Supporting Information

Facile Synthesis N-doped Fe_3C@CNT/Porous Carbon Hybrid for an Advanced Oxygen Reduction and Water Oxidation Electrocatalyst

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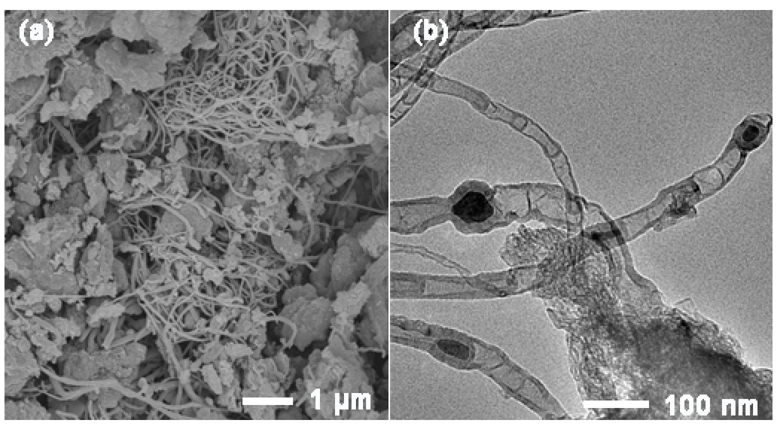

Figure S1. SEM (a) and TEM (b) images of the as-synthesized FeNC-800.

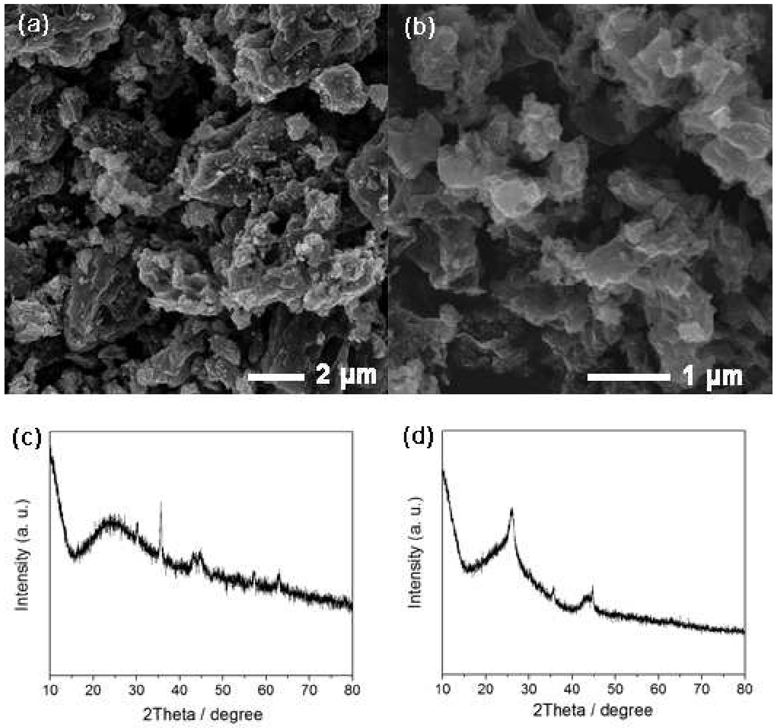

Figure S2. SEM images and XRD pattern of the FeNC-700 (a, c) and FeNC-900 (b, d).

