Supporting Information

Densely atomic Co–Nx moieties coupled hierarchical-carbon-microspheres for efficient oxygen reduction reaction in neutral media

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Electrochemical tests.

A conventional three-compartment electrochemical cell (Pine Electrochemical Station, Model AFCBP-1) was used for half-cell electrochemical characterizations with phosphate buffered saline (PBS) as electrolyte. A graphite rode, an Ag/AgCl, and a glass carbon electrode were employed as counter, reference and working electrode, respectively. All potentials were converted to reversible hydrogen electrode (RHE) scale. $E_{RHE}=E_{SCE}+0.056*pH+0.19$. Then, 3 mg of catalysts and 500 μL isopropanol with Nafion ionomer were sonicated for 1h. Then 30 μl ink was deposited onto a glassy carbon electrode to reach a catalyst loading of 0.6 mg cm^{-2}. Pt/C loading of 20 μg_{pt} cm^{-2}. Kinetic current was acquired from mass transfer correction using Levich equation.[1] Cyclic voltammetry (CV) was performed to determine the electrochemical double-layer capacitance.[2]

Mg–air battery tests. Liquid Mg–Air batteries were assembled and tested in homemade electrochemical cells. SA Co–Nx–HCM or commercial Pt/C (20 wt%) were loaded on carbon fiber paper to fabricate air cathodes with a catalyst loading of 1.2 mg cm^{-2}. A polished Mg foil was used as anode in PBS electrolyte. The effective electrode area is 0.8 cm^2. Discharge measurements were carried out on the constructed cell at room temperature with a Land CT2001A system.

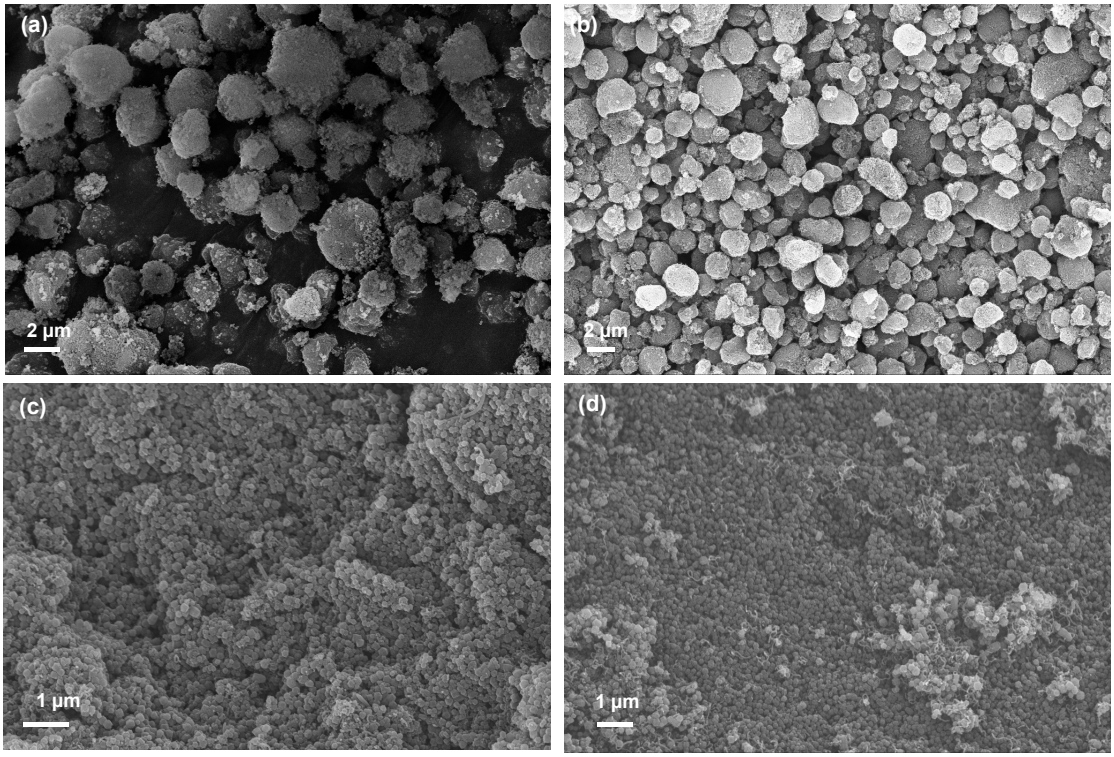

Fig. S1 SEM images of a) Spray-dried ZIF8 nanocrystals, and b) after carbonization. c) SA Co–Nx–C, d) Co-N-C.

