

A Fe-N-C hybrid electrocatalyst derived from bimetal-organic framework for efficient oxygen reduction

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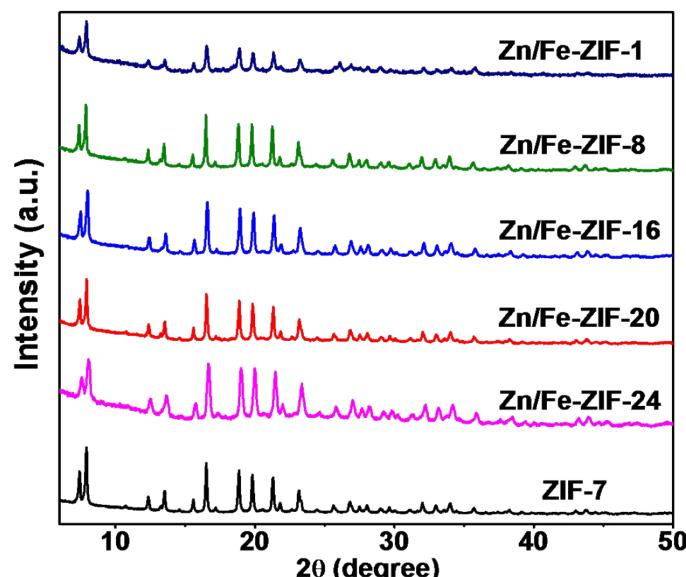


Figure S1. XRD survey of the Zn/Fe-ZIF-X.



Figure S2. Photographs of (a) ZIF-7, (b) Zn/Fe-ZIF-24, (c) Zn/Fe-ZIF-20, (d) Zn/Fe-ZIF-16, (e) Zn/Fe-ZIF-8 and (f) Zn/Fe-ZIF-1.

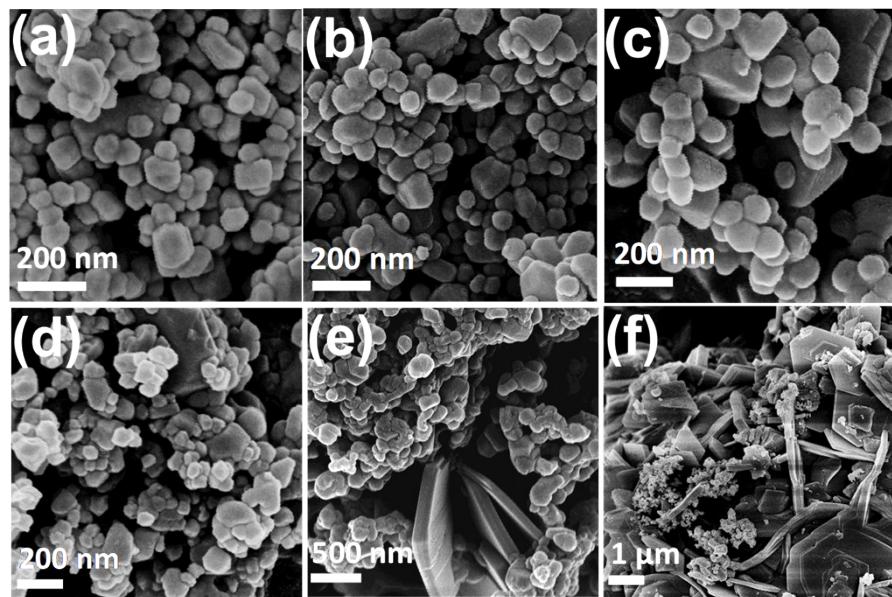


Figure S3. SEM images of (a) ZIF-7, (b) Zn/Fe-ZIF-24, (c) Zn/Fe-ZIF-20, (d) Zn/Fe-ZIF-16, (e) Zn/Fe-ZIF-8 and (f) Zn/Fe-ZIF-1.

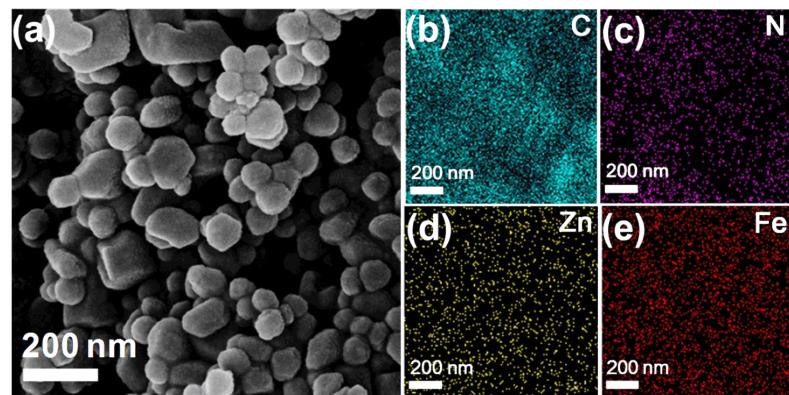


Figure S4. (a) SEM image of Zn/Fe-ZIF-20, (b-e) the elemental distribution of C,N, Zn and Fe.

