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Supporting Information

Flower balls cathode assembled by Cu doped Co_3S_4/Ni_3S_2 ultrathin nanosheets in photocatalytic fuel cell for efficient photoelectrochemical rifampicin purification and simultaneous electricity generation based on CuO QDs/TiO_2/WO_3 photoanode

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Experimental Section

Synthesis of WO_3 photoanode: Firstly, F-doped SnO_2 conductive glass（FTO） substrate was pre-treated with acetone, ethanol and deionized water successively.1.4 mmol of Na_2WO_4 and 1.2 mmol of $(NH_4)_2C_2O_4$ were mixed in 33 mL of deionized water. Then, 9ml HCl (37%) were added to the solution and vigorously stirred to make the solution yellow. Then 8 mL H_2O_2 (30%) was added and stirred for 10min to make the solution clear. Finally, 30 mL of ethanol was added into the solution. The FTO was immersed into a beaker containing the above solution with the conductive surface facing down. Then placed the sealed beaker in an electric blast drying oven at 85℃ for 3 h. After cooling to room temperature, the WO_3 was washed with deionized water and annealed at 500℃ for 2 h.

Synthesis of TiO_2/WO_3 photoanode: 0.9 mmol of $H_8F_6N_2Ti$ and 4.5 mmol of H_3BO_3 were mixed in 60 mL of deionized water. Then the prepared WO_3 photoanode was immersed into the beaker containing the above solution with the WO_3 side facing down. The sealed beaker was placed in a water bath at 25 ℃ for 60 h to prepare WO_3/TiO_2 photoanode. Finally, washed the photoanode with deionized water and dried.

Synthesis of CuO QDs/TiO_2/WO_3 photoanode: 0.5 mmol of $CuSO_4 \cdot 5H_2O$ was first dissolved into 20 mL of deionized water, and 2.5mmol of $Na_2S_2O_3$ was added into the above solution and stirred evenly. The solution gradually changed from blue to colorless and transparent, and the Cu^+ precursor was made. Immersed the WO_3/TiO_2 photoanode in the prepared solution, and added a drop of 0.5 M NaOH solution to convert Cu^+ into CuOH precipitation. After shaking the beaker for 10 s, the electrode was removed and washed with deionized water. Subsequently, CuOH on the electrode surface was oxidized to CuO by cyclic voltammetry. Finally, washed the photoanode with deionized water and dried. In addition, the effects of CuO modification on the PEC properties of WO_3/TiO_2 were investigated by preparing different concentrations of Cu^+ precursors.

Synthesis of CuO QDs/TiO_2/WO_3-buried junction silicon (BJS) photoanode: The

as-prepared CuO QDs/TiO_2/WO_3 was connected with the rear BJS through copper wire and silver glue.[1]

Synthesis of Cu doped Co_3S_4/Ni_3S_2 cathode: The nickel foam was first cut into 25 mm×50 mm in size, and then sonicated for 10 min in 1 mol/L of H_2SO_4 solution, ethanol, deionized water, respectively. The cathodes were prepared through simple hydrothermal method. Typically, 1 mmol of $CoCl_2 \cdot 6H_2O$ and 2 mmol of $Na_2S_2O_3$ were mixed with 40 mL of deionized water. Then, certain amount of $CuCl_2 \cdot 2H_2O$ were dissolved in the solution. After stirring for 20 min, the mixture was transferred to polytetrafluoroethylene reactor. At the same time, the pretreated nickel foam was immersed into the reactor and heated at 180 ℃ for 12 h. After cooling to room temperature, the prepared cathode was washed with ethanol and deionized water for several times, and dried at 60 ℃ under vacuum. In the following, for the convenience of description, Cu doped Co_3S_4/Ni_3S_2 cathodes are all marked as Cu/Co_3S_4/Ni_3S_2.

Synthesis of Co_3S_4/Ni_3S_2 cathode: Preparation of Co_3S_4/Ni_3S_2 cathode followed identical steps as the Cu doped Co_3S_4/Ni_3S_2 cathode except for only adding 1 mmol of $CoCl_2 \cdot 6H_2O$ and 2 mmol of $Na_2S_2O_3$ to form a mixed solution.

