

Supporting information

Nanoporous Carbon Derived from a Functionalized Metal–Organic Framework as Highly Efficient Oxygen Reduction Electrocatalyst

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The XRD peaks of MOF-253-Fe in Figure S1 correspond well to that of MOF-253 with only a slightly shifting which may be originated from a disorder in the crystal structure. X-ray photoelectron spectroscopy (XPS) analysis was performed to confirm the chemical state and coordination environment of Fe atom upon insertion within the framework. The high resolution N1s spectra of MOF-253-Fe in – Figure S2 demonstrate the presence of metal N fitting binding energies of 399.6 eV.^{1, 2} The binding energies of the Fe2p (around 711 eV) in Figure S2 could be ascribed to the N-coordinated Fe³⁺ or Fe²⁺.^{3, 4} These features are all attributed to the binding of FeCl₂ to pyridine, which may lead to Fe-2,2' -bipyridine distribution throughout of MOF-253.

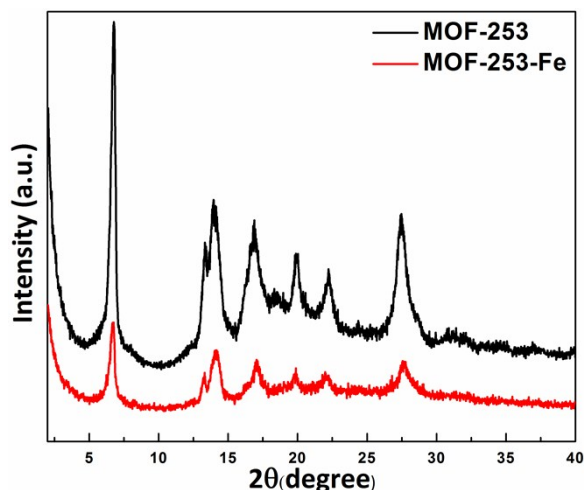


Figure S1. XRD patterns of MOF-253 and MOF-253-Fe.

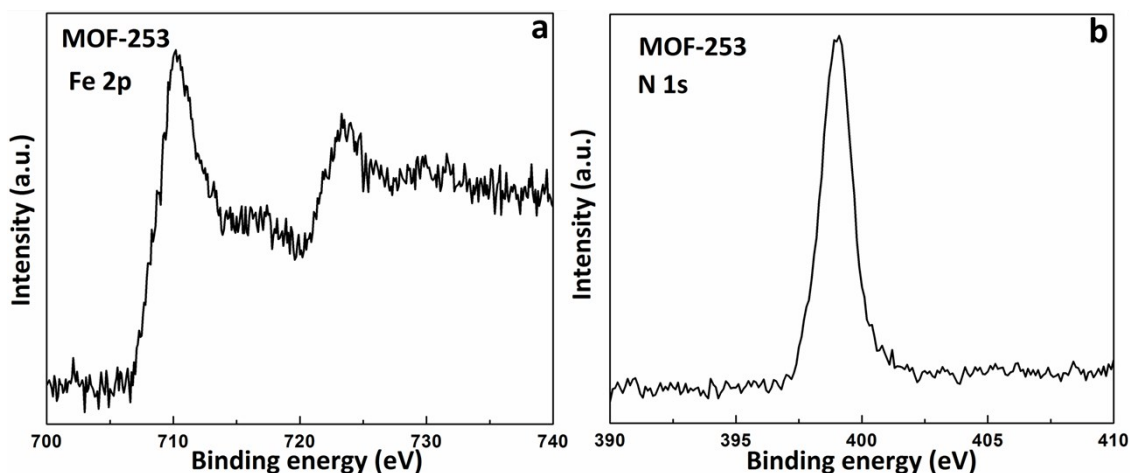


Figure S2. High-resolution Fe 2p and N 1s XPS spectra of MOF-253-Fe.

