Supporting Information

A Sulfur- and Nitrogen-Doped, Ferrocene-Derived Mesoporous Carbons with Efficient Electrochemical Reduction of Oxygen

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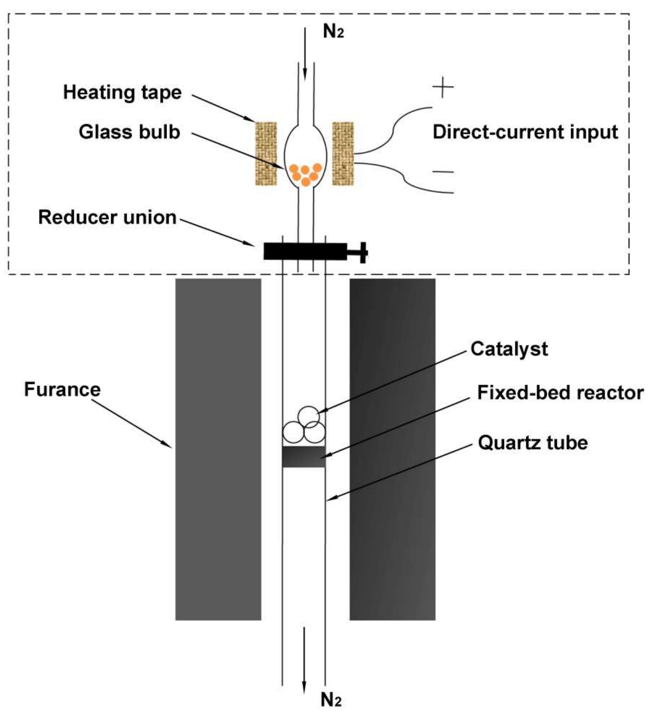
1. A schematic drawing of CVD reaction system



Scheme S1. Schematic drawings of the CVD reaction system equipped with a ferrocene sublimation-vapor generator (dashed-line section)

2. Additional experimental data

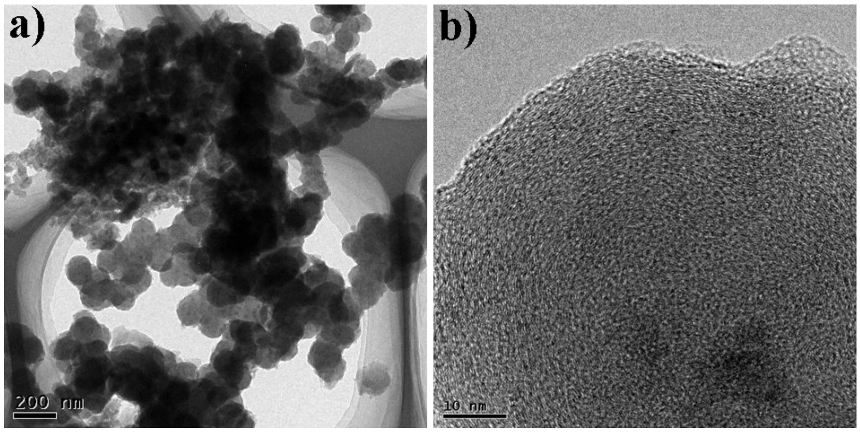


Figure S1. a) TEM image and b) HR-TEM image of the oligoporous SN-C prepared in template-free CVD condition.