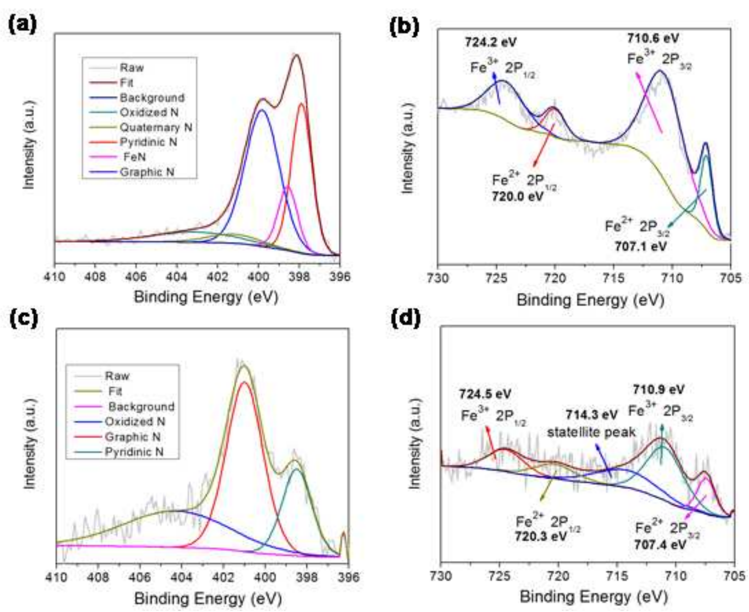

Figure S3. The high-resolution N 1s and Fe 2p spectrum of (a, c) FeNC-700, (b, d) FeNC-900.

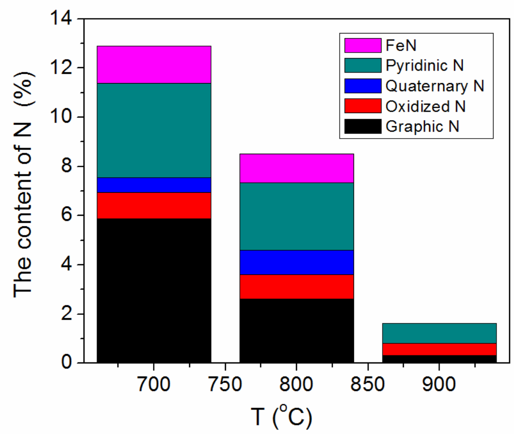

Figure S4. The content of N at different temperatures of 700,800 and 900 °C respectively.

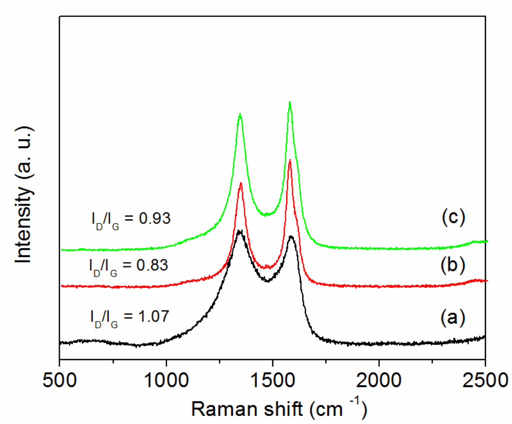

Figure S5. Raman spectrum of samples obtained at different temperatures of (a) FeNC-700, (b) FeNC-800 and (c) FeNC-900.

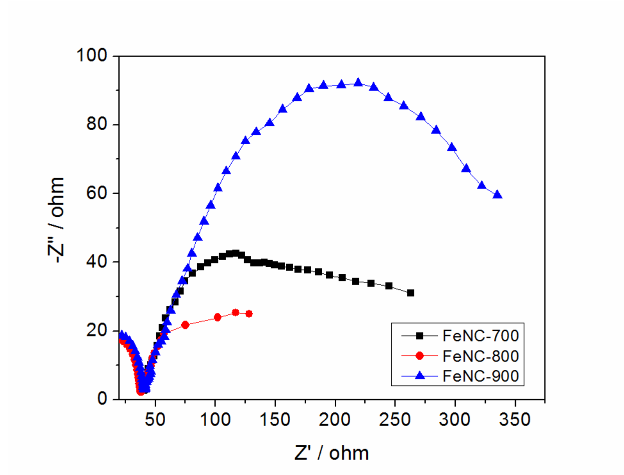

Figure S6. Impedance data for FeNC-X samples.

