Supporting Information for

Aligned N-doped Carbon Nanotube Bundles with Interconnected Hierarchical Structure as an Efficient Bi-functional Oxygen Electrocatalyst

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Experimental section:

The calculation of electron-transfer numbers: 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=nFkCo

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

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 (ω=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 =1.2x10^{-6} mo1 cm^{-3}), v is the kinematic viscosity of the electrolyte (v=0.01 cm^2 s^{-1}), D_o is the diffusion coefficient of O_2 in 0.1 mol L^{-1} KOH (1.9x10^{-5} cm^2 s^{-1}). According to equations (1) and (2), the number of electrons transferred (n) can be calculated to be 4.0, which indicates that the H-NCNTs lead to a four-electron-transfer reaction to reduce directly oxygen into OH^-.

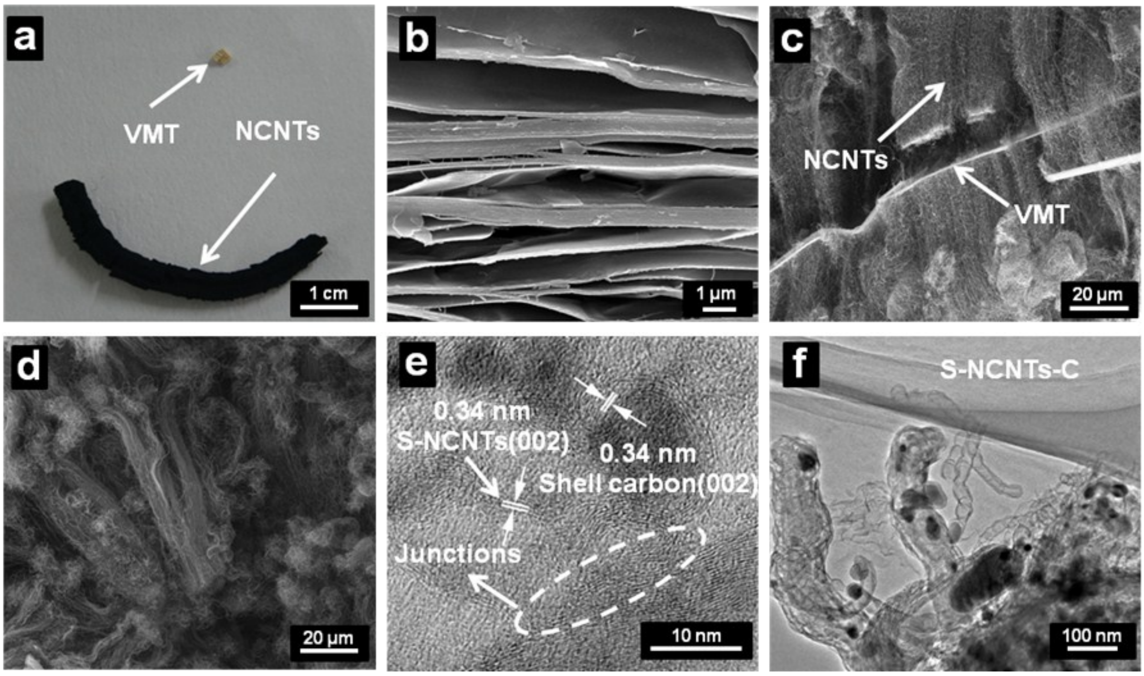

Figure S1. (a) Digital photograph of nature blocks of VMT and L-NCNTs/VMT. (b-d) Typical SEM images of VMT (b), L-NCNTs/VMT composites (c) and L-NCNTs after removal of VMT (d). (e, f) HRTEM images of h-NCNTs/Gr/TM (e) and S-NCNTs-C (f).

