Electronic Supplementary Information

Tunable doping of N and S in carbon nanotubes by retarding pyrolysis-gas diffusion to promote electrocatalytic hydrogen evolution

Hao Wu,^a Zhimin Chen,^{*a} Fei Xiao,^a Ying Wang,^a Erping Cao,^a Shuo Chen,^a Shichao Du,^a Yiqun Wu^{*ab} and Zhiyu Ren^a

^a Key Laboratory of Functional Inorganic Material Chemistry (Ministry of Education of China), School of Chemistry and Materials Science, Heilongjiang University, 74# Xuefu Road, Nangang District, Harbin 150080, People's Republic of China;
^b Shanghai Institutes of Optics and Fine Mechanics, Chinese Academy of Sciences, 390# Qinghe Road, Jiading District, Shanghai 201800, People's Republic of China.
* Corresponding author E-mail: <u>zmchen@hlju.edu.cn</u>; <u>yqwu@siom.ac.cn</u>.
Tel.: +86 451 86604331,

Fax: +86 451 86608616.

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1. Experimental Section

1.1 Reagents

Multi-walled carbon nanotube (CNT, purity > 95 %, 10-30 µm in length, 10-30 nm in diameter) was purchased from Chengdu Organic Chemicals Co., Ltd and, before use, CNT was acidified^{S1} and soaked in 6.0 M HCl, which was renewed every five days, for at least a month in order to completely remove metal impurities. Carbon fiber (CF, purity > 99 %, 10-20 µm in length, 150-200 nm in diameter) was received from Showa Denko and, before use, CF was pre-treated using the same procedure as used for the CNT. Flake graphite was obtained from Nanjing XFNANO Materials Tech Co., Ltd and graphene oxide (GO) was prepared using a modified Hummers' method reported in the literature (the mass ratio of graphite and KMnO₄ was 1 : 3).^{S2} Trithiocyanuric acid (TCY, 99.5 % purity) and sulfur powder (purity > 99.9 %) were bought from Aladdin Co. LLC. Melamine (99.5 % purity) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Commercial Pt/C (20 % Pt on Vulcan XC-72) and Nafion 117 solution (5 % (w/w) in low aliphatic alcohols and water) were obtained from Johnson Matthey Fuel Cells and Sigma-Aldrich LLC, respectively. Ultra-pure water (18.2 Ω m) used throughout all experiments was received from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA). All the other reagents were of analytical grade and used without further purification in this work.

1.2 Preparation of CNT-NS

CNT-NS was prepared by thermal-treating the mixture of CNT and TCY in a quasi-sealed quartz reactor, which consists of quartz tube (12.50 cm in length, 1.00 cm in outer diameter, 0.80 cm in inside diameter) and quartz rod (12.50 cm in length, 0.79 cm in diameter). Briefly, 40 mg of CNT was sonicated in 100 mL of ethanol at room temperature for 1 h. Subsequently, a certain amount of TCY was added under vigorous stirring (the amount of TCY was 10, 20, 40, 60, 80, 100, 120 and 140 mg for the synthesis of CNT-NS-1, CNT-NS-2, CNT-NS-3, CNT-NS-4, CNT-NS-5, CNT-NS-6, CNT-NS-7 and CNT-NS-8, respectively) and the mixture was continuously stirred for 1 h at room temperature. Next, the ethanol in the above mixture was removed by rotary evaporation and the product was filled to the bottom of the quartz tube and compacted with quartz rod. Finally, the quartz tube furnace with the bottom of

quartz reactor at the upstream side and heated to 900 °C with a ramp rate of 4 °C min⁻¹, and maintained for 2 h under a 100 mL min⁻¹ N_2 gas flow. After reaction, the furnace was naturally cooled down to room temperature under a flowing N_2 gas and the desired CNT-NS was obtained.

As a control, CNT-NS-9 and CNT-NS-10 were prepared using the same method as used for CNT-NS-4 except that 60 mg of TCY was replaced with 40 mg of TCY and 30 mg of melamine or 40 mg of TCY and 25 mg of sulfur powder, respectively; CNT was calcined at 900 °C, the same as CNT-NS, and the resulting product was denoted as CNT-900; N, S co-doped carbon fiber (CF-NS) and N, S co-doped graphene (G-NS) were prepared using the same procedure as used for the CNT-NS, and the amount of TCY was 10, 20, 40, 60, 80, 100, 120 and 140 mg for the synthesis of CF-NS-1 and G-NS-1, CF-NS-2 and G-NS-2, CF-NS-3 and G-NS-3, CF-NS-4 and G-NS-4, CF-NS-5 and G-NS-5, CF-NS-6 and G-NS-6, CF-NS-7 and G-NS-7 and CF-NS-8 and G-NS-8, respectively.

