Supporting Information Boosting Oxygen Activation by CoP/Carbon Nitride Photocatalyst in Low-Concentration H₂S Oxidation

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EXPERIMENTAL SECTIONS

S1 Synthesis of Co₃O₄ precursor

The Co₃O₄ precursor was prepared by a hydrothermal method reported before.¹ In a typical synthesis, 2.4 mL of 0.3M (Co(CH₃COO)₂·4H₂O) aqueous solution were added into 48 mL of ethanol with sonication for 5 minute. Subsequently, 1 mL of NH₃·H₂O were dropped into the system, which was under stirring at room temperature. After the suspension was heated at 353 K and continuous stirred for 20 h (the change of the reaction system was recorded in Fig. S1[†]), the whole mixture was transferred into a 100 mL Teflonlined stainless steel autoclave for 3-hour heating at 423 K. After that, the product was collected by vacuum filtration, washed with ethanol for 3 times and dried at 343 K in vacuum drying oven overnight.

S2 Characterizations

The X-ray diffraction (XRD) patterns was captured by Bruker D8 Advance equipped with Cu K α radiation. The actual amount of CoP loaded on CN was determined on the inductive coupled plasma emission spectrometer (ICP, PerkinElmer Avio 200 Avio 200). The microstructures of samples were surveyed on scanning electron microscope (SEM, FEI Nova NanoSEM 230) and transmission electron microscopy (TEM, Thermo Fisher Scientific, Talos F200). The specific areas and porous structures of catalysts were calculated by N₂ adsorption on Micromeritics ASAP 2460. X-ray photoelectron spectroscopy (XPS, Thermo ESCALB 250Xi) with an Al K α source was applied to explore the surface elements and the chemical state. The Fourier transform infrared (FTIR) spectrum and in-situ spectrum were recorded on Thermo Scientific Nicolet iS50 spectrometer. LabRAM HR Evolution Raman spectrometer system was used to obtain Raman spectrum. UV-vis diffuse reflectance spectroscopy (DRS, Varian Cary 500 Scan UV-visible system) and the photoluminescence (PL, PerkinElmer Luminescence Spectrometer LS 50 B) spectroscopy were used to investigate the optical properties. The photoelectrochemical testing was carried out on Bio-Logic VSP-300 electrochemical workstation and oxygen reduction reaction (ORR) characterization was achieved on Metrohm Autolab PGSTAT302N workstation. The temperatureprogrammed desorption (TPD) curves were obtained on Micromeritics AutoChem II 2920 Chemisorption Analyzer. BRUKER A300 spectrometer was applied to perform electron paramagnetic resonance (EPR) experiment.

S3 Photoelectrochemical test



Fig. S1. Evaluation system for photocatalytic H_2S oxidation performance. The detailed instructions were displayed as follow: 1. on-off valve, 2. mass flow meter, 3. gas mixture tank, 4. led light, 5. Self-designed quartz photoreactor, 6. Six-way valve, 7. exhaust gas collector, 8. gas chromatography.

S3 Photoelectrochemical test

1 mg of the sample was added into 1 mL DMF, and the mixture was sonicated for 40 min. Then, 5 μ L of the aqueous dispersion was dropped on the cleaned FTO and the cover area was constrained within 1cm². The working electrodes was prepared after repeating the procedure once. The photoelectrochemical experiments were performed on Bio-Logic VSP-300 electrochemical workstation using 0.2 M Na₂SO₄ as electrolyte, Ag/AgCl electrode as a reference electrode (in saturated KCl aqueous solution) and 1

cm² Pt electrode as a counter electrode.

S4 Electrochemical characterizations in quasi-reaction condition

The equipment and electrodes were similar to that in S2. The differences lay in the reaction atmosphere was created by bubbling gaseous reactants of O_2 molecules into the electrolyte with flow velocity of 10 mL/min and the electrolyte was replaced by 0.1 M NaOH. Meanwhile, the FTO base was replaced by carbon paper.

S5 Rotating disk electrode (RDE) measurement^{2, 3}

The 3CoP/CN and CN samples were prepared by mixing 5 mg of the catalyst in 1 mL of solution containing 470 μ L of ethanol, 20 μ L of H₂O and 10 μ L of 5% Nafion solution with ultrasonication for 30 min to obtain quasi-homogeneous inks. Then, 10 μ L of catalyst ink was cautiously dropped onto a polished glassy carbon RDE with work area of 0.196 cm² and the drop coating was repeated once.

