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Supporting Information

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Copper–Nickel Nitride Nanosheets as Efficient Bifunctional Catalysts for Hydrazine-Assisted Electrolytic Hydrogen Production

Zhaoyang Wang, Lin Xu, Fuzhi Huang,* Longbing Qu, Jiantao Li, Kwadwo Asare Owusu, Ziang Liu, Zifeng Lin, Binhua Xiang, Xiong Liu, Kangning Zhao, Xiaobin Liao, Wei Yang, Yi-Bing Cheng, and Liqiang Mai*

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1. Experimental Section

Materials: Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, >98%), copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, >99%), hexamethylene tetramine (C₆H₁₂N₄, >99%), methanol (CH₄O, >99.7%) and hydrazinehydrate (N₂H₄·xH₂O, 50.0 wt%) were bought from Sinopharm Chemical Reagent Co., Ltd. 5 wt % Nafion solution and commercial IrO₂ (99.9% Ir) were purchased from Sigma-Aldrich and Macklin Reagent, respectively. The Pt/C catalyst (20 wt% Pt on Vulcan XC-72 carbon) was obtained from Johnson Matthey. CFC was purchased from Shanghai He Seng Electric Co., Ltd. Unless specifically mentioned, all the reagents were used as-received without further purification. Deionized water was used throughout the experiments.

Preparation of CFC supported CuNi-LDH precursor: In a typical synthesis, 1 mmol of Cu(NO₃)₂·3H₂O, 2 mmol of Ni(NO₃)₂·6H₂O and 4 mmol hexamethylene tetramine were dissolved in 60 mL of methanol, thorough stirring is needed. The solution was transferred into a 100 mL Teflon-lined autoclave after being stirred for 20 min. A piece of CFC (2.5 cm × 5 cm) was washed with acetone, ethanol and deionized water for several times before use. The clean CFC was immersed into the autoclave and heated at 180 °C for 12 h. After cooling to room temperature, the substrate was taken out and washed thoroughly with ethanol and deionized water, followed by drying in vacuum at 60 °C overnight. This sample were denoted as Cu₁Ni₂-LDH. With different feed ratios of copper and nickel salt, such as 3:1, 2:1, 1:1, 1:3 and 0:1, Cu₃Ni₁-LDH, Cu₂Ni₁-LDH, Cu₁Ni₁-LDH, Cu₁Ni₃-LDH and Ni(OH)₂ samples were synthesized using the same procedure. The mass loading of precursors on the CFC is ~1.8 mg cm⁻².

Preparation of CFC supported Cu-precursor: In a typical hydrothermal synthesis, 3 mmol $Cu(NO_3)_2 \cdot 3H_2O$ and 7 mmol urea were dissolved in 36 mL of deionized water. The solution was transferred into a 50 mL Teflon-lined autoclave after being stirred for 25 min. A piece of

CFC (2.5 cm \times 5 cm) was immersed into the autoclave and heated at 120 °C for 12 h. After cooling to room temperature, the substrate was taken out and washed thoroughly with ethanol and deionized water, followed by drying in vacuum at 60 °C overnight. The mass loading of precursors on the CFC is ~1.7 mg cm⁻².

Preparation of CFC supported CuNi-N, Ni-N and Cu-N catalyst: The Cu₁Ni₂-LDH precursor was put in a porcelain boat, which was placed in the central region of a tubular furnace. The tube was purged for 30 min to exclude the air, and maintained at a steady flow of NH₃ at 20 sccm. Subsequently, the sample was heated to 400 °C with a heating rate of 5 °C min⁻¹ and kept at that temperature for 2 h. As control experiments, the Cu₁Ni₂-LDH precursor was also calcined at 350 °C and 450 °C to study the influence of calcination temperature on the catalytic activity. The samples of Cu₃Ni₁-N, Cu₂Ni₁-N, Cu₁Ni₁-N, Cu₁Ni₃-N, Ni-N and Cu-N were synthesized using the same procedure (400 °C) with the corresponding precursors. The mass loading of catalysts on the CFC is ~1.5 mg cm⁻².

