

Defect-Rich Walnut-like Copper-Doped Ni(PO₃)₂ Catalyst towards Ammonia Borane Electrooxidation Reaction with High Performance

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S1. Experimental section

The catalysts with different amounts of Cu were synthesized by one-pot hydrothermal method. In brief, 0.12 mmol Cu(NO₃)₂•3H₂O, 1.2 mmol Ni(NO₃)₂•6H₂O, 7.2 mmol urea were dissolved in 60 mL deionized water. The stirred-well solution was transferred to a 100 mL hydrothermal reactor and reacted at 160 °C for 20h. The precursor was collected by centrifugation and washed several times then dried in the vacuum oven at 80 °C overnight. Then, the product named 10% Cu-Ni₂CO₃(OH)₂•H₂O was annealed in air at 450 °C for 2h to get the metal oxide which was named 10% Cu-NiO. Finally, the oxide was placed in a porcelain boat and located downstream, meanwhile, another porcelain boat containing NaH₂PO₂ was placed upstream in the same tube (the mass ratio of 10% Cu-NiO and NaH₂PO₂ is 1:10). Under the nitrogen atmosphere, the tube furnace was heated to 350 °C (1 °C min⁻¹, 2 hours), and then cooled down to room temperature. The product was named 10% Cu-Ni(PO₃)₂. And other catalysts were synthesized through the same approach above by changing the addition of Cu(NO₃)₂•3H₂O, named Ni(PO₃)₂, 5% Cu-Ni(PO₃)₂ and 20% Cu-Ni(PO₃)₂, respectively.

S2. Characterization

X-ray diffraction (XRD) results were obtained on Bruker D8 Advance with a Cu K α radiation ($\lambda = 1.5408 \text{ \AA}$). Thermal gravimetric analyzer (TGA) data were obtained on Thermo Ecolab 250 at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer using Al K α monochromatic (100W, 30 eV pass energy). And the morphology of the catalysts was characterized by Scanning Electron Microscope (SEM, Quanta 250FEG), Transmission Electron Microscope (TEM, JEOL JEM-2100F), High-resolution TEM (HRTEM), and Energy Dispersive X-ray Spectroscopy (EDS mapping).

S3. Electrochemical measurements

The electrochemical measurements of ABOR were carried out on RRDE-3A Rotating Ring Disk Electrode Rotator Ver.1.2. The tests were conducted in a three-electrode system by using a rotating disk electrode (RDE, $\Phi 3\text{mm}$), a graphite rod, an Ag/AgCl (saturated KCl) as the working, counter, and reference electrodes, respectively. And all the measurements were performed in N₂-saturated 0.1 M KOH electrolyte with different amounts of AB at room temperature. 5 mg catalyst (Ni(PO₃)₂, 5% Cu-Ni(PO₃)₂, 10% Cu-Ni(PO₃)₂, or 20% Cu-Ni(PO₃)₂) and 0.5mg super P were dispersed in 1 mL aqueous solution (50 μL 5 wt% Nafion + 200 μL ethanol + 750 μL DI water) by ultrasonication for 1 hour. Then 5 μL ink was dropped onto the glassy carbon surface of the RDE, which served as the working electrode. The mass loading of the catalyst was $353 \mu\text{g cm}^{-2}$.

Cyclic voltammetry (CV) tests were conducted in 0.001 M AB ~ 0.02 M AB + 0.1 M KOH at 1600 rpm with a scan rate of 10 mV s^{-1} . Linear sweep voltammetry (LSV) curves were obtained in 2.5 mM AB + 0.1 M KOH at different rotating speeds with a scan rate of 10 mV s^{-1} . And the open circuit potential (OCP) of different catalysts were tested in 0.01 M AB + 0.1 M KOH under static conditions. To evaluate the stability of the catalyst, chronoamperometry with multipotential

steps was tested in 0.01 M AB + 0.1 M KOH at -0.3, 0.1, 0.5 and 0.1 V vs. RHE with a rotating speed of 1600 rpm. All the potential values in this work were converted to vs. RHE scale by Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.0591pH + 0.197$. The number transferred electron (n) was calculated by the following equations:

Levich equation:

$$i_{l,a} = 0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R^* \quad (S1)$$

where $i_{l,a}$ is the limiting anodic current at a given rotating rate, F is Faraday constant, A is the electrode area (cm^2), D_R is the diffusion coefficient ($8.45 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for AB), ω is the electrode rotating rate (rad s^{-1}), ν is the kinematic solution viscosity ($1.216 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ for AB), and C_R^* is the bulk concentration of the reduced species (mol cm^{-3}).

Koutecký-Levich (K-L) equation:

$$1/i = 1/i_k + 1/i_{l,a} = 1/i_k + 1/0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R^* \quad (S2)$$

where i is the disk current, i_k is the kinetically limited current.

CV was tested at the range of -0.4~0 V vs. RHE to avoid the oxidation of H₂ above 0 V in a same three-electrode system by using a rotating disk electrode, a graphite rod, an Ag/AgCl (saturated KCl) as the working, counter, and reference electrodes, respectively. After 500 CV cycles in N₂-saturated 0.1 M KOH or 0.1 M KOH + 0.1 M AB at 10 mV s⁻¹, 1 mL gas above the cell was sampled by gas-tight syringe and monitored by gas chromatograph (GC). And the gas product from 0.1 M KOH + 0.1 M AB without catalyst which was static for 6h was also monitored by GC.

S4. Computational methods

Spin-polarized density functional theory (DFT) computations were performed using the Vienna ab initio simulation package (VASP) with the projected augmented wave method. The exchange-correlation function was described by the parameterization scheme of Perdew-Burke-Ernzerhof of the generalized gradient approximation. The exchange-correlation function was described by the parameterization scheme of Perdew-Burke-Ernzerhof of the generalized gradient approximation. The vacuum layer is set to 20 Å to avoid interactions between the periodically repeated structures along the z direction. The Grimme DFT-D3 scheme of dispersion correction with zero damping is adopted to account for the vdW interactions. We calculated and analyzed the d-band center of the (010) plane in Cu-Ni(PO₃)₂ with a unit cell parameter change of 0.6%. The adsorption energy of AB and BO₂⁻ on the surface of Cu-Ni(PO₃)₂ and Ni(PO₃)₂ was also calculated on (010) plane.

S5. Supplementary data

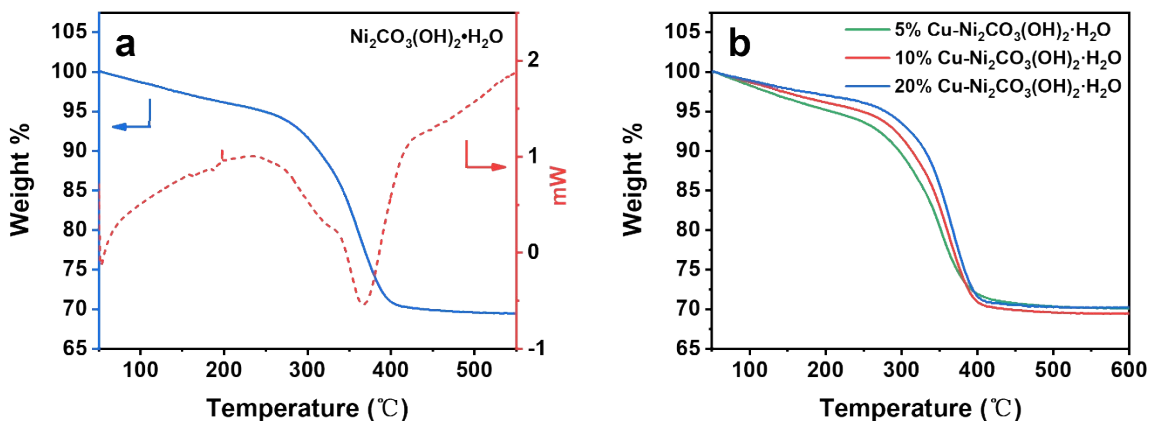


Fig. S1. (a) TGA and DSC curves of Ni₂CO₃(OH)₂·H₂O. (b) TGA curves of 5%, 10%, 20% Cu-doped Ni₂CO₃(OH)₂·H₂O.

