Electronic Supplementary Information

A pyrolysis-phosphorization approach to fabricate CoP nanoparticles-embedded carbon nanotubes for ambient electrosynthesis ammonia

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Experimental Section

Synthesis of ZIF-67. All of the chemical regents were analytical grade (AR) and were used without further purification. For the synthesis of ZIF-8, $Co(NO_3)_2.6H_2O$ (5.82 g) and 2-methylimidazole (6.16 g) were first dissolved in 150 mL of methanol respectively, forming two precursor solutions. Then the solution of 2-methylimidazole was poured into the $Co(NO_3)_2$ solution. After stirring at room temperature for 24 h, the obtained white precipitate was centrifuged and washed with methanol for several times and dried at 60 °C to obtain ZIF-67 product.

Synthesis of Co/CNs. The ZIF-67 as precursor was placed in a tube furnace, heated to 920 °C with a ramp rate of 2 °C min⁻¹ for 3 h in Ar atmosphere. The obtained black powdered product was subsequently washed using 0.8 M H₂SO4 solution at room temperature for 12 h to remove any accessible Co species, after drying at 60 °C to obtain Co/CNs.

Synthesis of CoP/CNs. The as-synthesized Co/CNs (10 mg) was then placed in a small crucible, which was put into a big crucible containing NaH₂PO₂.H₂O (100 mg) in a tube furnace. The reaction was performed at 350 °C for 2 h under Ar atmosphere. After that, CoP/CNs sample was obtained for further use.

Characterization. The crystalline structures of samples were identified by the X-ray

diffraction analysis (XRD, Philips X'pert PRO) using Nifiltered monochromatic CuKa radiation ($\lambda K\alpha 1 = 1.5418$ Å) at 40 kV and 40 mA. Transmission electron microscope (TEM) images of samples were obtained using JEMARM 200F operating at an accelerating voltage of 200 kV. High-resolution transmission electron microscope (HRTEM), scanning TEM images (STEM) and elemental mapping images of samples were obtained on a JEOL-2010 transmission electron microscope. Furthermore, the spherical aberration corrected (Cs-corrected) high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and the energydispersive X-ray (EDX) mapping experiments were performed using FEI Titan G2 microscope equipped with a Super-X detector at 300 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al Ka1, 2 monochromatized radiations at 1486.6 eV Xray source. Nitrogen adsorptiondesorption isotherms were measured using an automated gas sorption analyzer (Autosorb-iQ-Cx). XAFS spectra were obtained at the 1W1B station in the BSRF (Beijing Synchrotron Radiation Facility, People's Republic of China) operated at 2.5 GeV with a maximum current of 250 mA. XAS measurements at the Co K-edge were performed in fluorescence mode using a Lytle detector. All samples were pelletized as disks of 13 mm diameter with 1 mm thickness using graphite powder as a binder. The ¹⁵N isotopic labeling experiments were conducted using ¹⁵N₂ as the feeding gas (99% enrichment of ¹⁵N in ¹⁵N₂, Supplied by Hefei Ninte Gas Management Co., LTD). Prior to use for NRR measurements, ¹⁵N₂ feeding gas was purged through a 1.0 mM H₂SO₄ solution and distilled water to eliminate the potential NO_x and NH₃ contaminants. The ¹H NMR (nuclear magnetic resonance) spectra were obtained using superconducting Fourier transform nuclear magnetic resonance spectrometer (Bruker Avance-400). (15NH₄)₂SO₄ as reference samples was dissolved in 0.1 M Na₂SO₄ solution (D_2O/H_2O mixed solution, $V_{D2O}:V_{H2O} = 1:4$) for ¹H NMR measurements, and the electrolyte obtained from ¹⁵N₂-saturated 0.1 M Na₂SO₄ solution with the reaction time of 2 h and concentration time of 12 h at 80 °C (D₂O/electrolyte mixed solution, V_{D2O} : $V_{electrolyte} = 1:4$) for ¹H NMR measurements.

Electrochemical measurements. All electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH Instrumental Corporation, Shanghai, China) using a two-compartment cell, which was separated by Nafion 117 proton exchange membrane. Different catalyst inks were prepared by dispersing 0.5 mg sample into 100 µL of ethanol and 5.0 µL of Nafion (5 wt.%) under ultrasonic, and were then dropped on carbon cloth with 1×1 cm² used as the working electrode. A Ag/AgCl electrode was used as the reference electrode and a Pt wire was used as the counter electrode. The polarization curves were measured with a scan rate of 5.0 mV s⁻¹ at room temperature and all polarization curves were obtained at the steady-state ones after several cycles. For N₂ reduction reaction (NRR) experiments, the potentiostatic test was conducted for 2 h in N2-saturated 0.1 M Na2SO4 solution (30 mL, pH=6.3) by continuously supplying N₂ into the electrolyte under ambient conditions. Prior to NRR measurements, N2 feeding gas was first purged through a 1.0 mM H₂SO₄ solution and distilled water to eliminate the potential NO_x and NH₃ contaminants. In this work, all measured potentials (vs. Ag/AgCl) were transformed into the potentials vs. reversible hydrogen electrode (RHE) based on the following equation:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059 \rm pH + E^{\circ}_{\rm Ag/AgCl}$$

