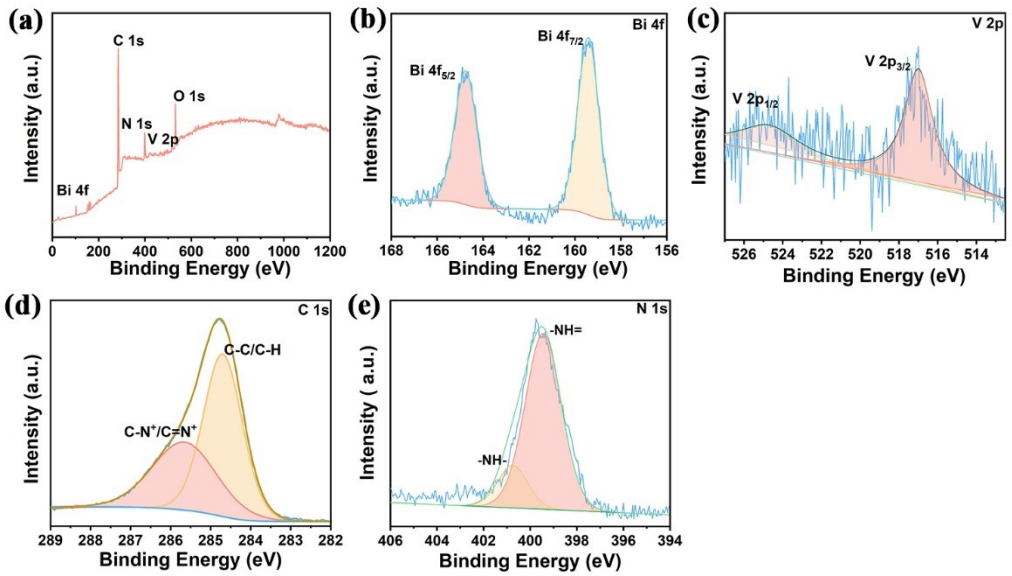

Figure S3. (a) Survey XPS spectra of BVO-PANI photoanode and high-resolution XPS spectra of (b) Bi 4f, (c) V2p, (d) C1s and (e) N 1s.

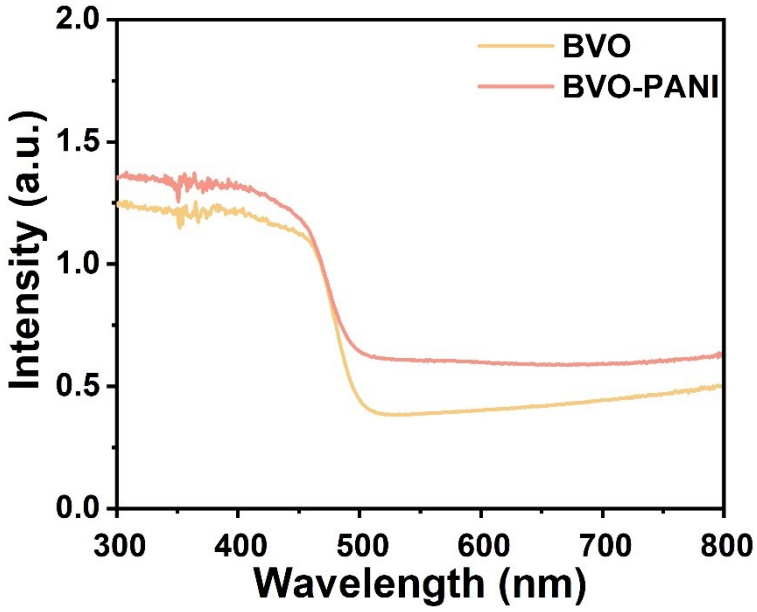

Figure S4. UV–vis DRS spectra of BVO and BVO-PANI photoanodes.