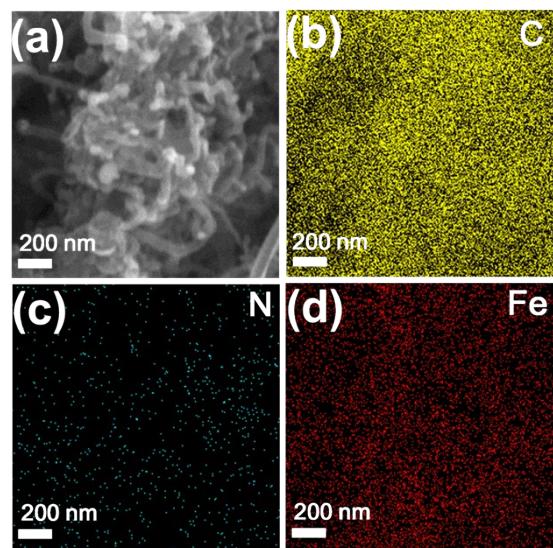


Figure S5. (a) SEM image of FeNC-20-1000, (b-d) the elemental distribution of C, N and Fe.

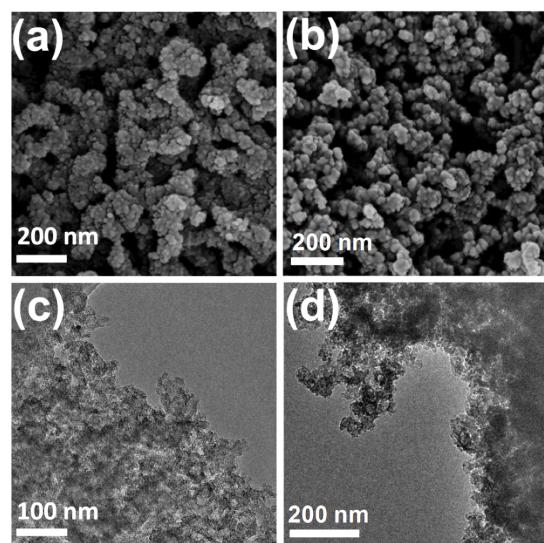


Figure S6. SEM image of (a) FeNC-20-900, (b) FeNC-20-1100. TEM image of (c) FeNC-20-900, (d) FeNC-20-1100.

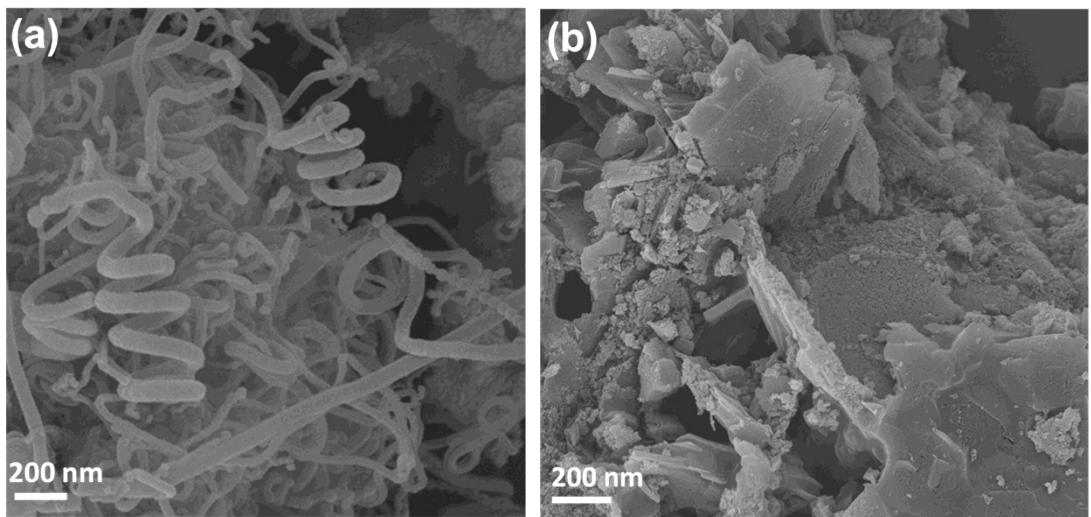


Figure S7. SEM images of (a) FeNC-20-1000-0, (b) FeNC-20-1000-con.

