Supplementary Materials

Nitrogen-doped truncated carbon nanotubes inserted into nitrogen-doped graphene nanosheets with a sandwich structure: a highly efficient metal-free catalyst for the HER

Shuwen Li(#)*, Zhounan Yu(#), Yang Liu, Yuanyuan yang, Hai Zou, Honglei Yang, Jun Jin and Jiantai Ma*

State Key Laboratory of Applied Organic Chemistry, Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

(#) These authors contributed equally to this work and should be considered co-first authors.

* Corresponding authors. Tel./fax: +86 931 8912577.

E-mail addresses: lishw@lzu.edu.cn (Shuwen Li), majiantai@lzu.edu.cn (Jianati Ma)

1. Experimental

1.1 Materials

The graphene oxide (GO) was purchased commercially from XFNANO (Nanjing, China). The water was doubly distilled and deionized in the experiments (18 MΩ cm^{-1}). All chemical reagents were bought commercially without further purification.

1.2 Preparation procedures

TCNT-ao. The MWCNTs (200 mg) were treated in mixed acid (200 mL) which contained concentrated sulfuric acid (150 mL) and concentrated nitric acid (50 mL) at 70^{o}Cfor 4 h. The mixture was diluted to 10 times and the product was washed with deionized water until neutral and collected by centrifugation and vacuum filtration, and then dried at 60 ^{o}C in vacuum oven.

N-TCNT@NGS. The GO was ultrasonicated in deionized water (20 mL) until uniformly dispersion. The TCNT-ao was pretreated through the same way. And then the urea (1.2 g) was added into this dispersion system, after the intermixture of TCNT-ao was doped in the GO aqueous dispersion while stirring. After being violently stirred for 30 min, this mixture was sealed in a Teflon-lined autoclave (50 mL) and maintained at 160 ^{o}C for 3 h in a muffle furnace. After then, the solid which was in this mixture was separated through membrane by vacuum filtration and washed with deionized water and absolute ethyl repeatedly. The product was dried in vacuum oven at 60 ^{o}C for 8 h. Finally we got N-TCNT@NGS as a kind of black powder. We prepared five kinds of product which have different mass ratios of TCNT-ao to GO, and they were 1:1 (N-TCNT@NGS1), 1:2 (N-TCNT@NGS2), 1:4 (N-TCNT@NGS4), 1:6 (N-TCNT@NGS6), 1:8 (N-TCNT@NGS8), respectively.The usage of every reagent was showed in the Table S1

NGS and N-TCNT. The similar method was used to prepare the NGS and N-TCNT, but the only difference was that there was no TCNT-ao in the preparation of NGS and vice versa.

2. Materials characterization

The morphologies and microstructures of synthesized catalysts were studied by transmission electron microscope (TEM, FEI Tecnai G^2 F^{30}, USA) operated at 300 kv, equipped with an energy-dispersive X-ray spectroscopy (EDS, AMETEK, USA) analyzer. More TEM pictures of N-TCNT@NGS2 are shown in Fig. S1 and the raw data of elemental mapping are shown in Fig. S2. Powder X-ray diffraction (XRD) data was collected by utilizating a Rigaku D/max-2400 diffractometer with Cu-Ka

radiation as the radiation source. Raman spectra were collected on a Jobin-Yvon LabRam HR80 spectrometer (Horiba Jobin Yvon, Inc.) with 532 nm laser as the excitation source. The surface chemical composition was evaluated by X-ray photoelectron apectroscopy (XPS, ESCALAB210, VG, UK). The typical XPS survey of NGS, N-TCNT and N-TCNT@NGS2 and the signal of the high resolution O1s are shown in Fig. S3.

3. Electrochemical measurement

All of the electrochemical measurements were performed on an electrochemical workstation (CHI model 760E, Shanghai Chenhua Instrument Factory, China). The used electrolyte was 0.5M H_2SO_4 which had been degassed with N_2 for half an hour. Every sample (4 mg) was scattered by 0.5 wt% Nafion solution (Alfa Aesar)(200 μL), isopropanol (1 mL) and deionized water(1 mL) and the catalyst ink(5μL) was doped onto a polished glass carbon electrode (GCE, diameter:3.0 mm) and then the ink was dried out in air. We used Pt electrodeas counter electrode and the reference electrode is Ag/AgCl (in 3 M KCl solution).