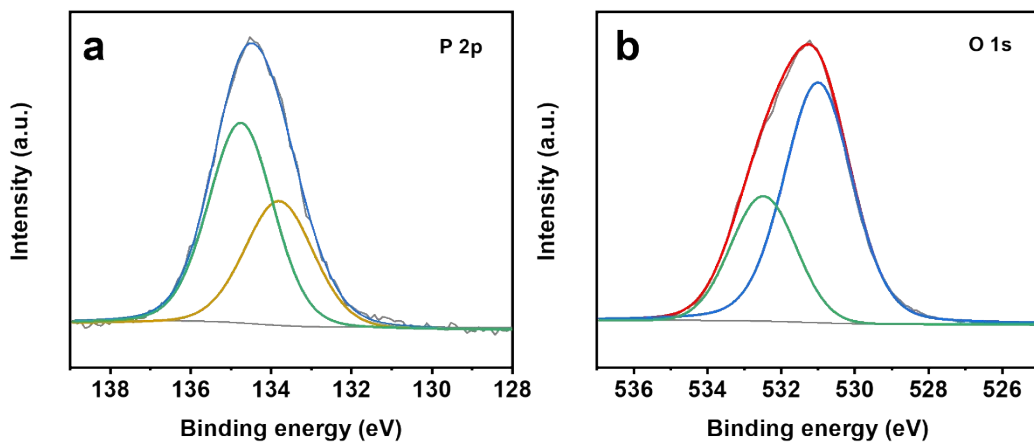


Fig. S2. High-resolution XPS spectrums of (a) O 1s and (b) P 2p of Ni(PO₃)₂.

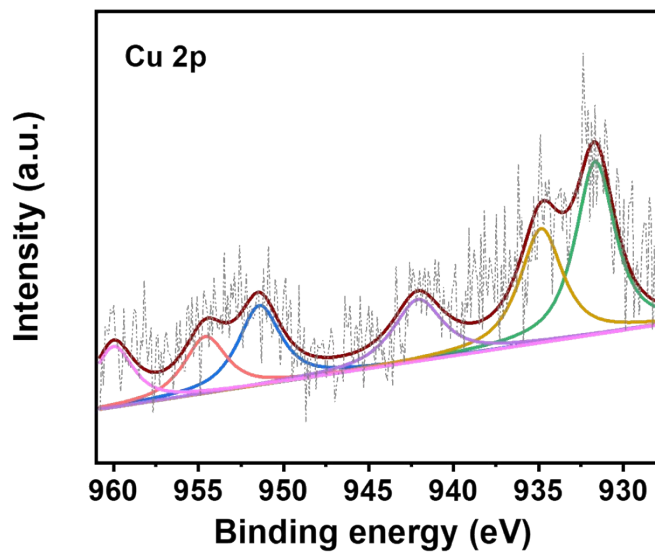


Fig. S3. High-resolution XPS spectrum of Cu 2p of 10% Cu-Ni(PO₃)₂.