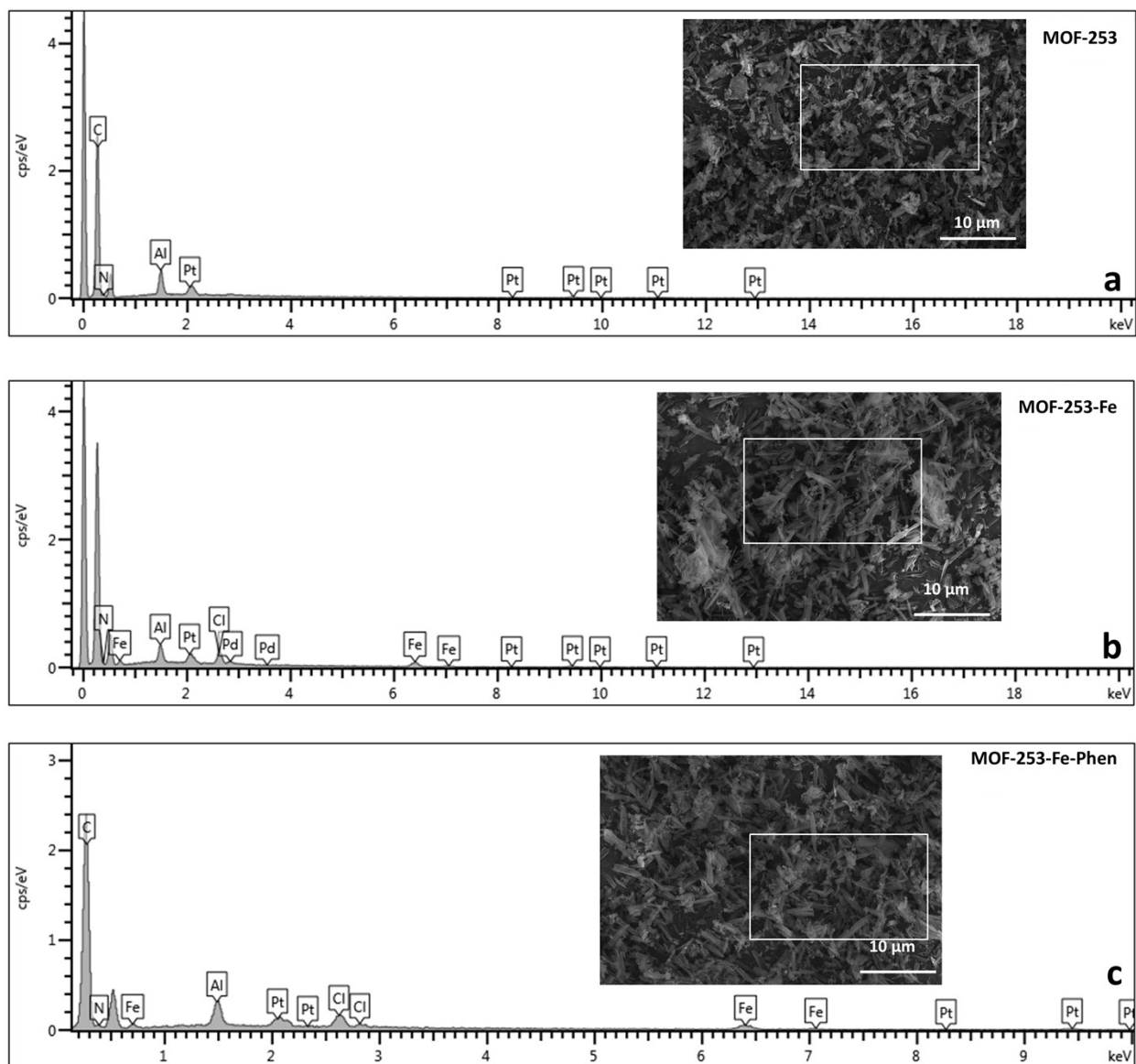


Figure S3. EDX spectrum of MOF-253, MOF-253-Fe and MOF-253-Fe-Phen.

MOF-253 (Al(OH)(bpydc) (Anal. Calcd for $C_{12}H_7AlN_2O_5$) is synthesized according to the procedure reported in literature. (For detailed synthetic procedures, please refer to the Experimental part.) EDS analysis showed that the molar ratio of Al/N was 1:2.25 which is close to the theoretical value of 1:2.

After MOF-253 is synthesized, it is modified with $FeCl_2$ in acetonitrile to form Fe incorporated compound which is named as MOF-253-Fe. The compounds Al(OH)(bpydc) (3.5 mmol) and $FeCl_2$ (3.5 mmol) were stirred and then collected by filtration and washing with acetonitrile. EDS analysis showed that the molar ratio of Fe/Al was 0.64:1, matching well with the atomic ratio of 0.7:1 measured by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (ESI). EDS analysis measure on the same sample showed that the molar ratio of Al/N was 1:2.12.

