

Electronic Supplementary Information for Space-Confinement-Induced Synthesis of Hierarchically Nanoporous Carbon Nanowire for the Enhanced Electrochemical Reduction of Oxygen

Jiaoxing Xu,^{a,b} Qiangmin Yu,^{a,b} Lunhui Guan^{a,b*}

^a Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China. Tel./Fax: 86-591-63173539. E-mail: guanlh@fjirsm.ac.cn.

^b Fujian provincial key laboratory of nanomaterials, Fuzhou, Fujian 350002, China

1. Details of experimental

The bimetallic oxide filled in the AAO channels was prepared through a vacuum-impregnation and oxidative decomposition. In brief, the AAO membrane with a diameter of 25 mm and channel size of 100 nm was first vacuum submerged in the nitrate aqueous solution (1.0 mL, 0.3 mol·L⁻¹, Fe/Co=1:2) at room temperature. The vacuum condition was kept until the water was completely evaporated. Then, another 1 mL distilled water was added to dissolve the residual metal nitrate and again vacuum-soaking. This procedure repeated for three times. After that, the AAO template with metal nitrate-bearing was heated at 500 °C in air for 2 hours to transform into bimetallic oxide-bearing AAO template according to literature.¹ In the supporting experimental, the AAO channel beard with trace Fe/Co metal oxide was prepared for one-time vacuum impregnation and then for the same oxidative decomposition.

2. Additional experimental data

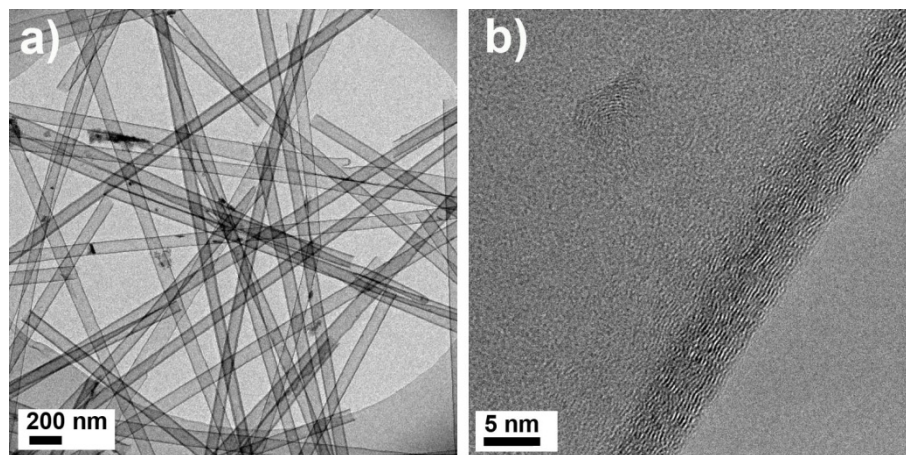


Fig. S1. (a)TEM and (b) HR-TEM image of N-CT sample.

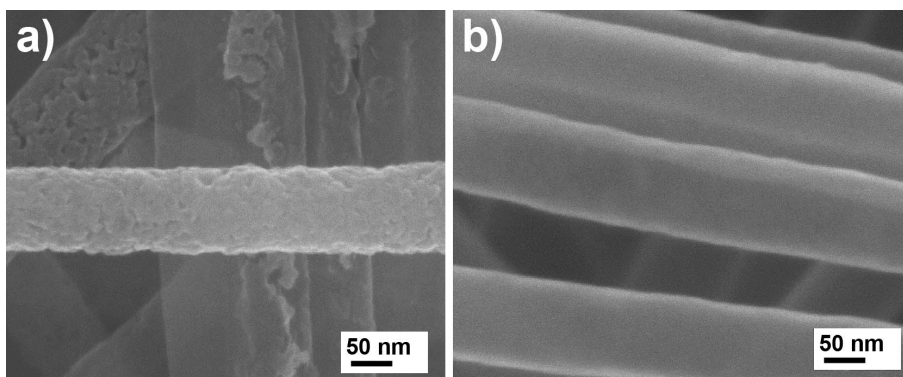


Fig. S2. SEM images of N-CW synthesized by using AAO channel beard with traces of metal oxide (a) and N-CT sample (b).