1.3 Characterization

Scanning electron microscopy (SEM) images were recorded on a S-4800 field-emission SEM (Hitachi) operating at 15 kV. Transmission electron microscopy (TEM) images and the scanning TEM-energy-dispersive X-ray spectroscopy (STEM-EDS) mapping were measured on a JEM-3010 TEM (JEOL) with an acceleration voltage of 300 kV. The Brunauer-Emmett-Teller (BET) surface area was investigated on ASAP 2010 (Micromeritics) with a nitrogen adsorption-desorption isotherms at 77 K. Thermogravimetric analysis (TGA-IR) was performed using a SDT-Q600 thermal analyzer (TA Instruments). Raman spectra were obtained on a HR800 UV spectrometer (Jobin Yvon) excited by a laser of 457.9 nm. X-ray photoelectron spectroscopy (XPS) was carried out on an AXIS Ultra spectrometer (Kratos) equipped with a delay line detector in an ultrahigh vacuum. The conductivity of the samples was received from a RM3000+ 4-point probe instrument (Jandel Engineering Ltd) by repeating the test in at least 10 different positions. Elemental analyses of C, H, N and S were determined on an elemental analyzer (Vario MICRO). Inductively coupled plasma-optial emission spectroscopy (ICP-OES) analysis was collected on Optima 7000 DV (PerkinElmer). Samples for ICP-AES were prepared by ashing 10 mg of sample in muffle furnace (air atmosphere) at 800 °C for 2 h, and then leached out with HCl (10 wt % in water) and volume

to 5 mL.

1.4 Electrochemical measurements

The electrochemical measurements were taken on the CHI 760D electrochemical workstation equipped with a three-electrode system (CH instruments, Shanghai, China) in 0.5 M H₂SO₄ aqueous solution at room temperature (25 ± 1 °C). A studied catalyst modified glassy carbon electrode (GCE) served as the working electrode, while graphite rod and saturated calomel electrode were used as the auxiliary and reference electrodes, respectively. The electrolyte was constantly bubbled with H₂ gas (99.999 % purity) to avoiding the effects of dissolved oxygen and maintain a constant reversible hydrogen electrode (RHE) potential. For the preparation of the working electrode, 1 mg of catalyst mixed with 10 µL of 5 wt.% Nafion ionomer was ultrasonically dispersed in 0.2 mL of ethanol until a homogenous catalyst ink was obtained. Then, 20 µL of this catalyst ink was evenly drop casted on the well-polished GCE surface (the catalyst loading ~ 0.378 mg cm^{-2}) and allowed to dry under an infrared lamp. All the potentials were manually *iR*-compensated and converted to the RHE scale by adding a value of (0.242 + 0.0592pH) V. Linear sweep voltammetry (LSV) was performed at 2 mV·s⁻¹ for the polarization curves and all the polarization curves were recorded with 100 % *iR* compensation. The Tafel slope is obtained from Tafel equation as follows: $\eta = b \times \log(j/j_0)$, where η is the overpotential, b is the Tafel slope, j is the current density, and j_0 is the exchange current density, respectively. Chronopotentiometry and chronoamperometry measurements were used to perform long-term durability tests. The Faradic efficiency of HER catalystsis defined as the ratio of the amount of experimentally determined H₂ to that of the theoretically expected H₂ from the reaction solution. Accordingly, the H₂ evolved from the reaction solution was measured by gas chromatography (GC2002, Shanghai, China) with CH₄ as internal standard and N₂ as carrying gas for quantitative analysis. The electrochemical double layer capacitance (C_{dl}) was determined by cyclic voltammetry (CV) method in a N₂-saturated 0.5 M H₂SO₄ aqueous solution and a non-Faradaic region at different scan rates of 20, 40, 60, 80, 100, 120, 140, 160, and 180 mV·s⁻¹. Electrochemical impedance spectra (EIS) were recorded at open circuit potential over a frequency range from 0.01 Hz to 100 kHz.

1.5 Calculation methods

DFT calculations were performed by using the CASTEP code.^{S3,S4} The form of computing was delineated by the Perdew-Burke-Ernzerh (PBE) functional of the generalized gradient approximation (GGA). The ion-electron interaction was modelled by the frozen core all-electron projector augmented wave pseudopotentials. The electron wave functions were expanded by using a plane wave basis set with a cutoff energy of 400 eV. The structure of model was fully optimized by taking 0.01 eV Å⁻¹ as the convergence threshold. The density of states (DOS) was computed by using a $7 \times 6 \times 1$ k-point mesh. The Gibbs free-energy of hydrogen adsorption (ΔG_{H^*}) at T = 298.15 K was obtained as $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_{H^*}$,^{S5} where ΔE_{H^*} is the hydrogen absorption energy, ΔE_{ZPE} is the difference in zero point energy between the adsorbed hydrogen and hydrogen in the gas phase and $\Delta S_{\rm H}$ is the entropy difference between the adsorbed state and the gas phase. Given that the vibrational entropy of hydrogen on the adsorbed state is extremely small,^{S6} the formula for ΔG_{H^*} can also be simplified as $\Delta G_{H^*} = \Delta E_{H^*} + 0.24$ eV. And ΔE_{H^*} can be defined as $\Delta E_{H^*} = (1/n) (\Delta E_{M+nH^*} - 1/n) (\Delta E_{M+nH^$ $\Delta E_{\rm M}$) – 0.5 $E_{\rm H2}$, where $\Delta E_{\rm M+nH^*}$ is the total energies of the doped graphene with *n* adsorbed H atoms on the surface, $\Delta E_{\rm M}$ is the total energy of the doped graphene and $E_{\rm H2}$ is the energy of a H₂ molecule.

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2. Supplementary Figures



Fig. S1. (A and B) Components and structure of the quartz reactor. (C) A quartz reactor filled with 100 mg mixture of CNT and TCY.