The curve of (LSV) was carried out with a scan rate of 5 mV s^{-1} from 0.1 V to -1.0 V. Every electrode was cycled with a scan rate of 50 mV s^{-1} until the catalytic effect is stable. According to the Tafel slop and the Bulter-Volmer formula, the exchange current density j^0 can be obtained:

$$\eta = -\frac{2.3RT}{\beta Fn}\lg j^0 + \frac{2.3RT}{\beta Fn}\lg j \quad (1)$$

The $\eta$is overpotential,βtransfer coefficient,R gas constant (8.314 J K^{-1}), T temperature, F Faraday constant (96500 C mol^{-1}), n the number of transferred electrons. j^0, the statistics of onset overpotential (E_S) and the operating overpotentials (E_P) at 10 mA cm^{-2} current are presented in Table S4.

The result of electrochemical impedance spectra (EIS) was obtained at -0.25V with 10^5 HZ as high frequency and 0.01 HZ as low frequency.

***IR* compensation** was expressed by following formulas:

$$E_{correction} = I \times R \quad (2)$$

$$E_{corrected} = E_{uncorrected} - I \times R \quad (3)$$

E is potential, I is momentary current and R is resistance, which could be measured from electrochemical workstation directly.

4. Figures and Tables.

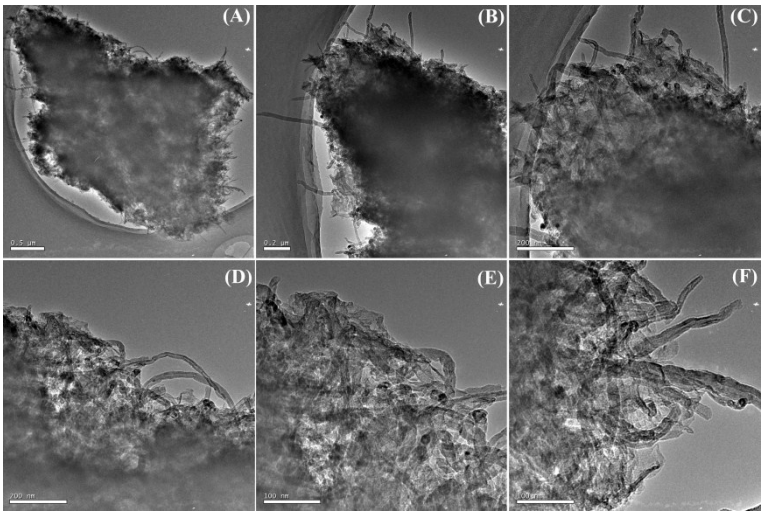

Fig. S1 (A-F) The TEM pictures of N-TCNT@NGS2 in different scales.