RDE measurements were carried out in a three-electrode system on Metrohm Autolab PGSTAT302N workstation in 0.1 M KOH electrolyte with catalyst-coating RDE as working electrode, Ag/AgCl electrode and Pt wire as a reference electrode and counter electrode, respectively. Before measurement, O_2 flow was purged into electrolyte for 30 min to saturate it with O_2 . The experiment was conducted at various rotating speed of 625 rpm \circ 900 rpm \circ 1225 rpm \circ 1600 rpm \circ 2025 rpm with a sweep rate of 10 mV s⁻¹. The electron transfer number (n) were calculated from the Koutecky-Levich equation :

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{\frac{1}{B\omega^2}} + \frac{1}{J_K}$$
$$B = 0.62nFC_0 D_0^{\frac{2}{3}} v^{-\frac{1}{6}}$$

J is the measured current density, J_K and J_L are the kinetic and limiting current

densities, ω is the rotating speed (r s⁻¹), F is the Faraday constant (96485 C mol⁻¹), v is the kinetic viscosity of water (0.01 cm² s⁻¹), C_0 is the bulk concentration of O₂ in 0.1 M KOH (1.26×10⁻³ mol cm⁻³), and D_0 is the diffusion coefficient of O₂ (2.7×10⁻⁵ cm² s⁻¹), respectively.

S6 Computational details

To verify the reliability of the experiment, we utilized the Density Functional Theory (DFT) to simulate calculation,⁴ and then adopt what is the Vienna Ab-initio Simulation Package (VASP) with the Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA). In the calculation, we used DFT-D3 to decorrect the van der Waals interaction \cdot besides, the kinetic cutoff energy of plane wave expansion was set to 420 eV, whereas the convergence criteria of energy and force for all geometry structures were fixed to 10⁻⁵ eV and 0.05 eV Å⁻¹. (1×1×1) Monkhorst-Pack mesh was used for k-point sampling of the Brillouin zone.⁵ Unit cell (2 × 2× 1) was periodically repeated on the x-y plane. Since the melon system loads large CoP clusters, to ensure that the interlayer effects can be eliminated, spacing between the adjacent slabs was set to about 15 Å. We need to use the binding energy formula when loading clusters, and the adsorption energy formula when comparing the adsorption capacity, as shown below :

$$E_{abs} = E_{(sub-gas)} - E_{(sub)} - E_{(gas)}$$
(1)

In this (1) formula, $E_{(sub-gas)}$ represents the energy of the with or without CoP clusters loaded after absorbing small gas molecules on the melon $\cdot E_{(sub)}$ represents the energy with or without CoP clusters loaded on the melon without adsorbing small molecules, $E_{(gas)}$ represents the energy of small gas molecules in a vacuum condition, If E_{abs} is negative, the adsorption process is exothermic, on the contrary, it is endothermic, so the smaller the value of E_{abs} , the more likely it is to adsorb small

molecules.

RESULTS AND DISCUSIION



Fig. S2. (a) Color changes of samples during the synthesis of Co_3O_4 by chemical precipitation method; (b, c) XRD patterns of lab-made Co_3O_4 and CoP.



Fig. S3. XRD pattern of CN and xCoP/CN.



Fig. S4. SEM images and EDS mapping images of 3CoP/CN.



Fig. S5. N_2 adsorption-desorption isotherms and BJH desorption plots of CN and xCoP/CN.



Fig. S6. ATR-FTIR spectra of CN and xCoP/CN.



Fig. S7. Raman spectra of CN and xCoP/CN.



Fig. S8. Full XPS spectra and enlarged version of the selected area of CN, 3CoP/CN and 5CoP/CN.



Fig. S9. High resolution XPS spectra of (a) C 1s, (b) N 1s, (C) Co 2p and (d) P 2p in CN, CoP and 5CoP/CN.



Fig. S10. The charge densities of CoP/CN. The white, grey, brown, lilac and navy-blue spheres were H, N, C, P and Co atoms, respectively. Yellow and blue regions represent the accumulation and depletion of electrons at 0.002 eÅ⁻³ isosurface value, respectively.



Fig. S11. High resolution XPS spectra of (a) Co 2p, (b) P 2p in 3CoP/CN and 3CoP/CN-Used.



Fig. S12. (a) XPS spectra of S 2p on 3CoP/CN-Regenerated and 3CoP/CN-Used, (b)

Photocatalytic H_2S oxidation performance of 3CoP/UCN-Regenerated.