Preparation of CFC supported Pt/C and IrO₂ catalyst: 10 mg of Pt/C or IrO₂ was dispersed in a mixed isopropanol (750 μ L) and deionized water (200 μ L) solution, and then 50 μ L of Nafion solution (5 wt %) was added. Sonication for 1 h was needed to form a relatively homogeneous suspension. Afterward, 150 μ L of catalyst ink was loaded on the CFC (Pt/C or IrO₂ mass loading is ~1.5 mg cm⁻²).

Materials Characterization: X-ray diffraction (XRD) patterns were characterized by a Bruker D8 Discover X-ray diffractometer with a Cu K α X-ray ($\lambda = 1.5418$ Å) at room temperature. The morphologies of the samples were investigated by scanning electron microscopy (SEM) on JEOL-7100F at an acceleration voltage of 15 kV. Transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) images were performed with a JEM-2100F microscope. EDS elemental mapping was recorded by an Oxford EDS IE250 system. X-ray photoelectron spectroscopy (XPS) analysis was done on VG Multilab 2000.

Brunauer–Emmett–Teller (BET) surface area was measured by using a Tristar II 3020 instrument. The contact angle measurements were performed using an OCA Automatic contact angle measurement device.

Electrochemical Measurements: Electrochemical measurements were performed in a standard three electrode system by CHI 760e electrochemical workstation. Catalysts modified CFC were directly utilized as the working electrodes. Graphite rod and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) measurements were carried out in 1.0 M KOH solution, and hydrazine oxidation reaction (HzOR) measurements were performed in 1.0 M KOH with 0.5 M N₂H₄. The polarization curves of catalysts were recorded by linear sweep voltammetry (LSV) at a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were collected in the range from 10^5 Hz to 10^{-2} Hz. The chronopotentiometric (CP) curve was conducted out at a fixed current density of 10 mA cm⁻². All measured potentials were converted to the reversible hydrogen electrode (RHE) by using the following equation: E (RHE) = E (Hg/HgO) + 0.098 V + 0.059 \times pH. For hydrazineassisted water electrolysis, a symmetrical full electrolyzer was fabricated by using Cu₁Ni₂-N/CFC electrode both as cathode and anode. LSV was measured at a scan rate of 5 mV s⁻¹ in 1.0 M KOH with 0.5 M N₂H₄. For comparison, the two-electrode tests of Cu₁Ni₂-N/CFC and Ni-N/CFC electrodes for water electrolysis without hydrazine can also been done by the same approach in 1.0 M KOH solution.

The electrochemical surface areas (ECSAs) were estimated by cyclic voltammograms (CVs) in a small potential range at the scan rates of 20, 40, 60, 80, 100, 120, 140, 160 and 180 mV s⁻¹, respectively. The current density differences ($\Delta j = j_a - j_c$) were plotted against scan rates, and the linear slope is twice the double-layer capacitance (C_{dl}). In addition, the roughness factors (R_f) were calculated by the following equation: R_f = C_{dl}/C_o, C_o is the capacitance of

ideal planar metal oxides (*i.e.* NiO) with smooth surfaces (60 μ F cm⁻²). ECSA can be calculated from the C_{dl} by using the specific capacitance value for a flat standard with 1 cm² of real surface area. Herein, CFC was used as the standard. ECSA was calculated as follows:

$$A_{ECSA}^{catalyst} = \frac{C_{dl}^{catalyst}(mF \text{ cm}^{-2})}{C_{dl}^{CFC}(mF \text{ cm}^{-2}) \text{ per } cm_{ECSA}^{2}} = 26.76 \text{ } cm_{ECSA}^{2}$$

$$A_{ECSA}^{Cu_{1}Ni_{2}-N} = \frac{42.02 (mF \text{ } cm^{-2})}{1.57 (mF \text{ } cm^{-2}) \text{ per } cm_{ECSA}^{2}} = 26.76 \text{ } cm_{ECSA}^{2}$$