Synthesis of Ni_3S_2 cathode: Preparation of Ni_3S_2 cathode followed identical steps as the Co_3S_4/Ni_3S_2 cathode except for only adding 2 mmol of $Na_2S_2O_3$ to form a mixed solution.

Supplementary figures

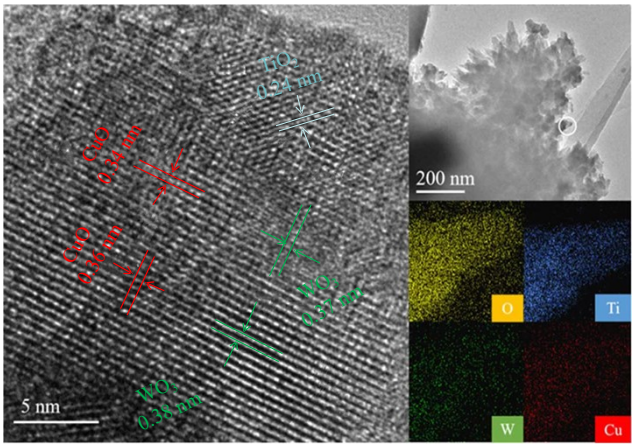

Fig. S1. TEM and EDS mapping images of CuO QDs/TiO_2/WO_3 photoanode.

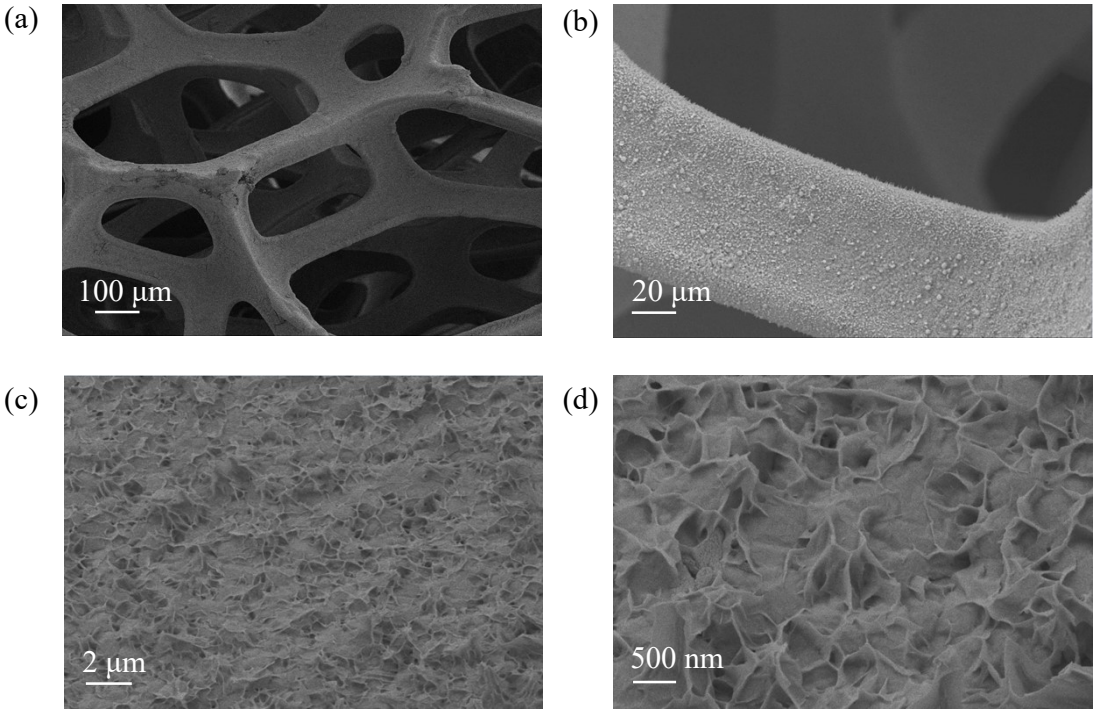

Fig. S2. (a) SEM images of pretreated Ni foam and (b-d) Ni_3S_2.

