

## Supporting Information

### O, N Co-doped 3D graphene Hollow Sphere Derived from Metal-Organic Frameworks as Oxygen Reduction Reaction Electrocatalysts for Zn-air batteries

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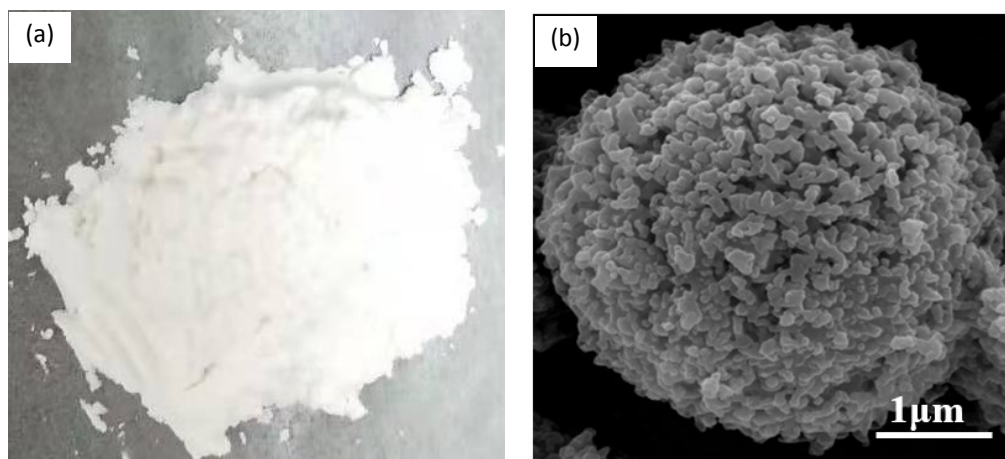


Figure S1. (a) Optical photo of Zn-BTC. (b) FESEM of Zn-BTC.

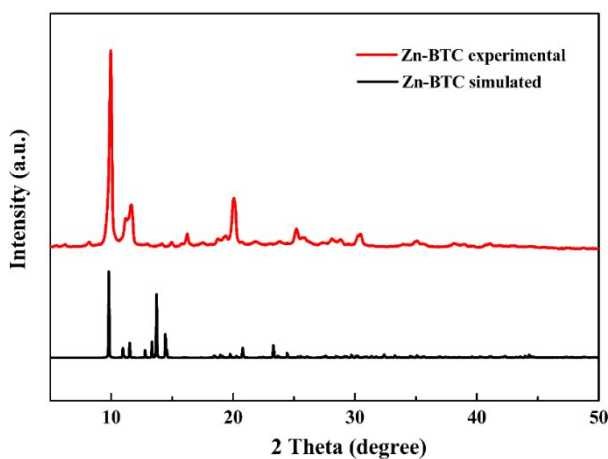


Figure S2. XRD pattern of Zn-BTC

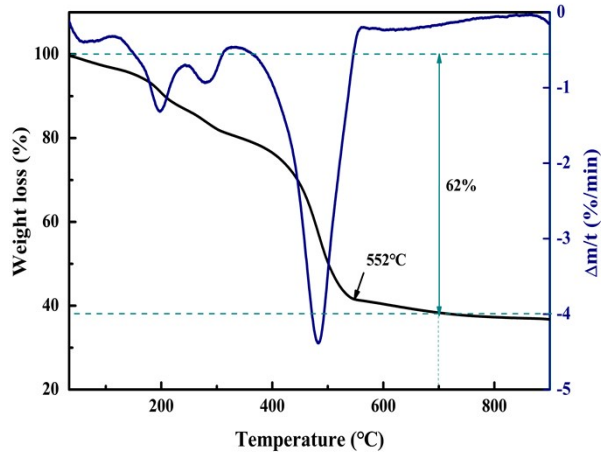


Figure S3. TGA curve of Zn-BTC precursor under nitrogen atmosphere.