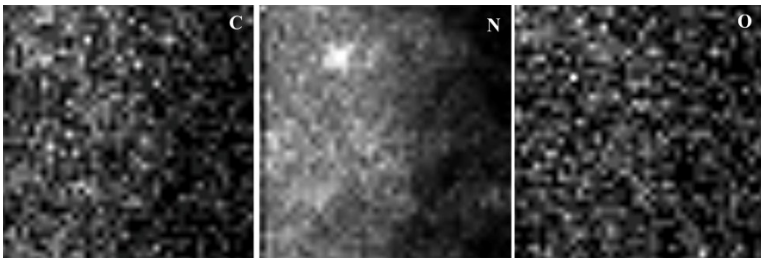

Fig. S2 The raw data of elements mapping

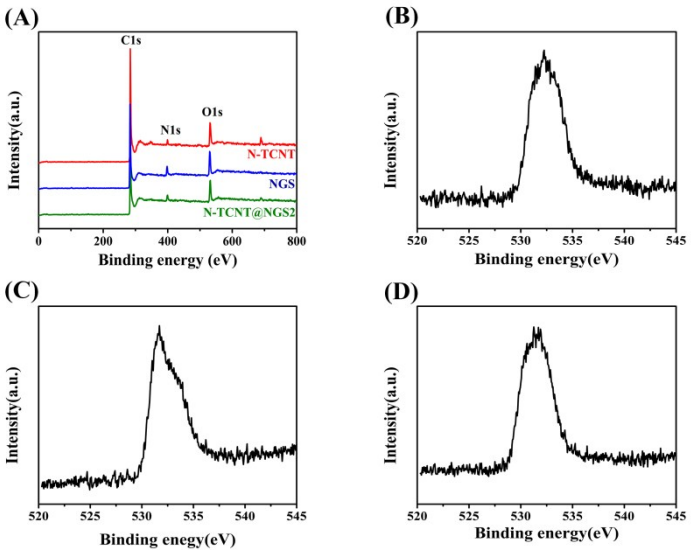

Fig. S3 (A) The XPS results of three kinds of samples. (B-D) The O1s results of N-TCNT@NGS2, N-TCNT, NGS respectively.

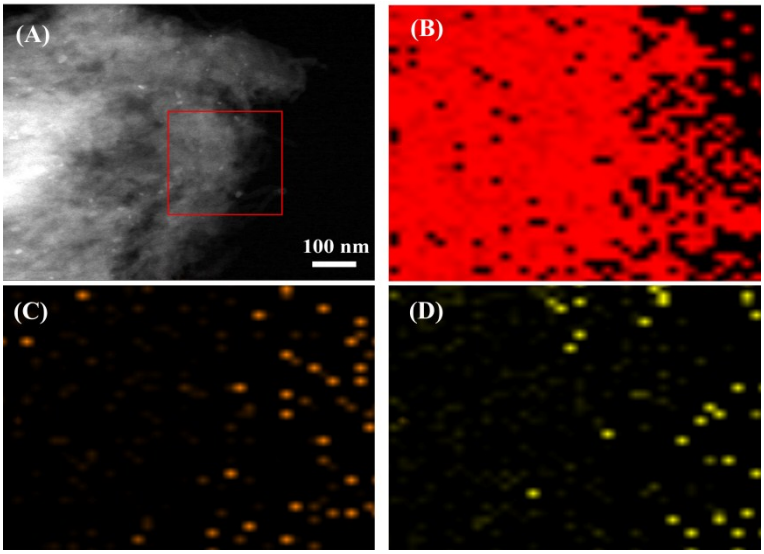

Fig. S4 The mapping result of C, N, O elements in TEM. (A) The mapping range is shown in red rectangle. (B, C, D) The carbon, oxygen and nitrogen distribution in the inside structure of N-TCNT@NGS2.

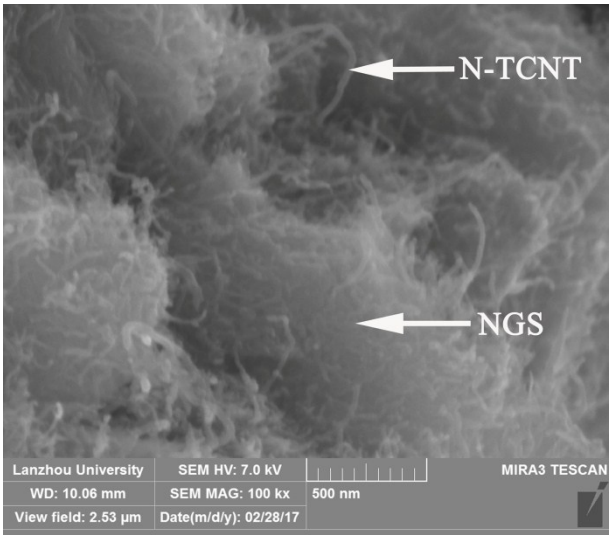

Fig. S5 The SEM picture of N-TCNT@NGS2.