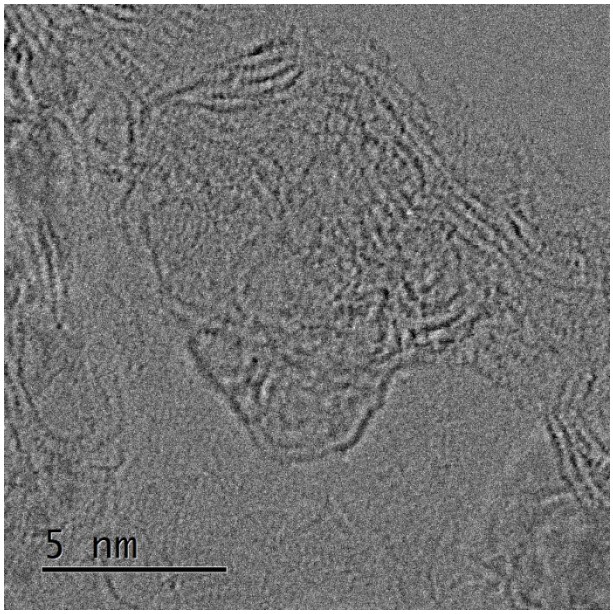

Fig. S2 TEM image of SA Co–Nx–HCM

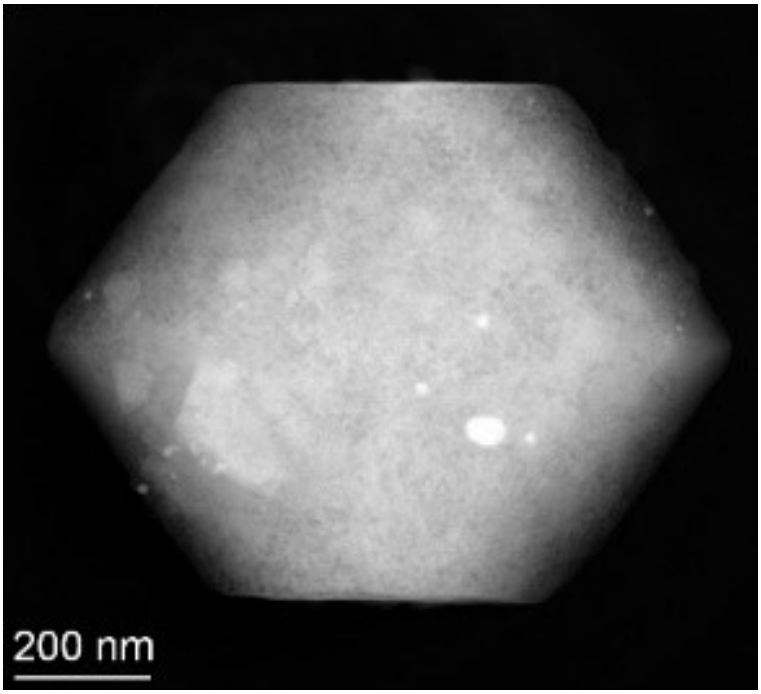

Fig. S3 STEM image of Co–N–C

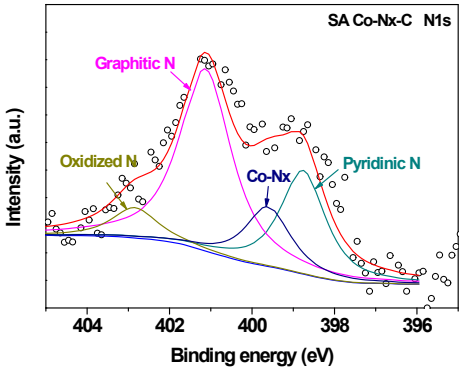

Fig. S4 N1s of SA Co–Nx–C

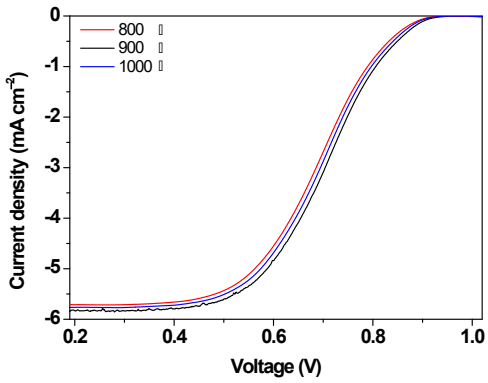

Fig. S5 ORR polarization plots of SA Co–Nx–HCM catalysts pyrolyzed at different temperatures.

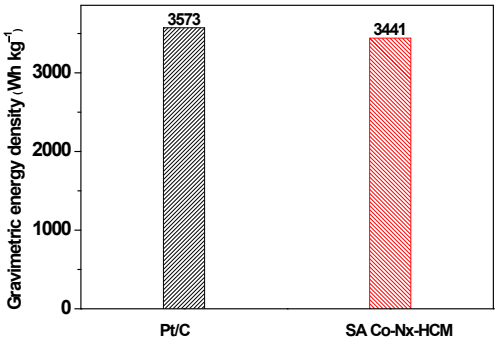

Fig. S6 Comparison of the gravimetric energy density

Table S1. Specific surface areas and pore volumes distributions of the prepared catalysts.

Samples	BET surface area $m^2\ g^{-1}$	Micropore surface area $m^2\ g^{-1}$	External surface area $m^2\ g^{-1}$
N-carbon sphers	480	390	90
Co–N–C	682	485	197
SA Co–Nx–C	712	499	213
SA Co–Nx–HCM	894	577	317

Table S2. Elemental composition of the samples obtained from XPS results.

Samples	C (at.%)	N (at.%)	O (at.%)	Co (at.%)
SA Co–Nx–HCM	89.12	4.41	6.25	0.22
SA Co–Nx–C	89.06	4.34	6.36	0.24
Co–N–C	87.91	4.61	7.13	0.35

Table S3. Atomic concentrations (at.%) of heterocyclic N components of samples in the N 1s binding energy region (395 ~ 4010 eV).

