

## Electronic Supplementary Information

# Metal-Organic Framework-Derived Hybrid of Fe<sub>3</sub>C Nanorods-Encapsulated, N-Doped CNT on Porous Carbon Sheet for Highly Efficient Oxygen Reduction and Water Oxidation

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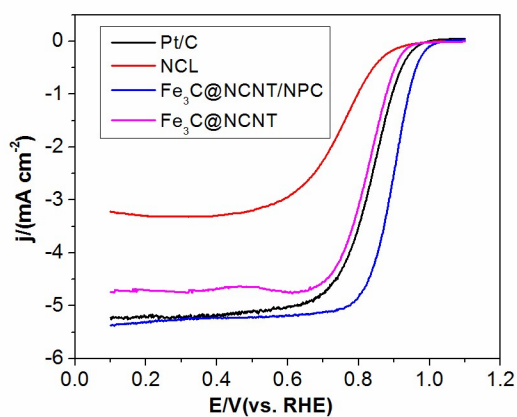


Figure S1. Steady-state polarization curves of ORR obtained with the samples prepared at different temperatures.

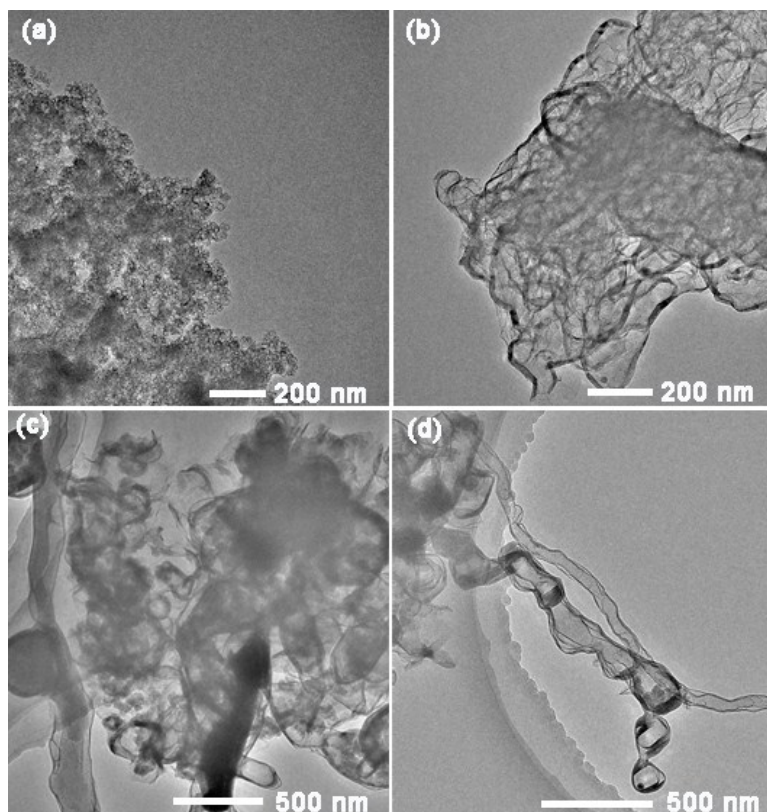


Figure S2. TEM images of the catalysts  $\text{Fe}_3\text{C}@\text{NCNT}/\text{NPC}$  obtained at different reaction stage (a, 0h), (b, 0.5h), (c-d, 1h).