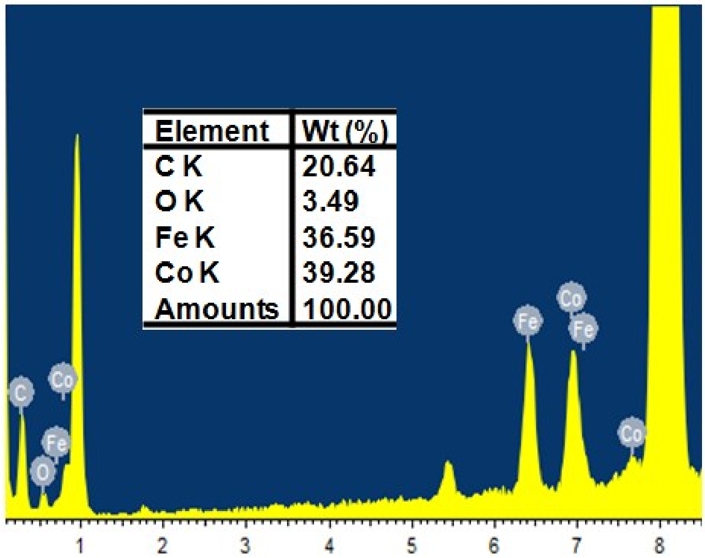

Figure S2. EDS spectrum for CoFe NPs in h-NCNTs/Gr/TM hybrid.