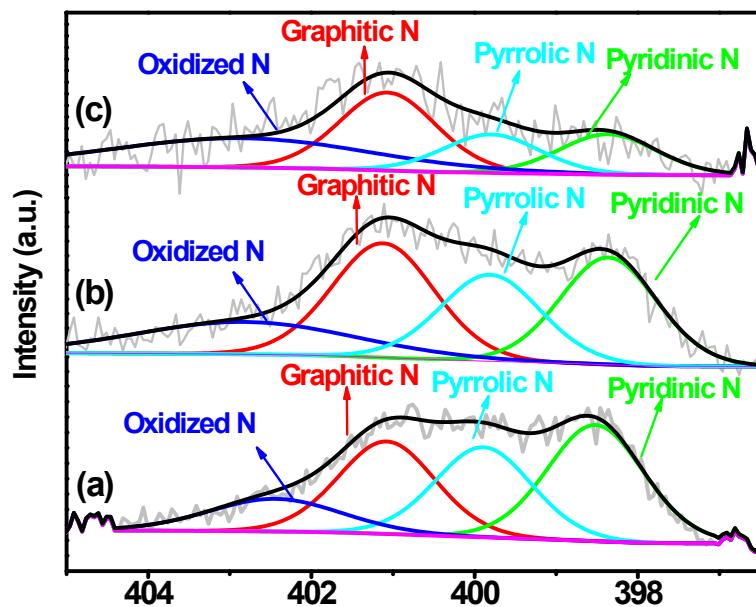


Figure S8. N 1s spectrum of FeNC-20-900 (a), FeNC-20-1000 (b), FeNC-20-1100 (c).

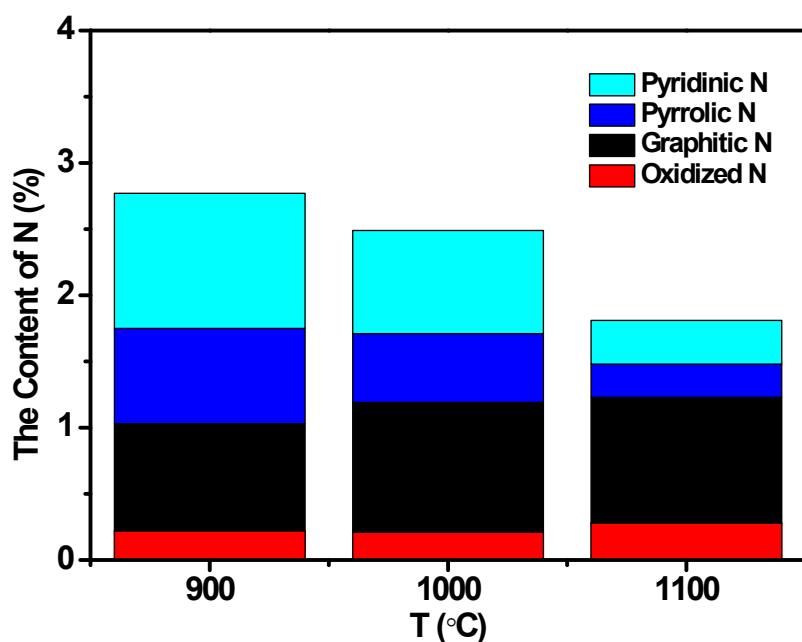


Figure S9. The content of N at different temperatures of 900, 1000 and 1100 °C respectively.