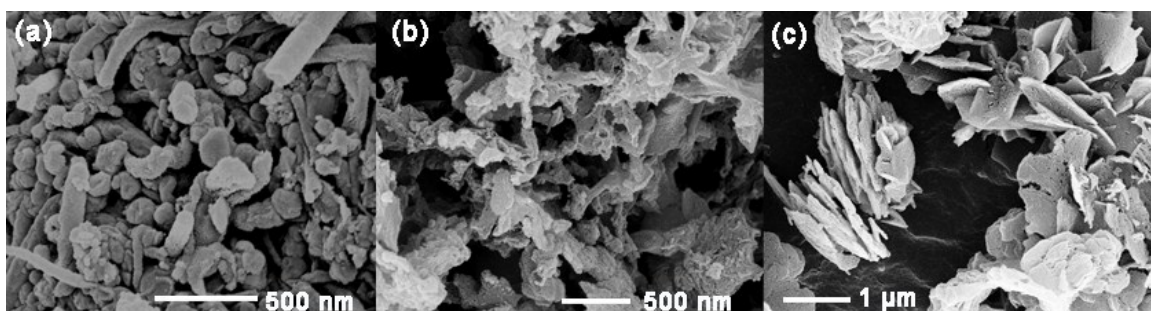


Figure S3. SEM images of the catalysts annealed at 800 °C: (a) with adding 50 wt% melamine; (b) with reducing 50 wt% melamine; (c) pure MOF.

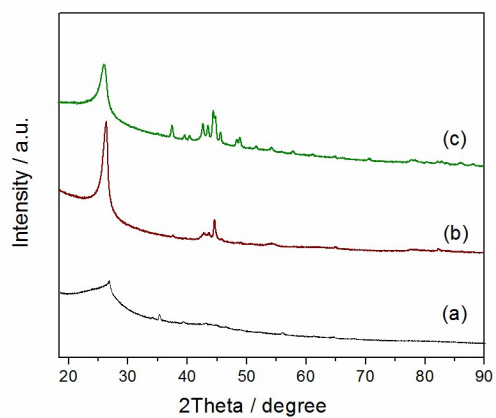


Figure S4. XRD of (a) NCL, (b)  $\text{Fe}_3\text{C@NCNT/NPC}$ , (c)  $\text{Fe}_3\text{C@NCNT}$ .

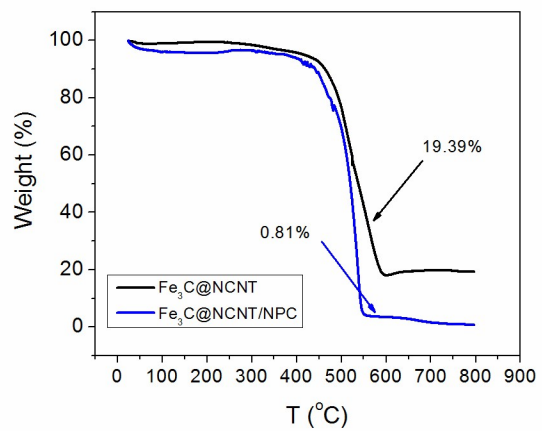


Figure S5. TGA of  $\text{Fe}_3\text{C@NCNT/NPC}$  and  $\text{Fe}_3\text{C@NCNT}$ .

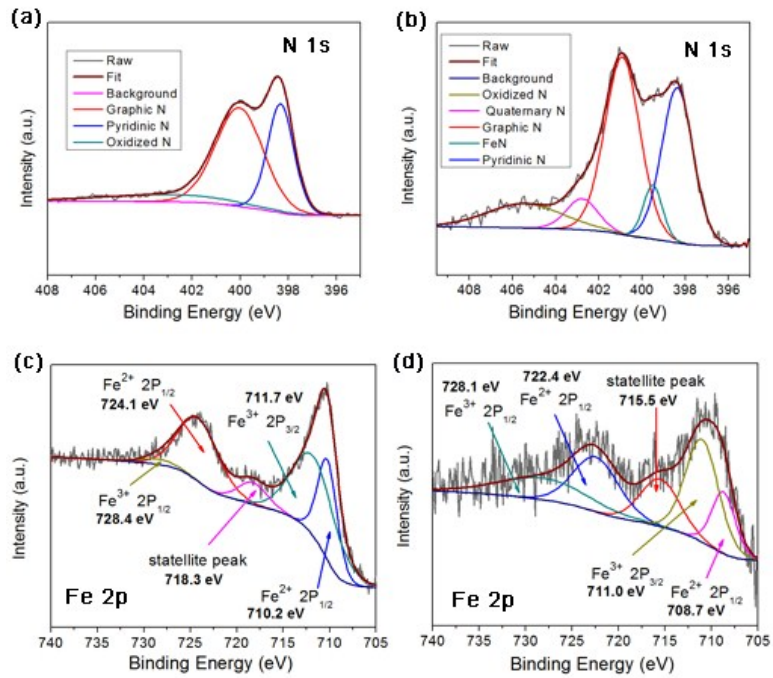


Figure S6. The high-resolution N 1s and Fe 2p spectrum of (a, c) NCL, (b, d) Fe<sub>3</sub>C@NCNT.