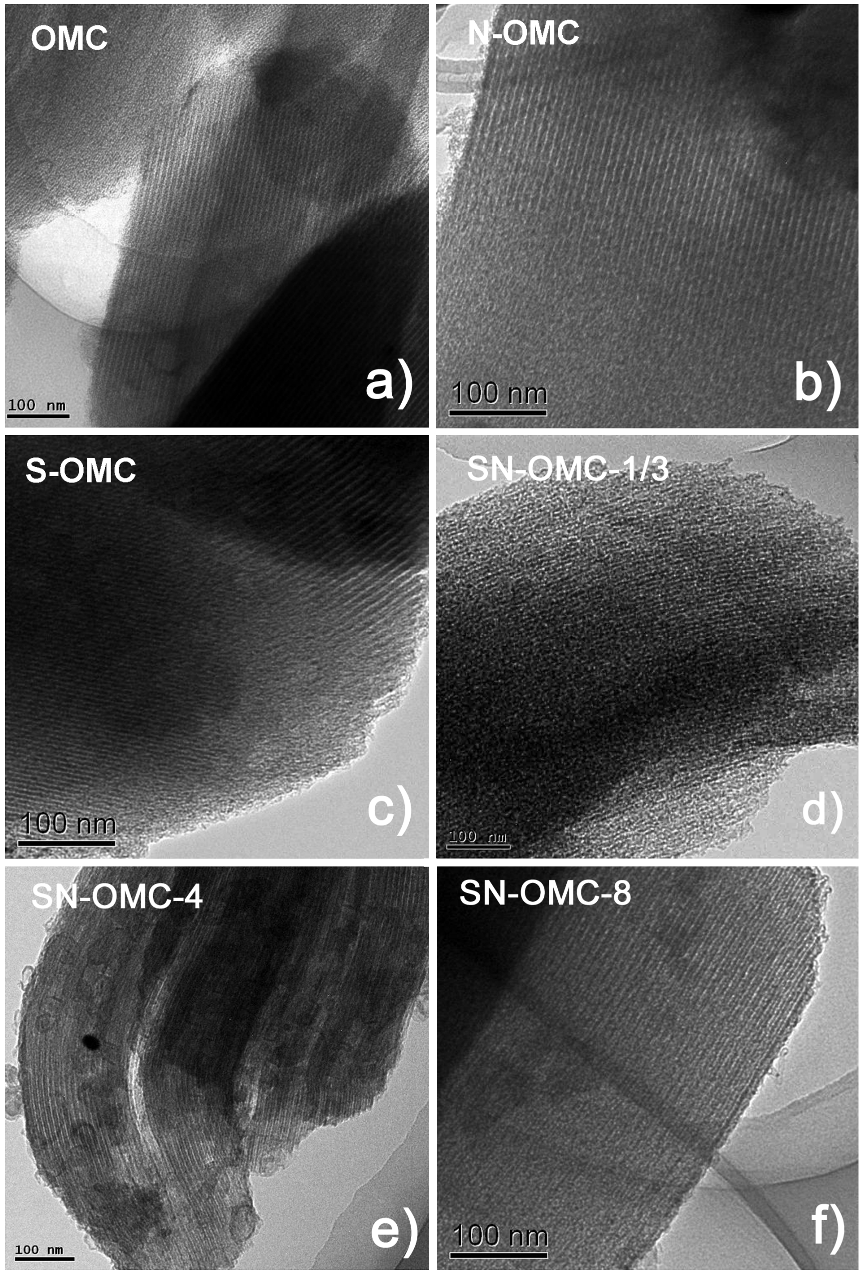


Figure S2. Typical TEM images of a) undoped OMC, b) N-OMC, c) S-OMC, d) SN-OMC-1/3, e) SN-OMC-4, and f) SN-OMC-8.