The above obtained dry MOF-253-Fe, mixed with 1,10-Phenanthroline (7 mmol) in acetonitrile was stirred, followed by filtration and dried under vacuum. The formed MOF-253-Fe-phen composite was also analysed by EDS. The molar ratio of Fe/Al was 0.53:1 which is a little bit smaller than that of MOF-253-Fe. This is because of the possible dissolution of some of Fe species into solutions after the subsequent stirring with 1,10-Phenanthroline. In our expectation, after the addition of 1,10-Phenanthroline, Fe which was chelated with the ligand of MOF-253 would chelate with two portion of 1,10-Phenanthroline. Thus, if the molar ratio of Fe/Al is 0.53:1, plus with the nitrogen atoms in the ligand, Fe/N ratio of the as-synthesized compound should be around 0.53: (0.53*4+2) = 0.53:4. EDS analysis showed that the molar ratio of Fe/Al/N in the formed compound was 0.53:1:3.5, which match well with the above calculated data.

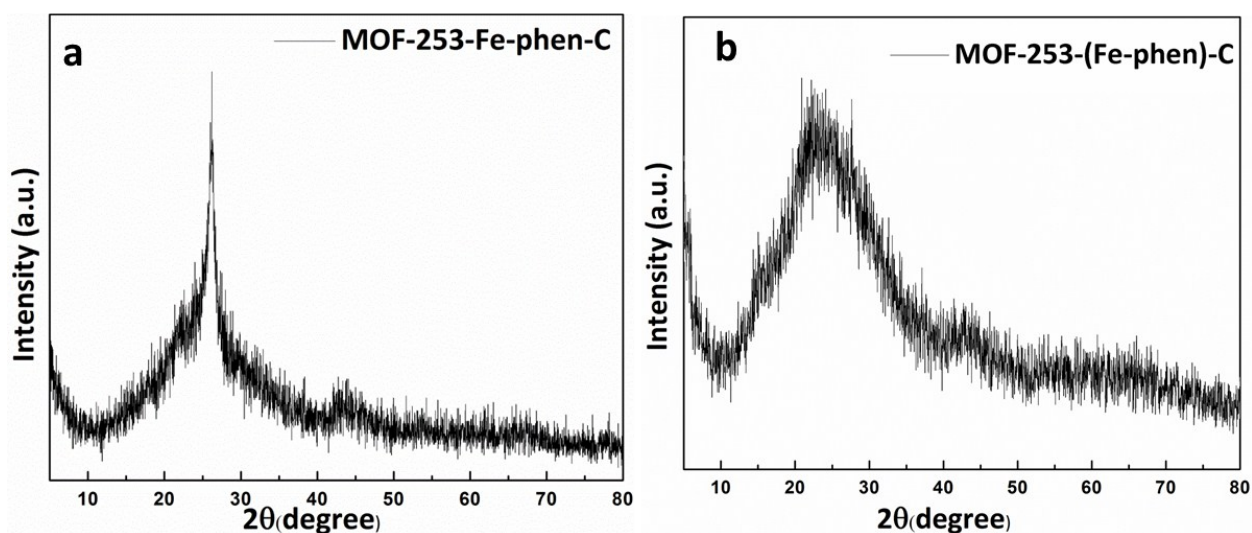


Figure S4. XRD patterns of MOF-253-Fe-phen-C (a), MOF-253-(Fe-Phen)-C (b).

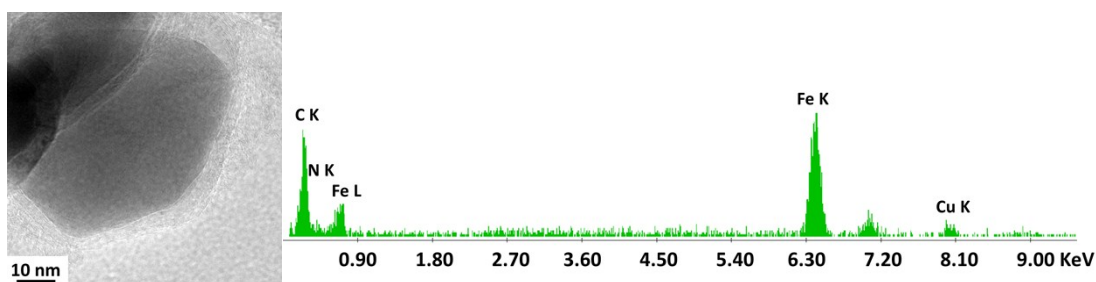


Figure S5. EDX spectrum of Fe₃C nanoparticles which are wrapped by carbon graphitic carbon layers in MOF-253-Fe-phen-C.