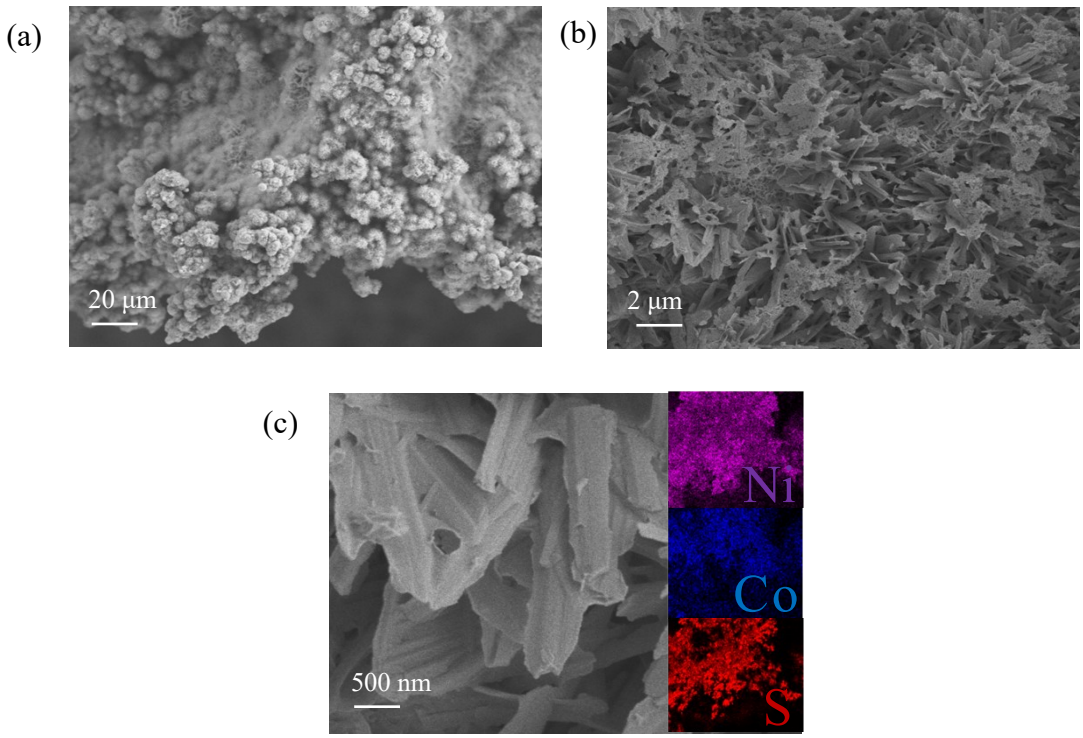

Fig. S3. SEM images of Co_3S_4/Ni_3S_2 (insert: EDS mapping images of Co_3S_4/Ni_3S_2)