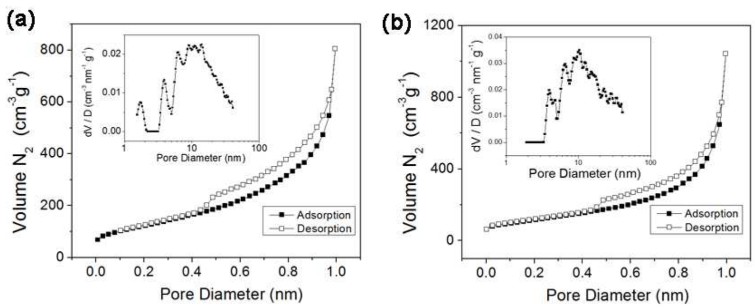

Figure S7. N_2 adsorption-desorption isotherms of (a) FeNC-700 and (b) FeNC-900 (inset) the pore size distribution by DFT method.

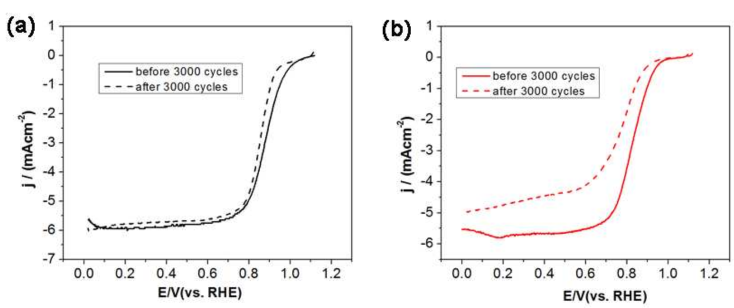

Figure S8. The activities after 3000 cycles of FeNC-800 and Pt/C in an O_2-saturated 0.1 M KOH solution.

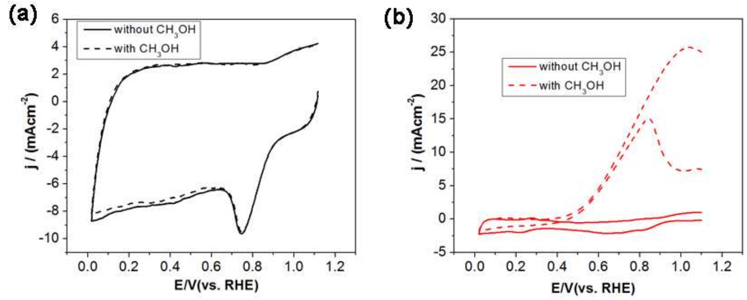

Figure S9. CV curves of (a) FeNC-800 and (b) Pt/C in an O_2-saturated 0.1 M KOH solution containing 1M methanol.

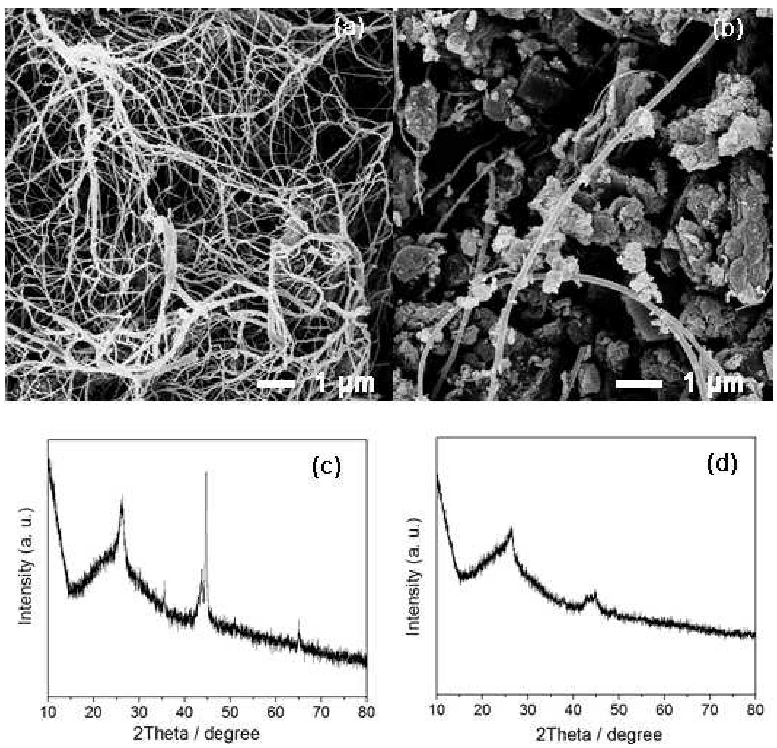

Figure S10. SEM images and XRD patterns of samples prepared with different amount of o-Phthalic anhydride in the precursors at 800 ^{o}C: (a, c) reducing 50% o-Phthalic anhydride and (b, d) adding 50% o-Phthalic anhydride.