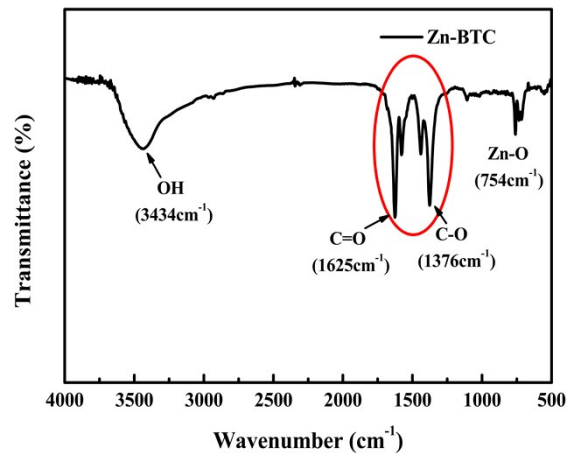


Figure S4. FTIR pattern of Zn-BTC precursor

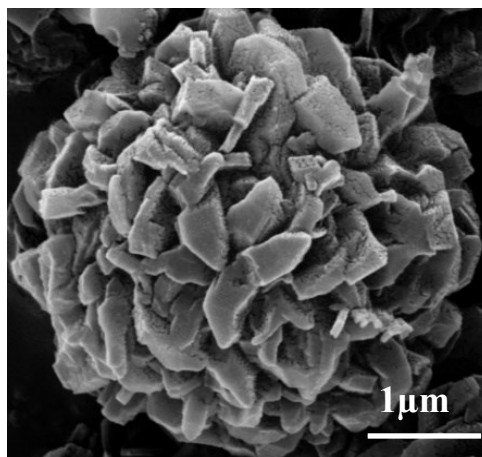


Figure S5. (a) FESEM of ZnO/C.

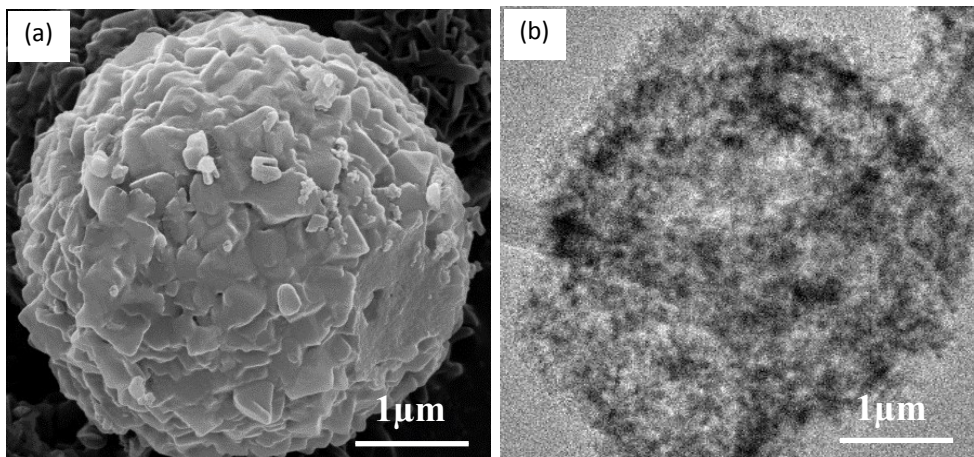


Figure S6. (a) FESEM of ZnO/C-HCl. (b) HRTEM of ZnO/C-HCl.

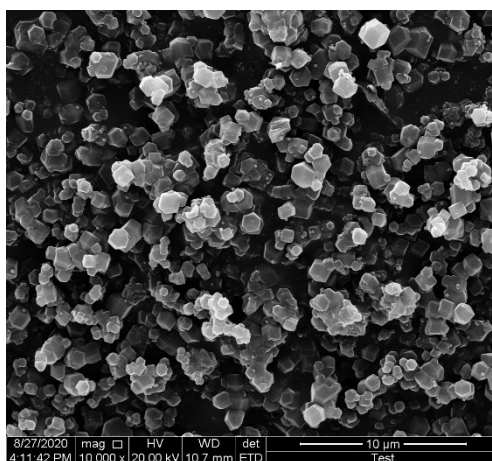


Figure S7. (a) FESEM of N-graphene.

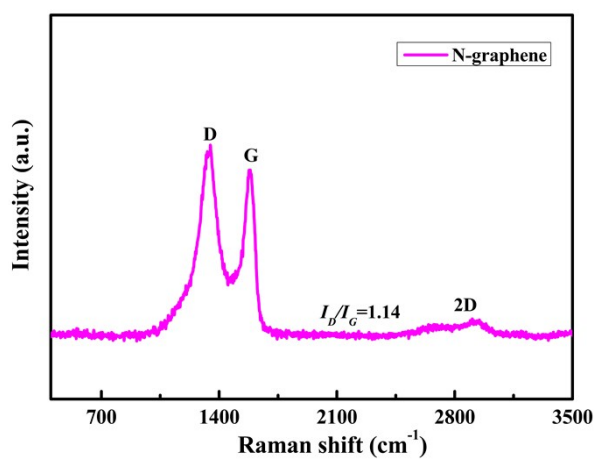


Figure S8. Raman spectra of N-graphene.