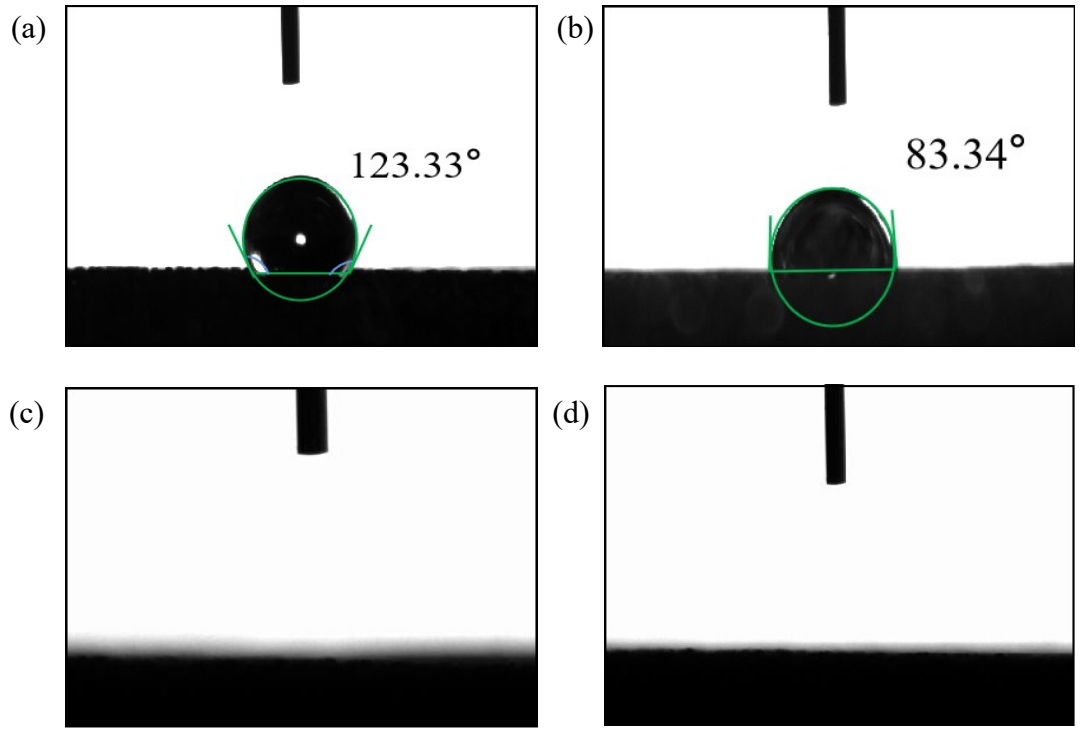

Fig. S4. Contact angle measurements of (a) Ni foam, (b) Ni_3S_2, (c) Co_3S_4/Ni_3S_2 and (d) $Cu/Co_3S_4/Ni_3S_2$.

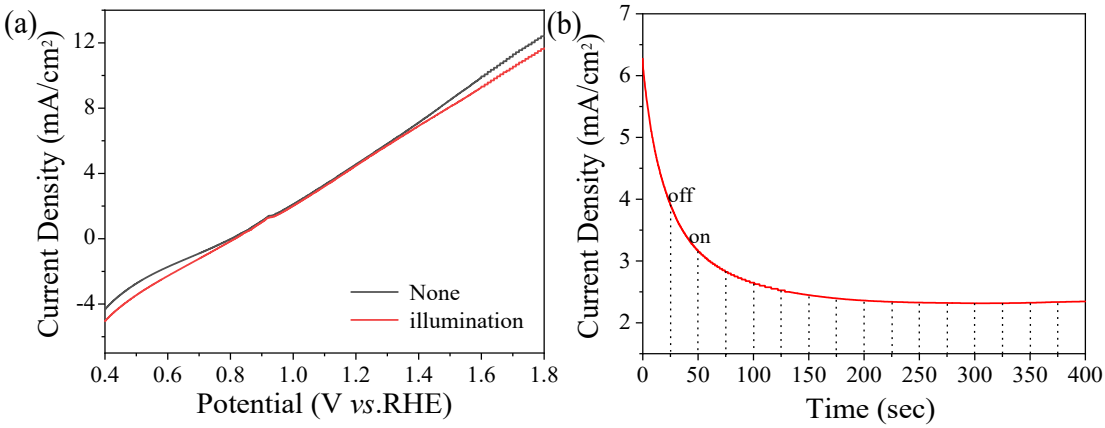

Fig. S5. (a) LSV curves of $Cu/Co_3S_4/Ni_3S_2$ cathode under different conditions. (b) Chopping photocurrent–time (J-t) plot of the $Cu/Co_3S_4/Ni_3S_2$ cathode (dashed line: switch on and off the simulated light source every 25 seconds).

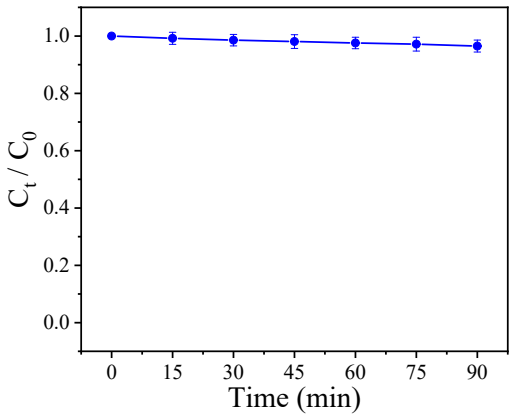

Fig. S6. Self-degradation of RFP under simulated sunlight in PFC system.

