Electronic Supplementary Information

Efficient metal-free carbon catalyst boosting hydrogen production below 1.23 V water electrolytic boundary

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Supplementary Equation, Figures and Tables

Synthetic metal-free catalysts:

The metal-free N@C was prepared by the bottom-up method. 1000 mg carbon nanotubes (CNTs, diameter: 20~40 nm, length: $1\sim2 \ \mu$ m), 1000 mg conductive carbon black (average primary particle size: $30\sim45$ nm, specific surface area: $\sim125 \ m^2/g$), 500 mg graphite (purchased from Macklin), 200 mg activated carbon (AG, particle size: $4\sim6 \ \mu$ m, specific surface area: $1700\sim1900 \ m^2/g$) and 1 ml polydimethyl diallyl ammonium chloride (PDDA) were placed in an agate mortar. The mixture was ground for 30 min. Then 300 mg of the mixed powder was pressed by a tablet press at the pressure of 20 MPa for 1 min. The obtained bulk with the diameter of 13 ± 0.2 mm and the thickness is 2 ± 0.1 mm was placed in the tube furnace, and heated to 900 °C with the heating rate of 5 °C/min. The ammonia flowed through the tube furnace during the entire heating process at a flow rate of 100 ml/min. After maintaining the temperature at 900 °C for 120 min, the tube furnace was naturally cooled to room temperature, and the catalyst N@C was obtained. The metal-free N@AG and N@CNTs were prepared by the similar steps with the N@C, except using only one carbon source of 2.7 g AG or 2.7 g CNTs.

Electrochemical performance

The electrochemical activities of the catalysts were tested using an Ivium-N-Stat potentiostat (Netherlands) in a standard three-electrode cell. Unless otherwise specified, all the electrolytes used in the experiment were 1.0 M KOH. Metal-free N@C was used as the working electrode (WE). The counter electrode (CE) and reference electrode (RE) used in this study were a platinum plate and Hg/HgO, respectively. The potential values reported in this article was referred to the reversible hydrogen electrode (RHE). The potential was calculated as follows:

 E_{RHE} (V) = $E_{Hg/HgO}$ (in 1.0 M KOH) + 0.098 V + 0.0592 × pH

Structure characterization

The structures of the materials were determined by X-ray diffraction (XRD, Rigaku Miniflex; 600, Japan), using Cu K radiation at 40 kV and 40 mA. Raman spectroscopy measurement was conducted using a Raman system (LabRAM Aramis, French) equipped with a 532 nm laser source. The morphology and chemical composition of the materials were obtained using a field emission scanning electron microscope (FESEM, Apreo S LoVac, Czech Republic) equipped with an energy dispersive X-ray spectrometer (EDS). X-ray photoelectron spectroscopy was performed using an X-ray photoelectron spectroscopy system (XPS, Axis Supra, Britain) with Al K X-ray irradiation as the X-ray source. The ion concentration was measured using an ion chromatography (Thermo Scientific ICS-5000+, USA). The three-dimensional morphology and roughness of the membrane electrode were measured using an optical profiler (Bruker Contour GT-K 3D, Germany). The metal content of N@C was measured by the inductively coupled plasma optical emission spectrometer (ULTIMA 2, France).

Gas analysis

The gas product was analyzed qualitatively and quantitatively by the thermal conductivity detector (TCD) in the gas chromatograph (GC9790 Plus, Fuli). Standard gas containing hydrogen with the concentration of 1% was used to calibrate the retention time and content of the hydrogen products. During the reaction, Ar was injected into the cathode cell and then take the cathode product into the gas chromatograph. The flow rate of Ar was measured using a gas flowmeter. The amount of the hydrogen produced was calculated as follows.

$$R_{H_2} = \frac{A_{test}}{A_{standard}} \times C_{standard} \times R_{Ar}$$

 R_{H_2} : gas flow rate of H_2

R_{Ar}: gas flow rate of Ar

 A_{test} : peak area of H_2 produced by TCD at a specific point in time

A_{standard}: peak area of H₂ in the standard gas samples

 $C_{standard}$: volume concentration of H_2 in the standard gas samples

Calculation of faraday efficiency

The faraday efficiency (FE) of hydrogen production is calculated by the following formula:

$$FE = \frac{V_{ex}}{V_{theo}} \times 100\%$$
$$N = \frac{Q}{nF}$$
$$Q = It$$

$$V_{theo} = N \times Vm = \frac{It}{nF} \times \frac{RT}{p}$$

Q: charge, C

N: theoretical hydrogen production, mol

I: current, A

t: reaction time, s

Vm: ideal gas volume, mL

R: ideal gas constant, J/mol K

T: absolute temperature, K

n: electron transfer number (n $_{\text{HER}}=2$)