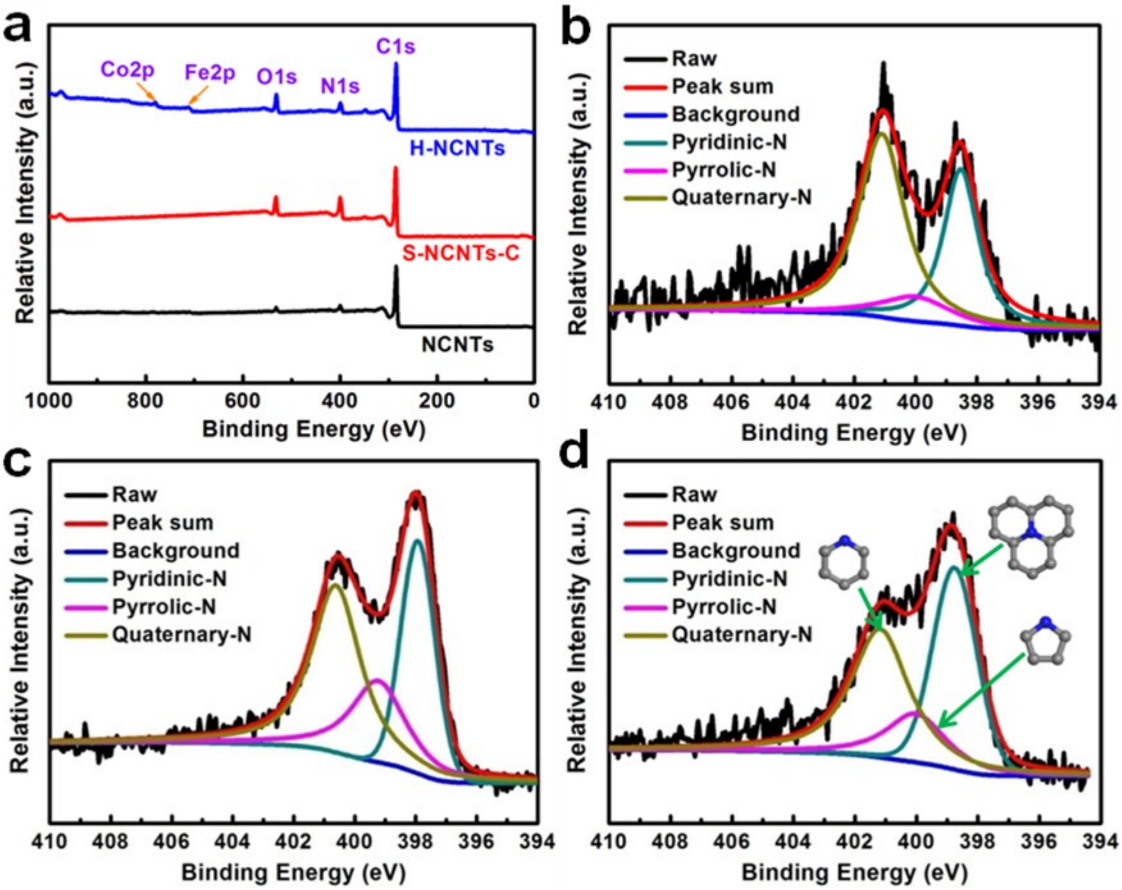

Figure S3. (a) XPS survey spectra of L-NCNTs, S-NCNTs-C, and h-NCNTs/Gr/TM; (b-d) N 1s binding energy region of L-NCNTs (b), S-NCNTs-C (c), and h-NCNTs/Gr/TM (d).

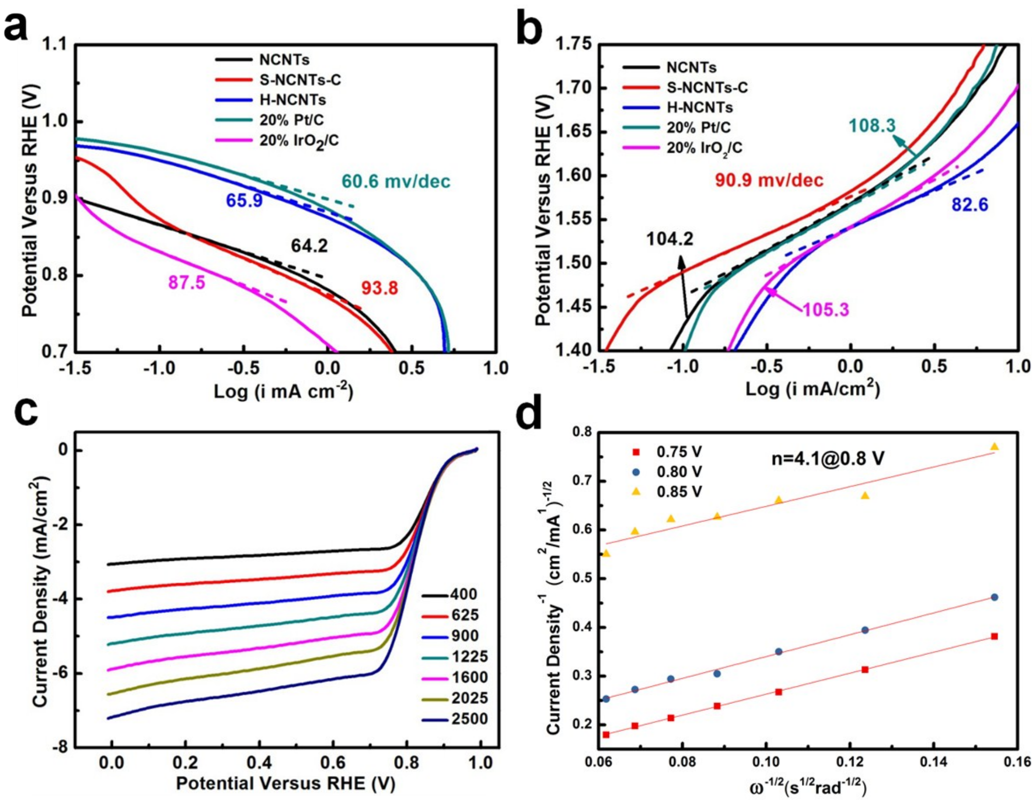

Figure S4. (a) ORR and (b) OER tafel plots of h-NCNTs/Gr/TM compared with L-NCNTs, S-NCNTs-C, Pt/C and IrO_2/C. Polarization curves (c) and K-L plots (d) of h-NCNTs/Gr/TM of ORR (Indicating the h-NCNTs/Gr/TM is four-electron-transfer reaction).