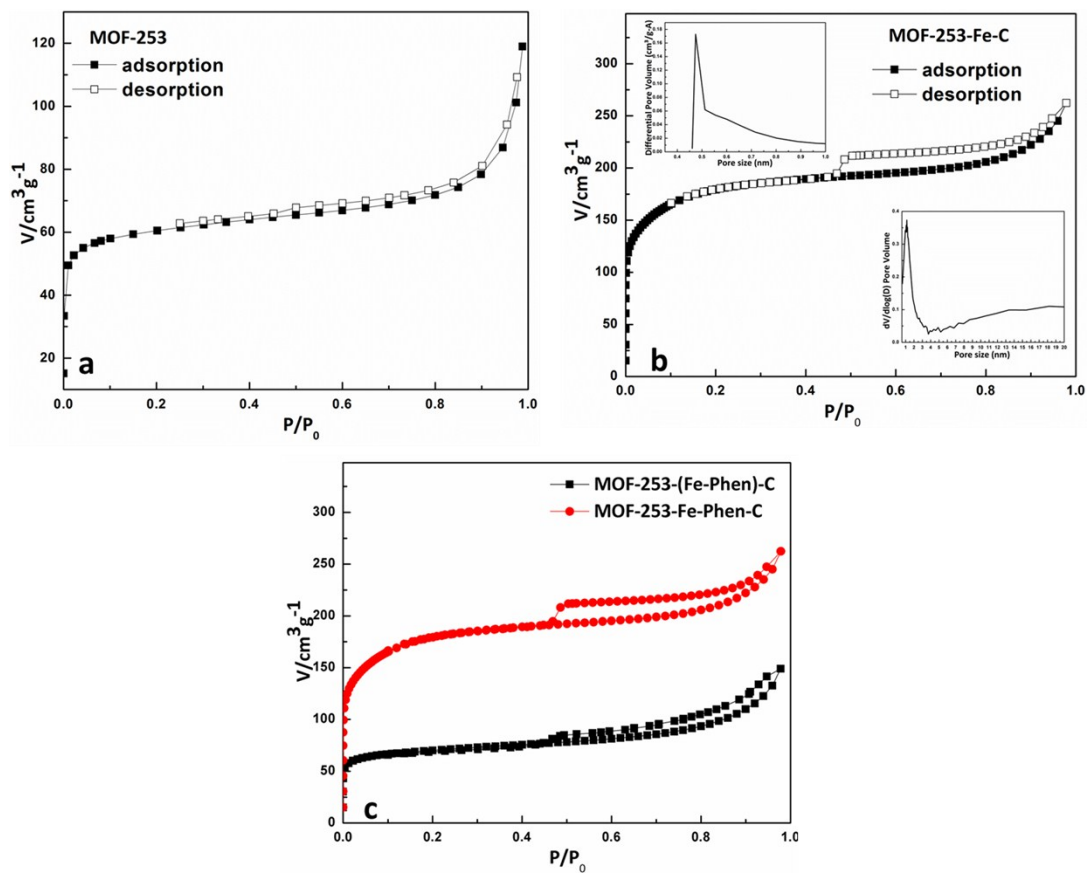


Figure S6. Nitrogen adsorption/desorption isotherms and the corresponding pore size distribution curves for a), MOF-253, b) MOF-253-Fe-Phen-C, c), MOF-253-(Fe-phen)-C.