Fig. S13. UV-Vis DRS spectra of CN and xCoP/CN.



Fig. S14. (a) H_2S -TPD of CN and 3CoP/CN; (b) H_2S adsorbed on CN and 3CoP/CN, respectively. The yellow, red, white, grey, brown, lilac and navy-blue spheres were S, O, H, N, C, O and Co atoms, respectively. The CoP was simplified as Co4P4 cluster in the calculation model. The E_{ads} represented the adsorption energy.



Fig. S15. Photocatalytic performance of 3CoP/CN under different conditions (with O₂ or without O₂).



Fig. S16. Schematic diagram on the conversion of reactive oxygen species⁶.



Fig. S17. LSV curves of CN and 3CoP/CN in 0.1 M NaOH purged with N₂.



Fig. S18. RDE polarization curves of CN and 3CoP/CN at different rotation rates.



Fig. S19. Photocurrent-Time curve of CoP/CN under different circumstances. (O₂ flow: 10 mL min⁻¹, the concentration of Na₂S: 5 mg L⁻¹)



Fig. S20. SO₂-TPD of CN and 3CoP/CN

Sample	Co ³⁺ (wt%)	Surface Area (m²/g)	Pore volume (cm ³ /g)		
CN	0.59	71	0.36		
2CoP/CN	1.07	75	0.40		
3CoP/CN	1.59	73	0.37		
4CoP/CN	2.38	75	0.39		
5CoP/CN	3.02	75	0.41		

Table S1 BET and ICP results of prepared catalysts

Table S2 Chemical nature of CN, CoP and xCoP/CN

Sample C specie		C 1s		N 1s		Co 2p			Р 2р		
	C species	С-N-Н	N-C=H	C-N=C	N-(C) ₃	C-N-H	Co 2p _{3/2}	Со-О	Co Sat.	P 2p _{3/2}	P-O
CN	284.80	286.03	288.29	398.75	399.82	401.05	/	1	/	/	/
CoP	284.80	/	/	/	/	/	778.73	781.38	784.81	129.44	133.55
3CoP/CN	284.80	286.09	288.45	398.85	399.75	401.14	778.63	781.25	785.11	129.69	13395
5CoP/CN	284.80	286.47	288.55	398.93	399.83	401.21	778.64	781.20	785.49	129.80	134.04

Table S3 Chemical nature of 3CoP/CN and 3CoP/CN-Used

Sample	Со 2р					s			
	Co 2p _{3/2} (at.%)	Co-O (at.%)	Co Sat. (at.%)	Co-O/ Co 2p _{3/2}	P 2p _{3/2} (at.%)	P-O (at.%)	P-O/P 2p _{3/2}	S 2p _{3/2} (at.%)	
3CoP/CN	0.12	0.08	0.11	0.67	0.17	0.29	1.71	/	
3CoP/CN-Used	0.07	0.10	0.09	1.43	0.26	1.05	4.04	0.64	

C species located at 284.80 eV was served as a calibration peak for other peaks.

a The center of Co $2p_{3/2}$ (778.5±0.1 eV), b The center of Co $2p_{1/2}$ (793.3±0.1 eV),

c The center of Co Sat. (785.2 \pm 0. 1 eV), d The center of P 2p_{3/2} (129.6 \pm 0.1 eV),

e The center of P-O (134.0 \pm 0.1 eV), f The center of P 2p_{3/2} (168.9 eV).

REFERENCES

(1) Z. Pan, Y. Zheng, F. Guo, P. Niu and X. Wang, ChemSusChem, 2017, 10, 87-90.

(2) Z. Zhu, H. Pan, M. Murugananthan, J. Gong and Y. Zhang, *Appl. Catal.*, *B*, 2018, **232**, 19-25.

(3) J. Wang, Z. Huang, W. Liu, C. Chang, H. Tang, Z. Li, W. Chen, C. Jia, T. Yao and S. Wei, *J. Am. Chem. Soc.*, 2017, **139**, 17281-17284.

(4) C. Dong, Z. Zheng, Z. Wang, J. He, Z. Ye, X. Gong and I. M. Lo, *J. Hazard. Mater.*, 2021, **416**, 125891.

(5) C. Zhu, S. Zhao, Z. Fan, H. Wu, F. Liu, Z. Chen and A. Li, *Adv. Funct. Mater.*, 2020, **30**, 2003947.

(6) Y. Nosaka and A. Y. Nosaka, Chem. Rev., 2017, 117, 11302-11336.