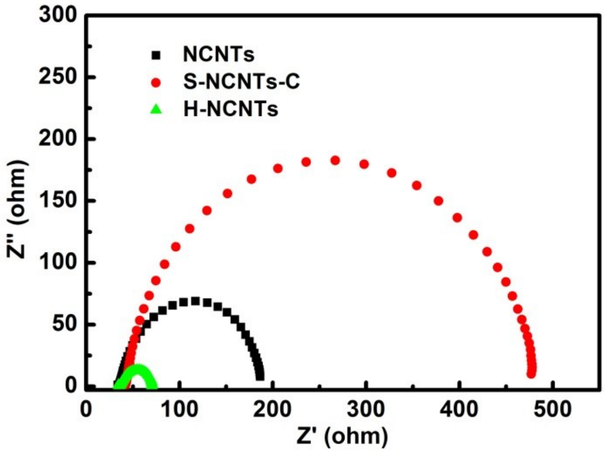

Figure S5. The electrochemical impedance spectra of h-NCNTs/Gr/TM, S-NCNTs-C and L-NCNTs.

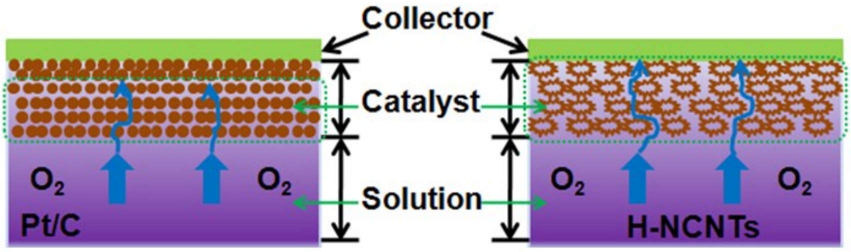

Figure S6. Graphical depiction of the transportation difference of solvated O_2 in catalyst layer of Pt/C and h-NCNTs/Gr/TM occurring in ORR.

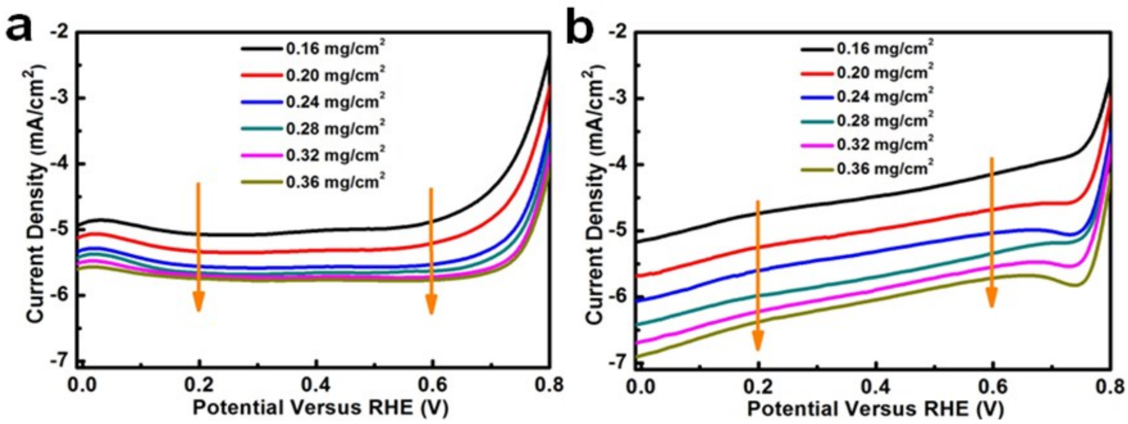

Figure S7. Investigations of the effect of catalyst's loading amount on ORR performance. (a) 20 wt% Pt/C and (b) h-NCNTs/Gr/TM.