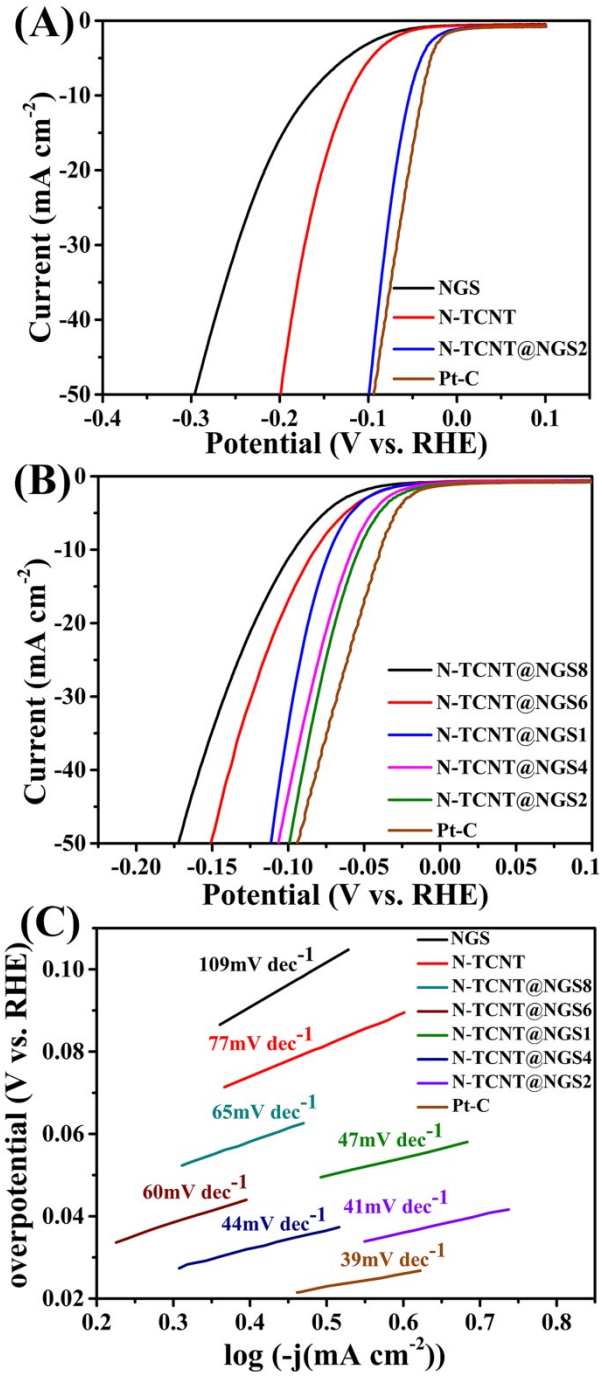

Fig. S6 (A) The LSV curves of NGS, N-TCNT and N-TCNT@NGS2 after IR compensation. (B) The LSV curves of N-TCNT@NGS in different mass rateswith IR compensation. (C) The Tafel slops of sampleswith IR compensation.

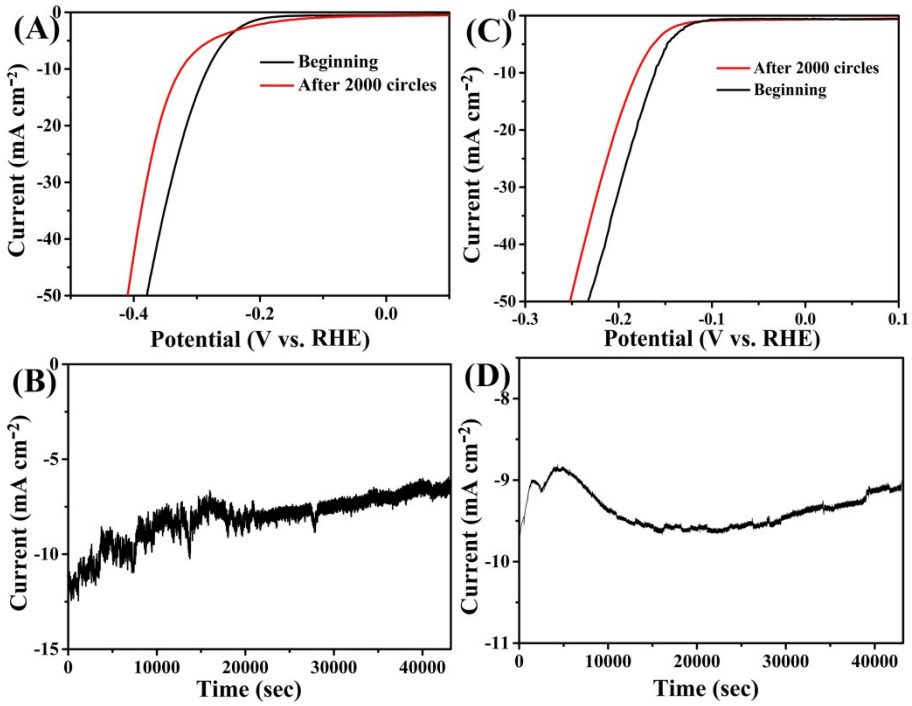

Fig. S7 The LSV curves of NGS (A) and N-TCNT (C) with different working circles.The i-t curve of NGS (B) and N-TCNT (D).