$$A_{ECSA}^{Ni-N} = \frac{13.18 (mF \text{ } cm^{-2})}{1.57 (mF \text{ } cm^{-2}) \text{ per } cm_{ECSA}^{2}} = 8.39 \text{ } cm_{ECSA}^{2}$$

$$A_{ECSA}^{Cu-N} = \frac{14.01 (mF \text{ } cm^{-2})}{1.57 (mF \text{ } cm^{-2}) \text{ per } cm_{ECSA}^{2}} = 8.92 \text{ } cm_{ECSA}^{2}$$

$$A_{ECSA}^{Cu-N} = \frac{2.72 (mF \text{ } cm^{-2})}{1.57 (mF \text{ } cm^{-2}) \text{ per } cm_{ECSA}^{2}} = 1.73 \text{ } cm_{ECSA}^{2}$$

$$A_{ECSA}^{Ni(OH)_{2}} = \frac{2.06 (mF \text{ } cm^{-2})}{1.57 (mF \text{ } cm^{-2}) \text{ per } cm_{ECSA}^{2}} = 1.31 \text{ } cm_{ECSA}^{2}$$

$$A_{ECSA}^{Ni(OH)_{2}} = \frac{7.19 (mF \text{ } cm^{-2})}{1.57 (mF \text{ } cm^{-2}) \text{ per } cm_{ECSA}^{2}} = 4.58 \text{ } cm_{ECSA}^{2}$$

Turnover frequency (TOF) calculation: The number of active sites (*N*) was first examined by an electrochemical method. CV curves were measured in phosphate buffer (pH = 7) at a scan rate of 50 mV s⁻¹. *N* (mol) and TOF (s⁻¹) were calculated with the following equations:

$$N = \frac{Q}{2F}$$
$$TOF = \frac{I}{2NF}$$

where Q is the number of voltammetric charges, F is Faraday constant (96485 C mol⁻¹), I (A) is the current of the polarization curve obtained by LSV measurements.

Density functional theory (DFT) calculations: The present calculations were carried out by using the projector augmented wave (PAW)^[1] method within DFT, as implemented in the Vienna ab initio simulation package (VASP)^[2, 3]. The generalized gradient approximation

(GGA) in the form of the Perdew-Burke-Ernzerhof (PBE)^[4] was used to treat the exchangecorrelation energy. A kinetic energy cut-off of 500 eV was used for wave functions expanded in the plane wave basis. All atoms were allowed to relax until the forces were less than 0.05 $eV Å^{-1}$. For the Brillouin-zone sampling, 4×4×4 k-points were adopted to ensure convergence of the total energy.



2. Supplementary Figures

Figure S1. (A) XRD pattern for Cu₁Ni₂-LDH/CFC. (B) Low-magnification and (C) highmagnification SEM images showing typical morphology for Ni-N/CFC (inset: the corresponding EDX spectrum). (D) XRD pattern for Ni(OH)₂/CFC. (E) Low-magnification and (F) high-magnification SEM images showing typical morphology for Ni(OH)₂/CFC (inset: the corresponding EDX spectrum).



Figure S2. SEM images of Cu_1Ni_2 -N/CFC (A-B) and Ni-N/CFC (C-D) under different magnifications.



Figure S3. (A) XRD pattern for Ni-N/CFC. (B) Low-magnification and (C) highmagnification SEM images of typical morphology for Ni-N/CFC. (D) TEM (inset shows the particle size distribution) and (E) HRTEM images of Ni-N/CFC. (F) HAADF-STEM image and corresponding elemental mapping of Ni-N/CFC.



Figure S4. (A) XRD pattern for Cu-pre/CFC. (B) Low-magnification and (C) highmagnification SEM images of typical morphology for Cu-pre/CFC. (D) XRD pattern for Cu-N/CFC. (E) Low-magnification and (F) high-magnification SEM images showing typical morphology for Cu-N/CFC.



Figure S5. *I-V* curves of Cu₁Ni₂-N (thickness of 0.22 mm) and Ni-N simples (thickness of 0.24 mm), which were tested by Agilent B1500A Semiconductor Device Analyzer. Corresponding conductance were calculated to be 8.1×10^3 S m⁻¹ for Cu₁Ni₂-N and 5.4×10^3 S m⁻¹ for Ni-N.