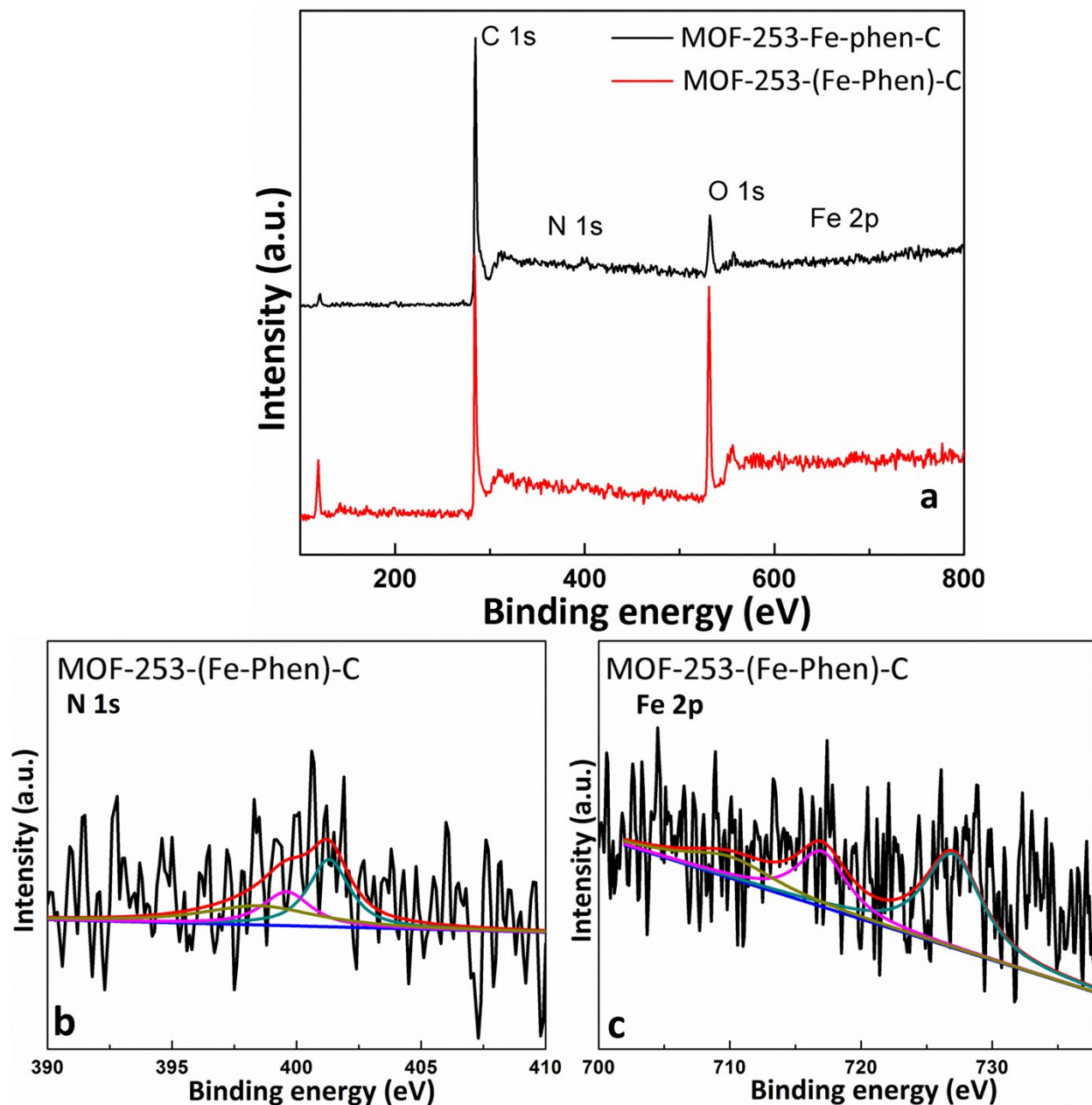


Figure S7. XPS survey scan of MOF-253-Fe-phen-C and MOF-253-(Fe-Phen)-C (a), high-resolution N 1s XPS spectra of MOF-253-(Fe-Phen)-C (b), high-resolution Fe 2p XPS spectra of MOF-253-(Fe-Phen)-C (c).