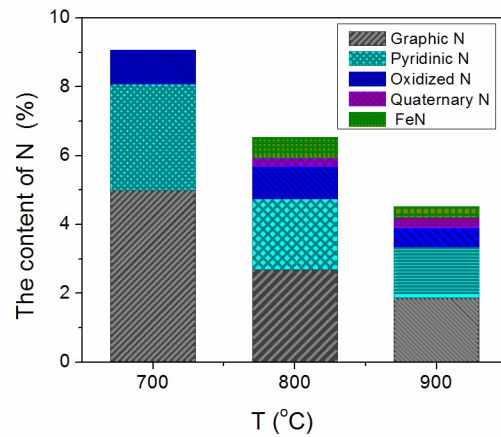


Figure S7. The content of N at different temperatures of 700, 800 and 900 °C for NCL, Fe<sub>3</sub>C@NCNT/NPC and Fe<sub>3</sub>C@NCNT respectively.

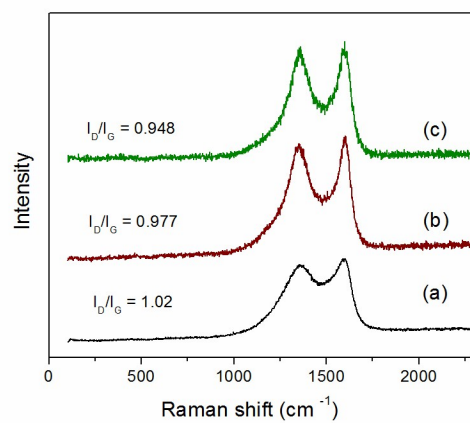


Figure S8. Raman spectrum of (a) NCL, (b) Fe<sub>3</sub>C@NCNT/NPC, (c) Fe<sub>3</sub>C@NCNT.

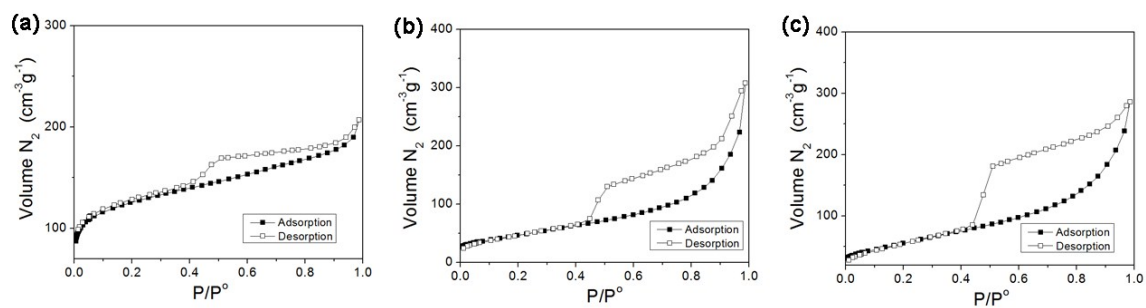


Figure S9. N<sub>2</sub> adsorption-desorption isotherms of (a) NCL, (b) Fe<sub>3</sub>C@NCNT/NPC, (c) Fe<sub>3</sub>C@NCNT.

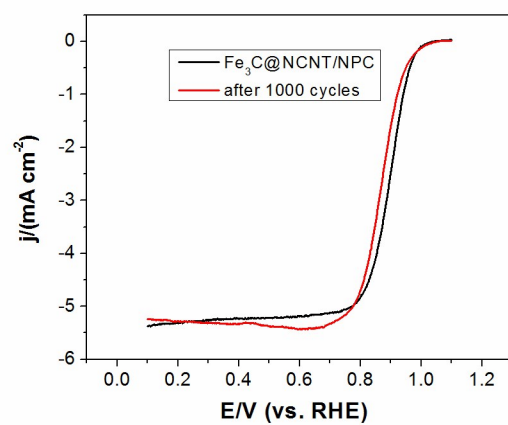


Figure S10. Steady-state polarization curves of ORR obtained with the samples of Fe<sub>3</sub>C@NCNT/NPC after 1000 cycles in 0.1M KOH solution.

