Electronic Supplementary Information for

Oxygen Reduction Electrocatalyst Based on Spatially Confined Cobalt Monoxide Nanocrystals on Holey N-Doped Carbon Nanowire : the Enlarged Interfacial Area for Performance Improvement

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1. Additional experimental data

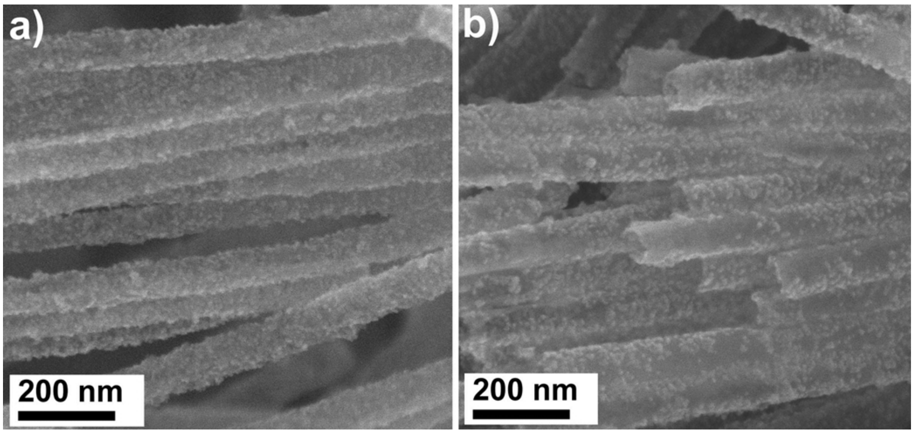

Fig. S1. SEM image of (a) CoO/NCW and (b) CoO/NCT sample.

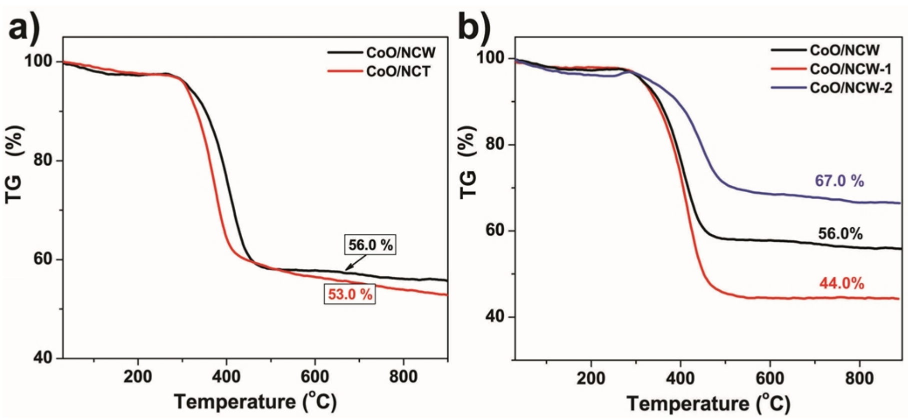

Fig. S2. TG analysis of (a) the CoO/NCW and CoO/NCT hybrids and (b) CoO/NCW samples with different CoO contents.

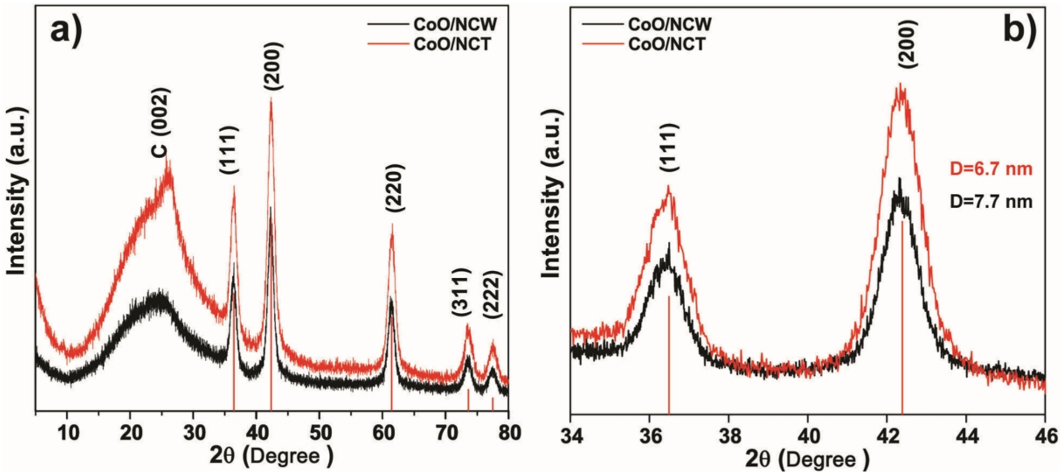

Fig. S3. (a) XRD patterns of the CoO/NCW and CoO/NCT hybrids and (b) The enlarged show of the diffraction peaks of (111) and (200), the crystalline diameter (*D*) calculated by Scherrer formula from the most intense diffraction peak (200) was 6-7 nm.