Table S1. BET surface areas and pore volumes of the N-graphene, ZnO/C, ZnO/C-HCl, and O, N-graphene

Sample	BET surface area ( $\text{m}^2\text{g}^{-1}$ )	$V_{\text{micropore}}/$ $V_{\text{micropore+mesopore}}$	$V_{\text{mesopore}}/$ $V_{\text{micropore+mesopore}}$	Total pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Pore size (nm)
N-graphene	697.6	19%	81%	0.394	2.26
ZnO/C	1577.44	30%	70%	1.01	2.50
ZnO/C-HCl	1621.58	21%	79%	1.11	2.81
O, N-graphene	1801.45	21.6%	78.4%	1.43	3.18

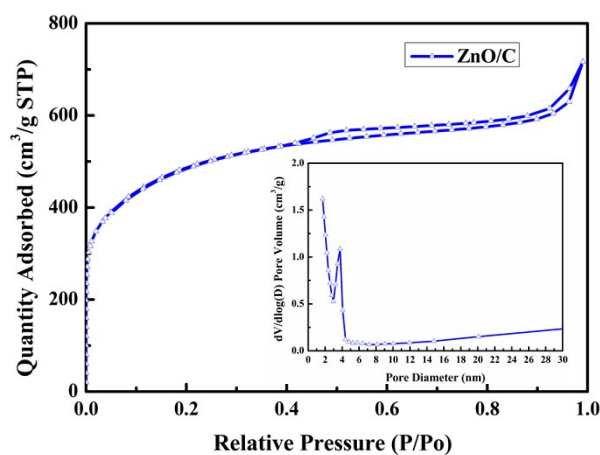


Figure S9. Nitrogen adsorption-desorption isotherm of ZnO/C, and inset shows the corresponding pore size distribution of ZnO/C.

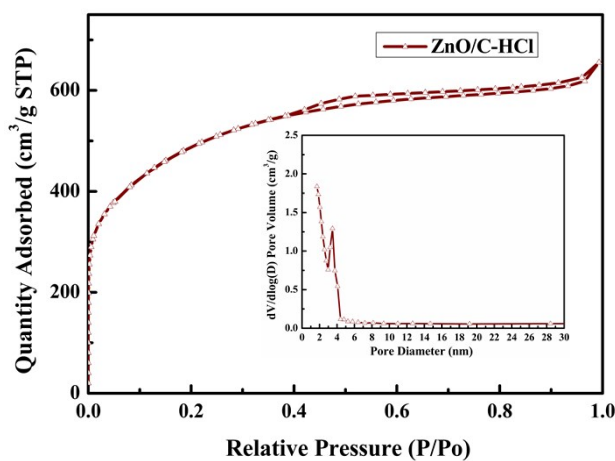


Figure S10. Nitrogen adsorption-desorption isotherm of ZnO/C-HCl, and inset shows the

corresponding pore size distribution of ZnO/C-HCl.

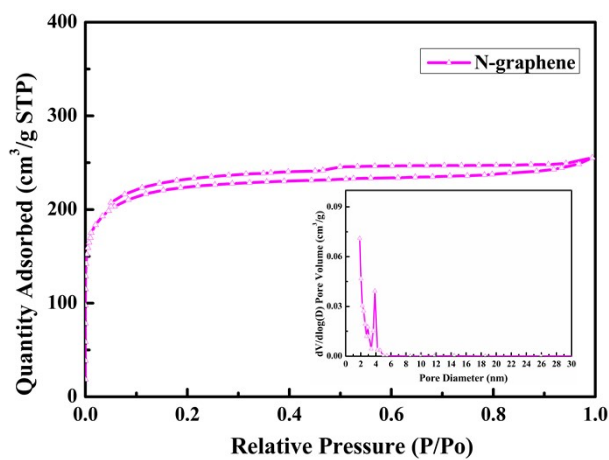


Figure S11. Nitrogen adsorption-desorption isotherm of N-graphene, and inset shows the corresponding pore size distribution of N-graphene.