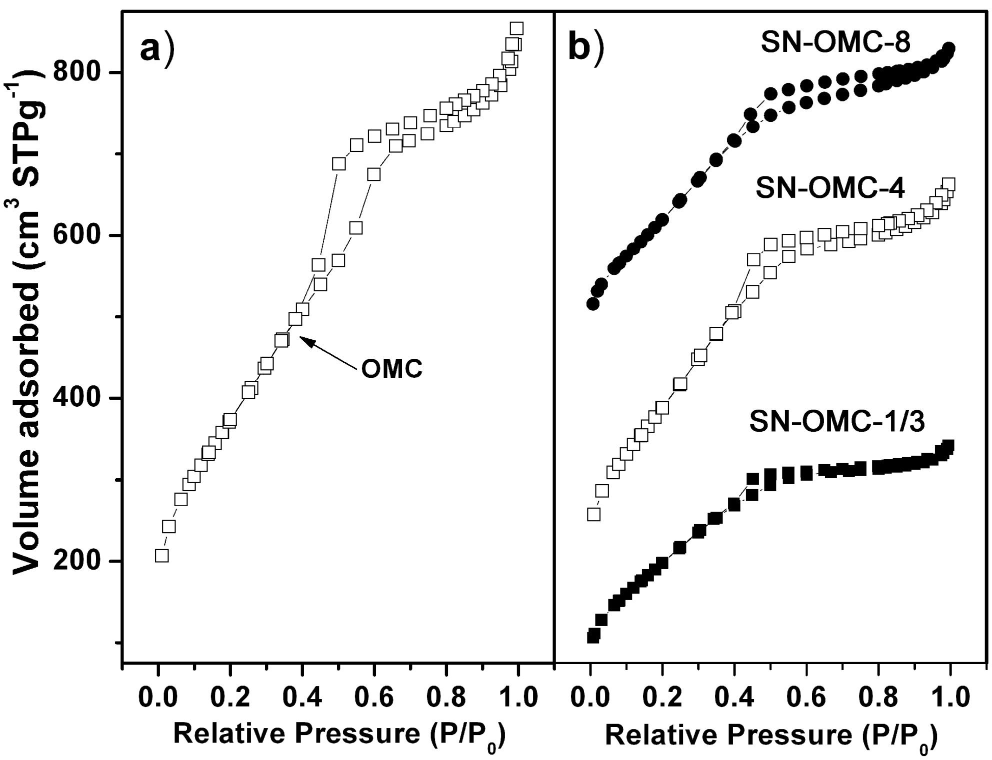


Figure S3. N_2-sorption isotherm curves of a) OMC for CVD-growth of 4 h and b) the SN-OMC-1/3, SN-OMC-4 and SN-OMC-8. The isotherms of SN-OMC-4 and SN-OMC-8 were offset vertically by 100 and 400 cm^3g^{-1}, respectively.

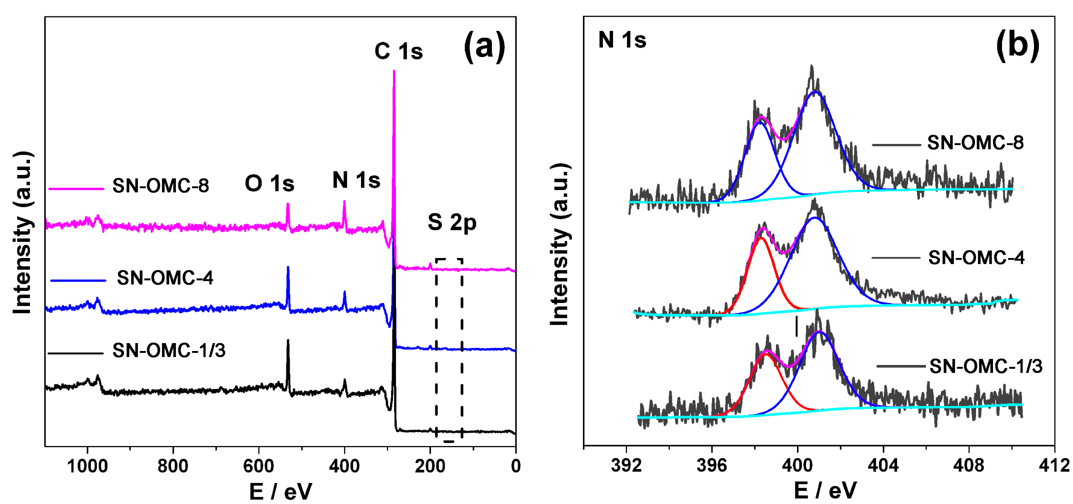


Figure S4. a) XPS survey spectra and b) high-resolution N1s spectra for SN-OMC-1/3, SN-OMC-4 and SN-OMC-8 samples: the black and purple lines are the raw and fitted spectra, respectively; the red and blue lines correspond to pyridinic-N (398.1 eV) and pyrrolic/graphitic-N (400.8 eV), respectively according to reference.[2]