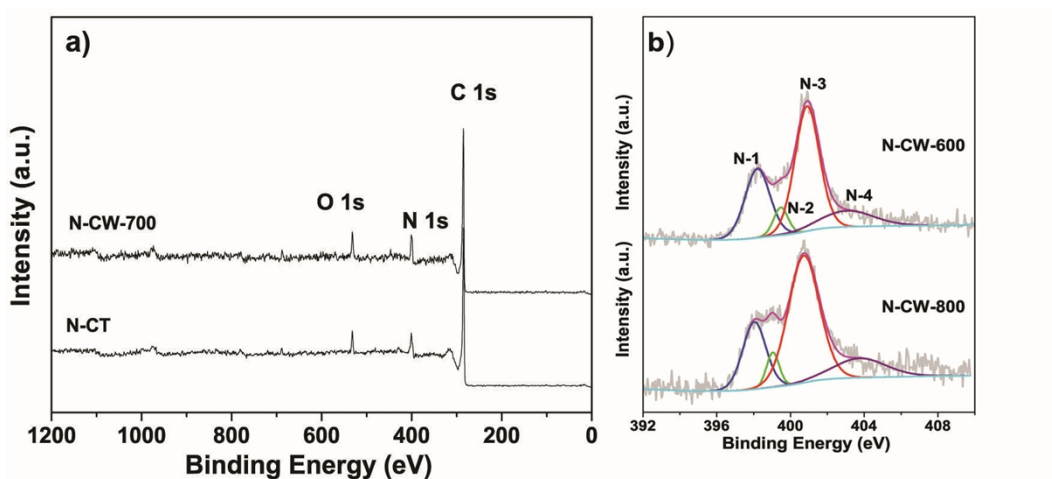


Fig. S3. (a) XP survey spectra of N-CW-700 and N-CT samples and (b) High-resolution N 1s spectra of N-CW-600 and N-CW-800.

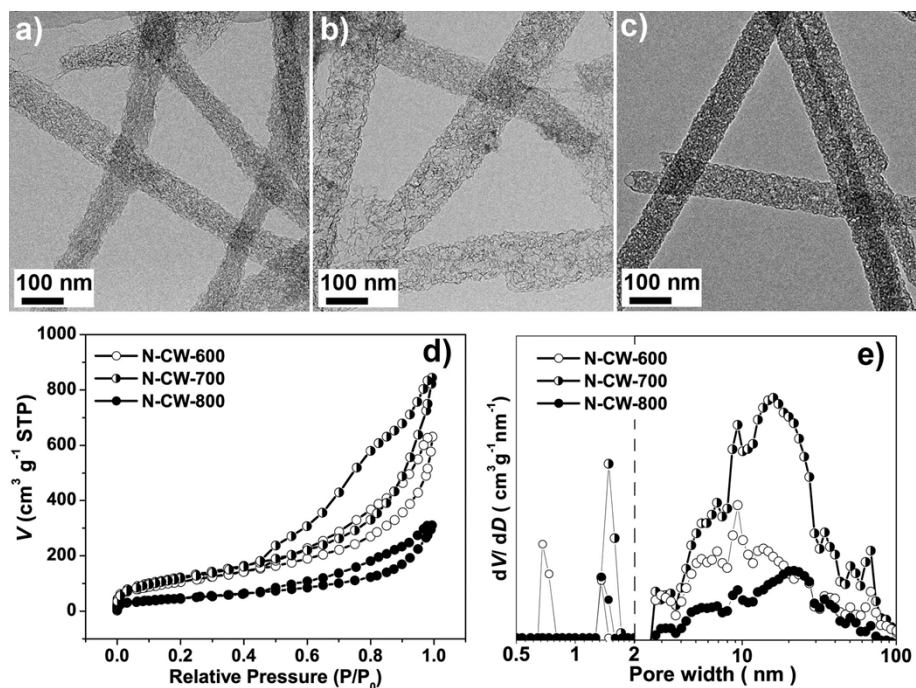


Fig. S4 (a-c) TEM image of the N-CW-600, N-CW-700 and N-CW-800 samples, (e) The corresponding N_2 sorption isotherms and (f) pore size distribution (PSD) calculated from nonlocal density functional theory (NLDFT) method.