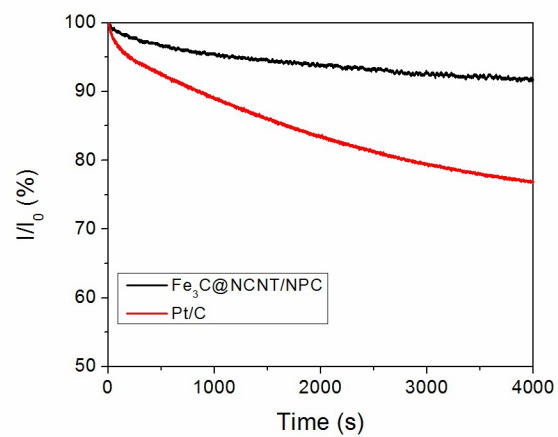


Figure S11. i-t result of Fe<sub>3</sub>C@NCNT/NPC and Pt/C in 0.1 M KOH solution.

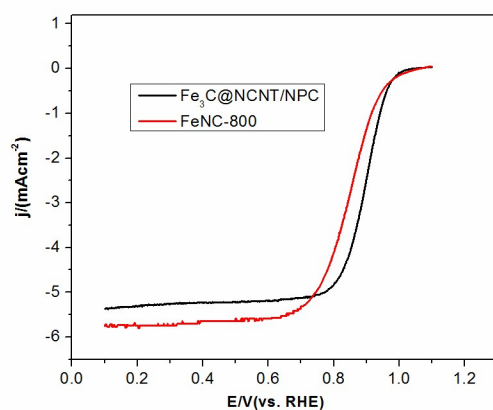


Figure S12. Steady-state polarization curves of ORR obtained with the samples of FeNC-800 and Fe<sub>3</sub>C@NCNT/NPC in 0.1M KOH solution.

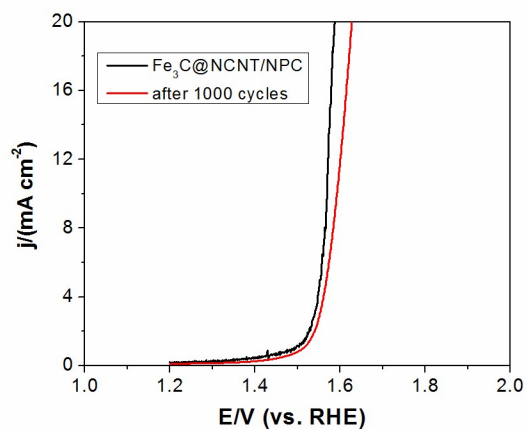


Figure S13. Steady-state polarization curves of ORR obtained with the samples of Fe<sub>3</sub>C@NCNT/NPC after 1000 cycles in 0.1M KOH solution.

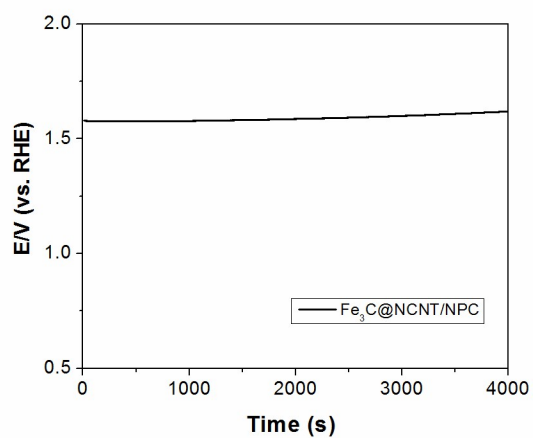


Figure S14. v-t result of  $\text{Fe}_3\text{C@NCNT/NPC}$  toward OER in 0.1 M KOH solution.