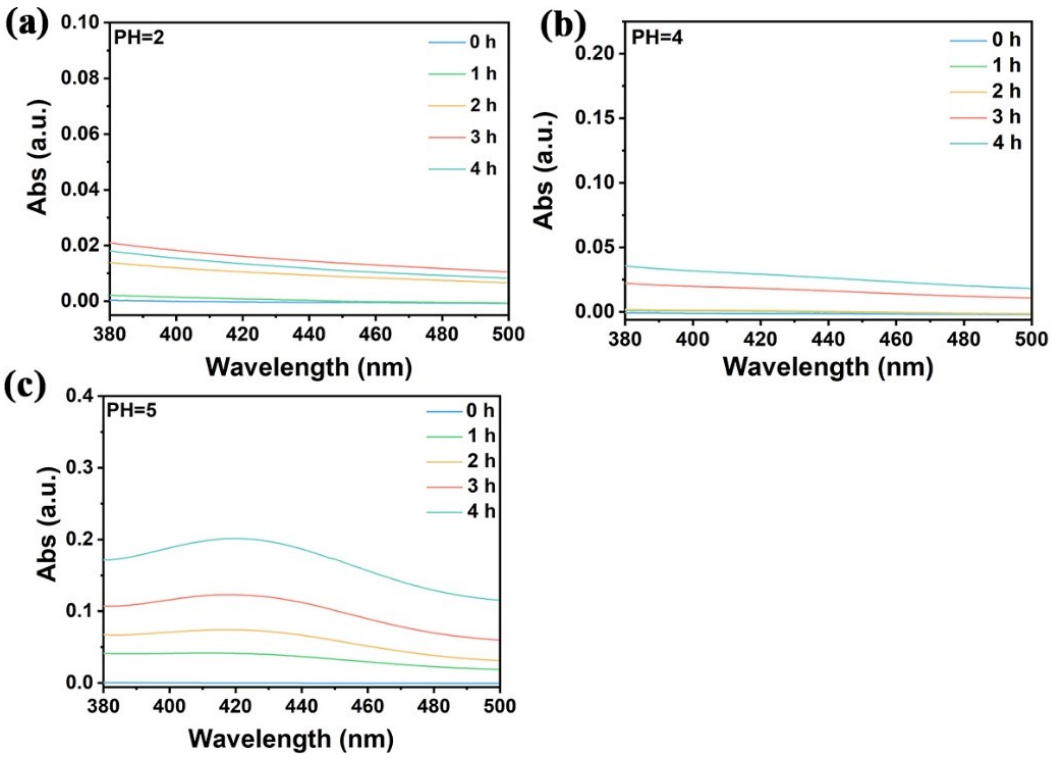

Figure S5. The UV-Vis absorption spectra of 5AT/Na_2SO_4 at (c) pH=2, (b) pH=4 and (c) pH=5 before and after PEC reaction.

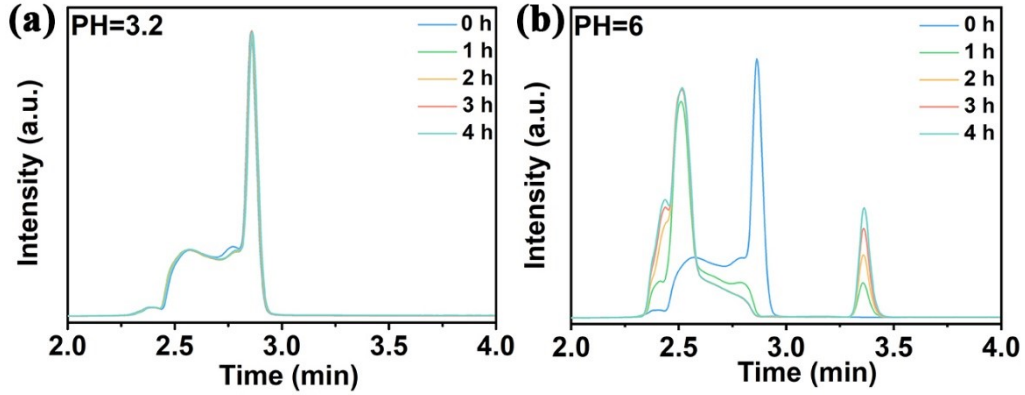

Figure S6. The HPLC spectra of 5AT/Na_2SO_4 at pH=3.2 and pH=6 before and after PEC reaction.

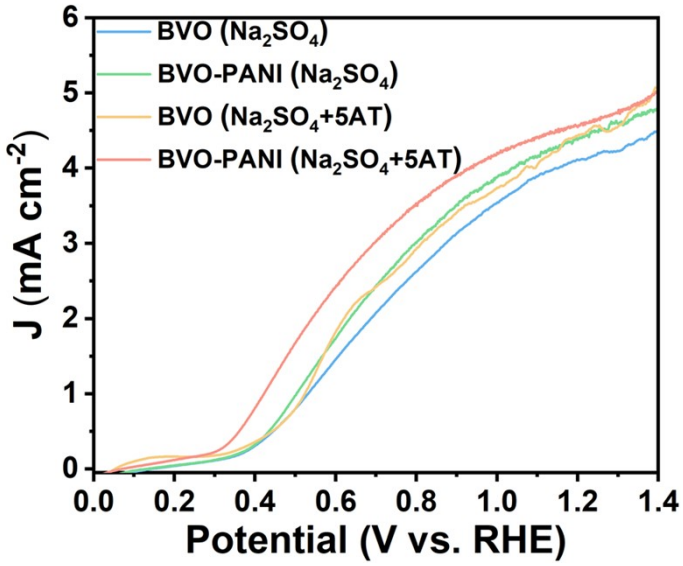

Figure S7. J-V plots of BVO and BVO-PANI photoanodes in Na_2SO_4 and 5AT/Na_2SO_4 electrolyte solution with 0.1 M Na_2SO_3.