Fig. S2. TG curves of TCY under N₂ atmosphere.

As shown in *Fig. S2*, a great loss of weight appears in the TG curve of TCY accompanied by the increasing of temperature. The loss of weight at 700 °C is about 98.71 %. And, when the temperature goes up to 900 °C, only a negligible TCY residue (about 0.05 %) is observed. Therefore, the pyrolysis temperature is selected as 900 °C. After treating the mixture of CNT and TCY at 900 °C for 2 h under N₂ atmosphere, TCY in the mixture can be gasified almost completely.



Fig. S3. TEM (A) and HRTEM (B) images of CNT.



Fig. S4. TEM and HRTEM images of CNT-NS-1 (A and B), CNT-NS-2 (C and D), CNT-NS-3 (E and F) and CNT-NS-5 (G and H).



Fig. S5. N₂ adsorption-desorption isotherms (A) and pore-size distribution curves (B) of the various CNT-NS catalysts.



Fig. S6. The survey XPS spectra of CNT and CNT-900. The inset is the corresponding atomic percentages of C and O.



Fig. S7. The high-resolution Fe 2p (A), Co 2p (B), Ni 2p (C) and Pt 4f (D) XPS spectra of CNT-NS-4.



Fig. S8. Raman spectra of the various CNT-NS catalysts obtained at $\lambda_{exc} = 457.9$ nm.



Fig. S9. (A) The survey XPS spectra of CNT-NS-6, CNT-NS-7 and CNT-NS-8. (B) The content of N and S in CNT-NS obtained from XPS analysis versus the amount of TCY in quartz reactor (the amount of CNT is 40 mg).



Fig. S10. (A) The content of N and P in CNT-NS obtained from XPS analysis versus the amount of TCY in porcelain boat (the amount of CNT is 40 mg). (B) The content of heteroatoms in CNT-NS obtained from XPS analysis versus the amount of TCY in quartz reactor or porcelain boat (the amount of CNT is 40 mg).



Fig. S11. Potential gas diffusion modes of TCY in quartz reactor (A) and porcelain boat (B).



Fig. S12. The content of heteroatoms in CF-NS (A) and G-NS (B) obtained from elemental analysis.



Fig. S13. HER polarization curves (scan rate: 2 mV s^{-1}) of the various CNT-NS and Pt/C catalysts in 0.5 M H₂SO₄ with (solid lines) and without iR correction (dashed lines).



Fig. S14. The content of N and S and the HER η values required for the current density of 10 mA cm⁻² for CNT-NS-6, CNT-NS-7 and CNT-NS-8.



Fig. S15. TEM images of CNT-NS-9 (A) and CNT-NS-10 (B). N₂ adsorption-desorption isotherms (C) and pore-size distribution curves (D) of CNT-NS-4, CNT-NS-9 and CNT-NS-10. (E) The survey XPS spectra of CNT-NS-4, CNT-NS-9 and CNT-NS-10. (F) The content of N and S and the HER η values required for the current density of 10 mA cm⁻² for CNT-NS-4, CNT-NS-9 and CNT-NS-4, CNT-NS-9 and CNT-NS-10.

As shown in *Fig. S15*, the morphology, surface area, and total amount of heteroatoms in CNT-NS-9 and CNT-NS-10 are similar to those of CNT-NS-4. However, the HER activity of CNT-NS-9 and CNT-NS-10 are less than that of CNT-NS-4. These results indicate that the doping atomic ratio of N/S also influences the catalytic activity of CNT-NS and a ratio of N/S close to 1/1 may be more advantageous.



Fig. S16. The measured j_0 of various CNT-NS catalysts by using an extrapolation method.



Fig. S17. TEM (A) and HRTEM (B) images of CNT-NS-4 after 100 h durability tests.



Fig. S18. The survey (A), high-resolution N 1s (B) and high-resolution S 2p (C) XPS spectra of CNT-NS-4 initially and after 100 h durability tests. The inset in (A) is the corresponding atomic percentages of N and S.



Fig. S19. The Faradic efficiency of CNT-NS-4 in 0.5 M H₂SO₄ (η = 200 mV).



Fig. S20. (A-E) CVs for various CNT-NS catalysts at different scan rate from 20 to 180 mV s⁻¹. (F) The differences in current density (Δj) at 0.265 V (vs. RHE) as a function of scan rate for various CNT-NS catalysts.



Fig. S21. iR-compensated HER polarization curves of various CNT-NS catalysts with current densities normalized to ECSA in $0.5 \text{ M H}_2\text{SO}_4$.



Fig. S22. TOFs of various CNT-NS catalysts in 0.5 M H₂SO₄.