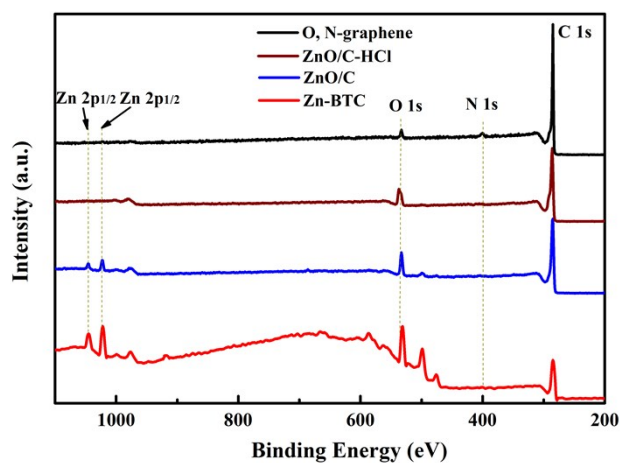


Figure S12. XPS survey spectra for Zn-BTC, ZnO/C, ZnO/C-HCl, and O, N-graphene.

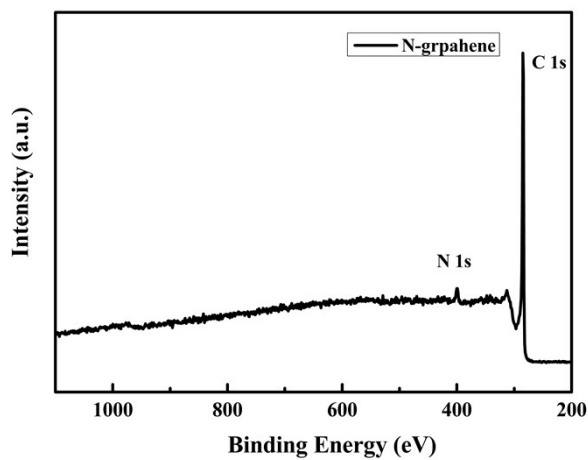


Figure S13. XPS survey spectra of N-graphene.

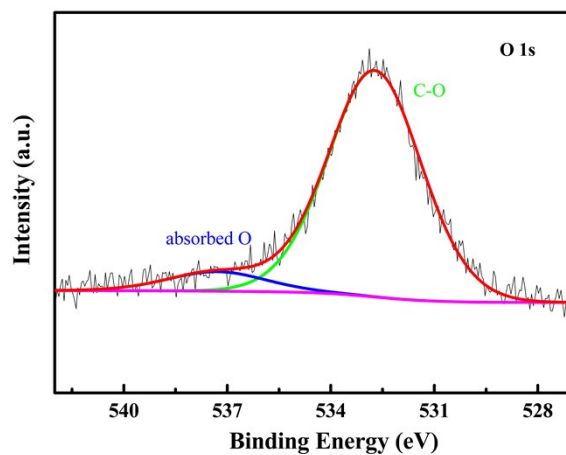


Figure S14. O 1s XPS spectra of O, N-graphene.

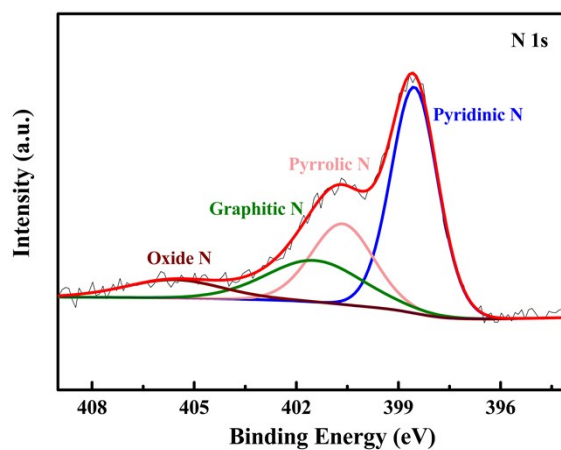


Figure S15. N 1s XPS spectra of N-graphene.