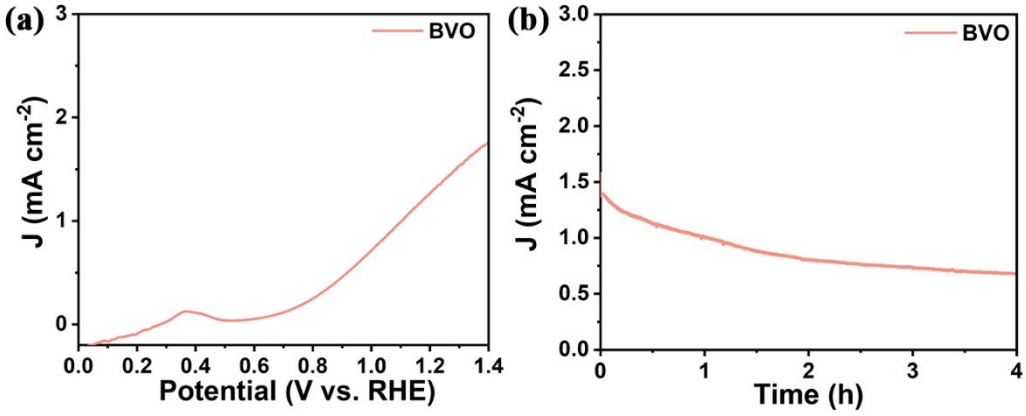

Figure S8. J-V and J-t curves of BVO photoanode in 0.1M Na_2SO_4 acidified with 0.1 M dilute H_2SO_4 (PH=3.2).

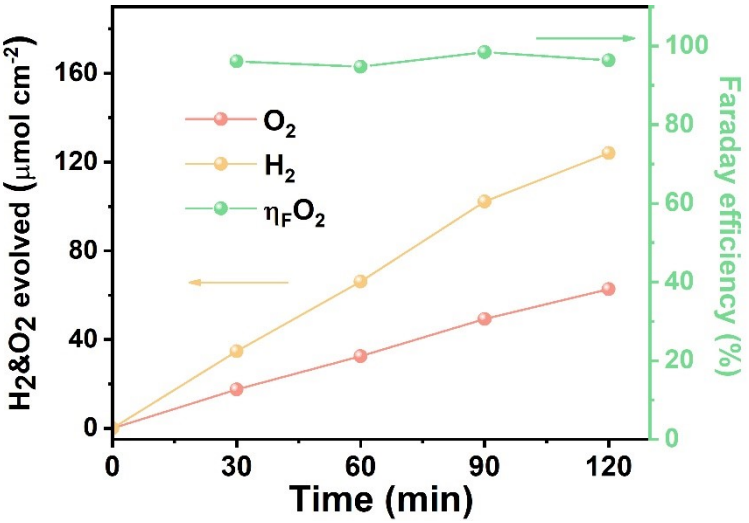

Figure S9. The actual amount of H_2 and O_2 produced by BVO in 5AT solution under AM1.5G illumination at 1.23V_{RHE}.