The TOFs of various CNT-NS catalysts in $0.5 \text{ M H}_2\text{SO}_4$ for the HER is calculated by the equation:

$$TOF = \frac{Total number of hydrogen turnover/geometric area (cm2)}{Number of active sites/geometric area (cm2)}$$

Total number of hydrogen turnover^{S7,S8}

$$= (j \text{ mA } \text{cm}^{-2}) \left(\frac{1 \text{ C } \text{s}^{-1}}{10^3 \text{ mA}} \right) \left(\frac{1 \text{ mol } \text{e}^-}{96485.3 \text{ c}} \right) \left(\begin{array}{c} \frac{1 \text{ mol } \text{H}_2}{2 \text{ mol } \text{e}^-} \right) \left(\begin{array}{c} \frac{6.022 \times 10^{23} \text{ molecules } \text{H}_2}{1 \text{ mol } \text{H}_2} \right)$$
$$= 3.12 \times 10^{15} \text{ H}_2 \text{ s}^{-1} \text{ cm}^{-2} \text{ per mA } \text{cm}^{-2}$$

The number of active sites is assumed to be equal to the number of heteroatoms (N and S) and all of these sites are accessible to the electrolyte. The real number of active and accessible sites should be considerably lower than the calculated value and the content of heteroatoms is revealed by the XPS measurements. Accordingly, number of active sites

$$= \left(W_{N} \times \frac{1 \text{ mmol}}{14.004 \text{ mg}} + W_{S} \times \frac{1 \text{ mmol}}{32.065 \text{ mg}} \right) \times 0.378 \text{ mg } \text{cm}^{-2} \times 6.022 \times 10^{20} \text{ sites } \text{ mmol}^{-1}$$

Where W_N is the mass content of N, and W_S is the mass content of S.

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Fig. S23. Conductivity of various CNT-NS catalysts measured by 4-point probe method. As shown in *Fig. S23*, the conductivity of CNT-NS first increases and then decreases with increasing the doping amount of N and S (as for CNT-NS-1, CNT-NS-2, CNT-NS-3, CNT-NS-4, CNT-NS-5, CNT-NS-6, CNT-NS-7 and CNT-NS-8), and the conductivity of CNT-NS decreases regardless of increasing or decreasing the doping atomic ratio of N/S (as for CNT-NS-4, CNT-NS-9 and CNT-NS-10). Therefore, the content and proportion of N and S in CNT-NS-4 are optimal for obtaining high conductivity.



Fig. S24. (A) Hydrogen adsorption sites and configurations on different N, S co-doped CNT models (N/S atomic ratio equals 1/1). The grey, orange, dark cyan and white balls represent C, N, S and H atoms, respectively, and the unit cells of various models are indicated by pink dashed line. (B) The calculated free energy (ΔG_{H^*}) diagram for HER at the equilibrium potential ($U_{RHE} = 0$ V) of different N, S co-doped CNT models (N/S atomic ratio equals 1/1).



Fig. S25. (A) Hydrogen adsorption sites and configurations on different N, S co-doped CNT models (N/S atomic ratio equals 1/1). The grey, orange, red, dark cyan and white balls represent C, N, O, S and H atoms, respectively, and the unit cells of various models are indicated by pink dashed line. (B) The calculated free energy (ΔG_{H^*}) diagram for HER at the equilibrium potential ($U_{RHE} = 0$ V) of different N, S co-doped CNT models (N/S atomic ratio equals 1/1).



Fig. S26. (A) Hydrogen adsorption sites and configurations on different N, S co-doped CNT models (N/S atomic ratio equals 1/1). The grey, orange, dark cyan and white balls represent C, N, S and H atoms, respectively, and the unit cells of various models are indicated by pink dashed line. (B) The calculated free energy (ΔG_{H^*}) diagram for HER at the equilibrium potential ($U_{RHE} = 0$ V) of different N, S co-doped CNT models (N/S atomic ratio equals 1/1).



Fig. S27. (A) Hydrogen adsorption sites and configurations on different N, S co-doped CNT models (N/S atomic ratio equals 1/1). The grey, orange, red, dark cyan and white balls represent C, N, O, S and H atoms, respectively, and the unit cells of various models are indicated by pink dashed line. (B) The calculated free energy (ΔG_{H^*}) diagram for HER at the equilibrium potential ($U_{RHE} = 0$ V) of different N, S co-doped CNT models (N/S atomic ratio equals 1/1).



Fig. S28. $|\Delta G_{H^*}|$ of different CNT doped with 2 at.% of N and S (N/S atomic ratio equals 1/1). Ortho, Meta, Para indicates the relative positions of N and S heteroatoms in one benzene heteroring. The grey, orange, red, dark cyan and white balls represent C, N, O, S and H atoms, respectively, and the unit cells of various models are indicated by pink dashed line.



Fig. S29. $|\Delta G_{H^*}|$ of different CNT doped with 2 at.% of N and S (N/S atomic ratio equals 1/1). Ortho, Meta, Para indicates the relative positions of N and S heteroatoms in one benzene heteroring. The grey, orange, red, dark cyan and white balls represent C, N, O, S and H atoms, respectively, and the unit cells of various models are indicated by pink dashed line.

2. Supplementary Tables

Samples	Fe (wt.%)	Co (wt.%)	Ni (wt.%)	Pt (wt.%)
CNT-NS-1	<0.0010	< 0.0010	<0.0010	<0.0010
CNT-NS-2	< 0.0010	< 0.0010	< 0.0010	< 0.0010
CNT-NS-3	< 0.0010	< 0.0010	< 0.0010	< 0.0010
CNT-NS-4	< 0.0010	< 0.0010	< 0.0010	< 0.0010
CNT-NS-5	< 0.0010	< 0.0010	< 0.0010	< 0.0010

Table S1. The ICP-AES results of various CNT-NS catalysts.

Table S2. The elemental analysis results of various CNT-NS catalysts.

