Sulfur–Nitrogen Co-doped Three-Dimensional Carbon Foams with Hierarchical Pore Structures as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reactions

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Supporting Information

Table S1   Physical parameters, electrochemical properties for various carbon materials

obtained at various annealing temperature and mass ratios of sucrose to TH

| Samples	Annealing temperature (°C)	Sucrose: TH	Specific surface area (m²/g)	S content (wt.%)	N content (wt.%)	Peak Potential (V)	Peak current density, (mA cm⁻²)	Number of electron transfer (n)
CMK-3-1000	1000	5:0	1127	0	0	-0.20	0.22	1.95
S-N-CF-1000-1	1000	4:1	1017	1.51	4.23	-0.18	0.29	2.07
S-N-CF-1000-2	1000	3:2	850	2.41	6.34	-0.18	0.48	2.43
S-N-CF-1000-3	1000	2:3	643	2.61	6.44	-0.17	0.89	3.09
S-N-CF-1000	1000	1:4	394	2.88	6.53	-0.16	2.35	3.96
S-N-CF-1000-4	1000	1:8	298	2.96	6.98	-0.15	1.27	3.52
S-N-CF-900	900	1:4	457	2.96	7.86	-0.18	1.59	3.58
S-N-CF-800	800	1:4	480	3.14	10.24	-0.19	1.19	3.16
S-N-CF-700	700	1:4	493	3.23	13.25	-0.20	0.86	2.45
S-N-CF-600	600	1:4	497	3.51	15.29	-0.37	0.20	1.89
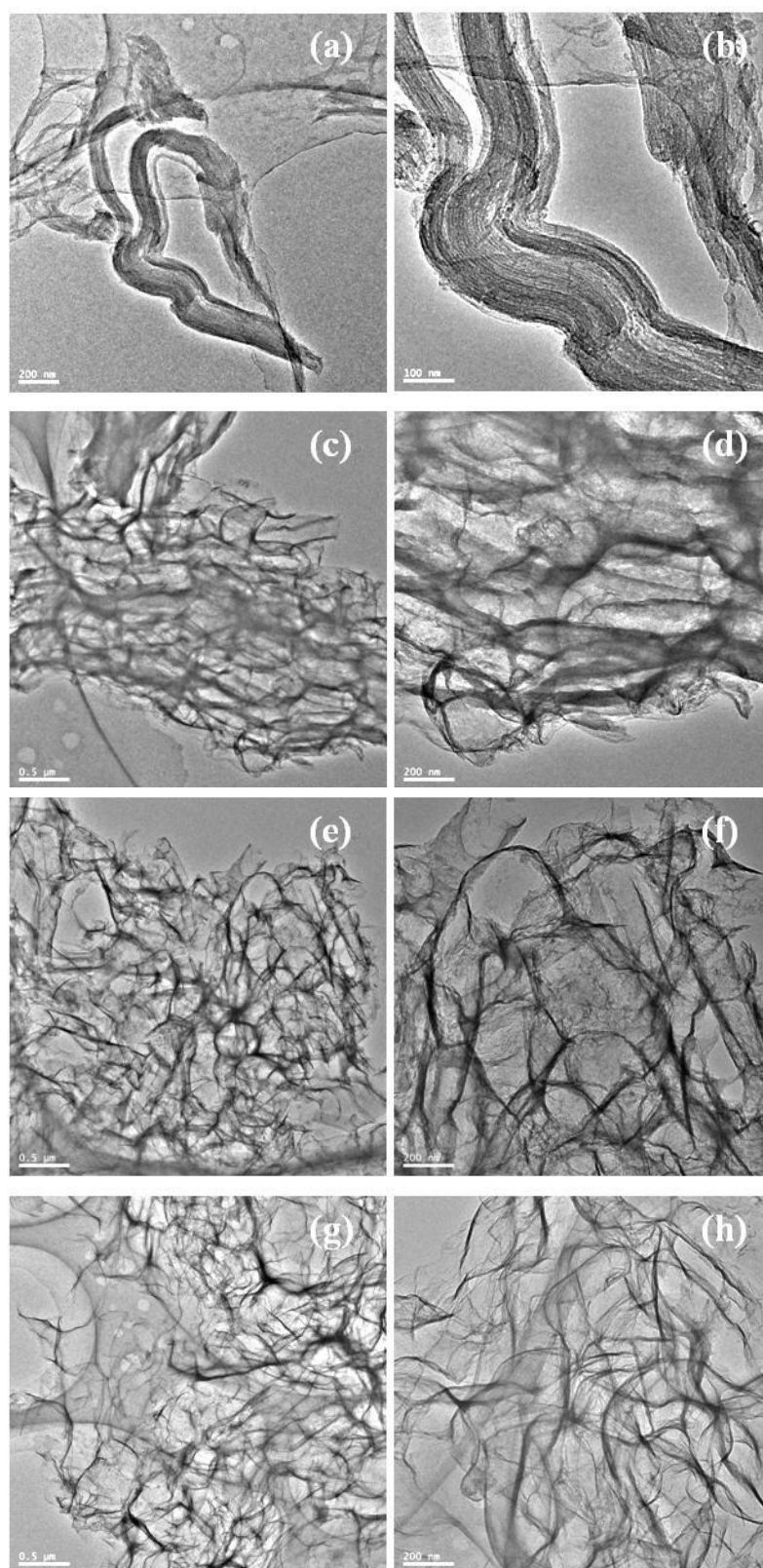
Figure S1 Typical TEM images of the resulting carbon materials obtained under different mass ratios of sucrose to TH: (a, b) 5:0, (c, d) 3:2, (e, f) 1:4, (g, h) 1:8
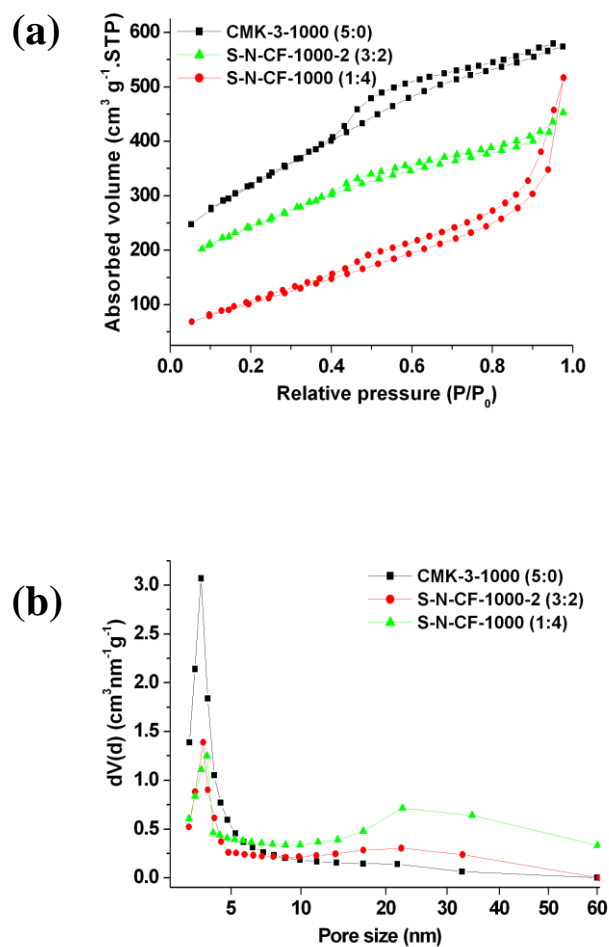
(a)