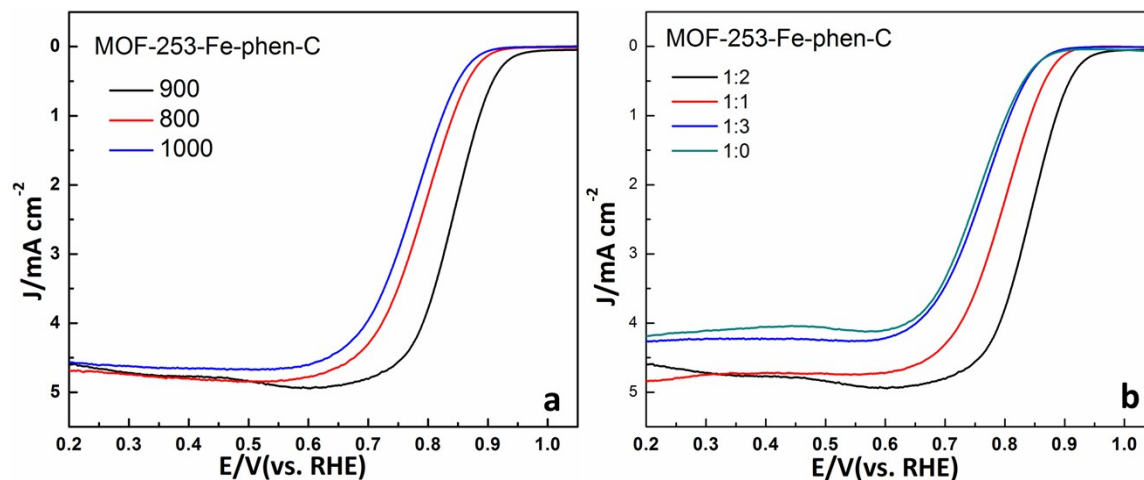


Figure S8. RDE voltammograms of MOF-253-Fe-phen-C pyrolyzed at different temperatures in O_2 -saturated 0.1 M KOH (a), RDE voltammograms of MOF-253-Fe-phen-C pyrolyzed by heating the mixtures containing different molar ratio of MOF-253-Fe and 1, 10-Phenanthroline at 900 °C and HCl etching in O_2 -saturated 0.1 M KOH. Note, 1:0 means that no 1, 10-Phenanthroline is added in MOF-253-Fe precursor (b).

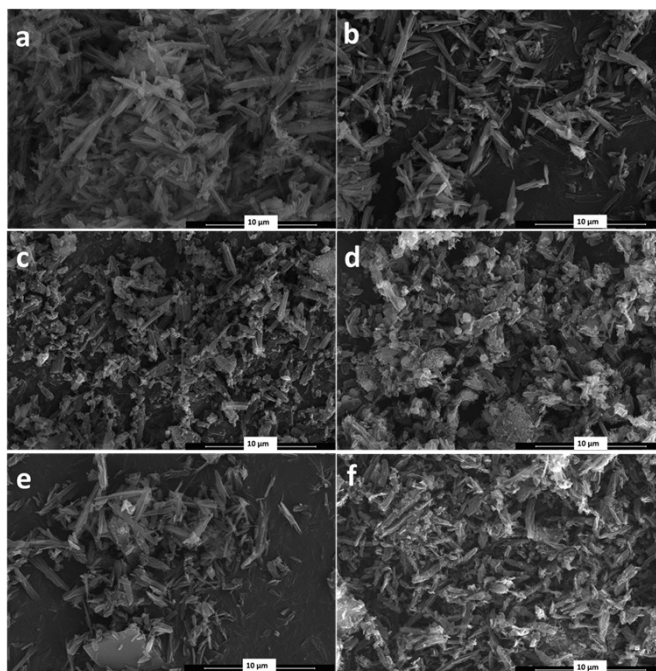


Figure S9. SEM images (a) MOF-253, (b) MOF-253-Fe, (c) MOF-253-Fe-Phen, (d) MOF-253-Fe-Phen-C, (e) MOF-253-(Fe-Phen), (f) MOF-253-(Fe-Phen)-C.