Somplog	Eleme	ntal ar	alysis (wt.%)	Elemental analysis (at.%)			
Samples	С	н	Ν	S	С	Н	Ν	S
CNT-NS-1	95.32	0.32	1.20	2.49	93.77	3.81	1.01	0.92
CNT-NS-2	89.46	0.37	2.71	5.95	89.84	4.45	2.33	2.24
CNT-NS-3	82.45	0.42	4.08	10.43	84.56	5.23	4.19	4.01
CNT-NS-4	74.34	0.49	5.86	15.35	78.38	6.24	6.18	6.07
CNT-NS-5	66.61	0.55	8.56	19.36	72.76	7.27	8.01	7.93
CNT-NS-6	62.64	0.58	9.64	21.60	69.54	7.69	9.17	8.99
CNT-NS-7	61.42	0.58	9.96	22.33	68.58	7.75	9.53	9.35
CNT-NS-8	61.23	0.58	10.03	22.41	68.41	7.78	9.61	9.39

Some los	Eleme	Elemental analysis (wt.%)			Elemental analysis (at.%)			
Samples	С	Н	N	S	С	н	Ν	S
CF-NS-1	97.88	0.15	0.53	1.08	97.12	1.76	0.45	0.40
CF-NS-2	96.40	0.16	0.90	1.96	96.14	1.93	0.77	0.73
CF-NS-3	91.56	0.20	2.18	4.76	92.89	2.41	1.89	1.81
CF-NS-4	87.23	0.24	3.28	7.33	89.79	3.01	2.90	2.83
CF-NS-5	84.44	0.27	3.98	8.98	87.79	3.35	3.54	3.50
CF-NS-6	82.04	0.28	4.62	10.37	86.13	3.51	4.16	4.08
CF-NS-7	81.18	0.28	4.86	10.86	85.53	3.57	4.39	4.29
CF-NS-8	81.01	0.28	4.87	10.98	85.41	3.59	4.40	4.34
G-NS-1	94.08	0.40	1.58	3.38	92.06	4.67	1.33	1.24
G-NS-2	86.07	0.48	3.65	8.16	86.40	5.79	3.14	3.07
G-NS-3	77.45	0.52	5.85	13.26	80.51	6.43	5.21	5.17
G-NS-4	66.50	0.63	8.73	19.74	71.69	8.20	8.07	7.98
G-NS-5	60.12	0.67	10.38	23.55	66.51	8.94	9.84	9.77
G-NS-6	55.14	0.70	11.69	26.45	62.31	9.46	11.32	11.21
G-NS-7	54.00	0.70	11.96	27.15	61.38	9.53	11.65	11.57
G-NS-8	53.75	0.70	12.00	27.33	61.16	9.57	11.71	11.66

Table S3. The elemental analysis results of various CF-NS and G-NS catalysts.

Catalysts	Substrate	η@10 mA·cm ⁻² (mV)	Tafel slope (mV/dec)	Reference
CNT-NS-4	GCE	131	71.9	This work
N, P codoped G	GCE	340	118	Adv. Sci. 2019, 6, 1900119.
N doped CNT	GCE	360	118	Catal. Lett. 2019, 149, 486.
Defect-rich and ultrathin N doped C nanosheet	GCE	90	43	Energy Environ. Sci. 2019, 12, 322.
N doped porous CF	GCE	248	135	J. Solid State Chem. 2019, 274, 207.
3D NG sponge	GCE	267	69.7	RSC Adv. 2019, 9, 99.
3D G	Si substrate	107	64	Angew. Chem. Int. Ed. 2018, 57, 192.
Ethylenediamine-functionalized multiwalled CNT	GCE	350	116	Electrocatalysis 2018, 9, 573.
$C_{3}N_{4}@G$	GCE	110	53	ACS Catal. 2018, 8, 3965.
B, S codoped G	GCE	230	72	Angew. Chem. Int. Ed. 2018, 57, 13302.
NG	GCE	210		ACS Energy Lett. 2018, 3, 1345.
Hexagonal BN-G	GCE	~390		Phys. Chem. Chem. Phys 2018, 20, 15007.
3D porous N doped C	GCE	143	64.3	ChemCatChem 2018, 10, 5194.
Pyrazine-incorporated graphdiyne	GCE	275	75	J. Mater. Chem. A 2018, 6, 22189.
NG	GCE	~580	133.8	Chem. Commun. 2018, 54, 13726.
Graphite CN/B doped G	GCE	260	90	Nanotechnology 2018, 29, 345705.
Maleimide edge-functionalized G	GCE	420	110	ChemistrySelect 2018, 3, 13070.
P nanodot incorporated G	GCE	440	46	J. Mater. Chem. A 2018, 6, 3141.
Amine functionalized NG	GCE	350	113	Carbon 2018, 138, 169.
N functionalized CNT	GCE	250		ChemCatChem 2018, 10, 3872.
NBC-ternary nanosheet	GCE	590	205	Appl. Surf. Sci. 2018, 448, 618.
3D S doped G	GCE	218	64	J. Mater. Sci. 2018, 53, 7767.
N, P codoped G	GCE	~500	88	ChemistrySelect 2018, 3, 6814.
S doped g-C ₃ N ₄	GCE	186	84	ACS Nano 2017, 11, 6004.
CN _x @NG	GCE	193	54	ChemElectroChem 2017, 13, 2643.