Figure S6. N_2 adsorption–desorption isotherms and pore size distribution (Inset) of (A) Cu_1Ni_2 -N and (B) Ni-N nanosheets.



Figure S7. Water contact angle photographs of (A) pristine CFC and (B) Cu₁Ni₂-N.



Figure S8. XPS survey of Cu₁Ni₂-N.



Figure S9. (A) HER polarization curves for Cu_1Ni_2 -N/CFC synthesized under different nitridation temperatures in 1.0 M KOH; (B) HER polarization curves for CuNi-N/CFC at the various ratios of copper to nickel in 1 M KOH.



Figure S10. (A-G) Cyclic voltammetry curves of Cu₁Ni₂-N, Ni-N, Cu-N, Cu₁Ni₂-LDH, Ni(OH)₂, Cu-pre and CFC for hydrogen evolution obtained at 20, 40, 60, 80, 100, 120, 140, 160 and 180 mV s⁻¹ scanning rate in the range of no Faradaic processes (0.074~0.174 V vs. RHE); (H) double layer capacitances (C_{dl}) and roughness factors (R_f) of different samples.



Figure S11. The CV curves of Cu₁Ni₂-N and Ni-N at a scan rate of 50 mV s⁻¹ in PBS solution (pH = 7.0).



Figure S12. Electrocatalytic performance of Cu-pre/CFC and Cu-N/CFC samples for the HER measured in 1.0 M KOH solution. (A) Polarization curves for Cu-pre and Cu-N at a scan rate of 5 mV s⁻¹; (B) the corresponding Tafel plots; (C) estimation of C_{dl} by plotting the current density difference at 0.124 V vs. RHE; (D) polarization curves of different samples normalized by the ECSA; (E) the TOFs at different potentials; (F) electrochemical impedance spectroscopy for Cu-pre and Cu-N.



Figure S13. Electrocatalytic performance of electrodes for the OER measured in 1.0 M KOH solution. (A) Polarization curves for Cu₁Ni₂-N, Ni-N, Cu-N, IrO₂ and CFC at a scan rate of 5 mV s⁻¹; (B) the corresponding Tafel plots; (C) estimation of C_{dl} by plotting the current density difference at 1.074 V vs. RHE; (D) electrochemical impedance spectroscopy for the corresponding electrocatalysts; (E) long-time stability test of the of Cu₁Ni₂-N and Ni-N at constant current densities of 10 mA cm⁻².

The Cu₁Ni₂-N exhibits higher OER activity and can deliver a current density of 20 mA cm⁻² at low overpotential of 312 mV. In contrast, Ni-N, Cu-N and IrO₂ require overpotential of 405 mV, 498 and 324 mV to deliver the same current density, respectively. Additionally, Cu₁Ni₂-N displays a Tafel slope of 89.6 mV dec⁻¹ (Figure S13B), which is smaller than that of Ni-N (120.3 mV dec⁻¹) and Cu-N (148.6 mV dec⁻¹). The corresponding ECSA are calculated to be 19.41, 13.99, 5.79 and 1.58 mF cm⁻² for Cu₁Ni₂-N, Ni-N, Cu-N and bare CFC, respectively (Figure S13C). In the Nyquist plots (Figure S13D), the Cu₁Ni₂-N electrode displays a smaller charge-transfer resistance, indicating more favorable reaction kinetics for OER process. Moreover, the potential of Cu₁Ni₂-N electrode driven at a constant current density of 10 mA cm⁻² increases from 1.55 to 1.61 V *vs.* RHE after 50 h (Figure S13E).



Figure S14. (A) OER polarization curves for Cu_1Ni_2 -N/CFC synthesized under different nitridation temperatures in 1.0 M KOH; (B) OER polarization curves for CuNi-N/CFC at the various ratios of copper to nickel in 1 M KOH.

The catalyst with a calcination temperature of 400 °C and a Cu/Ni molar ratio of 1:2 possesses the highest activity for OER, which is good accordance with HER performance.