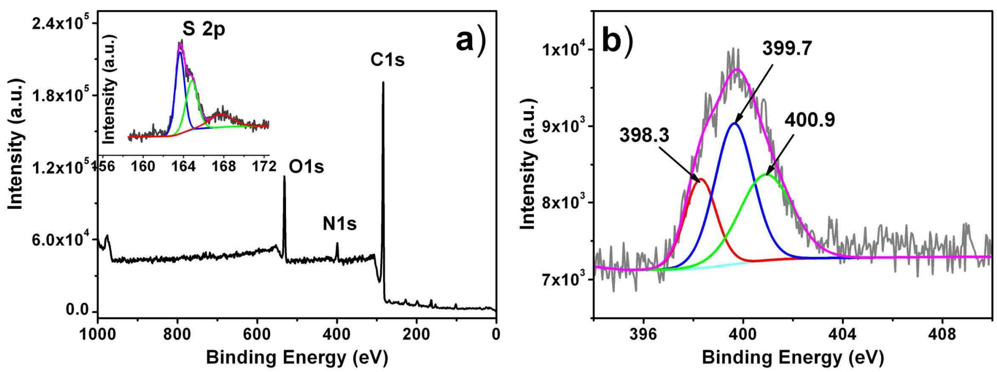


Figure S5. a) XPS survey spectrum of SN-C, the inset shows the corresponding S 2p spectrum. b) High resolution N 1s spectrum: the grey and purple lines are the raw and fitted spectra; the red, blue and green lines correspond to pyridinic-N (398.3 eV) and pyrrolic-N (399.7 eV) and graphitic-N (400.9 eV), respectively.

Table S1. Physicochemical properties of OMC, S-OMC, N-OMC, SN-C, SN-OMC-4 and SN-OMC-16 samples.

Catalyst	SA [a] $[m^2 \cdot g^{-1}]$	PV [b] $[cm^3 \cdot g^{-1}]$	PD [c] [nm]	At% [d] C	At% [d] O	At% [d] S	At% [d] N *N*-1 [e]	*N*-2 [f]
OMC	1390	1.32	3.9/2.4	88.5	11.5	--	--	--
S-OMC	688	0.71	3.5/2.4	89.8	9.2	1.0	--	--
N-OMC	556	0.5	3.5/2.4	81.1	15.4	--	2.8	3.4
SN-C	--	--	--	80.7	13.6	1.85	0.83	2.96
SN-OMC-16	680	0.70	3.2	74.8	4.9	2.1	4.6	12.75

[a] Specific surface area from multiple BET method; [b] Total pore volume at $P/P_0 = 0.99$; [c] Average pore diameter, estimated using the desorption branch of the isotherm and the Barrett–Joyner–Halenda formula; [d] Atomic ratio data from XPS analyses; [e] Pyridinc-N, at ~398.3 eV; [f] Pyrrolic-/graphitic-N, at ~400-~402 eV according to reference.[2]

Table S2. The electrochemical activity of OMC, SN-C, SN-OMC-4 and SN-OMC-16 sample for ORR.

Catalyst	$E_{onset} / E_{1/2}$ [a] [mV/mV]	J_{κ} [b] $[mA \cdot cm^{-2}]$	*n* [c]
OMC	-186/-229	5.4	2.4
S-OMC	-136/-203	14.2	2.1
N-OMC	-75/-138	26.0	3.8
SN-C	-280/-350	2.4	2.3
SN-OMC-16	-60/-144	22.5	4.0

a) Onset potential (E_{onset}) and half-wave potential ($E_{1/2}$), estimated LSV measurement curves; b) Kinetically limiting diffusion current density at -0.3 V vs. Ag/AgCl; c) The number of electron-transfer.

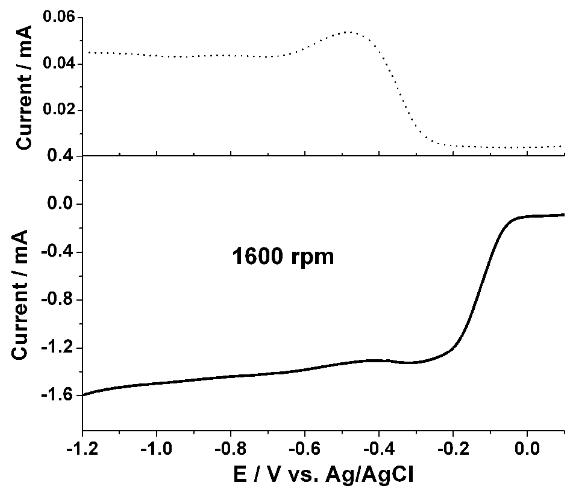


Figure S6. Polarization curves obtained with a rotating disk-ring electrode for ORR on SN-OMC-4 catalyst (0.306 mg/cm^2) in 0.1m NaOH. Rotation rates are indicated in the graph; sweep rate 10 mVs^{-1}; ring potential +500 mV vs. Ag/AgCl; ring and disk areas are 0.2467 cm^2 and 0.1867 cm^2, respectively; collection efficiency 37 %.