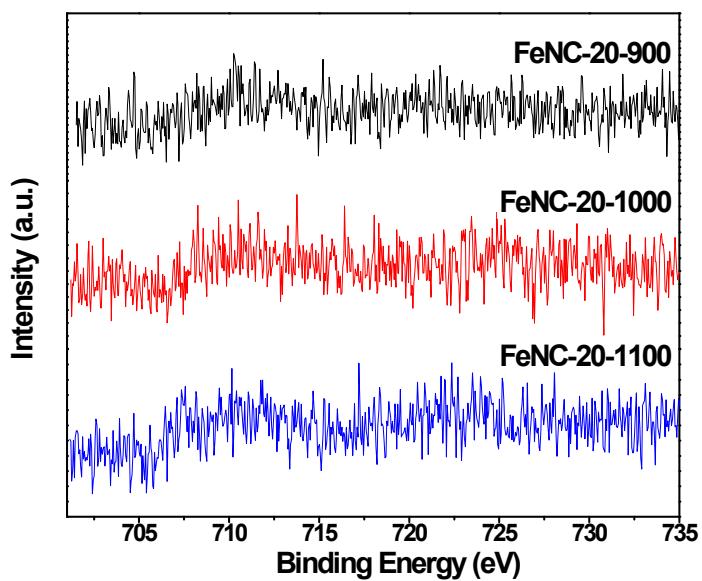


Figure S10. Fe 2p spectrum of FeNC-20-900, FeNC-20-1000, FeNC-20-1100.

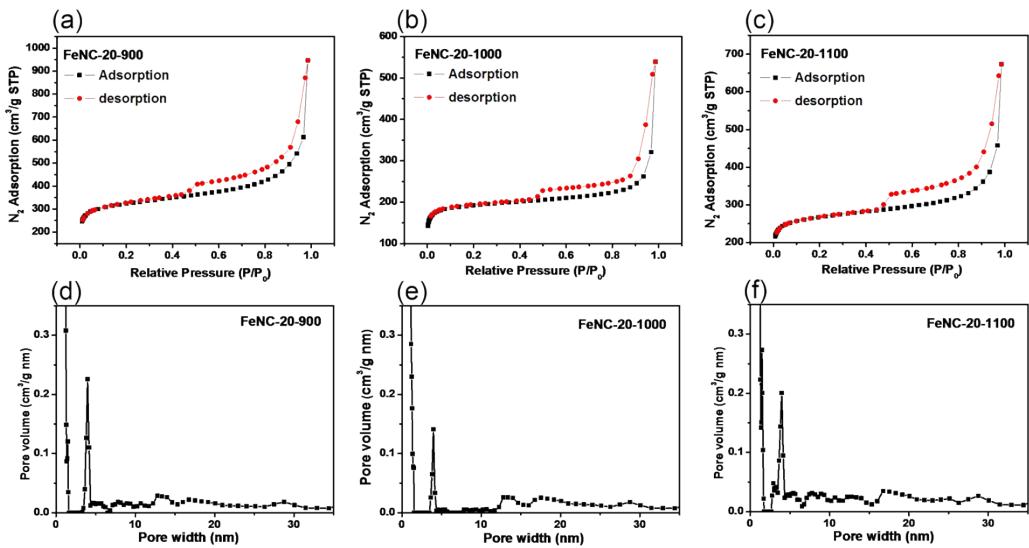


Figure S11. Nitrogen adsorption/desorption isotherms and pore distribution of FeNC-20-900, FeNC-20-1000, FeNC-20-1100.

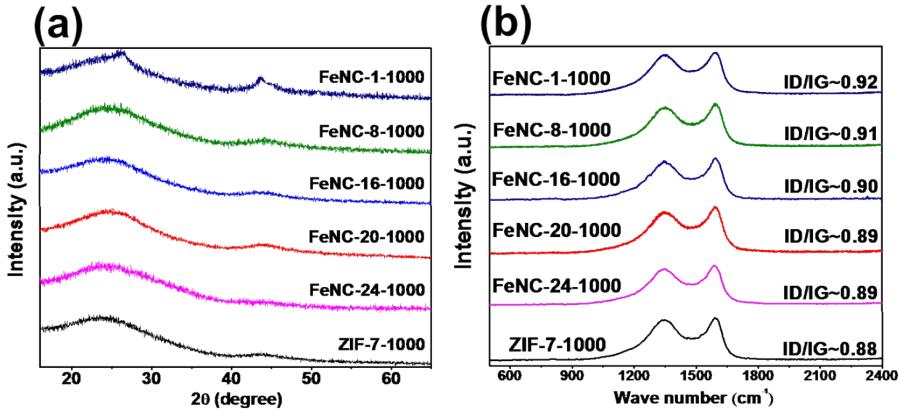


Figure S12. XRD pattern (a) and Raman spectra (b) of FeNC-X-1000.

