

Supporting Materials

Soft-template assisted synthesis of Fe/N-doped hollow carbon nanospheres as advanced electrocatalysts for oxygen reduction reaction in microbial fuel cells

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Table S1 Concentrations of the reagents for preparation of hollow or solid PACP nanosphere

Reagents	Hollow PACP (mM)	Hollow Fe-PACP (mM)	Solid Fe-PACP (mM)
Triton X-100	1.6	1.6	1.6
Aniline	50	50	50
Pyrrole	50	50	85
APS	100	100	100
FeCl ₃ ·6H ₂ O	--	50	50

Table S2 Characterizations of the as-prepared materials

Samples	C%	N%	O%	Fe%	S_{BET}^a (m²/g)	S_{micro}^b (m²/g)	S_{meso}^c (m²/g)	Pore diameter r (nm)	V_{total}^d (cm³/g)	V_{micro}^e (cm³/g)
HCN	87.8	4.3	6.9	-	893.3	723.0	170.3	3.39	0.76	0.37
Fe-HCN	86.2	4.2	7.5	1.8	853.1	675.1	178.1	4.73	0.75	0.34
Fe-SCN	85.8	4.0	7.6	1.5	322.8	249.8	73.0	4.32	0.35	0.13

S_{BET} is the surface area calculated by the Brunauer–Emmett–Teller equation.

S_{micro} is the microporous surface area calculated by the t-plot method.

S_{meso} is the mesoporous surface area (S_{meso}=S_{BET}-S_{micro}).

Total pore volume (V_{total}) is calculated at a relative pressure of 0.99.

Micropore volume (V_{micro}) is calculated by the t-plot method.

Table S3 Summary of performance of hollow carbon nanosphere-based catalysts for ORR

Catalysts	CV E_{peak} (V)	LSV $E_{\text{on-set}}$ (V)	LSV $E_{\text{half-wave}}$ (V)	n	Ref.
BHCSs-0.3-900	-0.17	-0.10	-0.15	3.7	[1]
HMCN-G	-0.30	-0.15	-0.23	3.7	[2]
S-PGHS-900	-0.26	-0.10	0.17	3.8	[3]
Fe/N/C HNSs-750	-0.17	-0.13	-0.15	3.8	[4]
PDA-HCS-Co	-0.31	-0.18	-0.27	3.8	[5]
HNCS71	\	-0.05	-0.20	3.9	[6]
Co ₃ O ₄ /HCS	-0.28	-0.13	-0.22	3.7	[7]
Fe/N-HCN	-0.09	0.02	-0.12	3.9	This work

The potentials were reported versus Ag/AgCl, which could be converted with the equations:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.2438 \text{ V} + 0.0591 \times \text{pH}$$

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH}$$

Reference:

- [1] H. Lu, Y. Li, L. Zhang, H. Li, Z. Zhou, A. Liu, Y. Zhang, S. Liu, RSC Adv, 5 (2015) 52126-52131.
- [2] Y. Qin, J. Li, J. Yuan, Y. Kong, Y. Tao, F. Lin, S. Li, J. Power Sources, 272 (2014) 696-702.
- [3] Xi'An Chen, X. H. Chen, X. Xu, Z. Yang, Z. Liu, L.J. Zhang, X.J. Xu, Y. Chen, S.M. Huang, Nanoscale, 22 (2014) 13740-13747.
- [4] Dan Zhou, L. P. Yang, L. H. Yu, J. H. Kong, X. Y. Yao, W. S. Liu, Z.C. Xu, X. H. Liu, Nanoscale, 7 (2015) 1501-1509.
- [5] H. Wang, X. Bo, A. Wang, L. Guo, Electrochem Commun, 36 (2013) 75-79.
- [6] J. Sanetuntikul, T. Hang, S. Shanmugam, Chem Commun, 50 (2014) 9473-9476.
- [7] Z. Chen, D. He, X. Xu, Z. Liu, M. Huang, X. Wang, H. Jiang, RSC Adv, 6 (2016) 34159-34164.

Figure S1

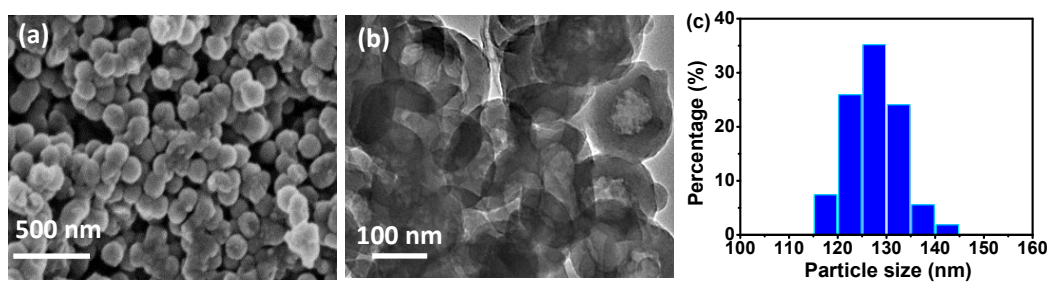


Figure S1 (a) SEM image of Fe-doped PACP; (b) TEM image of Fe-doped PACP; (c) diameter distribution histograms of Fe-doped PACP from analysis of TEM image.