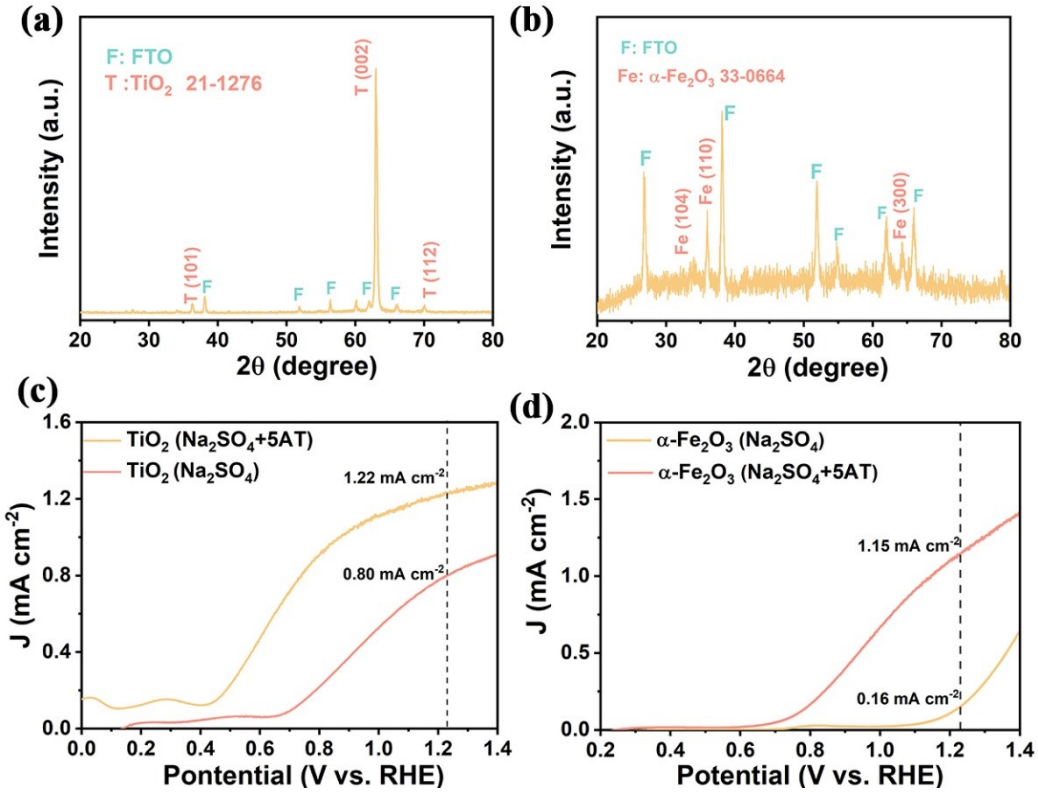

Figure S10. XRD images of (a) TiO_2 and (b) α-Fe_2O_3 photoanodes. J-V plots of (c) TiO_2 and (d) α-Fe_2O_3 photoanodes in Na_2SO_4 and 5AT/Na_2SO_4 electrolyte solution.

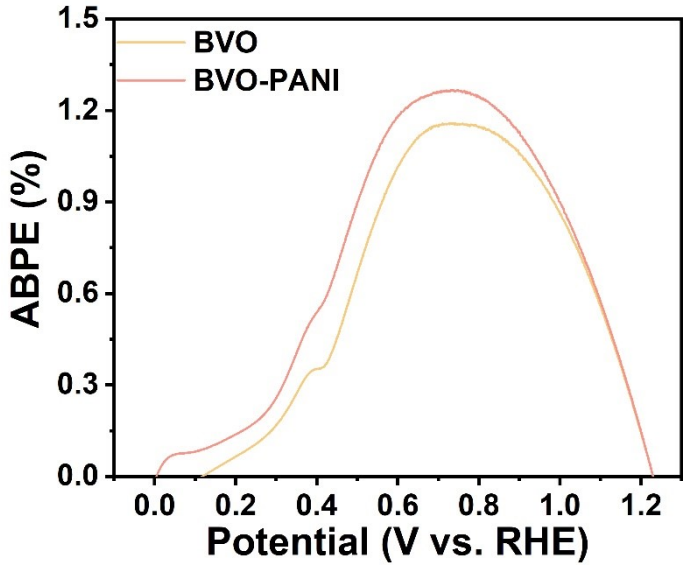

Figure S11. ABPE of BVO and BVO-PANI in 5AT/$NaVO_3$/Na_2SO_4.

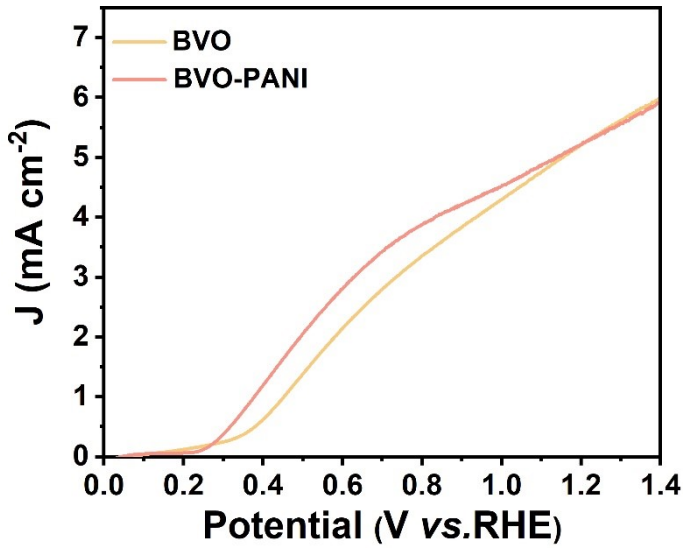

Figure S12. J-V plots of BVO and BVO-PANI photoanodes in 5AT/$NaVO_3$/Na_2SO_4 electrolyte solution with 0.1 M Na_2SO_3.

