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Supporting Information

Hierarchically Porous Nitrogen-Doped Carbon Nanotubes Derived

from Core-shell ZnO@Zeolitic Imidazolate Framework Nanorods for

Highly Efficient Oxygen Reduction Reactions

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Fig. S1 (a) N₂ sorption isotherms of ZnO@ZIF-8-24h and ZnO@ZIF-8-48h. (b) The pore size distribution of ZnO@ZIF-8-24h and ZnO@ZIF-8-48h based on H-K method. (c) N₂ sorption isotherms of NCNTs and C-ZIF-8-1000. (d) Pore size distribution plots of NCNTs and C-ZIF-8-1000 based on the non-local density functional theory (NLDFT).



Fig. S2 (a) AFM image of NCNT-24-1000. (b) Height profile along the line scan in a. (c) AFM image of NCNT-48-1000. (d) Height profile along the line scan in c.



Fig. S3 SEM images (a) NCNT-48-800, (b) NCNT-24-900, (c) NCNT-48-900, (d) NCNT-24-1000, (e) NCNT-48-1000, TEM image (f) NCNT-24-1000, (g) NCNT-48-1000, inset in g the SAED pattern of NCNT-48-1000. (h) HRTEM image of NCNT-48-1000.



Fig. S4 N content (at %) and C/N atomic ratios in NCNTs based on XPS.



Fig. S5 (a) CV curves of NCNT-48-1000, C-ZIF-8-1000, NCNT-24-800. (b) K-L plots of NCNT-24-800 at different voltages. (c) LSVs of NCNT-48-1000 with various rotation speeds. (d) K–L plots of NCNT-48-1000 at different voltages. (e) LSVs of NCNT-48-900 with various rotation speeds. (f) K–L plots of NCNT-48-900 at different voltages.

Table S1. Comparison of ORI	R catalytic performances u	under alkaline conditions	between metal-free
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Sample	Precursors	Onset	Half-wave	Current	Refs.
		potential	potential	density	
		(V) V vs	(V) V vs	(rpm)	
		RHE	RHE		
NCNT-24-800	ZnO@ZIF-8	1.025	0.862	5.68 (1600)	Present
					Work
NCNT-48-1000	ZnO@ZIF-8	0.995	0.831	5.5 (1600)	Present
					Work
GPC-1000-5	ZIF-8	0.876	0.705	5.66 (1600)	S 1
P-Z8-Te-1000	Te@ZIF-8	0.895	-0.161	Not	S2
				mentioned	
FeIM/ZIF-8	Fe-ZIF & ZIF-8	0.915	0.755 V	Not	S3
	mixture			mentioned	
NC900	ZIF-8	0.83	Not	4.9 (2500)	S4
			mentioned		
Co@Co3O4@C-CM	ZIF-9	0.93	0.81	Not	S5
				mentioned	
FePhen@MOF-ArNH ₃	ZIF-8 & 1,10-	1.03	0.86	Not	S 6
	phenanthroline			mentioned	
ZIF-67-900	ZIF-67	0.91	0.85	5 (1600)	S7
Carbon-L	ZIF-7	0.861	0.697	4.59 (1600)	S 8
MOFCN900	melamine & MOF-	0.99	Not	4.2 (1600)	S9
	5		mentioned		

NCNTs and carbons materials derived from MOFs in previous reports

The reversible hydrogen electrode (RHE) potential converts to the Ag/AgCl electrode using: E (RHE) = E (Ag/AgCl) + 0.965 V.



Fig. S6. A proposed mechanism of ORR catalyzed by NCNTs

Four-electron mechanism^{S10}:

 $O_{2} + * \rightarrow O_{2} * (a \rightarrow b)$ $O_{2}^{*} + H_{2}O + e^{-} \rightarrow OOH^{*} + OH^{-} (b \rightarrow c)$ $OOH^{*} + e^{-} \rightarrow O^{*} + OH^{-} (c \rightarrow d)$ $O^{*} + H_{2}O + e^{-} \rightarrow OH^{*} + OH^{-} (d \rightarrow e)$ $OH^{*} + e^{-} \rightarrow OH^{-} + * (e \rightarrow f)$ **Two-electron mechanism:** $O_{2} + * \rightarrow O_{2}^{*} (a \rightarrow b)$ $O_{2}^{*} + H_{2}O + e^{-} \rightarrow OOH^{*} + OH^{-} (b \rightarrow c)$ $OOH^{*} + e^{-} \rightarrow OOH^{-} + * (c \rightarrow g)$

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