Table S1 The weight of every raw material.

Sample	GO mg^{-1}	TCNT-ao mg^{-1}
NGS	70	0
N-CNT@NGS1	35	35
N-CNT@NGS2	46	23
N-CNT@NGS4	56	14
N-CNT@NGS6	60	10
N-CNT@NGS8	64	8
N-CNT	0	70

Table S2 N1s analysis of as-synthesized catalysts

Samples	Pyridinic N		Pyrrolic N		Graphitic N	
	E_B/eV	AP%	E_B/eV	AP%	E_B/eV	AP%
NGS	398.6	34.42	399.7	38.91	400.9	26.67
N-TCNT@NGS2	398.5	13.25	399.8	50.79	401.2	35.96
N-TCNT	398.8	22.01	399.8	41.11	400.9	36.88

E_B: binding energy; AP: atomic percentage. The quantitative analysis of N1s was obtained according to the XPS analysis.

Table S3 Elemental analysis of as-synthesized catalysts

Samples	N (wt%)	C (wt%)	H (wt%)
NGS	7.38	68.04	1.091
N-TCNT@NGS6	5.40	69.78	1.343
N-TCNT@NGS4	5.44	70.39	1.254
N-TCNT@NGS2	4.23	73.56	1.087
N-TCNT@NGS1	4.20	72.99	1.009
N-TCNT	2.05	77.91	0.537

The contents of atoms were determined using combustion CHN method.

Table S4 The exchange current density j^0, onset overpotential (E_S) and operating overpotentials at 10 mA cm^{-2} (E_P).

Samples	E_S mV	E_P mV	j^0 mA cm^{-2}
Pt-C	-1	-40	0.63
N-TCNT@NGS2	-16	-62	0.65
N-TCNT@NGS4	-23	-66	0.55
N-TCNT@NGS1	-35	-81	0.31
N-TCNT@NGS6	-36	-90	0.47
N-TCNT@NGS8	-48	-104	0.34
N-TCNT	-60	-129	0.30
NGS	-71	-175	0.38

Table S5 The date about j^0, E_S and $E_P$with IR compensation.

Samples	E_S mV	E_P mV	j^0 mA cm^{-2}
Pt-C	-1	-40	0.63
N-TCNT@NGS2	-8	-53	0.55
N-TCNT@NGS4	-16	-58	0.52
N-TCNT@NGS1	-26	-72	0.24
N-TCNT@NGS6	-27	-82	0.46
N-TCNT@NGS8	-39	-96	0.32
N-TCNT	-52	-122	0.27
NGS	-63	-170	0.37

To show the excellent catalytic performance of N-TCNT@NGS, the comparison of materials and performance of other carbon-based metal-free HER catalysts is shown in Table S6.

Table S6 Comparison of materials and performance of metal-free HER catalysts.