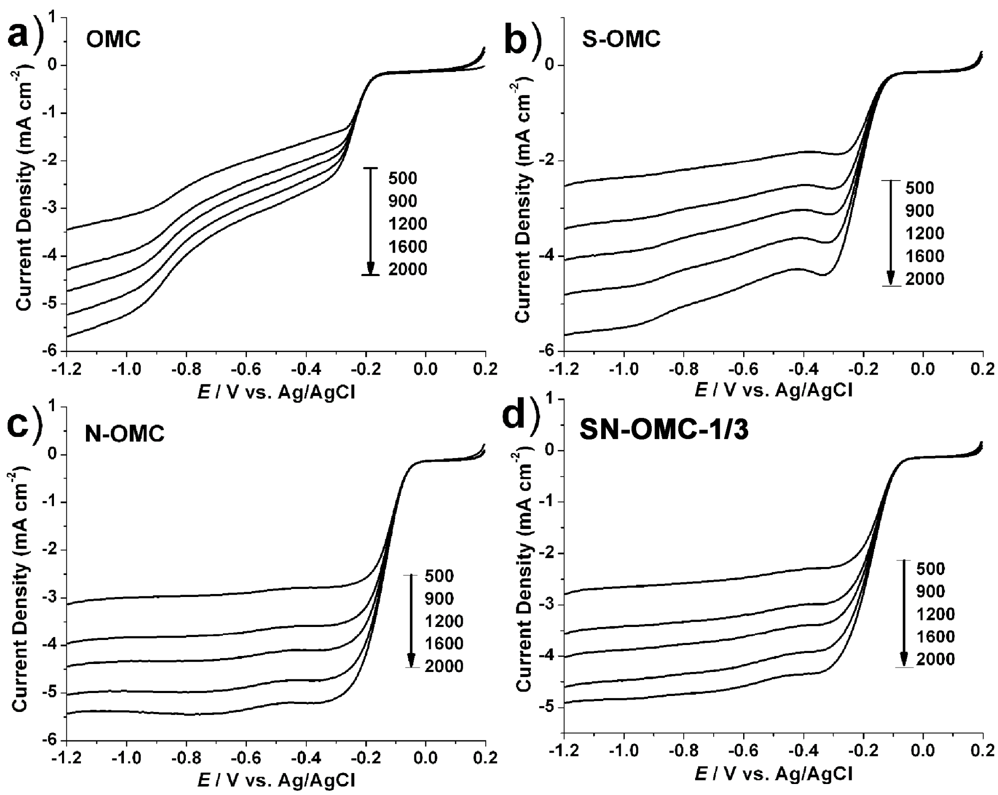


Figure S7. Linear sweep voltammograms of a) OMC, b) S-OMC, c) N-OMC, and d) dual-doped SN-OMC-1/3 on GC electrodes in O_2-saturated 0.1 M NaOH solution at different ratation speeds with a scan rate of 10 mV·S^{-1}.