Table S4. Comparison of HER performance of CNT-NS-4 with the recently reported metal-free catalysts in $0.5 \text{ M H}_2\text{SO}_4$.

N doped C	GCE	276	94	J. Mater. Chem. A 2017, 5, 6025.
g-C ₃ N ₄ @2D mesoporous G	GCE	219	53	Adv. Funct. Mater. 2017, 27, 1606352.
NG	GCE	128	66	Appl. Catal. A: General 2017, 529, 127.
3D CNT	GCE	~300		ACS Catal. 2017, 7, 2676.
NG	GCE	~380		ChemCatChem 2017, 9, 4049.
Defect-rich, N, B codoped C nanocage	GCE	175.3		Nano Energy 2017, 42, 334.
NSC	GCE	290	76.9	ACS Nano 2017, 11, 7293.
Covalent organic polymer	GCE	250	106	ACS Catal. 2017, 7, 6120.
NG	GCE	~380		ChemCatChem 2017, 9, 4049.
Pyrene-porphyrin-based crystalline covalent organic framework	GCE	380@5	116	ACS Appl. Mater. Interfaces 2017, 9, 23843.
N, S codoped G	Ni foam	298	75	Int. J. Hydrogen. Energ. 2017, 42, 27004.
N, F codoped G	GCE	290	87	Catal. Sci. Technol. 2017, 7, 2228.
N doped CNT@NG	GCE	62	50	J. Mater. Chem. A 2017, 5, 6405.
N doped C nanosheet	CC	320	198	Int. J. Hydrogen. Energ. 2017, 42, 14390.
BC7N2	GCE	70@20	100	Energy Environ. Sci. 2016, 9, 95.
S-C3N4/CNT/CF	CF	236	81.6	J. Mater. Chem. A 2016, 4, 12878.
N, S codoped G	GCE	~300	120	Nature Energy 2016, 1, 16130.
G nanostripe	GCE	560	85.3	Angew. Chem. Int. Ed. 2016, 55, 13965.
N, P, S tridoped G	GCE	240	90	Adv. Mater. 2016, 28, 10644.
Horizontally-aligned CNT and G	GCE	420	121	Carbon 2016, 107, 739.
N, P codoped CF	GCE	151	69	J. Mater. Chem. A 2016, 4, 13726.
Defect G	GCE	150	55	Adv. Mater. 2016, 28, 9532.
N, P codoped C network	GCE	163	89	Angew. Chem. Int. Ed. 2016, 55, 2230.
S doped C ₃ N ₄	GCE	145	51	J. Mater. Chem. A 2016, 4, 12205.
Plasma-etched N, S codoped G	GCE	149	78	Electrochimica Acta 2016, 219, 781.
Plasma-etched S doped G	GCE	178	86	Int. J. Hydrogen. Energ. 2016, 42, 4184.
N doped C nanosheet	GCE	137	131.6	Electrochimica Acta 2016, 215, 223.
Acid treated multiwalled CNT	GCE	~180	71.3	ACS Appl. Mater. Interfaces 2016, 8, 35513.
B, N codoped G	GCE	216	92	J. Mater. Chem. A 2016, 4, 16469.

Defective activated C	GCE	334	66	Chem. Commun. 2016, 52, 8156.
N, S codoped CNT	GCE	~270	126	Chem. Eur. J. 2016, 22, 10326.
$C_3N_4@NG$	GCE	80	49.1	ACS Nano 2015, 9, 931.
2D supramolecular polymer	GCE	333	80.5	Angew. Chem. Int. Ed. 2015, 54, 12058.
N, P codoped porous C	GCE	204	58.4	J. Mater. Chem. A 2015, 3, 7210.
N, S codoped carbon nanosheet	GCE	120	67.8	Nano Energy 2015, 16, 357.
N, S codoped G	GCE	276	81	Angew. Chem. Int. Ed. 2015, 54, 2131.
N, P codoped G	GCE	213	79	J. Mater. Chem. A 2015, 3, 12642.
Holey NG	GCE	340	99	Nano Energy 2015, 15, 567.
NSC	GCE	100	57.4	J. Mater. Chem. A 2015, 3, 8840.
g-C3N4/N, P codoped G	GCE	340	90	ChemCatChem 2015, 7, 3873.
$C_3N_4@NG$	GCE	~240	51.5	Nat. Commun. 2014, 5, 3783.
Activated CNT	GCE	220	71.3	Chem. Commun. 2014, 50, 9340.
NG	GCE	240	109	Sci. Rep. 2014, 4, 7557.
g-C3N4 nanoribbon/G	GCE	207	54	Angew. Chem. Int. Ed. 2014, 53, 13934.
B doped G	GCE	470	99	Catal. Sci. Technol. 2014, 4, 2023.
N, P codoped G	GCE	~420	91	ACS Nano 2014, 8, 5290.