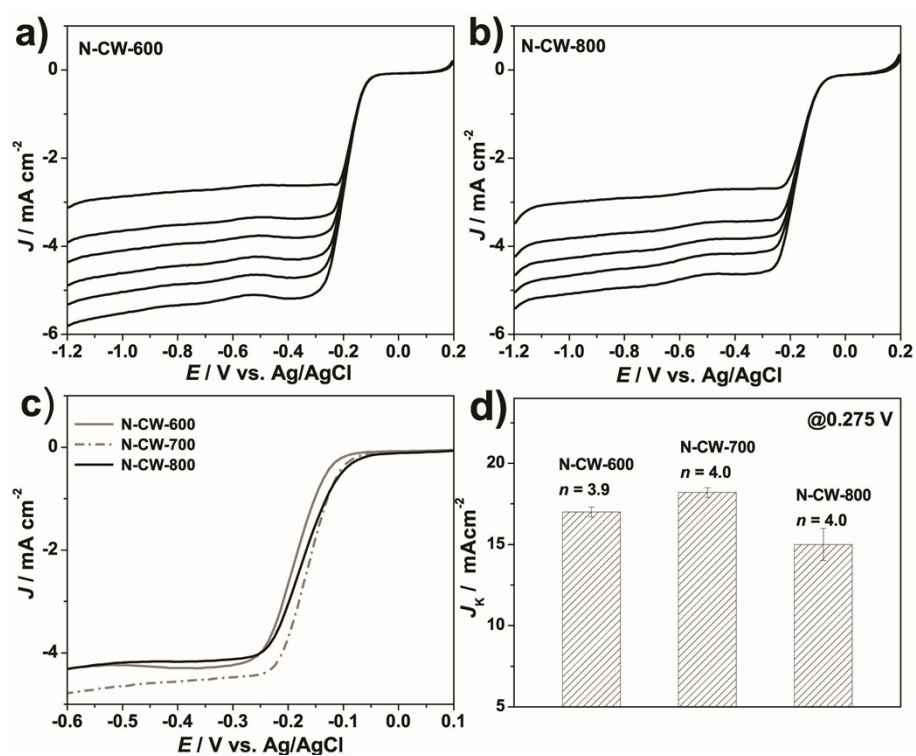


Fig. S5. (a,b) LSV curves of the N-CW-600 and N-CW-800 samples in 0.1 M NaOH alkaline media; (c) LSV curves of the N-CW-600, N-CW-700 and N-CW-800 samples at scan rate of 1600 rpm; (d) Electrochemical activity given for the kinetically limited current density (J_k) and the corresponding electron transfer number (n) of different samples at -0.275 V.

Table S1. Physicochemical properties and the electrocatalytic activity of the N-CT and N-CWs samples for ORR in comparison with the commercial Pt/C catalyst.

Catalysts	SA ^{a)}	PV ^{b)}	PSD ^{c)}	At% ^{d)} N				$E_{1/2}$ ⁱ⁾	J_k ^{j)}	n ^{k)}
	[m ² ·g ⁻¹]	[cm ³ ·g ⁻¹]	[nm]	N-1 ^{e)}	N-2 ^{f)}	N-3 ^{g)}	N-4 ^{h)}	[mV]	[mA·cm ⁻²]	
N-CT	109	0.91	65	2.5	0.4	6.1	1.6	-220	11.5	3.65
N-CW-600	396	0.98	0.7/1.4/10	2.8	0.7	4.9	1.4	-185	17	3.9
N-CW-700	455	1.30	1.5/15	3.2	0.4	6.3	2.1	-160	18.2	4.0
N-CW-800	176	0.48	1.4/22	1.6	0.5	4.0	1.0	-175	15.3	4.0
Pt/C	--	--	--	--	--	--	--	-155	23.1	4.0

^{a)} Specific surface area from multiple BET method; ^{b)} Total pore volume at $P/P_0 = 0.99$; ^{c)} Pore size distribution, estimated using the nonlocal density functional theory for N-CWs (assuming slit pore geometry) and the Barrett–Joyner–Halenda formula for N-CT (cylindrical pore geometry); ^{d)} Atomic ratio data from XPS analyses; ^{e)} Pyridinic-N, at ~398.2 eV; ^{f)} Amino-N, at ~399.3 eV; ^{g)} Pyrrolic-/graphitic-N, at ~400.5-~402 eV; ^{h)} Oxidized-N, at ~402-405 eV; ⁱ⁾ Half-wave potential ($E_{1/2}$), estimated from LSV curves; ^{j)} Limited kinetic current density at -0.275 V. ^{k)} The corresponding electron-transfer number.

Table S2. ICP analysis of the residual of Fe/Co metals in typical N-CW-700 sample.

Sample	Fe / wt.%	Co / wt.%	Al / wt.%
N-CW-700	0.38	0.33	0.12

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

The transfer electron number per oxygen molecule involved in the oxygen reduction at N-CW and N-CT electrodes was determined on the basis of the Koutechy-Levich equation^{2,3} given below:

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

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

$$J_K = nF\kappa C_0 \quad (3)$$

where J_K is the kinetics current density, J is the measured current density of the ORR, n represents the number of electrons transferred per oxygen molecule, F is the Faraday constant ($F = 96485 \text{ C}\cdot\text{mol}^{-1}$), C_0 is the bulk concentration of O_2 ($= 1.2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$), D_0 is the diffusion coefficient of O_2 in the NaOH electrolyte ($= 1.9 \times 10^{-5} \text{ cm}^2 \text{ S}^{-1}$), ν is the kinetic viscosity of the electrolyte ($= 0.01 \text{ cm}^2 \text{ S}^{-1}$), κ is the electron-transfer rate constant and ω is the angular

velocity of the the disk ($\omega = 2\pi N$, N is the linear rotation speed). According to Eqs. (1) and (2), the number of electrons transferred (n) and J_K can be obtained from the slope and intercept of the K-L plots, respectively.

Reference

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2. W. Chen, S. W. Chen, *Angew Chem Int Ed*, 2009, **48**, 4386-4389.
3. J. X. Xu, G. F. Dong, C. H. Jin, M. H. Huang, L. H. Guan, *ChemSusChem*, 2013, **6**, 493-499.