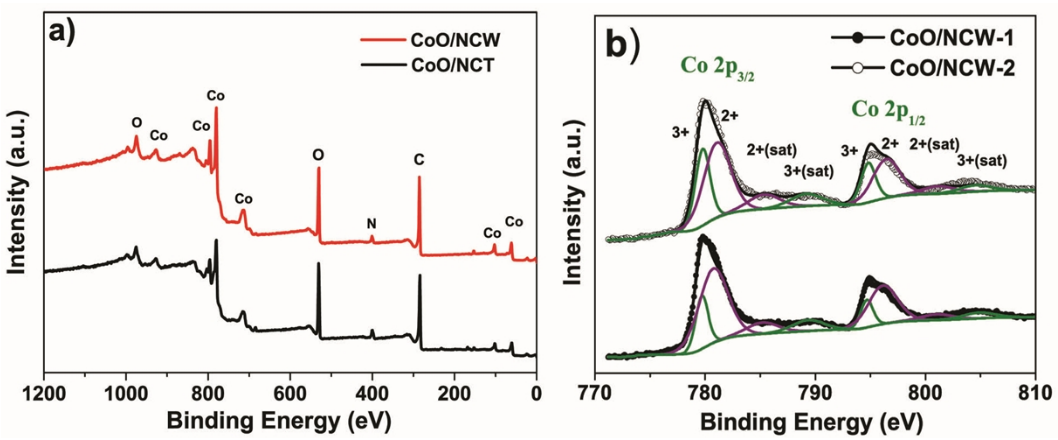

Fig. S4. (a) XP survey spectra of the CoO/NCW and CoO/NCT hybrids and (b) High-resolution Co 2p spectra of CoO/NCW-1 and CoO/NCW-2.

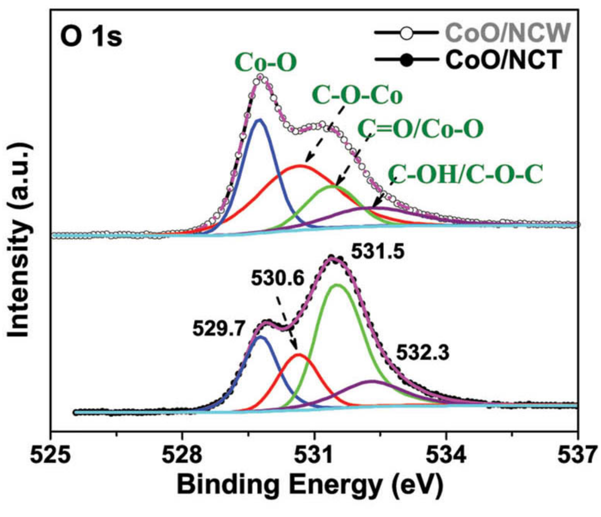

Fig. S5. High-resolution XP O 1s spectra of CoO/NCW and CoO/NCT.

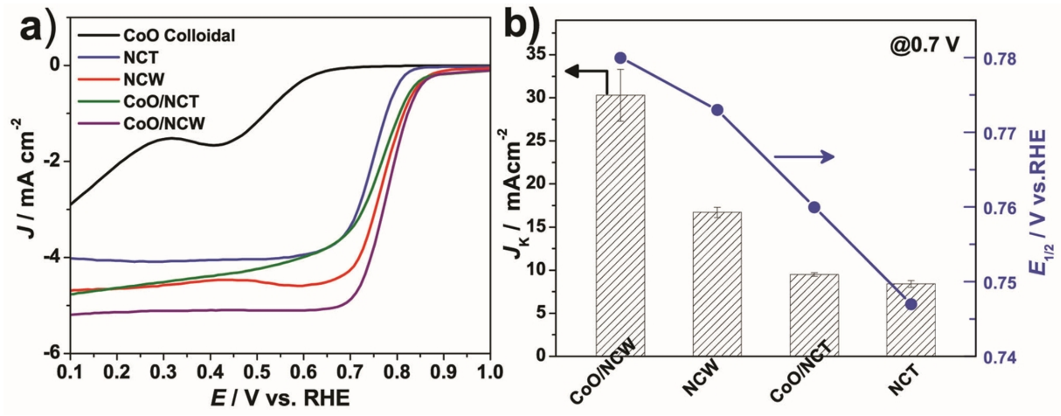

Fig. S6 (a) LSV Curves of the CoO NPs, NCT, NCW, CoO/NCT and CoO/NCW nanocomposite and (b) the corresponding given electrocatalytic acivity in term of half-wave potential ($E_{1/2}$) and kinetic-limiting current density.