Figure S15. (A-D) Cyclic voltammetry curves of Cu₁Ni₂-N, Ni-N, Cu-N and CFC for oxygen evolution obtained at 20, 40, 60, 80, 100, 120, 140, 160 and 180 mV s⁻¹ scanning rate in the range of no Faradaic processes ($1.024 \sim 1.124$ V vs. RHE).



Figure S16. (A) HzOR polarization curves of Cu_1Ni_2 -N toward different concentrations of hydrazine (0.5, 1 and 2 M). (B) HzOR polarization curves for CuNi-N/CFC at the various ratios of copper to nickel in 1 M KOH/0.5 M hydrazine electrolyte. (C) Polarization curves of Cu_1Ni_2 -N and Pt/C for HER and HzOR in 1 M KOH/0.5 M hydrazine electrolyte. (D) HER polarization curves of Cu_1Ni_2 -N toward different concentrations of hydrazine (0, 0.1, 0.3, 0.5, 1 and 2 M).



Figure S17. (A) HzOR polarization curves of Cu-pre and Cu-N in 1.0 M KOH/0.5 M

hydrazine electrolyte. (B) The corresponding Tafel plots.



Figure S18. Experimental and theoretical amounts of H_2 gas produced from cathode of Htype electrolyzer based on Cu₁Ni₂-N electrode at a current density of 20 mA cm⁻² in 1.0 M KOH/0.5 M hydrazine electrolyte.



Figure S19. Morphology and structural characterizations of the Cu₁Ni₂-N/CFC after HER test. (A-B) Low-magnification, (C) high-magnification SEM images. (D) TEM, (E) HRTEM images and (F) EDX spectrum. (G) HAADF-STEM image and corresponding elemental mapping. (H) The corresponding EDX spectrum.



Figure S20. Morphology and structural characterizations of the Cu₁Ni₂-N/CFC after HzOR test. (A-B) Low-magnification, (C) high-magnification SEM images. (D) TEM, (E) HRTEM images and (F) EDX spectrum. (G) HAADF-STEM image and corresponding elemental mapping. (H) The corresponding EDX spectrum.



Figure S21. DFT calculations. Schematic models, total and partial electronic density of states for Cu_4N -Ni₃N (A), Cu_4N (B) and Ni₃N (C).

3. Supplementary Tables

Catalysts	Mass loading (mg cm ⁻²)	Substrate	Electrolyte	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Reference
Cu ₁ Ni ₂ -N	1.2 mg cm ⁻²	Carbon cloth	1 М КОН	71.4	106.5	This work
Co-Ni ₃ N	2.91 mg cm ⁻²	Carbon cloth	1 M KOH	194	156	5
NiMoN	1.1 mg cm ⁻²	Carbon cloth	1 M KOH	109	95	6
NC@CuCo ₂ N _x	2.0 mg cm ⁻²	Carbon cloth	1 М КОН	105	76	7
Ni ₃ FeN/rGO	0.5 mg cm ⁻²	Aerogel	1 М КОН	94	90	8
FeNi ₃ N	NA	Nickel foam	1 M KOH	75	98	9
NC–NiCu–NiCuN	1.5 mg cm ⁻²	Nickel foam	1 M KOH	93	55	10
NiCo ₂ N	NA	Nickel foam	1 M KOH	180	79	11
PO-Ni/Ni-N-CFC	2.0 mg cm ⁻²	Glassy carbon	1 M KOH	262	97.42	12
Cu@NiFe-LDH	2.2 mg cm ⁻²	Copper foam	1 M KOH	116	58.9	13
NC/CuCo/CuCoO _x	1.5 mg cm ⁻²	Nickel foam	1 M KOH	112	55	14
Fe _{0.09} Co _{0.13} -NiSe ₂	NA	Carbon cloth	1 M KOH	92	89	15
NiFe LDH@NiCoP	2.0 mg cm ⁻²	Nickel foam	1 M KOH	120	88.2	16
Ni ₂ P/Ni ₃ S ₂	8.9 mg cm ⁻²	Nickel foam	1 M KOH	80	65	17
MoS_2/Ni_3S_2	9.7 mg cm ⁻²	Nickel foam	1 M KOH	110	83.1	18
NiFeSP	4.2 mg cm ⁻²	Nickel foam	1 M KOH	91	82.6	19
Se-(NiCo)S _x /(OH) _x	NA	Nickel foam	1 M KOH	103	87.3	20
MoS ₂ /FNS/FeNi	0.37 mg cm ⁻²	FeNi foam	1 M KOH	122	45.1	21
O-CoMoS	1	Carbon cloth	1 M KOH	97	70	22
PA-NiO	NA	Nickel foam	1 M KOH	138	81	23
Ni-BDT-A	NA	Carbon cloth	1 M KOH	80	70	24
NG-NiFe@MoC ₂	0.2 mg cm ⁻²	Glassy carbon	1 M KOH	150	88	25
Ni-doped FeP	0.4 mg cm ⁻²	Carbon fiber paper	1 M KOH	95	72	26