F: Faraday' s constant (96485 C/mol)

p: pressure, Pa

 V_{ex} : amount of evolved gas, L

 V_{theo} : calculated volume by the equation, L

Energy consumption per unit volume of hydrogen production

The energy consumption per unit volume of hydrogen production is calculated by the following formula:

$$w = \frac{W}{V_{ex}} = \frac{V_{\text{electroolytic voltage}} \times \int_0^t I \, \text{dt}}{V_{ex}}$$

w: energy consumption per unit volume of hydrogen production (kWh/Nm³ H₂)

W: power consumption (J)

I: electrolysis current (A)

Velectroolytic voltage : constant voltage (V)

t: reaction time (s)

Vex: actual gas production (L)

Oxidation potential and enthalpy of formation of carbon

Complete oxidation reaction is highly exothermic and has thermodynamic advantage.

 $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$, $E_1^0 = 0.207 \text{ V vs. RHE}$

 $C + 2H_2O \rightarrow CO + 2H^+ + 2e^-$, $E_2^0 = 0.518 V vs. RHE$

Complete oxidation: $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -393.5 \text{ kJ/mol}$

Incomplete oxidation: $2C(s) + O_2(g) \rightarrow 2CO(g)$, $\Delta H = -221.0 \text{ kJ/mol}$

Metal-free N@C preparation

To construct the membrane electrode assembly (MEA), the metal-free N@C or IrO₂ was used as the anode catalyst and the commercial Pt/C (40 wt%) was used as the cathode catalyst to prepare the catalysts' inks. The loadings of metal-free N@C or IrO₂ was 1.0 mg /cm² and Pt/C was 0.4 mg/cm², respectively. The nafion 115 proton membrane with the size of 10*10 cm² was selected as the coating substrate. The titanium felt with the thickness of 1 mm and the

carbon paper were used as the gas diffusion layer (GDL). Then, a proton exchange membrane water electrolysis (PEMWE) device was assembled to test the electrochemical performance of the N@C-Pt electrode compared to that of the IrO₂-Pt electrode.

Result and discussion



Fig. S1 (a, d) TEM images of N@AG. (b, e) TEM images of N@CNTs. (c, f) TEM images of N@C.



Fig. S2 Energy-dispersive X-ray spectroscopy analysis for (a) N@AG, (b) N@CNTs and (c) N@C.



Fig. S3 X-ray diffraction spectra of different carbon-based materials, including N@AG, N@CNTs and N@C.



Fig. S4 The XPS spectra of N@AG, N@CNTs and N@C for different elements including C, O and N.



Fig. S5 Atomic percentage of N@AG, N@CNTs and N@C.



Fig. S6 Image of the N@C electrode, whose actual electrolytic geometric area of the electrode is 1 cm².



Fig. S7 Contact angle tests for (a) N@AG, (b) N@CNTs and (c) N@C.



Fig. S8 Electrochemical impedance tests for N@AG, N@CNTs and N@C.



Fig. S9 Cyclic voltammetry (CV) and linear sweep voltammogram (LSV) were carried out to evaluate the oxidation activity of N@C compared to contrast materials N@AG, N@CNTs, IrO₂ and Raney Ni. The images show that under the same potential, the current density of N@C electrode is higher than other electrodes.



Fig. S10 No bubble production under 1.2 V commercial battery (anode IrO₂, cathode Pt).



Fig. S11 (a) SEM images of N@C after reaction; (b) XRD images of N@C after reaction.



Fig. S12 Anodic potential comparison of reported catalysts for OER with N@C for COR ^[1-14].



Fig. S13 Images of collected hydrogen by the drainage method, which are produced in a potentiostatic test with the potential of 2 V during 10 min by using different catalysts as the anode, (a) N@C; (b) N@AG; (c) N@CNTs; (d) IrO₂; (e) Raney Ni.



Fig. S14 The current density of different catalysts in the potentiostatic tests at the potential of 2 V in 10 min. (a) N@AG; (b) N@CNTs; (c) N@C; (d) IrO₂; (e) Raney Ni.