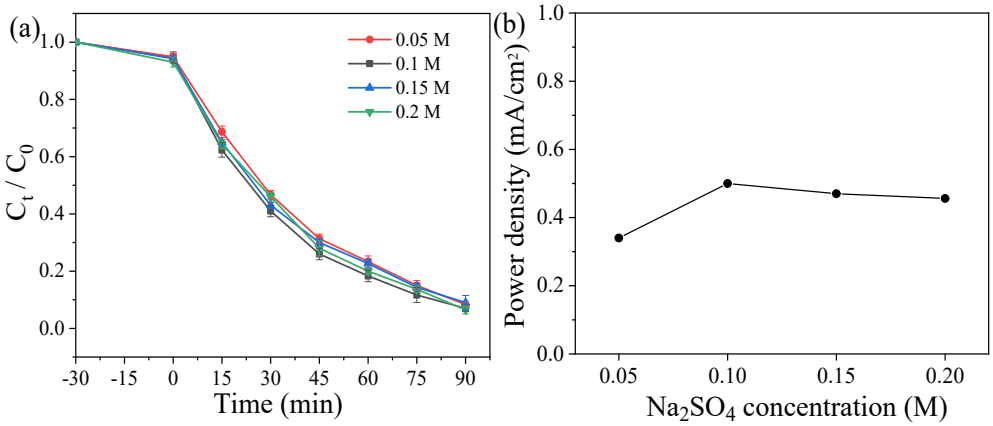

Fig. S7. (a) Degradation of 20 mg L^{-1} RFP in PFC systems with different concentrations of SO_4^{-2}. (b) Maximum power density (P_{max}) in diffffferent Na_2SO_4 concentrations.

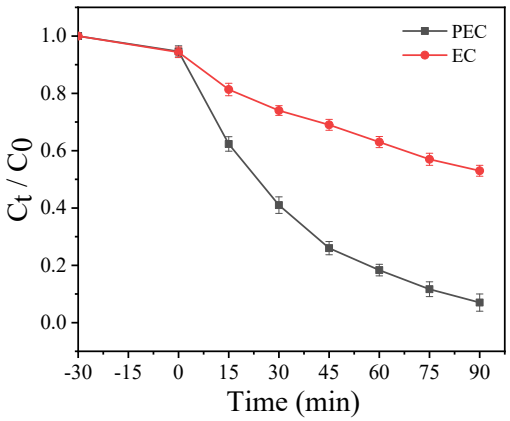

Fig. S8. RFP degradation curves in EC and PFC system.

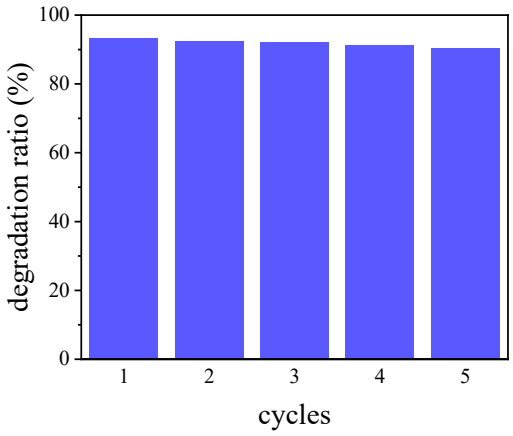

Fig. S9. Cyclic stability test for $Cu/Co_3S_4/Ni_3S_2$ cathode.

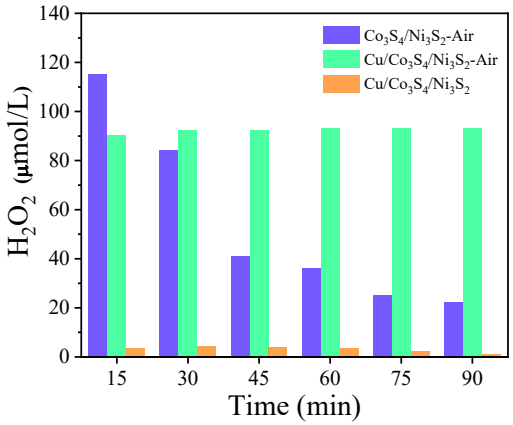

Fig. S10. Concentration of H_2O_2 in different systems.