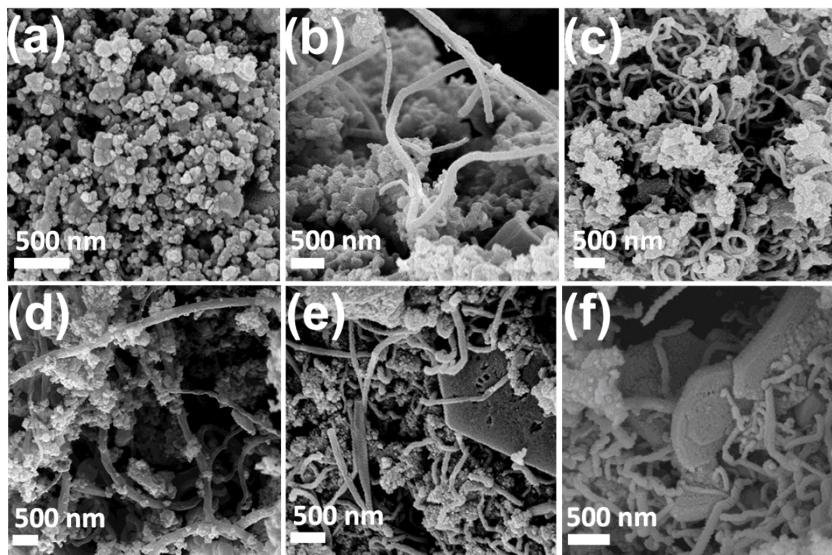


Figure S13. SEM image of (a) ZIF-7-1000, (b) FeNC-24-1000, (c) FeNC-20-1000, (d) FeNC-16-1000, (e) FeNC-8-1000, (f) FeNC-1-1000.

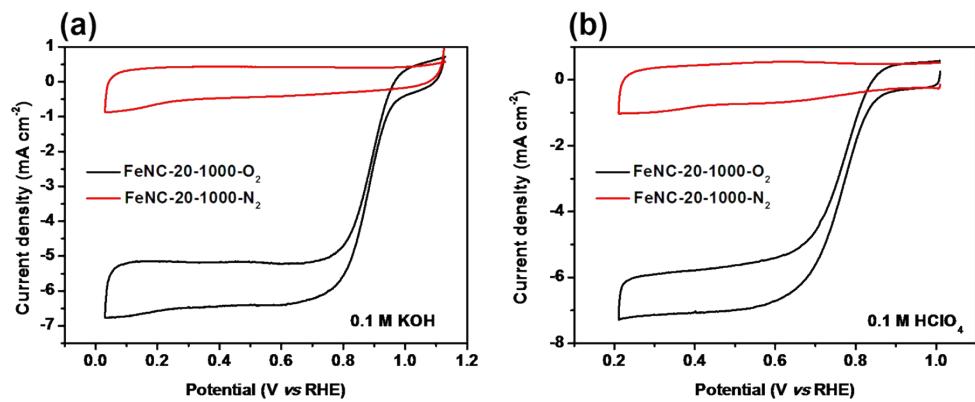


Figure S14. CV curve of FeNC-20-1000 in N_2 and O_2 , the catalyst loading is 0.75 mg cm^{-2} .