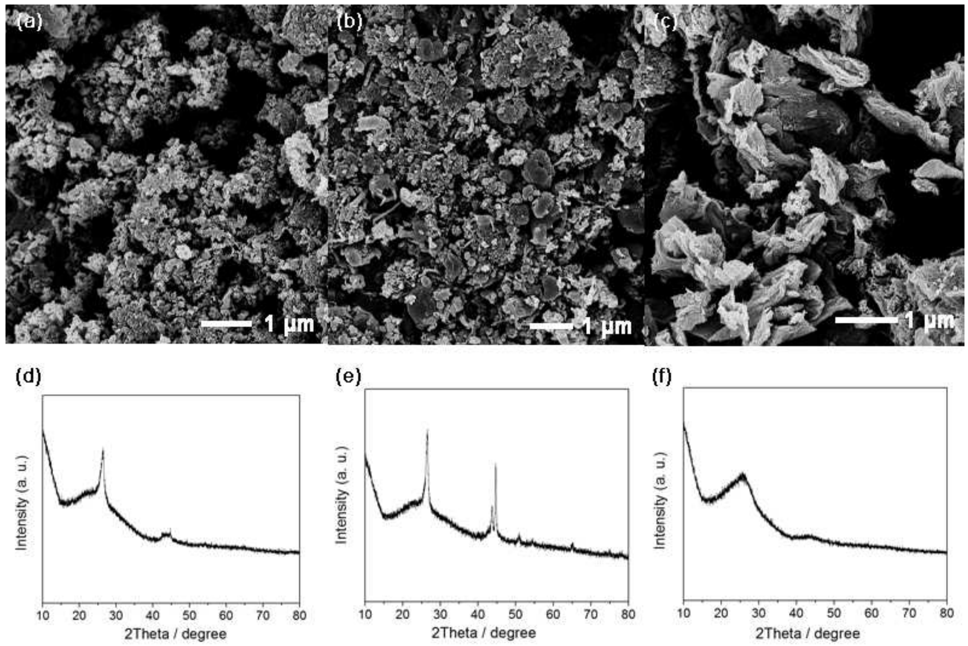

Figure S11. SEM images of samples prepared with different precursors at 800 ^{o}C: (a, d) without melamine, (b, e) without o-Phthalic anhydride and (c, f) without $FeCl_3$.

Table S1. N_2 adsorption-desorption characterization of the samples obtained at different temperatures.

Sample	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
FeNC-700	450.3	0.7	8.9
FeNC-800	275.7	0.5	14.1
FeNC-900	487.1	0.8	10.3

Table S2. Comparison of ORR catalytic performances in alkaline solution between FeNC-800 and other non-precious metal-based catalysts reported previously.

Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Ref.
FeNC-800	1.1	0.88	This work
N–Fe–CNT/CNP	-	0.87	1
FePhen@MOF-ArNH$_3$	1.03	0.86	2
N-CNT/N-G	-	0.85	3
N-GC	-0.05 (vs. Ag/AgCl)	-0.18 (vs. Ag/AgCl)	4
SN-OMC-8	-	-0.15 (vs. Ag/AgCl)	5
GFe-800a	-0.087 (vs. Ag/AgCl)	-0.29 (vs. Ag/AgCl)	6
ZIF-67-900	0.95	0.85	7
Fe_3C/C-800	1.05	0.83	8
Fe-N-CNFs	-0.02 (vs. Ag/AgCl)	-0.140 (vs. Ag/AgCl)	9
N-graphene/CNT	0.117	-	10
PMF-800	-	0.861	11

Table S3. Comparison of OER catalytic performances in alkaline solution between the FeNC-800 and other non-precious metal-based catalysts reported previously.