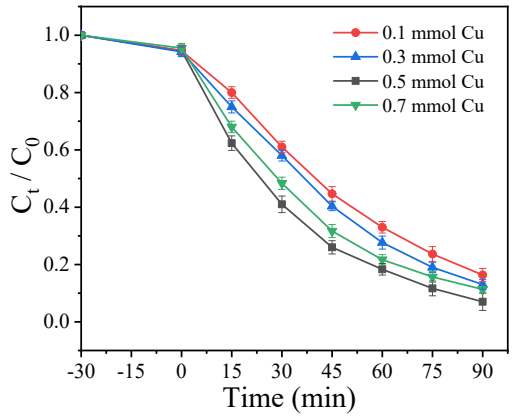

Fig. S11. Degradation performance of $Cu/Co_3S_4/Ni_3S_2$ electrodes with different copper content.

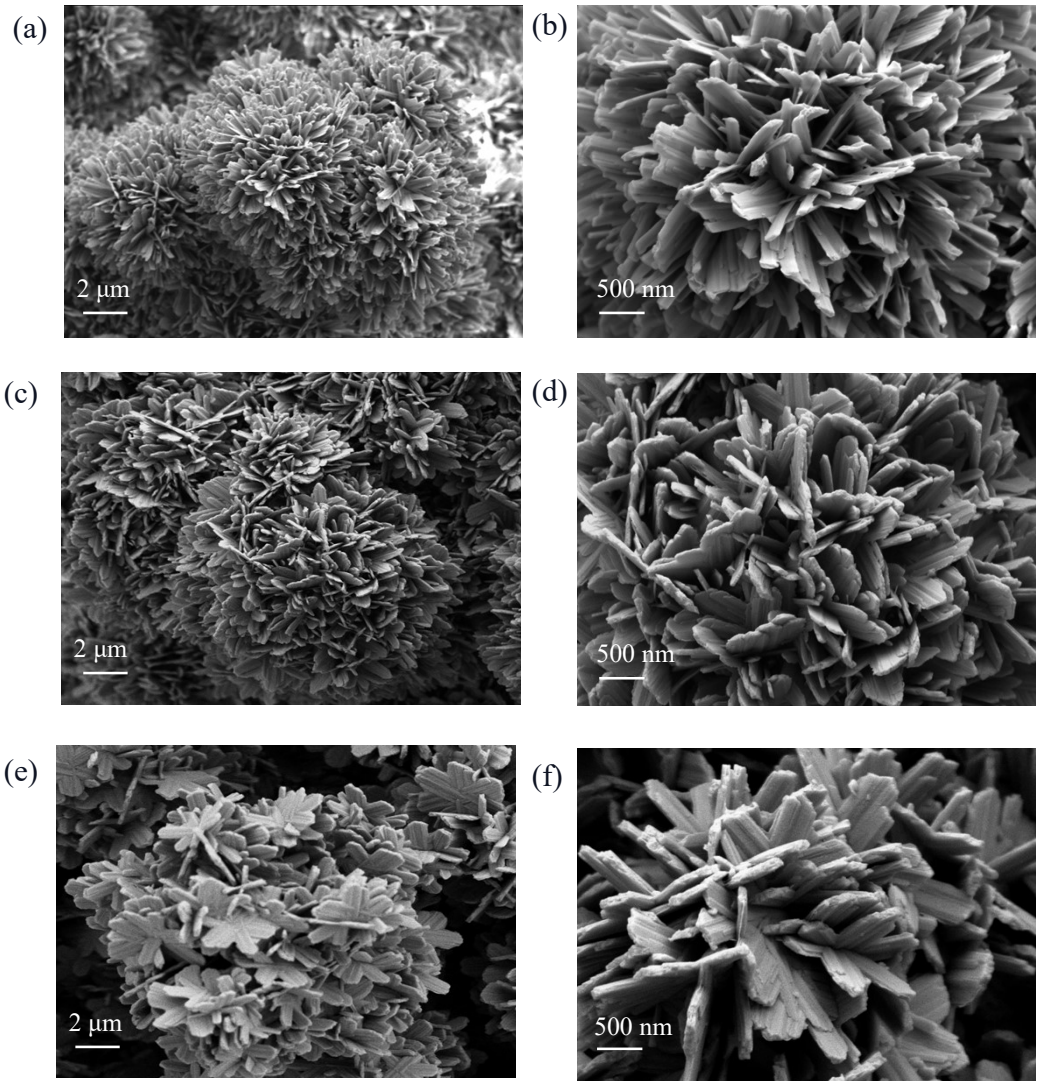

Fig. S12. SEM images of $Cu/Co_3S_4/Ni_3S_2$ with different Cu doping level (a-b) 0.1 mmol, (c-d) 0.3 mmol, (e-f) 0.7 mmol.

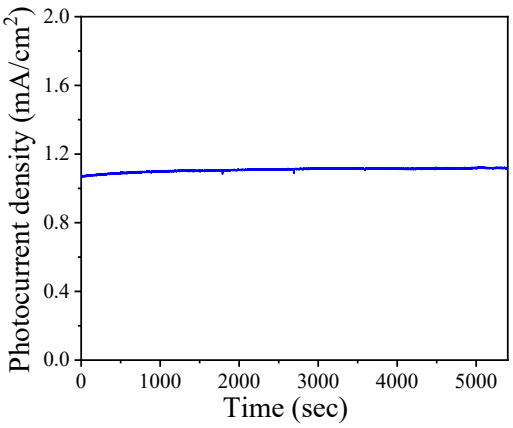