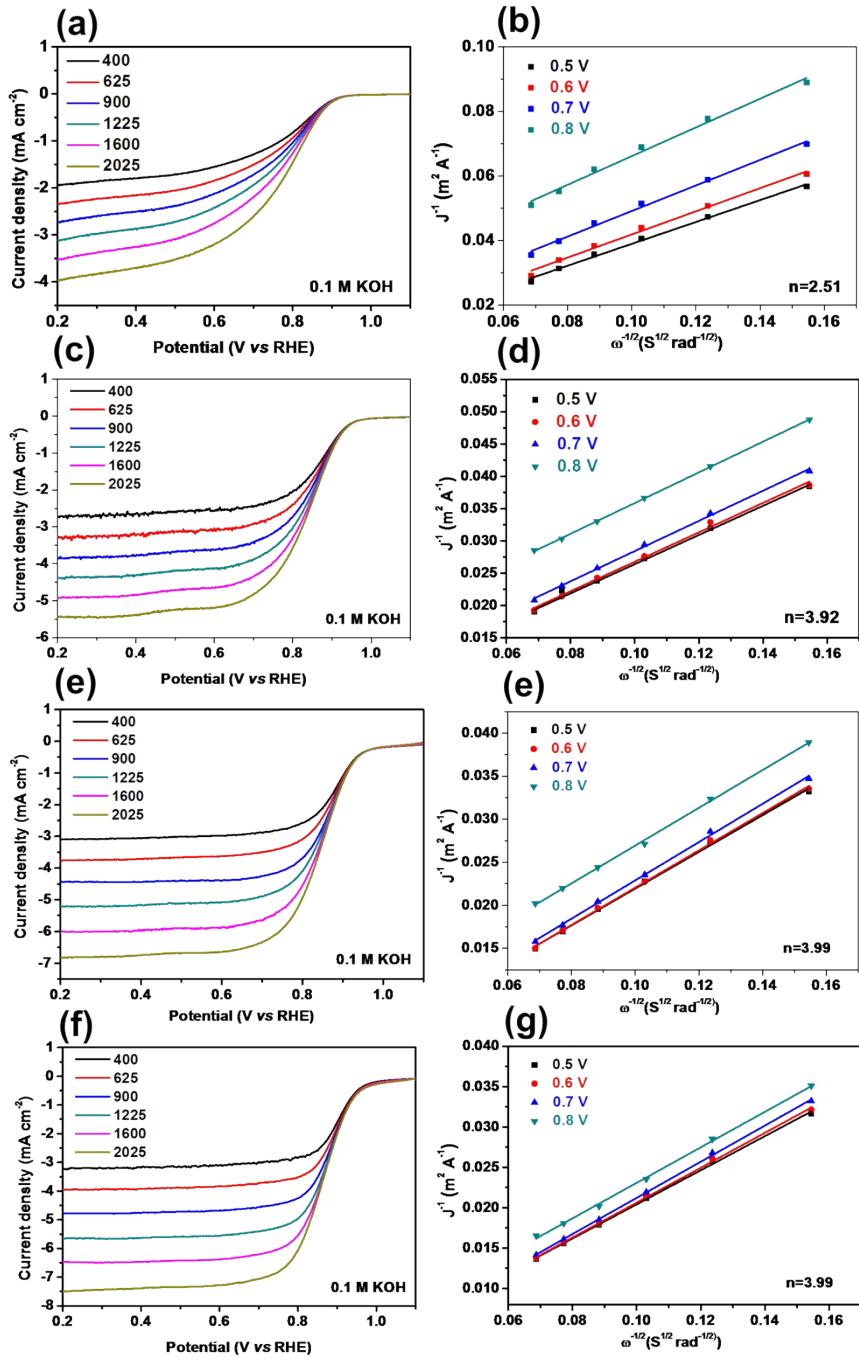


Figure S15. RDE voltammograms at different rotating speeds for FeNC-20-1000 with various catalyst loading and its corresponding Koutecky-Levich plots (a, b) 0.03 mg cm^{-2} , (c, d) 0.15 mg cm^{-2} , (e, f) 0.45 mg cm^{-2} and (f, g) 0.75 mg cm^{-2} in 0.1 M KOH with oxygen saturated.