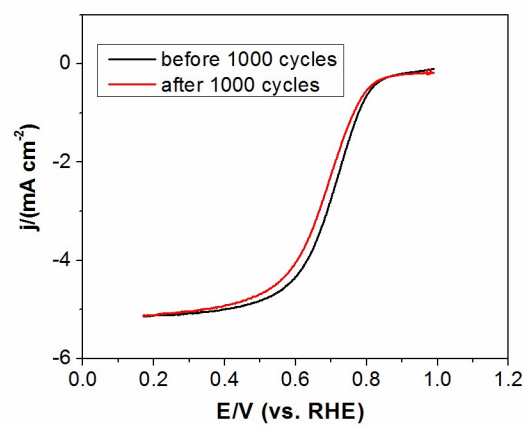


Figure S15. Steady-state polarization curves of ORR obtained with the samples of  $\text{Fe}_3\text{C@NCNT/NPC}$  after 1000 cycles in 0.5 M  $\text{H}_2\text{SO}_4$  solution.



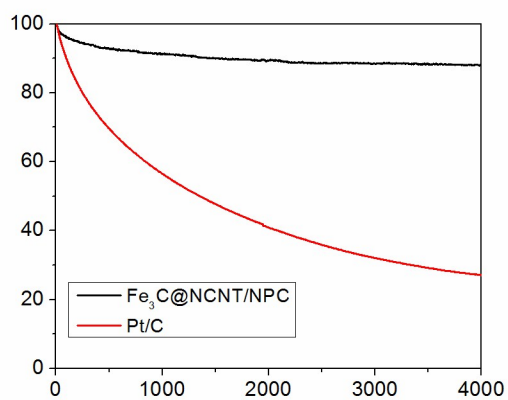


Figure S16. i-t result of Fe<sub>3</sub>C@NCNT/NPC and Pt/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

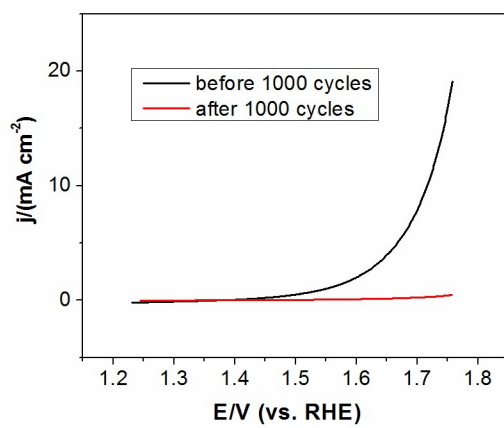


Figure S17. Steady-state polarization curves of OER obtained with the samples of Fe<sub>3</sub>C@NCNT/NPC after 1000 cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

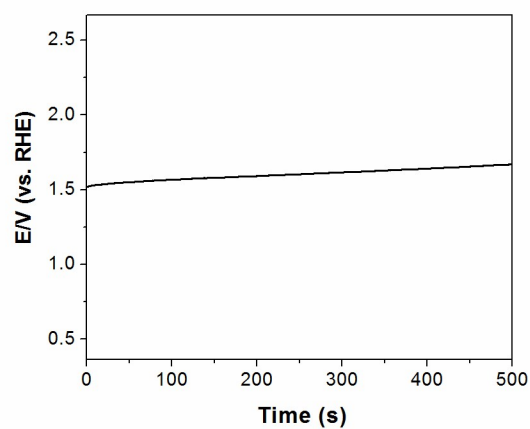


Figure S18. v-t result of Fe<sub>3</sub>C@NCNT/NPC toward OER in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

Table S1. N<sub>2</sub> adsorption-desorption characterization of the samples obtained at different temperatures.

Sample	Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore size (nm)
NCL	413.1	0.279	1.289
Fe <sub>3</sub> C@NCNT/NPC	175.1	0.417	3.79
Fe <sub>3</sub> C@NCNT	211.4	0.403	3.969

Table S2. Comparison of ORR catalytic performances in alkaline solution between Fe<sub>3</sub>C@NCNT/NPC and other non-precious metal-based catalysts reported previously.

Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE )	Ref.
Fe <sub>3</sub> C@NCNT/NPC	1.0	0.90	This work
P-CNC <sub>Co</sub> -20	0.93	0.85	1
Co@Co <sub>3</sub> O <sub>4</sub> @ C-CM	0.93	0.81	2
NC-900	0.83	0.68	3
GNPCSS-800	0.957	0.82	4
CNPs	1.03	0.85	5
Fe <sub>3</sub> C/C-800	1.05	0.83	6
Fe-N-CNFs	-0.02	-0.140	7
	(vs. Ag/AgCl)	(vs. Ag/AgCl)	
N-graphene/CNT	0.117	-	8
PMF-800	-	0.861	9
FePhen@MOF-ArNH <sub>3</sub>	1.03	0.86	10
Fe-N-GC-900	1.01	0.86	11
Fe-NCB-900	-	0.8	12
Fe <sub>3</sub> C/NG-800	1.03	0.86	13
NCNT/CoO-NiO-NiCo	1.0	0.83	14
Fe-N/C-800	0.92	0.81	15
Fe-N <sub>4</sub> /C	-	0.87	16
Co <sub>3</sub> O <sub>4</sub> -N-rmGO	-	0.83	17
N-Fe-CNT/CNP	-	0.87	18

Table S3. Comparison of OER catalytic performances in alkaline solution between the Fe<sub>3</sub>C@NCNT/NPC and other non-precious metal-based catalysts reported previously.

Catalyst	Overpotential (V)	KOH (M)	Tafel slope (mV dec <sup>-1</sup> )	Ref.
Fe <sub>3</sub> C@NCNT/NPC	0.34	1	62	This work
Fe/C/N	0.36	0.1	-	19
Fe@N-C-700	0.48	0.1	-	20
Co <sub>3</sub> O <sub>4</sub> /rm-GO	0.31	1	67	17
α-MnO <sub>2</sub> -SF	0.49	0.1	77.5	21
Ca <sub>2</sub> Mn <sub>2</sub> O <sub>5</sub> /C	0.47	0.1	149	22
CoO/NG	0.34	1	71	23
Fe-Ni oxides	0.38	1	51	24
NiFe-B	0.35	1	67	25
LiNi <sub>1-x</sub> Fe <sub>x</sub> PO <sub>4</sub> @C	0.31	1	78	26
Co(OH) <sub>2</sub>	0.35	1	-	27
Co <sub>0.5</sub> Fe <sub>0.5</sub> S@N-MC	0.34	1	159	28
Co-P film	0.34	1	47	29
CoCo LDH	0.39	1	59	25
N-CG-Co	0.34	1	71	23
Ni <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub> nanowire	0.37	1	64	30
ZnCo LDH	0.51	0.1	83	31
graphitic C <sub>3</sub> N <sub>4</sub> nanosheets/carbon nanotubes	0.37	0.1	83	32
P-doped graphitic C <sub>3</sub> N <sub>4</sub>	0.4	0.1	62	33