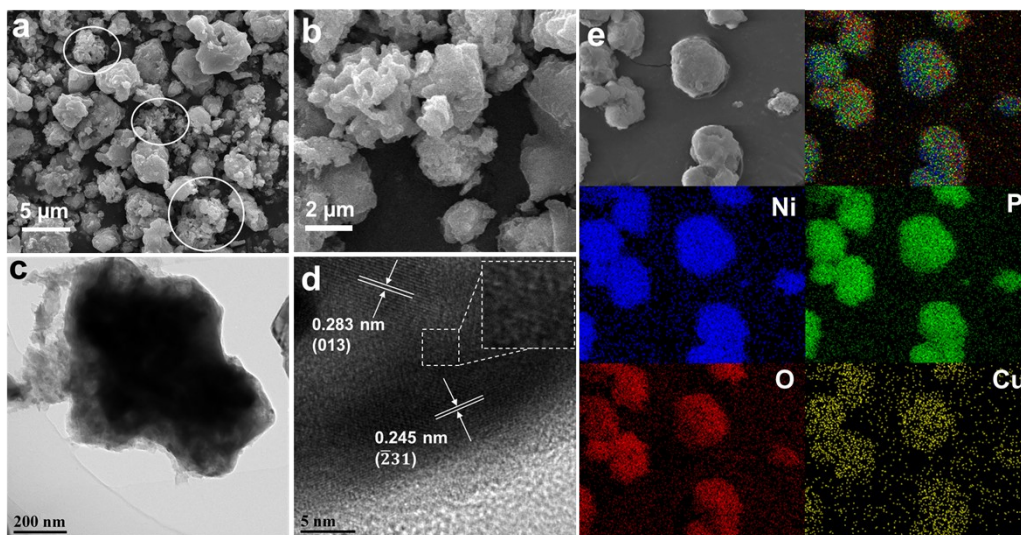


Figure S4. (a, b) SEM, (c) TEM, (d) HRTEM images and (e) corresponding EDS mapping images of 10% Cu-Ni(PO₃)₂ catalyst after stability test.

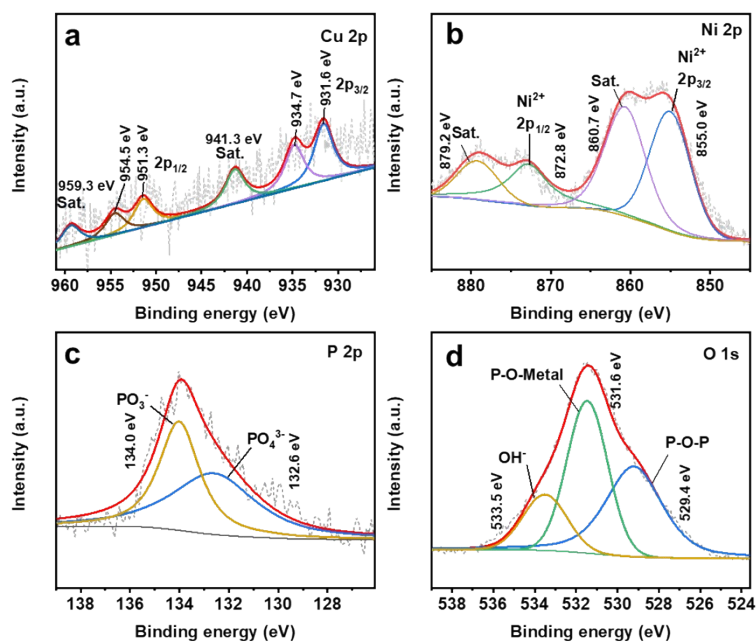


Figure S5. High-resolution XPS spectra of (a) Cu 2p, (b) Ni 2p, (c) P 2p and (d) O 1s in 10% Cu-Ni(PO₃)₂ after stability test.