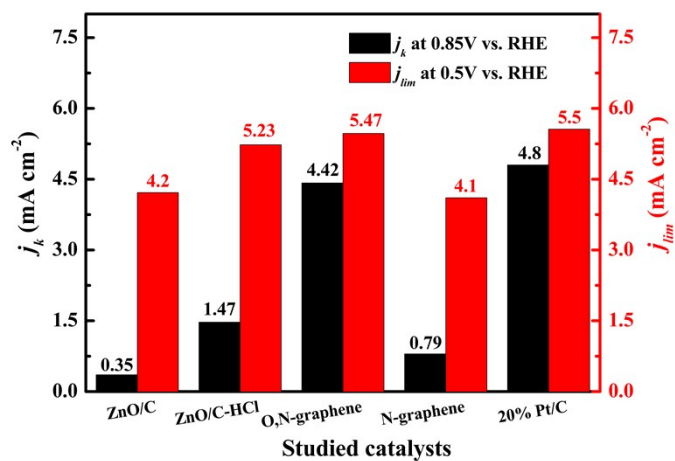


Figure S16. Onset potential and half-wave potential of ZnO/C, ZnO/C-HCl, O, N-graphene, N-graphene, and 20wt% Pt/C.

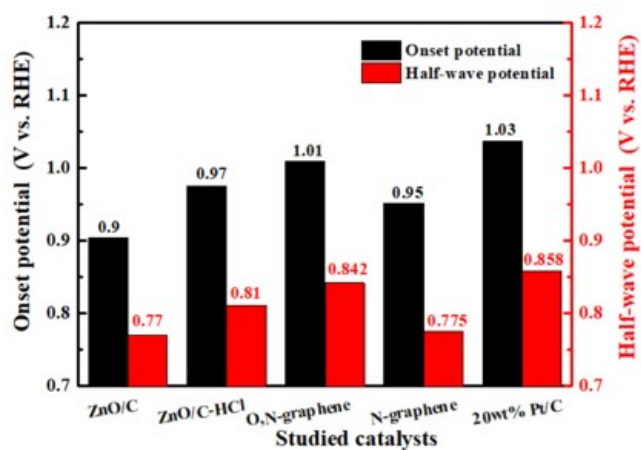


Figure S17. Kinetic current density at 0.85 V vs. RHE and limiting current density at 0.5 V vs. RHE of ZnO/C, ZnO/C-HCl, O, N-graphene, N-graphene, and 20wt% Pt/C.

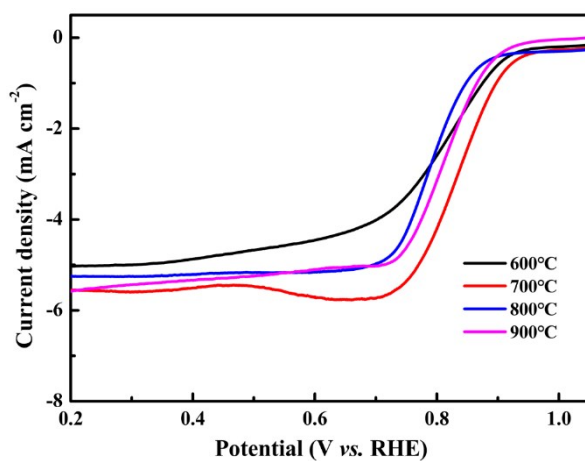


Figure S18. LSV curves of O, N-graphene pyrolyzed at different temperatures at  $10 \text{ mV s}^{-1}$ .

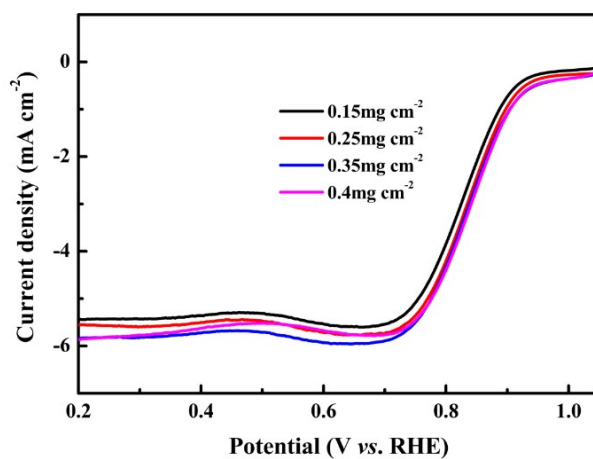


Figure S19. LSV curves of O, N-graphene under different loads at  $10 \text{ mV s}^{-1}$  and a rotating speed of 1600 rpm.