Fig. S13. J-t curve of $Cu/Co_3S_4/Ni_3S_2$ PEC system in degrading 20 mg L^{-1} RFP.

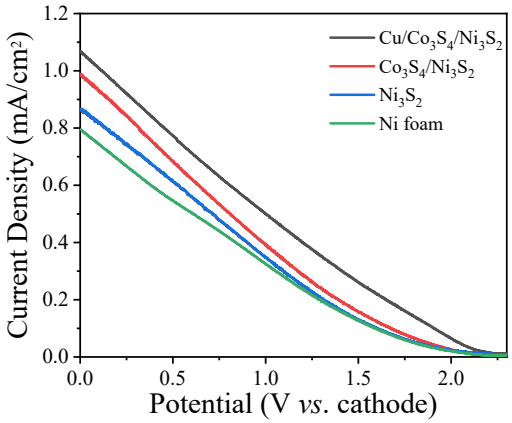

Fig. S14. J-v curves of different PFC system.

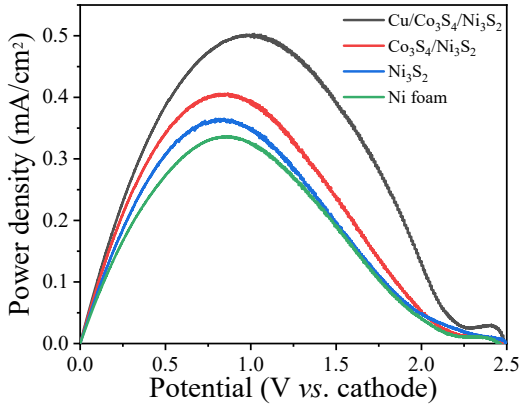

Fig. S15. Power output curves of PFC system with different cathodes.

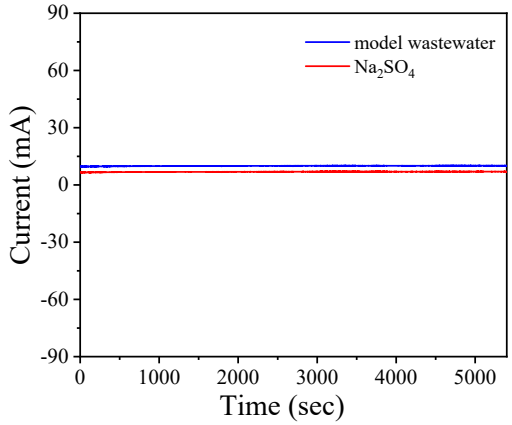

Fig. S16. J-t curves of $Cu/Co_3S_4/Ni_3S_2$ PEC system in simulated wastewater and 0.1M Na_2SO_4 solution.