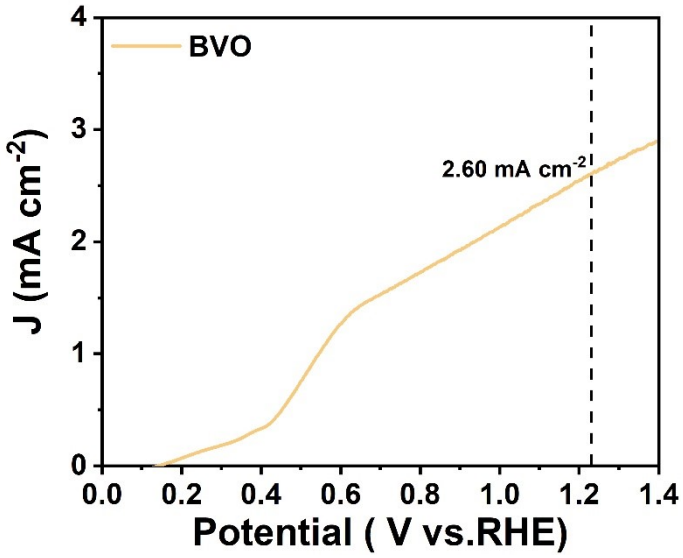

Figure S13. J-V curve of BVO in $NaVO_3/Na_2SO_4$ electrolyte solution.

Table S1. Onset potentials and photocurrent densities at $1.23V_{RHE}$ of BVO photoanode in Na_2SO_4+5AT electrolyte solutions with different pH.

Electrolyte	Onset potential	J (mA cm^{-2}) at $1.23V_{RHE}$
Na_2SO_4+5AT (pH=2)	0.4 V_{RHE}	3.71
Na_2SO_4+5AT (pH=3.2)	0.36 V_{RHE}	3.60
Na_2SO_4+5AT (pH=4)	0.32 V_{RHE}	3.45
Na_2SO_4+5AT (pH=5)	0.32 V_{RHE}	3.64
Na_2SO_4+5AT (pH=6)	0.32 V_{RHE}	3.93

Table S2. Fitting results of Electrochemical Impedance Spectra (at $1.23V_{RHE}$, AM 1.5G irradiation).

Photoanode	Electrolyte	R_s (Ω)	R_{ct} (Ω)
BVO	Na_2SO_4 (pH=6.8)	34.51	178.7
BVO-PANI	Na_2SO_4 (pH=6.8)	34.29	169.1
BVO	Na_2SO_4+5AT (pH=3.2)	38.0	116.8
BVO-PANI	Na_2SO_4+5AT (pH=3.2)	35.44	101.5

Table S3 Recent reports on electrolyte composition regulation to promote PEC water splitting of $BiVO_4$ (BVO) photoanode.

Photoanode	Electrolyte	Onset potential	J (mA cm^{-2}) at 1.23 V_{RHE}	Stability	Reference
NiFe OER/Mo:BVO/Ni/Sn	1 M KBi+Fe^{2+}	0.17 V_{RHE}	2.6 (0.6 V_{RHE})	1100 h (0.6 V_{RHE})	[1]
Etched-NiOOH/BVO	1 M KBi+Fe^{2+}	0.3 V_{RHE}	5.43	200 h (0.8 V_{RHE})	[2]
BVO/FeOOH/NiOOH	1 M KBi+0.1 M V_2O_5 (pH=9.3)	0.24 V_{RHE}	4.8	500 h (0.6 V_{RHE})	[3]
β-FeOOH-B-BVO	0.5 M KBi+0.1M $NaVO_3$(pH=9.3)	0.28 V_{RHE}	4.96	20 h (1.23 V_{RHE})	[4]
BVO/Co-Sil	0.5 M KBi+0.1M $NaVO_3$ (pH=9.5)	0.22 V_{RHE}	5.0	20 h (1.23 V_{RHE})	[5]
Ov-BVO@NiFe-MOFs	0.5 M KBi+0.05 V_2O_5 (pH=9)		5.3±0.15	10 h (0.7 V_{RHE})	[6]

Reference

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[4] Z. Kang, X. Lv, Z. Sun, S. Wang, Y.-Z. Zheng, X. Tao, *Chemical Engineering Journal* **2021**, *421*, 129819.

[5] Q. Sun, T. Cheng, Z. Liu, L. Qi, *Applied Catalysis B: Environmental* **2020**, *277*, 119189.

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