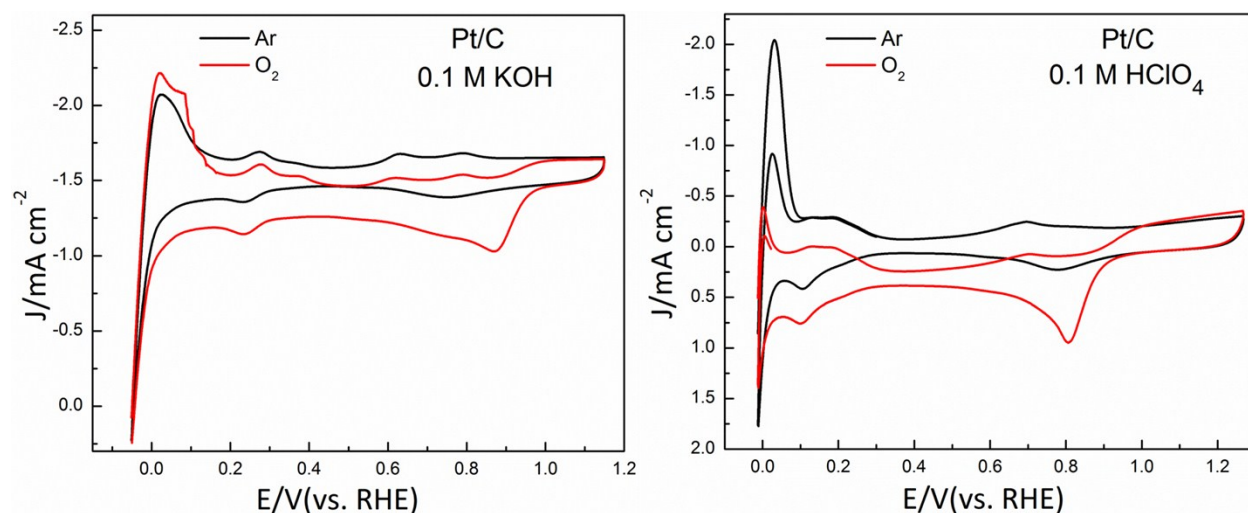


Figure S10. Cyclic voltammograms of Pt/C in O₂-saturated 0.1 M KOH and HClO₄.

Table S1. Summarized iron contents by ICP-OES measurements.

Samples	MOF-253-Fe-phen	MOF-253-(Fe-Phen)	MOF-253-Fe-phen-C	MOF-253-(Fe-Phen)-C
Fe wt.%	5.50	0.63	0.77	0.27

Table S2. The XPS surface species analyses of MOF-253-Fe-phen-C and MOF-253-(Fe-Phen)-C determined by XPS.

Samples	Graphitic nitrogen atom %	Metal nitrogen atom %	Pyridinic nitrogen atom %
MOF-253-Fe-phen-C	60.68	22.31	17.01
MOF-253-(Fe-Phen)-C	42.05	24.76	33.19

Table S3. Elemental compositions of MOF-253-Fe-phen-C and MOF-253-(Fe-Phen)-C determined by elemental analysis.

Samples	C wt. %	H wt. %	N wt. %
MOF-253-Fe-phen-C	53.53	0.99	1.34
MOF-253-(Fe-Phen)-C	47.82	1.766	0.68

Table S4. Electrocatalytic activity of carbon materials derived from pyridine as nitrogen source.

Catalyst	Electrolyte	Onset potential, V	Reference
[Zn(bpdc)DMA] ·DMF /C	0.1 M KOH	-0.14 (SCE)	5
4,4'-bipyridine and FeCl ₃ ·6H ₂ O /C	0.1 M KOH	0.98 (RHE)	6
Pyridine and CoSO ₄ ·7H ₂ O /C	0.1 M KOH	0.014 (SCE)	7
Current work	0.1 M KOH	0.98 (RHE)	

1. R. Kothandaraman, V. Nallathambi, K. Artyushkova and S. C. Barton, *Applied Catalysis B: Environmental*, 2009, 92, 209-216.
2. W. Gang, C. M. Johnston, N. H. Mack, K. Artyushkova, M. Ferrandon, M. Nelson, J. S. Lezama-Pacheco, S. D. Conradson, K. L. More, D. J. Myers and P. Zelenay, *J. Mater. Chem.*, 2011, 21, 11392-11405.
3. A. Kong, Y. Kong, X. Zhu, Z. Han and Y. Shan, *Carbon*, 2014, 78, 49-59.
4. Y. Zhao, K. Watanabe and K. Hashimoto, *J. Am. Chem. Soc.*, 2012, 134, 19528-19531.
5. D. Zhu, L. Li, J. Cai, M. Jiang, J. Qi and X. Zhao, *Carbon*, 2014, 79, 544.
6. Y. Wang, A. Kong, X. Chen, Q. Lin, and P. Y. Feng. *Acs Catal.*, 2015, 5, 3887.
7. J. Qiao, L. Xu, L. Ding, L. Zhang, R. Baker, X. Dai, J. Zhang. *Appl. Catal., B.*, 2012, 125, 197.