Sample	Onset potential (V)	Potential at 10 mA cm^{-2} (V)	Tafel slope ($mV\ dec^{-1}$)	Electrolyte	Ref.
N-TCNT@NGS2	**-0.016**	**-0.062**	**50**	**0.5 M H_2SO_4**	**In work**
Activated CNTs	-0.05	-0.22	71.3	0.5 M H_2SO_4	[1]
N,S codoped nanoporous graphene	-0.14	-0.39	80.5	0.5 M H_2SO_4	[2]
N,S codoped CNTs	-0.05	-0.12	67.8	0.5 M H_2SO_4	[3]
N,P codoped nanoporous carbon	-0.076	-0.204	58.4	0.5 M H_2SO_4	[4]
g-C_3N_4 nanoribbon graphene	-0.08	-0.2	54	0.5 M H_2SO_4	[5]
g-C_3N_4 and N,P codoped graphene	-0.076	-0.34	90	0.5 M H_2SO_4	[6]
N-rich holey graphene monoliths	-180	-340	99	0.5 M H_2SO_4	[7]
g-C_3N_4@N-doped graphene	-120	-240	51.5	0.5 M H_2SO_4	[8]
C_3N_4-nanolayers@N-graphene porous films	-8	-80	49.1	0.5 M H_2SO_4	[9]
g-C_3N_4 and S, Se codoped graphene	-96	-300	86	0.5 M H_2SO_4	[10]
N, P codoped graphene	-200	-420	91	0.5 M H_2SO_4	[11]
B-substituted graphene	-220	-470	99	0.5 M H_2SO_4	[12]
N-doped mesoporous graphene	-150	-240	109	0.5 M H_2SO_4	[13]
N,P codoped nanoporous graphene	-120	-213	79	0.5 M H_2SO_4	[14]
Poly(3,4-dinitrothiophene)/SWCNTs	-32	-120	---	1 M H_2SO_4	[15]

For the convenience of comparison, the measure potentials vs. Ag/AgCl were converted to a

reversible hydrogen electrode (RHE) scale according to the Nerst equation ($E_{RHE}=E_{Ag/AgCl}+0.059\times pH+0.198$)

References

1. N. Y. Cheng, Q. Liu, J. Q. Tian, Y. R. Xue, A. M. Asiri, H. F.Jiang, Y. Q. Hee, X. P. Sun, *Chem. Commun.*, 2014, 50, 9340-9342.

2. Y. Ito, W. T. Cong, T. Fujita, Z. Tang, M. W. Chen, *Angew.Chem. Int. Ed.*, 2015, 54, 2131-2136.

3. Y. C. Zhou, Y. H. Leng, W. J. Zhou, J. L. Huang, M. W. Zhao, J.Zhan, C. H. Feng, Z. H. Tang, S. W. Chen, H. Liu, *Nano Energy*, 2015, 16, 357-366.

4. L. Wei, H. E. Karahan, K. Goh, W. C. Jiang,. Birer,R. R. Jiang, Y. Chen, *J. Mater. Chem. A*, 2015, 3, 7210-7214.

5. Y. Zhao, F. Zhao, X. P. Wang, C. Y. Xu, Z. P. Zhang, G. Q. Shi,L. T. Qu, *Angew. Chem. Int. Ed*., 2014, 53, 13934-13939.

6. S. S. Shinde, A. Sami, J. H. Lee, *ChemCatChem*, 2015, 7, 3873-3880.

7. J. M. Ge, B. Zhang, L. B. Lv, H. H. Wang, T. N. Ye, X. Wei, J. Su,K. X. Wang, X. H. Lin, J. S. Chen, *Nano Energy*, 2015, 15, 567-575.

8. Y. Zheng, Y. Jiao, Y. H. Zhu, L. H. Li, Y. Han, Y.Chen, A. J. Du, M. Jaroniec, S. Z. Qiao, *Nat. Commun.*, 2014, 5,3783.

9. J. J. Duan, S. Chen, M. Jaroniec, S. Z. Qiao, *ACS Nano*, 2015, 9,931-940.

10. S. S. Shinde, A. Sami, J. H. Lee, *J. Mater. Chem. A*, 2015, 3,12810-12819.

11. Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec, S. Z.Qiao, *ACS Nano*, 2014, 8, 5290-5296.

12. B. R. Sathe, X. X. Zou, T. Asefa, *Catal. Sci. Technol.*, 2014, 4,2023-2030

13. X. D. Huang, Y. F. Zhao, Z. M. Ao, G. X. Wang, *Sci. Rep.*, 2014,4, 7557.

14. H. L. Jiang, Y. H. Zhu, Y. H. Su, Y. F. Yao, Y. Y. Liu, X. L.Yang, C. Z. Li, *J. Mater. Chem. A*, 2015, 3, 12642-12645.

15. K. Xie, H. P. Wu, Y. N. Meng, K. Lu, Z. X. Wei, Z. Zhang, *J.Mater. Chem. A*, 2015, 3, 78-82.