Determination of ammonia. Concentration of the produced ammonia was spectrophotometrically detected by the indophenol blue method. In detail, 2.0 mL of sample was taken, and then diluted with 8.0 mL of deionized water. Subsequently, 100 μ L of oxidizing solution (sodium hypochlorite (ρ Cl=4~4.9) and 0.75 M sodium hydroxide), 500 μ L of colouring solution (0.4 M sodium salicylate and 0.32 M sodium hydroxide) and 100 μ L of catalyst solution (0.1g Na₂[Fe(CN)₅NO]·2H₂O diluted to 10 mL with deionized water) were added respectively to the measured sample solution. After the placement of 1 h at room temperature, the absorbance measurements were performed at wavelength of 697.5 nm. The obtained calibration curve was used to calculate the ammonia concentration.

Determination of hydrazine. The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp. A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCI (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 2 mL of sample was taken, and then diluted with 8 mL 0.1 M HCl solution. Subsequently, 5.0 mL of the prepared color reagent was added to the above sample solution. Subsequently, the absorbance measurements were performed after the placement of 20 min at wavelength of 455 nm. The obtained calibration curve (Fig. S8) was used to calculate the N₂H₄·H₂O concentration.

Calculations of NH₃ yield rate and Faradaic efficiency.

The equation of NH₃ yield rate:

$$R(NH_3)(\mu g h^{-1} mg^{-1}_{cat}) = \frac{C(NH_4^+ - N)(\mu g mL^{-1}) \times V(mL) \times 17}{t(h) \times m(mg) \times 14}$$

where $R(NH_3)$ is the ammonia yield rate; C (NH_4^+ -N) is the measured mass concentration of NH_4^+ -N; V is the electrolyte solution volume; t is the reaction time; 14 is the molar mass of NH_4^+ -N atom; 17 is the molar mass of NH_3 molecules; and mwas the loading mass of catalysts.

The equation of Faradaic efficiency:

$$FE(NH_3)(\%) = \frac{3 \times n(NH_3)(mol) \times F}{Q} \times 100\%$$

where F is the Faradaic constant (96485.34); Q is the total charge during the NRR.

Supplementary Tables and Figures

 Table S1. The comparable results of our work and other recently reported NRR electrocatalysts.

References	Catalyst	System /Conditions	NH ₃ Production Rate	Faradaic Efficiency (%)	Detection method		
Noble metal electrocatalyst							
1	Pd nanoparticles	0.1 M PBS	4.2 μg mg ⁻¹ h ⁻¹ (0.1 V <i>vs.</i> RHE)	8.2	Indophenol method		
2	Au nanorods	0.1 M KOH	1.648 μg h ⁻¹ cm ⁻² (-0.2 V vs. RHE)	4.02	Nessler's reagent		
3	Au/TiO ₂	0.1 M HCl	21.4 μg mg ⁻¹ h ⁻¹ (-0.2 V <i>vs.</i> RHE)	8.11	Indophenol method		
4	α-Au/CeO _x -RGO	0.1 M HCl	8.3 μg mg ⁻¹ h ⁻¹ (-0.2 V <i>vs.</i> RHE)	10.1	Indophenol method		
5	Pd _{0.2} /Cu _{0.8} nanoclusters	0.1 M KOH	1.66 μg mg ⁻¹ h ⁻¹ (-0.2 V vs. RHE)	4.52	Indophenol method		
6	Ag nanosheets	0.1 M HCl	2.8µg h ⁻¹ cm ⁻² (-0.6 V vs. RHE)	4.8	Indophenol method		
7	Rh nanosheet	0.1 M KOH	23.88 μg cm ⁻² h ⁻¹ (-0.2 V <i>vs.</i> RHE)	0.217	Indophenol method		
8	Au nanocages	0.5 M LiClO ₄	3.74 μg cm ⁻² h ⁻¹ (-0.4 V <i>vs.</i> RHE)	35.9	Nessler's reagent		
9	Ru/MoS ₂	0.01M HCl	$1.14 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ (-0.15 V vs. RHE)	17.6	Indophenol method		
10	Ag-Au@ZIF	LiCF ₃ SO ₃ 1% EtOH in THF	10 pmol cm ⁻² s ⁻¹ (-2.9 V <i>vs.</i> Ag/AgCl)	18±4	Indophenol method		
11	pAu/NF	0.1 M Na ₂ SO ₄	9.42 μg cm ⁻² h ⁻¹ (-0.2 V <i>vs.</i> RHE)	13.36	Indophenol method		
12	AuSAs-NDPCs	0.1M HCl	2.32 μg cm ⁻² h ⁻¹ (-0.3 V <i>vs.</i> RHE)	12.3	Indophenol method		
13	BiNCs	0.5 M K ₂ SO ₄	$200 \text{ mmol g}^{-1} \text{ h}^{-1}$	66	Nessler's reagent		