Catalyst	Potential at current density of 10 mA cm^{-2} (V vs. RHE)	KOH (M)	Ref.
FeNC-800	1.64	0.1	This work
Fe/Fe_3C@NGL-NCNT	1.16 (vs. Ag/AgCl)	0.1	12
ZnCo LDH	1.74	0.1	13
α-MnO_2-SF	1.72	0.1	14
$Ca_2Mn_2O_5/C$	1.7	0.1	15
V–Co–Fe oxide	1.54	1	16
Fe-Ni oxides	1.61	1	17
γ-Fe_2O_3/CNT	1.61	0.1 NaOH	18
P-doped graphitic C_3N_4	1.63	0.1	19
α-$Ni(OH)_2$ hollow spheres	1.56	0.1	20
β-$Ni(OH)_2$ nanoplates	1.67	0.1	20
CoCo LDH	1.62	1	21
$NixCo_3$-xO_4 nanowire	1.6	1	22

Reference

(1) Chung, H. T.; Won, J. H.; Zelenay, P. Active and stable carbon nanotube/nanoparticle composite electrocatalyst for oxygen reduction. *Nat. Commun.* **2013,** *4* (May), ncomms2944, 2945 pp.

(2) Strickland, K.; Miner, E.; Jia, Q.; Tylus, U.; Ramaswamy, N.; Liang, W.; Sougrati, M. T.; Jaouen, F.; Mukerjee, S. Highly active oxygen reduction non-platinum group metal electrocatalyst without direct metal-nitrogen coordination. *Nat Commun* **2015,** *6*, 7343.

(3) Zhang, S.; Zhang, H.; Liu, Q.; Chen, S. Fe–N doped carbon nanotube/graphene composite: facile synthesis and superior electrocatalytic activity. *J. Mater. Chem. A* **2013,** *1* (10), 3302-3308.

(4) Yao, Y.; You, Y.; Zhang, G.; Liu, J.; Sun, H.; Zou, Z.; Sun, S. Highly Functional Bioinspired Fe/N/C Oxygen Reduction Reaction Catalysts: Structure-Regulating Oxygen Sorption. *Acs Appl. Mater. Interfaces* **2016**, 10.1021/acsami.1025b11870.

(5) Xu, J.; Zhao, Y.; Shen, C.; Guan, L. Sulfur- and nitrogen-doped, ferrocene-derived mesoporous carbons with efficient electrochemical reduction of oxygen. *Acs Appl. Mater. Interfaces* **2013,** *5* (23), 12594-12601.

(6) Dong, Q.; Zhuang, X.; Li, Z.; Li, B.; Fang, B.; Yang, C.; Xie, H.; Zhang, F.; Feng, X. Efficient approach to iron/nitrogen co-doped graphene materials as efficient electrochemical catalysts for the oxygen reduction reaction. *J. Mater. Chem. A* **2015,** *3* (15), 7767-7772.

(7) Wang, X.; Zhou, J.; Fu, H.; Li, W.; Fan, X.; Xin, G.; Zheng, J.; Li, X. MOF derived catalysts for electrochemical oxygen reduction. *J. Mater. Chem. A* **2014,** *2* (34), 14064.

(8) Hu, Y.; Jensen, J. O.; Zhang, W.; Cleemann, L. N.; Xing, W.; Bjerrum, N. J.; Li, Q. Hollow spheres of iron carbide nanoparticles encased in graphitic layers as oxygen reduction catalysts. *Angew. Chem. Int. Ed.* **2014,** *53* (14), 3675-3679.

(9) Wu, Z. Y.; Xu, X. X.; Hu, B. C.; Liang, H. W.; Lin, Y.; Chen, L. F.; Yu, S. H. Iron Carbide Nanoparticles Encapsulated in Mesoporous Fe-N-Doped Carbon Nanofibers for Efficient Electrocatalysis. *Angew. Chem. Int. Ed.* **2015**.