Figure S2

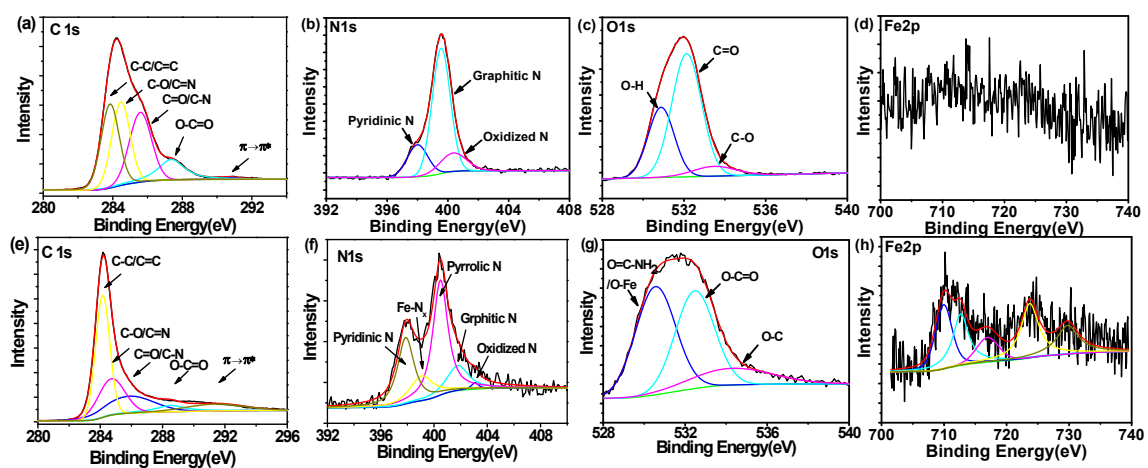


Figure S2 High-resolution C1s, N1s and O1s XPS spectra of HCN (a~d), and Fe-SCN (e~h), respectively.

Figure S3

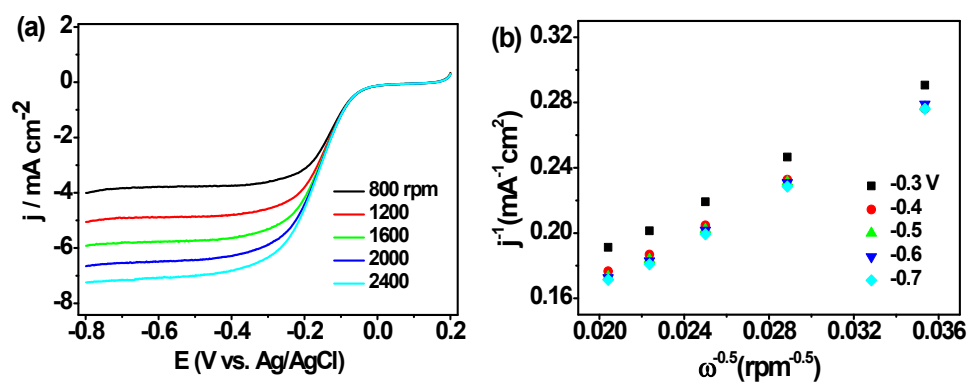


Figure S3 LSV curves of the Pt/C at different rotation rates in O₂-saturated 0.1 M KOH solutions at a scan rate of 10 mV/s (a), and the corresponding K-L plots at different potentials for the Pt/C (b).

Figure S4

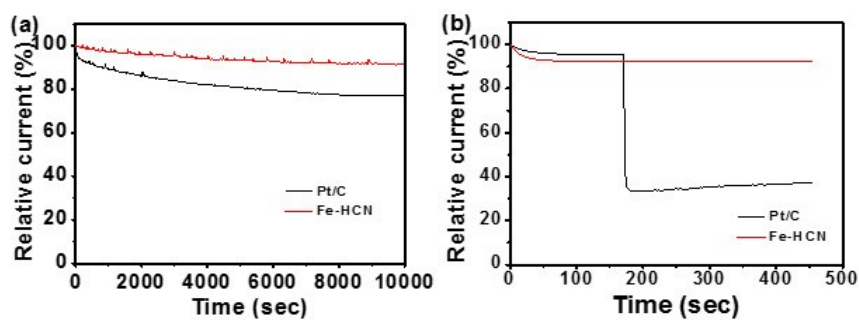


Figure S4 (a) Stability test of the Fe/N-HCN and Pt/C electrodes at - 0.3 V (vs. Ag/AgCl) in O₂-saturated 0.1 M KOH solutions at a rotation rate of 1600 rpm, normalized to the initial current responses; (b) Chronoamperometric responses to the injection of 3M methanol into an O₂-saturated 0.1 M KOH solution at the Fe/N-HCN and Pt/C electrodes, normalized to the initial current responses.