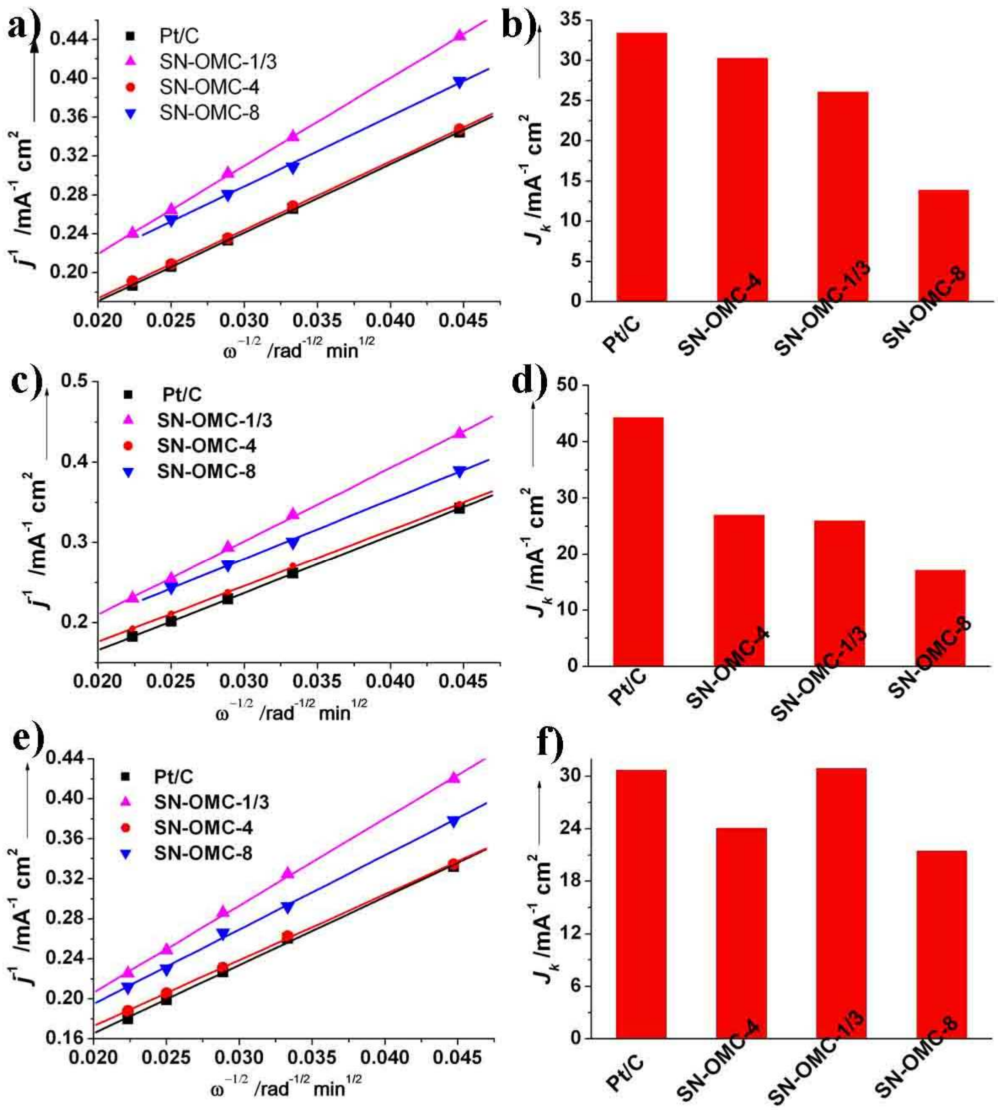


Figure S8. K-L plots and the corresponding kinetic limiting currents of SN-OMC-1/3, SN-OMC-4, SN-OMC-8 as well as Vulcan Pt/C obtained at different potentials: a, b) -0.3 V; c, d) -0.4 V; e,f) -0.5 V.

3. Koutechy-Levich equations and the transfer electron number calcualtions

The transfer electron number per oxygen molecule involved in the oxygen reduction at SN-OMCs electrodes was determined on the basis of the Koutechy-Levich equation[1,2] given below:

$I^{-1} = I_k^{-1} + (0.62nFCD^{2/3}\upsilon^{-1/6}\,\omega^{1/2})^{-1}$

where I_k is the kinetics current density, I is the measured current density of the ORR, n represents the number of electrons transferred per oxygen molecule, F is the Faraday constant (F=96485 $C{\cdot}mol^{-1}$), C is the bulk concentration of O_2 (= 1.2×10^{-3} $mol{\cdot}\,L^{-1}$), D is the diffusion coefficient of O_2 in the KOH electrolyte (=$1.9*10^{-5}$ cm^2 S^{-1}), υ is the kinetic viscosity of the electrolyte (=0.01 cm_2 S^{-1}), and ω is the angular velocity of the the disk (ω = 2πN, N is the linear rotation speed).

Reference

1. Chen, W. & Chen, S. W. Oxygen Electroreduction Catalyzed by Gold Nanoclusters: Strong Core Size Effects. *Angew Chem Int Edit* **48**, 4386-4389 (2009).
2. Xu, J. X. Dong, G. F. Jin, C. H. Huang, M. H. & Guan, L.H. Sulfur and Nitrogen Co-Doped, Few-Layered Graphene Oxide As a Highly Efficient Electrocatalyst for the Oxygen Redution Reaction. *ChemSusChem* **6**, 493-499 (2013).