Abbreviations: GCE = Glassy carbon electrode; G = Graphene; CNT = Carbon nanotube; C = Carbon; CF = Carbon fiber;

 $NG = N \ doped \ G; \ g-C_3N_4 = graphitic- \ C_3N_4; \ NSC = N, \ S \ codoped \ carbon; \ CC = Carbon \ cloth.$

Catalysts	Substrate	η@10 mA·cm ⁻² (mV)	Tafel slope (mV/dec)	Reference
CNT-NS-4	GCE	131	71.9	This work
G-supported single atom Co	GCE	230	99	Adv. Energy Mater. 2019, 9, 1803689.
Co-N doped carbon@Mo ₂ C	GCE	143	60	Nano Energy 2019, 57, 746.
S-vacancy MoS2	GCE	194	73	Angew. Chem. Int. Ed. 2019, 58, 2029.
MoS ₂ /WTe ₂	GCE	140	40	Small 2019, 15, 1900078.
N, P codoped MoS ₂	CC	116	58.4	Nano Energy 2019, 58, 862.
Amorphous MoS _x	GCE	145	40	Adv. Funct. Mater. 2019, 29, 1806229.
O2 plasma treated MoS2	GCE	~535	138	Nano Energy 2019, 57, 535.
MoS2/rGO	GCE	186	49	Small 2019, 15, 1804903.
Meso-CoS ₂	GCE	110	52	ACS Catal. 2019, 9, 456.
Monolayer MoS2	GCE	200	75	Nat. Commun. 2019, 10, 1348.
W_2C	GCE	~268	65	Small 2019, 15, 1900248.
$[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$	GCE	~114	~52	Nat. Commun. 2019, 10, 370.
Co-N/C	GCE	~202	82	ACS Catal. 2019, 9, 83.
p-(CH ₃ CH ₂) ₂ NPh-MoS ₂	GCE	~348	~75	J. Am. Chem. Soc. 2018, 140, 441.
Thiomolybdate [Mo3S13]2-cluster	GCE	137	51	ACS Catal. 2018, 8, 5221.
Co doped WS ₂ /W ₁₈ O ₄₉ nanotube	FTO	210	49	Energy Environ. Sci. 2018, 11, 2270.
Mo/Co@N doped carbon	GCE	187	148	Small 2018, 14, 1704227.
Cu ₂ Se sheet	Cu foam	~212	32	ACS Catal. 2018, 8, 5686.
Li ⁺ activated WSe ₂ nanoflower	CFP	243		Nano Lett. 2018, 18, 2329.
MoSe2 flake/single-wall CNT	GCE	100	63	Adv. Energy Mater. 2018, 8, 1703212.
$2D MoS_{2-x}O_x$	GCE	~255	67	Nat. Chem. 2018, 9, 810.
N-MoSe2/TiC-C	TiC-C	106	32	Adv. Mater. 2018, 30, 1802223.
MoSSe nanodot	GCE	140	40	Adv. Mater. 2018, 30, 1705509.
Er ₂ Si ₂ O ₇ :IrO ₂	GCE	130	49	ACS Catal. 2018, 8, 8830.
S. N codoped Fe2N	GCE	123	90	Small 2018, 14, 1803500.

Table S5. Comparison of HER performance of CNT-NS-4 with recently reported metallic catalysts in $0.5 \text{ M H}_2\text{SO}_4$.

Single-atomic Co/N doped carbon	GCE	137	52	Proc. Natl. Acad. Sci. USA 2018, 115, 12692.
Core-shell N-C-NiFe nanoparticle	CW	179	52.8	Adv. Energy Mater. 2018, 8, 1801289.
CoP@N doped carbon/N doped G	GCE	135	59.3	Small 2018, 14, 1702895.
Multi-channel carbon matrix nanofibers@MoS2-Ni	GCE	161	81	Adv. Funct. Mater. 2018, 8, 1807086.
Ultrathin CoP nanosheet aerogel	GCE	113	72	Small 2018, 14, 1802824.
Mo ₂ N–Mo ₂ C/holey reduced GO	GCE	157	55	Adv. Mater. 2018, 30, 1704156.
Monolayer MoS ₂	GCE	126	67	Adv. Energy Mater. 2018, 8, 1800734.
$Mo_{0.5}W_{0.5}S_2$	GCE	138	55	ACS Catal. 2018, 8, 9529.
1T-MoS ₂	GCE	230	45	ACS Energy Lett. 2018, 3, 7.
WS2/WO3/rGO	GCE	113	37	Nano Energy 2018, 47, 66.
NPNi-MoS2/rGO	GCE	205	71.3	ACS Catal. 2018, 8, 8107.
2D MoSe2 nanosheet	GCE	126	38	Small 2018, 14, 1704150.
MoS ₂ /hydrogenated G	GCE	124	41	ACS Catal. 2018, 8, 1828.
Ternary NiCo ₂ P _x Nanowire	Carbon felt	104	58.8	Adv. Mater. 2017, 29, 1605502.
Mo_2B_4	GCE	~260@3.5	80	J. Am. Chem. Soc. 2017, 139, 12915.
Crumpled MoS ₂	CC	193	66	Adv. Mater. 2017, 29, 1703863.
a-MoB2	GCE	149		J. Am. Chem. Soc. 2017, 139, 12370.
PtO _x /TiO ₂	GCE	~125	40	Energy Environ. Sci. 2017, 10, 2450.
Zn-MoS ₂	GCE	~140	51	J. Am. Chem. Soc. 2017, 139, 15479.
2D WC single crystal/G	GCE	120	38	Nano Energy 2017, 33, 356.
Monolayer MoS ₂	GCE	~220		J. Am. Chem. Soc. 2017, 139, 16194.
MoB_2	GCE	~240@3.5	75	Angew. Chem. Int. Ed. 2017, 56, 5575.
MoS ₂	Cu foil	~100	39	Sci. Adv. 2017, 3, e1602215.
1T-MoSe2 nanosheet	GCE	152	52	Adv. Mater. 2017, 29, 1700311.
MoSe2/Mo core-shell nanoscrew	Mo substrate	166	34.7	Adv. Mater. 2016, 28, 9831.
Metallic-phase MoS ₂	GCE	175	41	Nat. Commun. 2016, 7, 10672.
Mn doped CoSe2ultrathin nanosheet	GCE	174	36	J. Am. Chem. Soc. 2016, 138, 5087.
WS2/WO2.9	Graphite paper	~110	36	Adv. Mater. 2016, 29, 1603617.
1T-phase MoS2	GCE	~300@5	58	Adv. Mater. 2016, 28, 10033.