## Reference

- 1 Y. Z. Chen, C. Wang, Z. Y. Wu, Y. Xiong, Q. Xu, S. H. Yu and H. L. Jiang, *Adv. Mater.*, 2015.
- 2 W. Xia, R. Zou, L. An, D. Xia and S. Guo, *Energy Environ. Sci.*, 2015, **8**, 568-576.
- 3 A. Aijaz, N. Fujiwara and Q. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 6790-6793.
- 4 H.-x. Zhong, J. Wang, Y.-w. Zhang, W.-l. Xu, W. Xing, D. Xu, Y.-f. Zhang and X.-b. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 14235-14239.
- 5 S. Zhao, H. Yin, L. Du, L. He, K. Zhao, L. Chang, G. Yin, H. Zhao, S. Liu and Z. Tang, *ACS Nano*, 2014, **8**, 12660-12668.
- 6 Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum and Q. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 3675-3679.
- 7 Z. Y. Wu, X. X. Xu, B. C. Hu, H. W. Liang, Y. Lin, L. F. Chen and S. H. Yu, *Angew. Chem. Int. Ed.*, 2015.
- 8 Z. Wen, S. Ci, Y. Hou and J. Chen, *Angew. Chem. Int. Ed.*, 2014, **53**, 6496-6500.
- 9 W. Yang, X. Liu, X. Yue, J. Jia and S. Guo, *J. Am. Chem. Soc.*, 2015, **137**, 1436-1439.
- 10 K. Strickland, E. Miner, Q. Jia, U. Tylus, N. Ramaswamy, W. Liang, M. T. Sougrati, F. Jaouen and S. Mukerjee, *Nat Commun*, 2015, **6**, 7343.
- 11 A. Kong, X. Zhu, Z. Han, Y. Yu, Y. Zhang, B. Dong and Y. Shan, *ACS catal.*, 2014, **4**, 1793-1800.
- 12 A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M.-T. Sougrati, Q. Jia, S. Mukerjee and P. Atanassov, *Nano Energy*, 2015, **16**, 293-300.
- 13 M. Xiao, J. Zhu, L. Feng, C. Liu and W. Xing, *Adv. Mater.*, 2015, **27**, 2521-2527.
- 14 X. Liu, M. Park, M. G. Kim, S. Gupta, G. Wu and J. Cho, *Angew. Chem. Int. Ed.*, 2015, **54**, 9654-9658.
- 15 L. Lin, Q. Zhu and A. W. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 11027-11033.
- 16 N. Ramaswamy, U. Tylus, Q. Jia and S. Mukerjee, *J. Am. Chem. Soc.*, 2013, **135**, 15443-15449.
- 17 Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, **10**, 780-786.
- 18 T. Chung Hoon, H. Won Jong and P. Zelenay, *Nat Commun*, 2013, **4**, 1922.
- 19 Y. Zhao, K. Kamiya, K. Hashimoto and S. Nakanishi, *J. Phys. Chem. C*, 2015, **119**, 2583-2588.
- 20 J. Wang, H. Wu, D. Gao, S. Miao, G. Wang and X. Bao, *Nano Energy*, 2015, **13**, 387-396.
- 21 Y. Meng, W. Song, H. Huang, Z. Ren, S.-Y. Chen and S. L. Suib, *J. Am. Chem. Soc.*, 2014, **136**, 11452-11464.
- 22 J. Kim, X. Yin, K.-C. Tsao, S. Fang and H. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 14646-14649.
- 23 S. Mao, Z. Wen, T. Huang, Y. Hou and J. Chen, *Energy Environ. Sci.*, 2014, **7**, 609-616.
- 24 J. Landon, E. Demeter, N. Inoglu, C. Keturakis, I. E. Wachs, R. Vasic, A. I. Frenkel and J. R. Kitchin, *ACS catal.*, 2012, **2**, 1793-1801.
- 25 F. Song and X. Hu, *Nat. Commun.*, 2014, **5**, 4477.
- 26 S. Ma, Q. Zhu, Z. Zheng, W. Wang and D. Chen, *Chem. Commun.*, 2015, **51**, 15815-15818.
- 27 M. S. Burke, M. G. Kast, L. Trotochaud, A. M. Smith and S. W. Boettcher, *J. Am. Chem. Soc.*, 2015, **137**, 3638-3648.
- 28 M. Shen, C. Ruan, Y. Chen, C. Jiang, K. Ai and L. Lu, *Acs Appl. Mater. Interfaces*, 2015, **7**, 1207-1218.
- 29 N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251-6254.
- 30 Y. Li, P. Hasin and Y. Wu, *Adv. Mater.*, 2010, **22**, 1926-1929.
- 31 Y. Li, L. Zhang, X. Xiang, D. Yan and F. Li, *J. Mater. Chem. A*, 2014, **2**, 13250-13258.
- 32 T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *Angew. Chem., Int. Ed.*, 2014, **53**, 7281-7285.
- 33 T. Y. Ma, J. Ran, S. Dai, M. Jaroniec and S. Z. Qiao, *Angew. Chem., Int. Ed.*, 2015, **54**, 4646-4650.