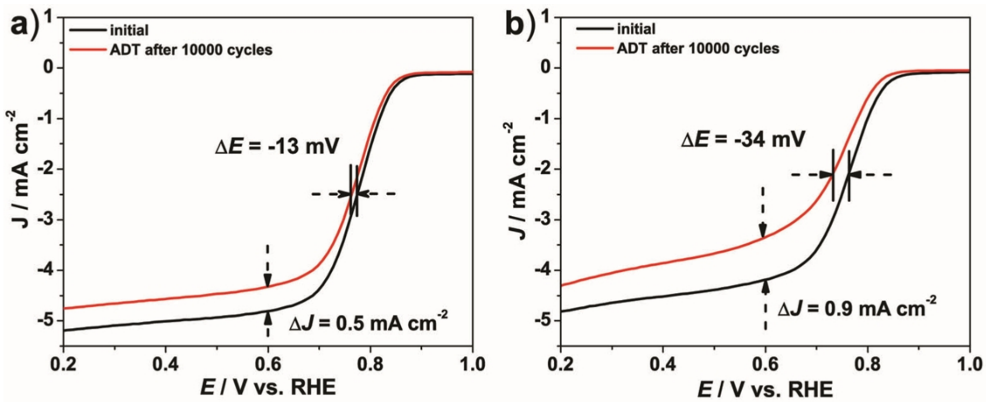

Fig.7 The accelerated durability by CV-cycling the catalyst of CoO/NCW (a) and CoO/NCT (b) between 0.6 and 1.0 V at 100 mVs^{-1} under O_2-atmosphere.

Table S1. ICP analysis of the residual of Fe/Co metals in NCW sample.

Sample	Fe / wt.%	Co / wt.%	Al / wt.%
NCW	0.38	0.33	0.12

Table S2. Physicochemical properties and the electrocatalytic activity of the N-CT and N-CW sample for ORR.

Catalysts	SA[a)] $[m^2 \cdot g^{-1}]$	PV [b)] $[cm^3 \cdot g^{-1}]$	PSD [c)] [nm]	At%[d)] *N*	*C*	*O*
N-CT	109	0.91	65	9.2	84	6.4
N-CW	176	0.48	1.4/22	7.2	86	6.2

[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.

Table S3. The interfacial area characterized by the amounts of the electrochemically-avaiable Co(II)/ Co(III) redox centers and the electrocatalytic activity of the CoO/KB, CoO/NCT and CoO/NCW samples for ORR in comparison with the commercial Pt/C catalyst.

Catalyst	**The charge of the oxidizing peak @1.1 V [C]**	E_{onset} **/** $E_{1/2}$ **[mV/mV]**	J_K **@ 0.7V** **[mA·cm^{-2}]**	n **(RRDE)**
CoO/KB	**1.46 x 10 $^{-3}$**	**0.875/0.75**	**5.6**	**3.3**
CoO/NCT	**1.04x 10 $^{-3}$**	**0.875/0.76**	**9.7**	**3.67**
CoO/NCW	**2.46x10 $^{-3}$**	**0.895/0.78**	**30.3**	**3.83**
Pt/C	**--**	**0.950/0.80**	**23.1**	**4.0**

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

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:

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

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

$$J_K=\mathrm{n}F\kappa C_0 \qquad (3)$$

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 C·mol^{-1}), C_0 is the bulk concentration of O_2 (= 1.2×10^{-3} mol· L^{-1}), D_0 is the diffusion coefficient of O_2 in the NaOH electrolyte (=1.9*10^{-5} cm^2 S^{-1}), υ is the kinetic viscosity of the electrolyte (= 0.01 cm^2 S^{-1}), κ is the electron-transfer rate constant and ω is the angular velocity of the the disk (ω = 2πN, 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

1. H. Chen, Y. Yang, Z. Hu, K. F. Huo, Y. W. Ma, Y. Chen, X. S. Wang and Y. N. Lu, *J Phys Chem B*, 2006, **110**, 16422-16427.
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.