Table S1. Cell parameters of Co_3S_4 and Ni_3S_2.

substance	Formula	cell parameters (Co_3S_4/Ni_3S_2.)	cell parameters (Cu/Co_3S_4/Ni_3S_2.)
Co_3S_4	$\frac{1}{d^2}=\frac{h^2+k^2+l^2}{a^2}$	a=b=c=9.392 Å, α=β=γ=90°	a=b=c=9.394 Å, α=β=γ=90°
Ni_3S_2	$\frac{1}{d^2}=\frac{4(h^2+hk+k^2)}{3a^2}+\frac{l^2}{c^2}$	a=b=5.738 Å, c=7.136 Å, α=β=90°、γ=120°	a=b=5.738 Å, c=7.136 Å, α=β=90°、γ=120°

Table S2. Comparison with reported PFC systems in electric production and pollutant degradation.

photoanode	(photo) cathode	Pollutant substrate	J_{sc} (mA·cm^{-2})	V_{oc} (V)	P_{max} (mW·cm^{-2})	Degradation eff./time taken	Ref.
$BiVO_4/WO_3/W$	Pt	Tetracycline	0.26	0.78	0.20	78%/4 h	S2
TiO_2/Ti	Cu_2O/Cu	Methylene blue	0.17	0.62	0.25	88%/8 h	S3
$TiO_2/WO_3/W$	Pt/BJS	Tetracycline	0.38	0.77	0.06	92%/3 h	S4
$TiO_2/BiVO_4$	Pt	Rhodamine B	0.29	0.34	0.002	30%/3 h	S5
$BiVO_4/WO_3$	Pt/C	Tetracycline	0.09	0.15	0.009	87%/8 h	S6
Ag_3PO_4/C_3N_4	Cu_2O	Tetracycline	0.09	0.36	0.006	76%/4 h	S7
NiFe/$BiVO_4$	Cu_2O/Cu	Methyl blue	0.14	0.58	0.02	81%/6 h	S8
ZnO/Zn	CuO/Cu	Methyl green	0.23	0.95	0.05	91%/6 h	S9
WO_3/W	Pt	Methyl orange	0.51	0.03	0.003	70%/2 h	S10
CuO QDs/TiO_2/WO_3-BJS	Cu/Co_3S_4/Ni_3S_2	Rifampicin	1.07	2.49	0.50	93%/1.5 h	This work
		Tetracycline	1.03	2.42	0.50	96%/1.5 h	
		Rhodamine B	0.98	2.28	0.54	95%/1.5 h	

Reference

[S1] L. Li, S. Chen, Y. Zhang, J. Li, J. Bai, T. Zhou, J. Wang, C. Zhou, L. Xia, Q. Xu, M. Rahim, B.

Zhou, Appl. Catal. B., 2020, 268, 118471.

[S2] L. Xia, J. Bai, J. Li, Q. Zeng, X. Li, B. Zhou, Appl. Catal. B., 2016, 183, 224–230.

[S3] J. Li, J. Li, Q. Chen, J. Bai, B. Zhou, J. Hazard. Mater., 2013, 262, 304–310.

[S4] Q. Zeng, J. Bai, J. Li, L. Li, L. Xia, B. Zhou, Y. Sun, Appl. Energy., 2018, 220, 127–137.

[S5] M. Khalil, F. Naumi, U. Pratomo, T.A. Ivandini, G.T.M. Kadja, J.Y. Mulyana, Appl. Surf. Sci., 2021, 542, 148746.

[S6] S Xie, K yang, X Ye, J. Colloid Interface Sci., 2018, 532, 758–766.

[S7] H Yu, Y Xue, Y Lu, X Wang, S Zhu, W Qin, M Huo, J. Environ. Manage., 2020, 254, 109738.

[S8] Y He, C Zhang, J Hu, Applied Energy., 2019, 255, 113770.

[S9] M Kee, J Soo, S Lam, J. Environ.Manage., 2018, 228, 383.

[S10] D Pan, S Xiao, X Chen, R Li, Y Cao, D Zhang, S Pu, Z Li, G Li, H Li, Environ. Sci. Technol., 2019, 53, 3697-3706.