MoS2 with S-vacancy	GCE	170	60	Nat. Mater. 2016, 15, 48.
W ₂ C nanoparticle	GCE	123	45	Nat. Commun. 2016, 7, 13216.
MoO _x /MoS ₂ Core-Shell Nanotubular	GCE	259	63	Angew. Chem. Int. Ed. 2016, 55, 12252.
CoMoS3 hollow prism	GCE	171	56.9	Adv. Mater. 2016, 28, 92.
Rh ₂ S ₃	GCE	137	44	Energy Environ. Sci. 2016, 9, 850.
MoS0.94P0.53	GCE	~150	57	Adv. Mater. 2016, 28, 1427.
Se-enriched NiSe2 nanosheet array	CF	117	32	Angew. Chem. Int. Ed. 2016, 55, 6919.
Cu7S4@MoS2	GCE	133	48	Angew. Chem. Int. Ed. 2016, 55, 6502.
CoNi@N-doped carbon	GCE	142	105	Angew. Chem. Int. Ed. 2015, 54, 2100.
CoN _x /C	GCE	133	57	Nat. Commun. 2015, 6, 7992.
FeCo alloy@N-doped G	GCE	262	74	Energy Environ. Sci., 2015, 8, 3563.
β -Mo ₂ C nanotube	GCE	172	62	Angew. Chem. Int. Ed. 2015, 54, 15395.
Mo ₂ C@N-doped carbon	GCE	~120	60	Angew. Chem. Int. Ed. 2015, 54, 10752.
Edge-terminated MoS ₂	GCE	149	49	Nat. Commun. 2015, 6, 7493.
Ni5P4-Ni2P	Ni foam	120	79.1	Angew. Chem. Int. Ed. 2015, 54, 8188.
H-MoS ₂	GCE	167	98	Adv. Mater. 2015, 27, 7426.
Ni-doped G	GCE	~150	45	Angew. Chem. Int. Ed. 2015, 54, 14031.
MoCx	GCE	142	53	Nat. Commn. 2015, 6, 6512.
Co-C-N	GCE	138	55	J. Am. Chem. Soc. 2015, 137, 15070.
Co-N-doped G	GCE	~147	82	Nat. Commun. 2015, 6, 8668.
Fe-Ni-S	GCE	105	40	J. Am. Chem. Soc. 2015, 137, 11900.
MoCN	GCE	140	46	J. Am. Chem. Soc. 2015, 137, 110.
MoP	GCE	~130	54	Energy Environ. Sci. 2014, 7, 2624.
Cu ₃ P nanowire Array	CF	143	67	Angew. Chem. Int. Ed. 2014, 53, 9577.
МоР	GCE	125	54	Adv. Mater. 2014, 26, 5702.
CoP/CNT	GCE	122	54	Angew. Chem. Int. Ed. 2014, 53, 6710.
CoSe2 nanoparticle	CFP	137	41	J. Am. Chem. Soc. 2014, 136, 4897.
WS ₂ nanosheet	GCE	142	70	Energy Environ. Sci. 2014, 7, 2608.

Abbreviations: GCE = Glassy carbon electrode; G = Graphene; CC = Carbon cloth; FTO = Fluorine doped tin oxide; CFP = Carbon fiber paper; CW = Carbonized wood; GO = Graphene oxide; rGO = Reduced graphene oxide; CNT = Carbon nanotube.

Samples	$R_{ m s}\left(\Omega ight)$	$R_1(\Omega)$	CPE1 (F)	$R_{ m ct}\left(\Omega ight)$	CPE2 (F)
CNT-NS-1	2.28	0.49	3.56×10 ⁻¹²	54.37	2.83×10 ⁻⁷
CNT-NS-2	2.20	0.25	6.98×10 ⁻¹²	43.85	3.51×10-7
CNT-NS-3	2.15	0.20	8.72×10 ⁻¹²	33.65	4.57×10 ⁻⁷
CNT-NS-4	2.05	0.19	9.18×10 ⁻¹²	12.16	1.26×10 ⁻⁶
CNT-NS-5	2.11	0.23	7.58×10 ⁻¹²	23.63	6.51×10 ⁻⁷

Table S6. Parameters obtained by fitting the Nyquist plots of various CNT-NS catalysts using the equivalent circuit in *Fig. 4B*.