(b)

Figure S2   Adsorption−desorption isotherm and pore size distribution for the resulting carbon materials obtained under different mass ratios of sucrose to TH
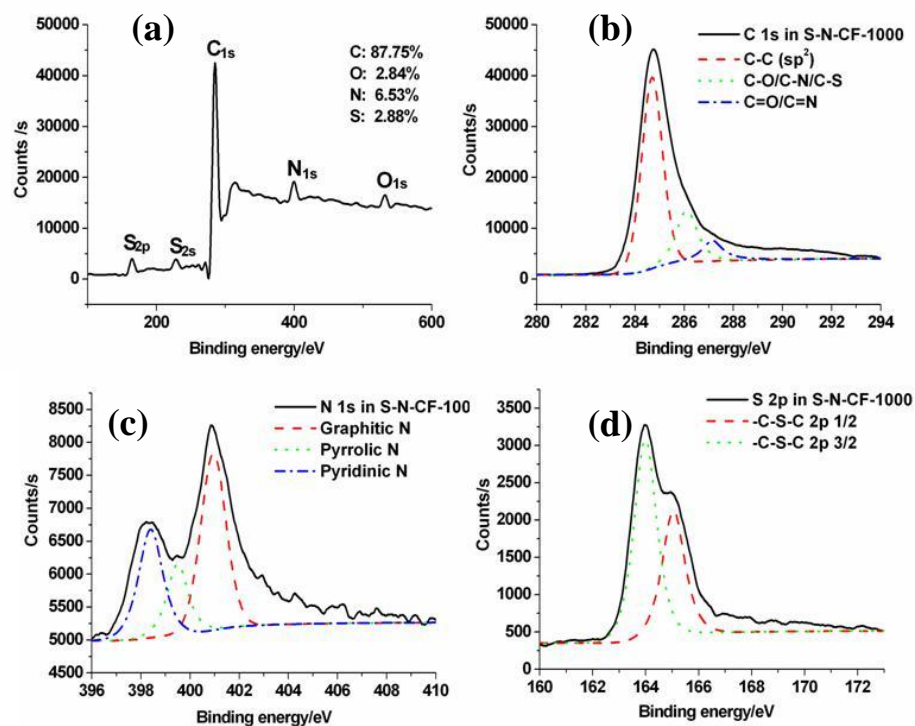
Figure S3   (a) XPS spectra survey scan, high-resolution (b) C_{1s}, (c) N_{1s} and (d) S_{2p} for S-N-CF-1000

S4. Rotating-disk voltammetry measurements

To further study the ORR electrochemical procedures of S-N-CF-1000, we performed rotating-disk electrode (RDE). The RDE current-potential curves at various rotating speeds are shown in Figure S4a .The limited diffusion currents are dependent on the rotating rates. The number of electrons involved in the ORR can be calculated from the Koutecky-Levich (K-L) equation:

(1) $J^{-1}=J_L^{-1}+J_K^{-1}=(B\omega^{1/2})^{-1}+ J_K^{-1}$

(2) $B=0.62nFC_0(D_0)^{2/3}v^{-1/6}$

(3) $B=nFkC0$

(4) $J_K^{-1} = J^{-1} -(0.62nFC_0(D_0)^{2/3}v^{-1/6}\omega^{1/2})^{-1}$.