The energy consumption of hydrogen production was calculated by as following formula:

(1) N@C:

$$w = \frac{W}{V_{ex}} = \frac{V_{\text{electroolytic voltage}} \times \int_0^t I \, \text{dt}}{V_{ex}}$$
$$= \frac{2 \, \text{V} \times \int_0^{1/6} 359.97 \times 10^{-3} \, \text{A dt}}{34.0 \times 10^{-3} \, \text{L}}$$
$$= 3.530 \, \text{kWh/Nm}^3$$

(2) N@AG:

$$w = \frac{W}{V_{ex}} = \frac{V_{\text{electroolytic voltage}} \times \int_0^t I \, \text{dt}}{V_{ex}}$$
$$= \frac{2 \, \text{V} \times \int_0^{1/6} 193.15 \times 10^{-3} \, \text{A dt}}{17.0 \times 10^{-3} \, \text{L}}$$
$$= 3.788 \, \text{kWh/Nm}^3$$

(3) N@CNTs:

$$w = \frac{W}{V_{ex}} = \frac{V_{\text{electroolytic voltage}} \times \int_0^t I \, \text{dt}}{V_{ex}}$$
$$= \frac{2 \, \text{V} \times \int_0^{1/6} 313.00 \times 10^{-3} \, \text{A dt}}{27.0 \times 10^{-3} \, \text{L}}$$
$$= 3.865 \, \text{kWh/Nm}^3$$

(4) IrO₂:

$$w = \frac{W}{V_{ex}} = \frac{V_{\text{electroolytic voltage}} \times \int_0^t I \, \text{dt}}{V_{ex}}$$
$$= \frac{2 \, \text{V} \times \int_0^{1/6} 253.15 \times 10^{-3} \, \text{A dt}}{23.0 \times 10^{-3} \, \text{L}}$$
$$= 3.670 \, \text{kWh/Nm}^3$$

(5) Raney Ni:

$$w = \frac{W}{V_{ex}} = \frac{V_{\text{electroolytic voltage}} \times \int_0^t I \, \text{dt}}{V_{ex}}$$
$$= \frac{2 \, \text{V} \times \int_0^{1/6} 229.36 \times 10^{-3} \, \text{A dt}}{20.0 \times 10^{-3} \, \text{L}}$$
$$= 3.823 \, \text{kWh/Nm}^3$$



Fig. S15 Field emission SEM and EDS mapping images of N@C treated at different temperatures, (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C.



Fig. S16 XPS images for N@Cs prepared under different temperatures. (a) XPS C1s spectra. (b) XPS N1s spectra. (c) XPS O1s spectra. (d) Full spectrum of XPS.



Fig. S17 Theoretical calculation simulation structure, including the original graphene, and the modified pyridinic nitrogen, pyrrolic nitrogen, and graphitic nitrogen sites on the graphene. The blue atoms represent nitrogen atoms and the red atoms represent oxygen atoms.



Fig. S18 Content comparison of different types of nitrogen before and after reaction.



Fig. S19 Possible reaction pathways of COR on the N@C catalyst.



Fig. S20 Scanning electron microscopy and EDS mapping images of membrane electrodes (ah) Pt/C and (i-p) N@C.



Fig. S21 The three-dimensional morphology and roughness images of (a) cathode Pt/C (40%) and (b) anode N@C of membrane electrode were measured by optical profilometer.

No.	Carbon source	Press		Burn		Obtained sample
1	AG (Artificial graphite)		M		Ø	N@AG
2	AC (Active carbon)	.0			\boxtimes	X
3	CCB (Conductive carbon black)		X	_	\boxtimes	X
4	CNTs (Carbon nanotubes)	0	N	0	V	N@CNTs
5	Composite carbon		M		Ø	N@C

Table S1. Preparation results of carbon-based materials by using different carbon sources.

Sample	Fe	Ni	Cu	Mn	Zn	Co	Total
	(ppm)						
Blank	0.009	0.004	-	0.002	-	0.000	0.015
N@C-1	0.259	0.048	0.003	0.046	-	0.922	1.278
N@C-2	0.245	0.047	0.001	0.046	-	0.922	1.261

Table S2. The metal content of the N@C was measured by inductively coupled plasmaemission spectrometer (ICP-OES).

Table S3. Comparison of OER properties in alkaline electrolytes.