(10) Wen, Z.; Ci, S.; Hou, Y.; Chen, J. Facile one-pot, one-step synthesis of a carbon nanoarchitecture for an advanced multifunctonal electrocatalyst. *Angew. Chem. Int. Ed.* **2014,** *53* (25), 6496-6500.

(11) Yang, W.; Liu, X.; Yue, X.; Jia, J.; Guo, S. Bamboo-like carbon nanotube/Fe_3C nanoparticle hybrids and their highly efficient catalysis for oxygen reduction. *J. Am. Chem. Soc.* **2015,** *137* (4), 1436-1439.

(12) Li, J.-S.; Li, S.-L.; Tang, Y.-J.; Han, M.; Dai, Z.-H.; Bao, J.-C.; Lan, Y.-Q. Nitrogen-doped Fe/Fe3C@graphitic layer/carbon nanotube hybrids derived from MOFs: efficient bifunctional electrocatalysts for ORR and OER. *Chem. Commun. (Cambridge, U. K.)* **2015,** *51* (13), 2710-2713.

(13) Li, Y.; Zhang, L.; Xiang, X.; Yan, D.; Li, F. Engineering of ZnCo-layered double hydroxide nanowalls toward high-efficiency electrochemical water oxidation. *J. Mater. Chem. A* **2014,** *2* (33), 13250-13258.

(14) Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S.-Y.; Suib, S. L. Structure-property relationship of bifunctional MnO2 nanostructures: highly efficient, ultra-stable electrochemical water oxidation and oxygen reduction reaction catalysts identified in alkaline media. *J. Am. Chem. Soc.* **2014,** *136* (32), 11452-11464.

(15) Kim, J.; Yin, X.; Tsao, K.-C.; Fang, S.; Yang, H. Ca2Mn2O5 as oxygen-deficient perovskite electrocatalyst for oxygen evolution reaction. *J. Am. Chem. Soc.* **2014,** *136* (42), 14646-14649.

(16) Gao, T.; Jin, Z.; Liao, M.; Xiao, J.; Yuan, H.; Xiao, D. A trimetallic V-Co-Fe oxide nanoparticle as an efficient and stable electrocatalyst for oxygen evolution reaction. *J. Mater. Chem. A* **2015,** *3* (34), 17763-17770.

(17) Landon, J.; Demeter, E.; Inoglu, N.; Keturakis, C.; Wachs, I. E.; Vasic, R.; Frenkel, A. I.; Kitchin, J. R. Spectroscopic Characterization of Mixed Fe-Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes. *ACS catal.* **2012,** *2* (8), 1793-1801.

(18) Tavakkoli, M.; Kallio, T.; Reynaud, O.; Nasibulin, A. G.; Sainio, J.; Jiang, H.; Kauppinen, E.; Laasonen, K. Maghemite nanoparticles decorated on carbon nanotubes as an efficient electrocatalyst for oxygen evolution reaction. *J. Mater. Chem. A* **2016**, 10.1039/c1036ta01472k.

(19) Ma, T. Y.; Ran, J.; Dai, S.; Jaroniec, M.; Qiao, S. Z. Phosphorus-doped graphitic carbon nitrides grown in situ on carbon-fiber paper: flexible and reversible oxygen electrodes. *Angew. Chem., Int. Ed.* **2015,** *54* (15), 4646-4650.

(20) Gao, M.; Sheng, W.; Zhuang, Z.; Fang, Q.; Gu, S.; Jiang, J.; Yan, Y. Efficient water oxidation using nanostructured alpha-nickel-hydroxide as an electrocatalyst. *J. Am. Chem. Soc.* **2014,** *136* (19), 7077-7084.

(21) Song, F.; Hu, X. Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis. *Nat. Commun.* **2014,** *5*, 4477.

(22) Li, Y.; Hasin, P.; Wu, Y. NixCo3-xO4 Nanowire Arrays for Electrocatalytic Oxygen Evolution. *Adv. Mater.* **2010,** *22* (17), 1926-1929.