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the disk ($\omega=2pN$, N is the linear rotation speed), n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (F=96485 C·mol^{-1}), C_0 is the bulk concentration of O_2, ($C_0 =1.2\times10^{-6}$mol·cm^{-3}),v is the kinematic viscosity of the electrolyte (v=0.01 cm^2·s^{-1}), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2·s^{-1}). According to Equations (1) and (2), the number of electrons transferred (n) can be calculated to be 3.96, which indicates that the S-N-CF-1000 lead to a four-electron-transfer reaction to reduce directly oxygen into OH$^-$.
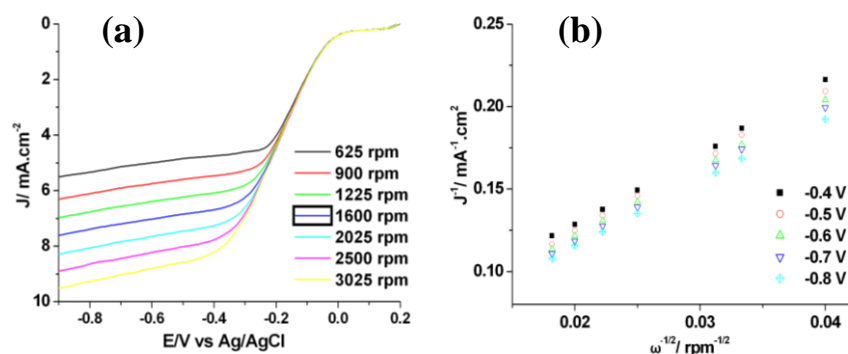

Figure S4 (a) Rotating-disk voltammograms recorded for the S-N-CF-1000 electrode in an O$_2$-saturated 0.1M solution of KOH at different rotation rates. (b,) Koutecky–Levich plot of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials and the experimental data were obtained from (Figure S4a).

S5. Estimation of Electrochemical Active Surface Area.

The current density (j) can be calculated though j=ip/A. Where ip is ORR current, A is the area of the electroactive surface area (cm^2). The electrochemical active surface areas (EASA) of the carbon catalyst samples are calculated using the Randles-Sevcik equation: $I_p = 2.69 \times 10^5 AD^{1/2} n^{3/2} \gamma^{1/2} C$. In this equation, I_p is peak current. A is the electroactive surface area (cm^2), D is the diffusion coefficient of the molecule in dilute aqueous solution, which is $6.7 \pm 0.02 \times 10^{-6}$ cm^2 s^{-1} (Hrapovic, S., Luong, J.H., 2003. Anal. Chem. 75, 3308-3315). n is 1 in our case which is the number of electrons appearing in half-reaction for the redox couple (Fe^{2+}/Fe^{3+}), γ is the scan rate which is 0.05 V s^{-1}, C is the concentration for the redox couple which is 5x10^{-6} mol/cm^3. Based on the data of peak currents in Figure S5, the calculated electrochemical active areas for CMK-3-1000 (5:0), S–N–CF-1000-2 (3:2), S–N–CF-1000 (1:4), and S–N–CF-1000-4 (1:8) are 0.115, 0.131, 0.156, 0.148 cm^2, respectively.
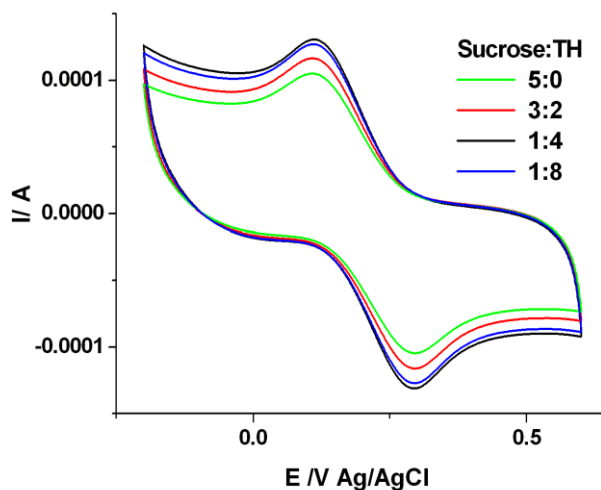

Figure S5 Cyclic voltammograms of various carbon materials in 5 mM K$_3$[Fe(CN)$_6$] solution containing 0.1 M KCl as supporting electrolyte.