Table S1. Comparison of HER performances of Cu_1Ni_2 -N with other reported electrocatalysts.

Table S2.	Comparison	of the p	performances	of different	catalysts f	or overall	water	electrolysis.
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Catalysts	Substrate	Electrolyte	Cell voltage (V)	Current density (mA cm ⁻²)	Stability (h)	Reference
Cu ₁ Ni ₂ -N	Carbon cloth	1 M KOH	1.63	10	60	This work
Cu ₁ Ni ₂ -N	Carbon cloth	1 M KOH + 0.5 M N ₂ H ₄	0.24	10	75	This work
NC@CuCo ₂ N _x	Carbon cloth	1 M KOH	1.62	10	60	7
Ni ₃ FeN/rGO	Acrogel	1 M KOH	1.6	10	100	8
FeNi ₃ N	Nickel foam	1 M KOH	1.62	10	400	9
NC-NiCu-NiCuN	Nickel foam	1 M KOH	1.56	10	50	10
NiCo ₂ N	Nickel foam	1 M KOH	1.7	10	80	11
PO-Ni/Ni-N-CFC	Glassy carbon	1 M KOH	1.71	10	40	12
Cu@NiFe-LDH	Copper foam	1 M KOH	1.54	10	48	13
NC/CuCo/CuCoO _x	Nickel foam	1 М КОН	1.53	10	100	14
Fe _{0.09} Co _{0.13} -NiSe ₂	Carbon cloth	1 M KOH	1.52	10	30	15
NiFe LDH@NiCoP	Nickel foam	1 M KOH	1.57	10	100	16
Ni ₂ P/Ni ₃ S ₂	Nickel foam	1 M KOH	1.5	10	12	17
MoS_2/Ni_3S_2	Nickel foam	1 M KOH	1.56	10	10	18
NiFeSP	Nickel foam	1 M KOH	1.58	10	20	19
Se-(NiCo)S _x /(OH) _x	Nickel foam	1 M KOH	1.6	10	66	20
O-CoMoS	Carbon cloth	1 M KOH	1.6	10	10	22
PA-NiO	Nickel foam	1 M KOH	1.56	10	10	23
CoSe ₂	Nickel foam	1 M KOH + 0.5 M N ₂ H ₄	0.164	10	14	27
Ni ₂ P	Nickel foam	1 M KOH + 0.5 M N ₂ H ₄	0.45	100	10	28
NiS ₂	Ti mesh	1 M KOH + 0.5 M N ₂ H ₄	0.49	30	10	29
CoS_2 - MoS_2	Nickel foam	1 M KOH + 0.5 M Urea	1.29	10	60	30
$NiCo_2S_4$	Carbon cloth	1 M KOH + 0.33 M Urea	1.45	10	20	31
Ni ₂ P	Nickel foam	1 M KOH + 0.5 M Urea	1.35	50	8	32
NiMoO	Nickel foam	1 M KOH + 0.5 M Urea	1.38	10	50	33
S-MnO ₂	Nickel foam	1 M KOH + 0.5 M Urea	1.41	10	20	34

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