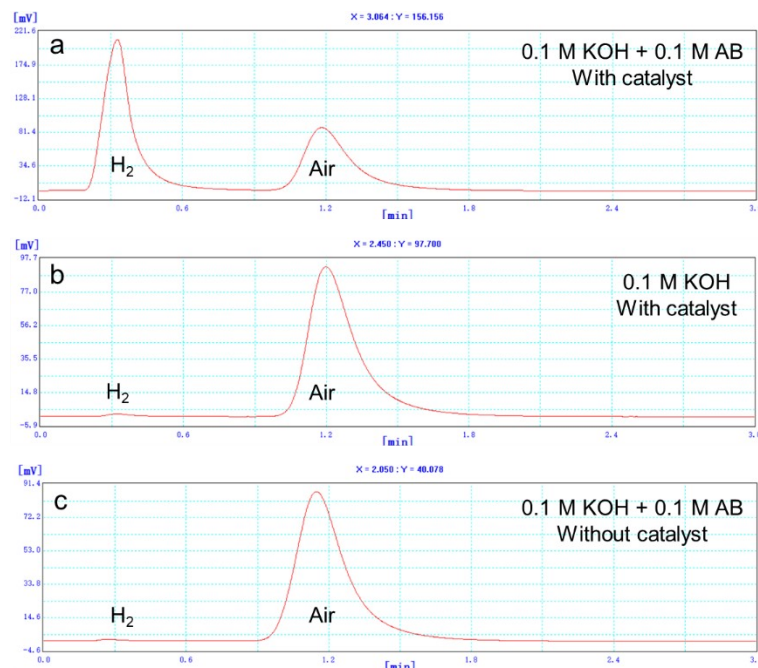


Figure S6. Gas chromatograms of the gas products of (a) 0.1 M KOH + 0.1 M AB, (b) 0.1 M KOH with catalyst, and (c) 0.1 M KOH + 0.1 M AB without catalyst.

Table S1. Comparison of electrocatalytic parameters of 10% Cu-Ni(PO₃)₂ catalyst and other electrocatalysts reported in the literature for ABOR.

Samples	E _{onset} (V vs. RHE)	Current density (mA cm ⁻²)	Electrolyte solution	Scan rate (mV s ⁻¹)	Ref.
10% Cu-Ni(PO ₃) ₂	-0.282	7.07 (at 0.298 V)	0.01 M AB+ 0.1 M KOH	10	This work
Ni _{1-x} Cu _x O/CFP	-0.267	4.65 (at 0.3 V)	0.01 M AB+ 0.1 M KOH	10	1 ¹
Ni _{1-x} Cu _x Se ₂ /CFP	-0.148	7.05 (at 0.3 V)	0.01 M AB+ 0.1 M KOH	10	2 ²
Ni _{1-x} Fe _x Se ₂ /CFP	-0.071	6.90 (at 0.3 V)	0.01 M AB+ 0.1 M KOH	10	2 ²
Ni _{1-x} Co _x Se ₂ /CFP	0.041	6.80 (at 0.3 V)	0.01 M AB+ 0.1 M KOH	10	2 ²
Au-Ag/PAP/GCE	-0.147	0.54 (at 0.5 V)	1 mM AB+ 2 M NaOH	50	3 ³
BNPs ^{s*}	-0.195	17.3 (at 0.5 V)	5 mM AB+ 0.1 M NaOH	10	4 ⁴
Pd/C	-0.200	7.5 (at 0.5 V)	5 mM AB+ 0.1 M NaOH	10 (1600 rpm)	5 ⁵
Pt/C	-0.030	7.5 (at 0.5 V)	5 mM AB+ 0.1 M NaOH	10 (1600 rpm)	5 ⁵

Ni ₃ Co/C	-0.090	5 (at 0.3 V)	5 mM AB+ 0.1 M NaOH	10 (1600 rpm)	6 ⁶
Ni ₃ Ag/C	-0.050	6.3 (at 0.5 V)	5 mM AB+ 0.1 M NaOH	10 (1600 rpm)	6 ⁶
Ni ₃ Pd/C	-0.030	10 (at 0.5 V)	5 mM AB+ 0.1 M NaOH	10 (1600 rpm)	6 ⁶
Pt/C	-0.060	30 (at 0.669 V)	0.01 M AB+ 0.1 M NaOH	25 (1000 rpm)	7 ⁷
Pd/C	-0.275	30 (at 0.641 V)	0.01 M AB+ 0.1 M NaOH	25 (1000 rpm)	7 ⁷

The potential value corresponds to the oxidation current density and is expressed on the RHE scale.

* The abbreviation of bimodal nano porous Ag.

Table S2. The calculated lattice parameters for Cu-Ni(PO₃)₂.

Scale factor	Lattice parameters	
	a (Å)	b (Å)
0.998	9.80	11.05
1.004	9.86	11.12

S6. References

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