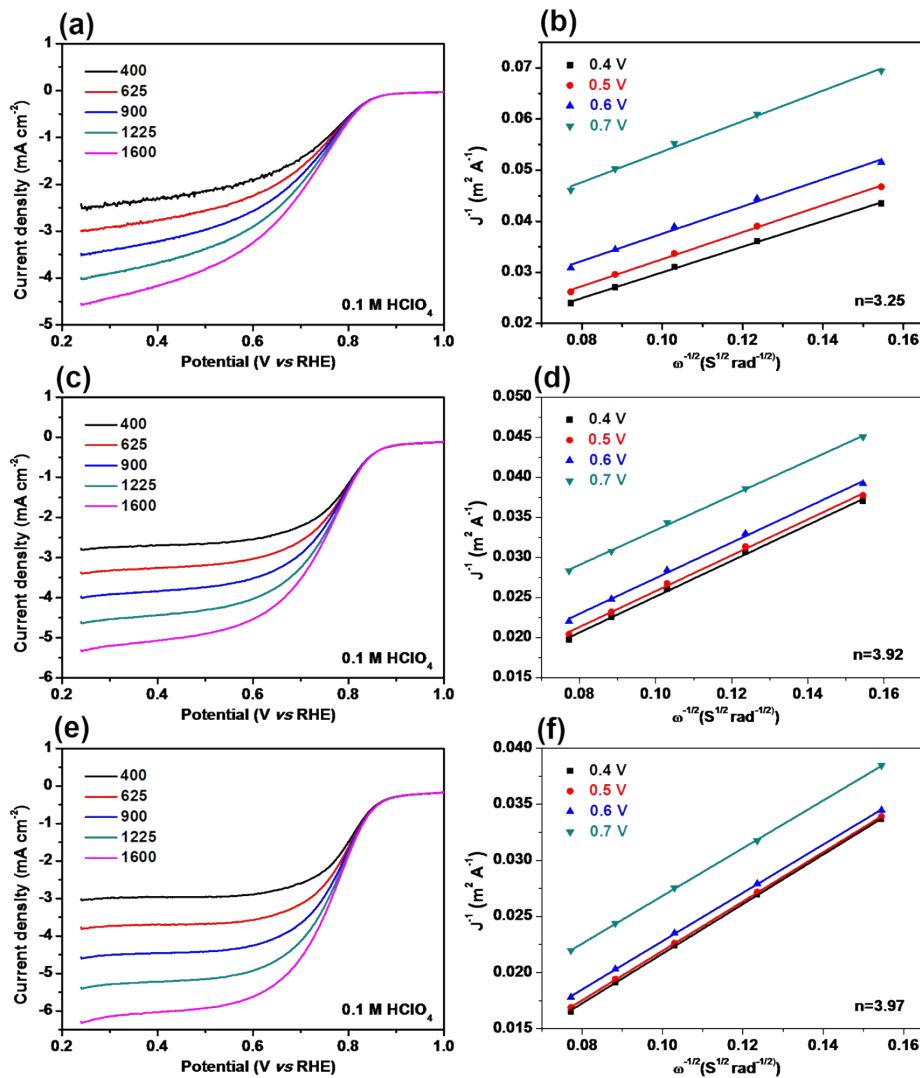


Figure S16. RDE voltammograms at different rotating speeds for FeNC-20-1000 with various catalyst loading and the corresponding Koutecky-Levich plots in 0.1 M HClO₄: (a, b) 0.15 mg cm⁻², (c, d) 0.45 mg cm⁻², (e, f) 0.75 mg cm⁻².

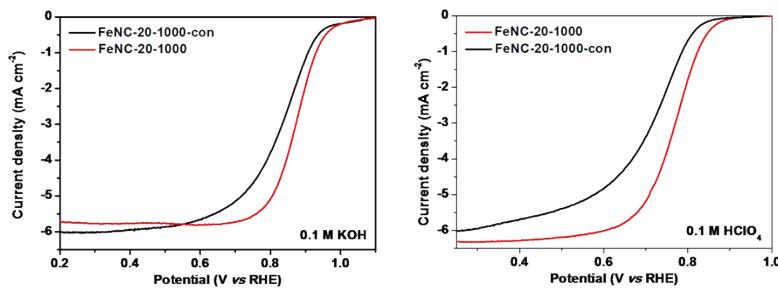


Figure S17. LSV curve of (a) FeNC-20-1000-con and (b) Pt/C carried in (a) 0.1 M KOH, (b) 0.1 M HClO₄ with oxygen saturated, rotating speed of 1600 rpm and a scan rate of 5 mV s⁻¹. Catalysts loading was 0.75 and 0.15 mg cm⁻² for FeNC-20-1000-con and Pt/C respectively.

Table S1. Comparison of the E_{onset} and $E_{1/2}$ toward ORR for non-noble metal catalysts reported and this work in alkaline medium.

| Catalyst | E_{onset}/V | $E_{1/2}/V$ | e | Referenc | References |
|---|----------------------|-------------|------------|---|------------|
| | | | | electrode | |
| Fe-N/C-800 | 0.923 | 0.809 | vs RHE | <i>J. Am. Chem. Soc.</i> 2014 , 136, 11027 | |
| Fe ₃ C/C-800 | 1.05 | 0.83 | vs RHE | <i>Angew. Chem. Int. Ed.</i> 2014 , 53, 3675 | |
| N-doped Fe/Fe ₃ C@C | 0.91 | 0.83 | vs RHE | <i>Adv. Energy Mater.</i> 2014 , 4, 1400337 | |
| PCN-FeCo/C | 1 | 0.85 | vs RHE | <i>Adv. Mater.</i> 2015 , 27, 3431 | |
| Fe ₃ C/C-800 | 1.03 | 0.86 | vs RHE | <i>Adv. Mater.</i> 2015 , 27, 2521 | |
| Fe-N-CNS | 0.98 | 0.85 | vs RHE | <i>ACS Catal.</i> 2015 , 5, 3887 | |
| Fe-N/C-800 | 0.98 | / | vs RHE | <i>J. Am. Chem. Soc.</i> 2015 , 137, 5555 | |
| CoFe ₂ O ₄ /NG | -0.03 | -0.144 | vs Ag/AgCl | <i>Small</i> 2015 , 11, 5833 | |
| Fe-N-CNFs | -0.02 | -0.14 | vs Ag/AgCl | <i>Angew. Chem. Int. Ed.</i> 2015 , 54, 8179 | |
| Co@Co ₃ O ₄ @C-CM | 0.93 | 0.81 | vs RHE | <i>Energy Environ. Sci.</i> 2015 , 8, 568 | |
| FePhen@MOF-ArNH ₃ | 1.03 | 0.86 | vs RHE | <i>Nat. Commun.</i> 2015 , 6, 7343 | |