Samples	Pyridinic N	Co-Nx	Graphitic N	Oxidized N
	~398 eV	~399 eV	~401 eV	~402 eV
SA Co–Nx–HCM	1.10	0.78	2.22	0.31
SA Co–Nx–C	1.07	0.73	2.24	0.30
Co–N–C	1.24	0.63	2.29	0.45

Table S4. Comparison of the Co content of SA Co–Nx–HCM material with published SA Co-N-C catalysts.

Samples	Co (ICP) (wt.%)	Ref.
SA-Fe-Nx-MPCS	1.13	This work
Co-SAC/NC	2.5	eScience[3]
Co−N−C	2.2	J. Am. Chem. Soc.[4]
Fe-NGM/C-Fe	0.14	Angew. Chem. Int. Ed.[5]
ZIF-NC-10Co	0.5	Angew. Chem. Int. Ed.[6]
IrCo-N-C	1.02	ACS Catal.[7]
Co-N/S-DSHCN	2.91	Nano Lett.[8]
PtZn–CoNC	0.13	J. Mater. Chem. A[9]

Table S5 Outline of recently reported electrocatalysts for Mg-air batteries.

Catalysts	Electrolyte	Half-wave potential (V)	Ref.
SA-Fe-Nx-MPCS	0.1 M PBS	**0.71**	**This work**
FeSAs/SN-C/rGO	0.1 M PBS	0.60	Nano Res.[10]
Fe1/d-CN	0.1 M PBS	0.605	Energy Environ. Sci.[11]
Co-N-C-10	0.1 M PBS	0.65	Electro. Acta [12]
e@G-800/100e	0.1 M PBS	0.83	ACS Sustainable Chem. Eng.[13]
Co−N−C	0.1 M PBS	0.731	ACS Catal.[14]

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