Catalyst	Electrolyte	J (mA·cm ⁻²)	Potential (V _{OER})	Ref.
N@C	1.0 M KOH	10	COR below 1.23 V	This work
NDCO	1.0 M KOH	10	1.47	1
P-CC	1.0 M KOH	10	1.68	2
Ir/Ni-Co ₃ O ₄	1.0 M KOH	10	1.41	3
CoFePO _x @CNQD	1.0 M KOH	10	1.47	4
NiFe-G	1.0 M KOH	10	1.48	5
O-CNT	1.0 M KOH	10	1.59	6
Co ₃ N@AN-CNCs	1.0 M KOH	10	1.51	7
Co ₃ O ₄	1.0 M KOH	10	1.53	8
W ₂ N/WC	1.0 M KOH	10	1.55	9
Se-FeOOH	1.0 M KOH	10	1.52	10
BP-CNT	1.0 M KOH	10	1.55	11
1100-CNS	1.0 M KOH	10	1.69	12
PEMAc@CNTs	1.0 M KOH	10	1.53	13
S, S'-CNT _{1000 °C}	1.0 M KOH	10	1.58	14

Catalyst	Electrolyte	$J(mA \cdot cm^{-2})$	Cell voltage ($V_{HER+OER}$)	Ref.
N@C	1.0 M KOH	10	1.16	This work
CoMoP/CoP/NF	1.0 M KOH	10	1.50	15
CoFe@NiFe-200/NF	1.0 M KOH	10	1.59	16
Co/CNFs (1000)	1.0 M KOH	10	1.69	17
MoS ₂ /LDH	1.0 M KOH	10	1.57	18
Ni ₃ S ₂ @Ni	1.0 M KOH	10	1.61	19
CVN/CC	1.0 M KOH	10	1.64	20
VOOH	1.0 M KOH	10	1.62	21
NiSe ₂ /3DSNG/NF	1.0 M KOH	10	1.59	22
ONPPGC/OCC	1.0 M KOH	10	1.66	23
NFPMO	1.0 M KOH	10	1.41	24
EBP@NG	1.0 M KOH	10	1.54	25
Co ₂ P@Co ₃ O ₄	1.0 M KOH	10	1.57	26

 Table S4. Performance comparison of catalysts for overall water splitting.

Potential (V)	Graphene-C	Pyridinic N-C	Pyrrolic N-C	Graphitic N-C
0	1.361795	0.963798	1.00527	2.036993
0.1	1.261795	0.863798	0.90527	1.936993
0.2	1.161795	0.763798	0.80527	1.836993
0.3	1.061795	0.663798	0.70527	1.736993
0.4	0.961795	0.563798	0.60527	1.636993
0.5	0.861795	0.463798	0.50527	1.536993
0.6	0.761795	0.363798	0.40527	1.436993
0.7	0.661795	0.263798	0.30527	1.336993
0.8	0.561795	0.163798	0.20527	1.236993
0.9	0.461795	0.063798	0.10527	1.136993
1	0.361795	-0.036202	0.00527	1.036993
1.1	0.261795	-0.136202	-0.09473	0.936993
1.2	0.161795	-0.2362	-0.19473	0.836993
1.23	0.131795	-0.2662	-0.22473	0.806993
1.3	0.061795	-0.3362	-0.29473	0.736993
1.4	-0.0382	-0.4362	-0.39473	0.636993
1.5	-0.13821	-0.5362	-0.49473	0.536993
1.6	-0.23821	-0.6362	-0.59473	0.436993
1.7	-0.33821	-0.7362	-0.69473	0.336993
1.8	-0.43821	-0.8362	-0.79473	0.236993

Table S5. The adsorption free energy profiles of the OH^{*} on the carbon atom adjacent to different nitrogen sites under the oxidation potential from 0 to 1.8 V.

Table S6. Ion chromatographic tests for the electrolyte before and after the reaction (chronoamperometry test at the potential of 2 V over 60 min). The amounts of both CO_3^{2-} and NO_3^{-} increased after the reaction, which might be part of the oxidation products of COR on N@C.

Sample	CO ₃ ²⁻ (ppm)	NO ₃ ⁻ (ppm)
Before	0.8325	0.2676
After	1.2395	0.4525

Table S7. Costs structure of N@C and noble metal IrO₂. (Source: www.inno-chem.com.cn and www.cbcie.com).

Catalyst	Constituent	USD/g	Electrode/g	USD/10*10cm ²
	Carbon nanotubes	0.050	0.0400	
	Conductive carbon black	0.042	0.0333	
N@C	Artificial graphite	0.054	0.0213	0.009
	Active carbon	0.077	0.0122	
	PDDA (1.04 g/ml)	0.108	0.0854	
IrO ₂	IrO ₂	165.28	0.1	16.528

Video S1. Video of the COR-HER device for producing hydrogen at the potential of 1.2 V.Video S2. Video of the Hoffman device for producing hydrogen by water electrolysis.

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