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|---------------------------------------|------|-------|---------------|---|
| $\text{Co}_3\text{O}_4@\text{CMWCNT}$ | 0.89 | 0.81 | <i>vs RHE</i> | <i>J. Mater. Chem. A</i> 2015 , <i>3</i> , 17392 |
| Co -S/G-3 | 0.93 | 0.83 | <i>vs RHE</i> | <i>ACS Appl. Mater. Interfaces</i> 2015 , <i>7</i> , 21373 |
| GNS/MC | / | 0.85 | <i>vs RHE</i> | <i>Adv. Energy Mater.</i> 2016 , <i>1501794</i> |
| pPMF-800 | 1.05 | 0.879 | <i>vs RHE</i> | <i>Nanoscale</i> 2016 , <i>8</i> , 959 |
| Fe/N/CNT | 1.04 | 0.86 | <i>vs RHE</i> | <i>Appl. Catal. B: Environ.</i> 2016 , <i>183</i> , 185 |
| FeNC-20-1000 | 1.04 | 0.88 | <i>vs RHE</i> | This work |

Table S2. Comparison of the E_{onset} and $E_{1/2}$ toward ORR for non-noble metal catalysts reported and this work in acid medium. The mole concentration in the table is 0.5 M for H_2SO_4 and 0.1 for HClO_4 .

| Catalyst | $E_{\text{onset}}/\text{V}$ | $E_{1/2}/\text{V}$ | Electrolyte | References |
|---------------------------|-----------------------------|--------------------|-------------------------|--|
| PANI-Fe-C | 0.93 | / | H_2SO_4 | <i>Science</i> 2011 , <i>332</i> , 443 |
| NT-G | 0.89 | 0.76 | HClO_4 | <i>Nat. Nanotech.</i> 2012 , <i>7</i> , 394 |
| PFeTTPP-1000 | 0.93 | 0.76 | HClO_4 | <i>Angew. Chem. Int. Ed.</i> 2013 , <i>125</i> , 8507 |
| Fe-AAPyr | 0.9 | 0.75 | H_2SO_4 | <i>Electrochimi. Acta</i> 2013 , <i>90</i> , 656 |
| PpPD-Fe-C | 0.826 | 0.718 | H_2SO_4 | <i>Angew. Chem. Int. Ed.</i> 2014 , <i>53</i> , 2433 |
| Zn(elm) ₂ TPIP | 0.914 | 0.78 | HClO_4 | <i>Adv. Mater.</i> 2014 , <i>26</i> , 1093 |

Angew. Chem. Int. Ed. **2014**, 53,

| | | | | |
|--------------------------|-------|-------|-------------------|--|
| Fe ₃ C/C-700 | 0.9 | 0.73 | HClO ₄ | |
| | | | | 3675 |
| Fe-N-GC-900 | / | 0.74 | HClO ₄ | <i>ACS Catal.</i> 2014 , 4, 1793 |
| PMF-800 | 0.886 | / | HClO ₄ | <i>J. Am. Chem. Soc.</i> 2015 , 137, 1436 |
| PCN-FeCo/C | 0.9 | 0.76 | HClO ₄ | <i>Adv. Mater.</i> 2015 , 27, 3431 |
| Fe ₃ C/NG-800 | 0.92 | 0.77 | HClO ₄ | <i>Adv. Mater.</i> 2015 , 27, 2521 |
| CPANIFe-NaCl | 0.91 | 0.74 | HClO ₄ | <i>J. Am. Chem. Soc.</i> 2015 , 137, 5414 |
| N-Fe/G (60)- 900-S | 0.834 | 0.716 | HClO ₄ | <i>Nanoscale</i> 2015 , 7, 14707 |
| pPMF-800 | 0.89 | 0.71 | HClO ₄ | <i>Nanoscale</i> 2016 , 8, 959 |
| ZIF-TAA-p | 0.88 | 0.78 | HClO ₄ | <i>J. Mater. Chem. A</i> 2016 , 4, 4457 |
| FeNC-20-1000 | 0.90 | 0.77 | HClO ₄ | This work |