14	$Pt_{93}Ir_7$	1 mM HCl	28 μg h ⁻¹ cm ⁻² (-0.3 V <i>vs.</i> RHE)	40.8	Indophenol method				
15	Pd ₃ Cu ₁ alloys	1 M KOH	39.9 μg h ⁻¹ mg ⁻¹ (-0.25 V <i>vs.</i> RHE)	1.22	Nessler's reagent				
	Metal free catalyst								
16	N-doped porous carbon	0.05 M H ₂ SO ₄	23.8 μg mg ⁻¹ h ⁻¹ (-0.9 V <i>vs.</i> RHE)	1.42	Indophenol method				
17	Polymeric carbon nitride	0.1 M HCl	8.09 μg mg ⁻¹ h ⁻¹ (-0.2 V <i>vs.</i> RHE)	11.59	Indophenol method				
18	NPC-500	0.005 M H ₂ SO ₄	22.3 μg mg ⁻¹ h ⁻¹ (-0.4 V <i>vs.</i> RHE)	9.58	Indophenol method				
19	B ₄ C nanosheet	0.1 M HCl	26.57 μg mg ⁻¹ h ⁻¹ (-0.75 V <i>vs.</i> RHE)	15.95	Indophenol method				
20	Fluorine-doped carbon	$0.05~M~\mathrm{H_2SO_4}$	6.9 μg h ⁻¹ cm ⁻² (-0.55 V <i>vs.</i> RHE)	12.1	Indophenol method				
21	Boron phosphide	0.1 M HCl	26.24 μg mg ⁻¹ h ⁻¹ (-0.6 V <i>vs.</i> RHE)	12.7	Indophenol method				
		Transition m	etal catalyst						
22	Fe ₂ O ₃ -CNTs	diluted KHCO ₃ aqueous solution	$0.22 \ \mu g \ mg^{-1} \ h^{-1}$ (-1.0V vs. Ag/AgCl)	0.15	Indophenol method				
23	MoS ₂ /CC	0.1 M Na ₂ SO ₄	4.94 μg mg ⁻¹ h ⁻¹ (-0.5 V <i>vs.</i> RHE)	1.17	Indophenol method				
24	Mo nanofilm	0.01 M H ₂ SO ₄	1.89 μg mg ⁻¹ h ⁻¹ (-0.14 V vs. RHE)	0.72	Indophenol method				
25	MoS ₂ nanosheet	0.1 M Li ₂ SO ₄	43.4 μg h ⁻¹ mg _{MoS2} ⁻¹ (-0.2 V <i>vs.</i> RHE)	9.81	Indophenol method				
26	CoS ₂ /NS-G	0.05 M H ₂ SO ₄	25.0 μg mg ⁻¹ h ⁻¹ (-0.2 V <i>vs.</i> RHE)	25.9 (-0.05 V <i>vs.</i> RHE)	Indophenol method				
27	CuO/RGO	0.1 M Na ₂ SO ₄	$1.8 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ (-0.75 V vs. RHE)	3.9	Indophenol method				
28	FeMoS	0.1 M HCl	8.45 μg mg ⁻¹ h ⁻¹ (-0.5 V <i>vs.</i> RHE)	2.96	Indophenol method				
29	W ₂ N ₃	0.1 M HCl	11.66 ± 0.98 μg mg ⁻¹ h ⁻¹ (-0.2 V <i>vs.</i> RHE)	11.67 ± 0.93	Indophenol method				