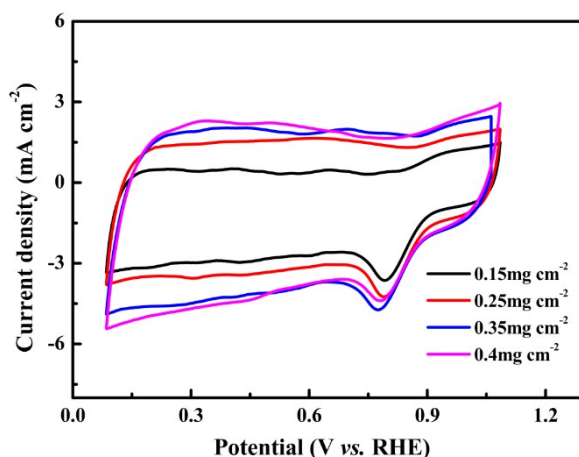


Figure S20. CV curves of O, N-graphene under different loads at 50 mV/s.

Table S2. Comparison of electrocatalytic activities of O, N-graphene with the state-of-the-art catalysts

Items	Catalyst	Dopped elements	Onset potential	Half-wave potential	Diffusion-limited Current density	Loading (0.1 M KOH)	Reference
1	O, N-graphene	O, N	1.01 vs. RHE	0.842 vs. RHE	5.47 mA cm <sup>-2</sup>	0.25	This work
2	NOGB-800	N, O	0.92 vs. RHE	0.84 vs. RHE	5.5 mA cm <sup>-2</sup>	0.4	1
3	BNPC-1100	N, P	0.894 vs. RHE	0.803 vs. RHE	4.73 mA cm <sup>-2</sup>	0.4	2
5	N, S-CN	N, S	0.92 vs. RHE	0.77 vs. RHE	5.35 mA cm <sup>-2</sup>	0.2	3
6	N-doped graphene	N	0.95 vs. RHE	-	-	0.2	4
7	GH-BGQD	B	0.93 vs. RHE	-	5.74 mA cm <sup>-2</sup>	-	5
8	N-graphene/CNT	N	0.98 vs. RHE	0.69 vs. RHE	-	0.2	6
9	BCN Graphene	B, N	-	-0.25 V vs. SCE	-	-	7
10	PG	P	0.92 vs. RHE	-	-	0.051	8
11	N-RGO-800	N	0.876 vs. RHE	0.725 vs. RHE	5.21 mA cm <sup>-2</sup>	-	9
12	S <sub>1</sub> N <sub>6</sub> C-900	N, S	0.95 vs. RHE	0.83 vs. RHE	4.86 mA cm <sup>-2</sup>	-	10
13	N-GA-150	N	-	0.77 vs. RHE	-	0.102	11



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- 1 Q. Hu, G. Li, G. Li, X. Liu, B. Zhu, X. Chai, Q. Zhang, J. Liu, C. He, *Advanced Energy Materials*, 2019, **9**(14), 1803867.
  - 2 J. Zhang, Z. Zhao, Z. Xia, L. Dai, *Nature Nanotechnology*, 2015, **10**, 444-452.
  - 3 K. Qu, Y. Zheng, S. Dai, S. Z. Qiao, *Nano Energy*, 2016, **19**, 373-381.
  - 4 H. Cui, M. Jiao, Y. Chen, Y. Guo, L. Yang, Z. Xie, Z. Zhou, S. Guo, *Small Methods*, 2018, **2**(10), 1800144.
  - 5 T. V. Tam, S. G. Kang, M. H. Kim, S. G. Lee, S. H. Hur, J. S. Chung, W. M. Choi, *Advanced Energy Materials*, 2019, **9** (26), 1900945.
  - 6 Z. Wen, S. Ci, Y. Hou, J. Chen, *Angew. Chem. Int. Ed.*, 2014, **53**, 6496-6500.
  - 7 S. Wang, L. Zhang, Z. Xia, A. Roy, D. W. Chang, J. B. Baek, L. Dai, *Angewandte Chemie International Edition*, 2012, **51**(17), 4209-4212.
  - 8 C. Zhang, N. Mahmood, H. Yin, F. Liu, Y. Hou, *Advanced materials*, 2013, **25**(35), 4932-4937.
  - 9 H. Miao, S. Li, Z. Wang, S. Sun, M. Kuang, Z. Liu, J. Yuan, *International Journal of Hydrogen Energy*, 2017, **42**(47), 28298-28308.
  - 10 J. Li, Y. Zhang, X. Zhang, J. Huang, J. Han, Z. Zhang, X. Han, P. Xu, B. Song, *ACS applied materials & interfaces*, 2017, **9**(1), 398-405.
  - 11 Q. Xue, Y. Ding, Y. Xue, F. Li, P. Chen, Y. Chen, *Carbon*, 2018, **139**, 137-144.