**Electronic Supplementary Material (ESI)** 

## Hierarchically porous Fe-N-C derived from covalent-organic material

## as highly efficient electrocatalyst for Oxygen Reduction<sup>+</sup>

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Fig. S1. SEM images of the catalysts pyrolysis at different target temperatures. (a, b) FeNC-800 (c, d) FeNC-1000



Fig. S2. TEM images of (a, b) FeNC-800 (c, d) FeNC-1000



Fig. S3. The high-resolution N 1s and Fe 2p spectrum of (a, c) FeNC-800, (b, d) FeNC-1000



Fig. S4. Pore size distribution of FeNC-based catalysts



Fig. S5. Steady-state polarization curves of FeNC-based catalysts.



Fig. S6. SEM images of the FeNC-900 catalyst after accelerated durability test: (a) in 1M KOH solution, (b) in 1M  $HCIO_4$  solution.



Fig. S7. Methanol-tolerance evaluation of FeNC-900 tested by the current–time chronoamperometric responses at 0.6 V versus RHE in O  $_2$  -saturated (commercial 20% Pt/C is used for comparison) in 0.1 M KOH solution. The arrow represents the addition of 3 M methanol into the electrolyte.



Fig. S8. Methanol-tolerance evaluation of FeNC-900 tested by the current–time chronoamperometric responses at 0.6 V versus RHE in O  $_2$  -saturated (commercial 20% Pt/C is used for comparison) in 0.1 M HClO<sub>4</sub> solution. The arrow represents the addition of 3 M methanol into the electrolyte.



Fig. S9. (a) XRD and (b) Steady-state polarization curves of ORR of catalysts in 0.1 M KOH solution from different metal.



Fig. S10. SEM images of the catalysts (a) CoNC-900 and (b) NiNC-900.



Fig. S11. (a) N<sub>2</sub> adsorption-desorption isotherms of CoNC-900 and NiNC-900 catalyst, (b) Pore size distribution of CoNC-900 catalyst, (C) Pore size distribution of NiNC-900 catalyst.



Fig. S12. The high-resolution N 1s and Co 2p (Ni 2p) spectrum of (a, c) CoNC-900, (b, d) NiNC-900







Fig. S14. XRD of CTF



Fig. S15. (a) XRD and (b) Steady-state polarization curves of ORR of catalysts in 0.1 M KOH solution from different precursors.



Fig. S16. SEM images of the catalysts (a) TTF-900, (b) Fe-TPN-900 and (c) Fe-CTF-900.

Table S1. (	Comparison	of ORR	catalytic	performances	in	alkaline	solution	between	FeNC-900	and	other	noble-
metal-free	electrocatal	ysts repo	orted pre	viously.								

Catalyst	Onset potential	Half-wave potential	The diffusion-limited	Ref.
	(V vs. RHE)	(V vs. RHE )	current density (mA/cm <sup>2</sup> )	
FeNC-900	1.00	0.88	6.25	This work
Fe-N/C-800	0.98	0.81	4.81	[1]
Fe-N/C-800	0.92	0.81	6.06	[2]
Fe-N-C	0.95	0.86	6.60	[3]
Fe-N/G	0.87	0.78	5.21	[4]
Co-N-HPC	0.91	0.83	5.00	[5]
N:C-MgNTA	0.89	0.75	5.70	[6]
NCNTFs	0.95	0.87	5.30	[7]
NPC-F	0.94	0.84	5.50	[8]
Fe <sub>2</sub> N/N-GAs-20	1.02	0.88	4.80	[9]

pPMF-800	1.05	0.88	6.20	[10]

Catalyst	Onset potential	Half-wave potential	The diffusion-limited	Ref.
	(V vs. RHE)	(V vs. RHE )	current density (mA/cm2)	
FeNC-900	0.85	0.72	5.95	This work
Fe-N/C-800	0.80	0.68	6.09	[2]
Fe2N/N-GAs-20	0.82	0.65	3.79	[9]
pPMF-800	0.89	0.71	6.10	[10]
Fe/Co-CMP-800	0.88	0.76	4.70	[11]
Co-N-C	0.85	0.76	5.90	[12]
Co-Zn-ZIF/GO-800	0.85	0.70	4.20	[13]
H–Fe@N–C/RGO	0.89	0.67	7.80	[14]
Fe-N/C-900	0.58	0.40	5.78	[15]
	(V vs. Ag/AgCl)	(V vs. Ag/AgCl)		

Table S2. Comparison of ORR catalytic performances in acid solution between FeNC-900 and other noble-metalfree electrocatalysts reported previously.

## Notes and references

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