30	Co/NC	0.1 M KOH	5.1 μg mg ⁻¹ h ⁻¹ (-0.4 V vs. RHE)	10.1 (-0.1 V vs. RHE)	Indophenol method		
31	PC/Sb/SbPO ₄	0.1 M HCl	25 μg mg ⁻¹ h ⁻¹ (-0.15 V <i>vs.</i> RHE)	31	Indophenol method		
32	C-Ti _x O _y /C	0.1 M LiClO ₄	14.8 μg mg ⁻¹ h ⁻¹ (-0.4 V vs. RHE)	17.8	Indophenol method		
33	Zr-TiO ₂	0.1 M KOH	8.9 μg h ⁻¹ cm ⁻² (-0.45 V <i>vs.</i> RHE)	17.3	Indophenol method		
34	Mo-500 °C- 8h/CC@CN	0.1 M KOH	7.02 μg mg ⁻¹ h ⁻¹ (0 V <i>vs</i> . RHE)	22.3	Indophenol method		
35	FePc/C	0.1 M Na ₂ SO ₄	137.95 μg mg ⁻¹ h ⁻¹ (-0.3 V vs. RHE)	10.5	Indophenol method		
Single-atom catalyst							
36	Au SAs/C ₃ N ₄	0.005 M H ₂ SO ₄	1305 μ g h ⁻¹ mg _{Au} ⁻¹ (-0.2 V vs. RHE)	11.1	Indophenol method		
37	Ru SAs/N-C	0.05 M H ₂ SO ₄	120.9 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs. RHE)	29.6	Indophenol method		
38	Ru@ZrO ₂ /NC	0.1 M HCl	3665 μg h ⁻¹ mg _{Ru} ⁻¹ (-0.21 V vs. RHE)	21	Indophenol method		
39	SA-Mo/NPC	0.1 M KOH	$34.0 \pm 3.6 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$ (-0.3 V vs. RHE)	14.6 ± 1.6	Indophenol method		
40	Fe _{SA} -N-C	0.1 M KOH	7.48 μg h ⁻¹ mg _{cat} ⁻¹ (0 V vs. RHE)	56.55	Indophenol method		
41	ISAS-Fe-N-C	0.1 M PBS	$62.9 \pm 2.7 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$ (-0.4 V vs. RHE)	18.6 ± 0.8	Indophenol method		
42	Mo ⁰ /GDY	0.1 M Na ₂ SO ₄	145.4 μg mg ⁻¹ h ⁻¹ (-1.2 V vs. SCE)	21	Indophenol method		
This work	CoP/CNs	0.1 M Na ₂ SO ₄	or 48.9 μg h ⁻¹ mg _{cat} ⁻¹ (-0.4 V <i>vs.</i> RHE)	11.3 (-0.1 V <i>vs.</i> RHE)	Indophenol method		



Fig. S1 (a) SEM and (b) TEM images of Co/CNs.



Fig. S2 (a) The Nitrogen adsorption and desorption isotherms and (b) pore size distribution curve of CoP/CNs sample.



Fig. S3 The surface survey XPS spectrum of CoP/CNs.



Fig. S4 (a) UV-Vis absorption spectra of various NH_4^+ -N concentrations (0, 0.25, 0.50, 0.75, 1, 2 and 4 µg mL⁻¹) after incubated for 1 h at room temperature. (b) The calibration curve used for calculation of NH_4^+ -N concentration.



Fig. S5 (a) UV-Vis absorption spectra of various $N_2H_4 \cdot H_2O$ concentrations (0, 0.05, 0.10, 0.25, 0.50, 0.75 and 1 µg mL⁻¹) after incubated for 20 min at room temperature. (b) The calibration curve used for calculation of $N_2H_4 \cdot H_2O$ concentrations



Fig. S6 UV-Vis absorption spectra of the electrolytes stained with indicator after electrolysis at different potentials for 2 h.



Fig. S7 Chrono-amperometry curves of CoP/CNs catalyst obtained at different applied potentials in N_2 -saturated 0.1 M Na_2SO_4 solution.



Fig. S8 UV-Vis absorption spectra of the electrolytes colored with indophenols indicator after electrolysis at different potentials for 2 h.



Fig. S9 (a) XRD patterns and (b) TEM image of the CoP/CNs catalyst after durability test.



Fig. S10 (a) Co 2p and (b) P 2p XPS spectra of CoP/CNs after NRR.



Fig. S11 (a) Normalized Co K-edge XANES and (b) FT-EXAFS curves of Co foil, CoO, Co₃O₄, CoP/CNs after NRR.



Fig. S12 UV-Vis absorption spectra of N₂-saturated 0.1 M Na₂SO₄ solution (blank solution), N₂-saturated 0.1 M Na₂SO₄ solution with the electrocatalyst for 2 h at opencircuit condition (open-circuit), and Ar-saturated 0.1 M Na₂SO₄ solution with the electrocatalyst at -0.2 V (*vs.* RHE) for 2 h (Ar-saturated electrolyte). All solutions were incubated with NH₃ color agent for 1 h before measurement.



Fig. S13 XRD patterns of the P-CNs sample.



Fig. S14 NH₃ yield rates and corresponding FEs for CoP/CNs, Co/CNs and P-CNs at -0.4 V *vs.* RHE after 2 h electrolysis under ambient conditions.

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