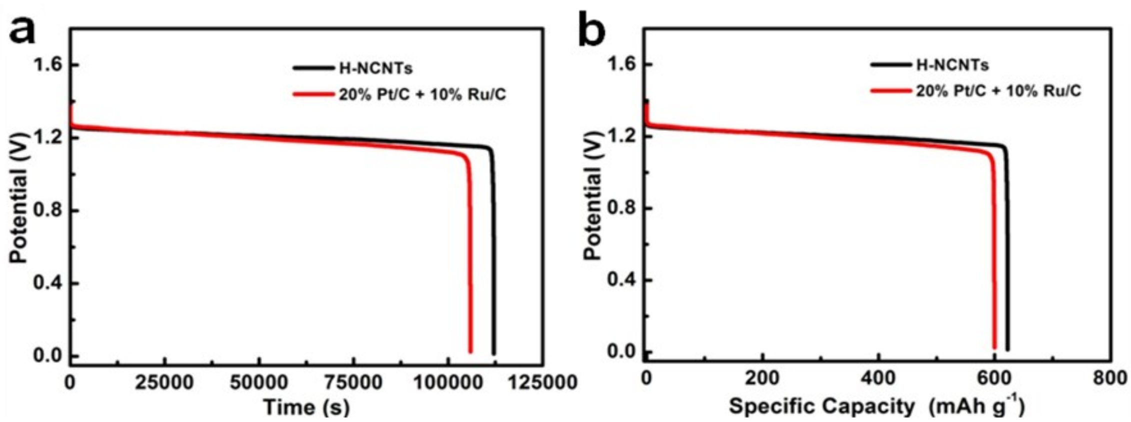

Figure S8. (a) The galvanostatic discharge curve of the primary zinc-air batteries at the current density of 7 mA cm^{-2}. (b) Specific capacities of the primary zinc-air batteries normalized to the mass of the consumed Zn at the current density of 7 mA cm^{-2}.

Table S1. The element content of L-NCNTs, S-NCNTs-C and h-NCNTs/Gr/TM obtained by XPS.

L-NCNTs	Atomic (%)	S-NCNTs-C	Atomic (%)	h-NCNTs/Gr/TM	Atomic (%)
C1s	93.99	C1s	81.68	C1s	88.18
N1s	6.01	N1s	16.91	N1s	9.73
		Fe2p3	1.68	Co2p3	0.97
				Fe2p3	1.12

Table S2. Specific surface area and total pore volume of different samples.

Sample	L-NCNTs	S-NCNTs-C	h-NCNTs/Gr/TM
Specific surface area (m^2 g^{-1})	73.6	62.6	95.0
Total pore volume (cm^3 g^{-1})	0.23	0.15	0.25

Table S3. ORR and Zn-air battery performance of some carbon based system.

Catalysts	Catalyst loading for ORR / Zn-air battery (mg cm^{-2})	ORR Half-wave potential (V vs. RHE)	E_{gap} values (V@mA cm^{-2})	Power density (mW cm^{-2})	Reference
Co@N-CNT	0.3728 / 2.5	0.805	N/A	244.0	[1]
Co/N/O tri-doped graphene	0.25 / 0.5	0.95	0.70@1	152	[2]
Co-based metal hydroxysulfides	N/A	0.721	1.12@5	113.1	[3]
Cobalt-Based nanocomposites	0.3 / 0.9	0.89	0.91@10	118.27	[4]
FeCo-Nx -carbon nanosheets	N/A	0.85	0.78@10	150	[5]
Co, N-Codoped carbon nanoframes	0.12 / N/A	0.79	0.752@25	N/A	[6]
Co-Nx-By-C carbon nanosheets	N/A / 0.5	0.83	0.83@10	100.4	[7]
Strung Co_4N and Intertwined N−C Fibers	N/A	0.8	0.84@10	174	[8]
Nanoporous carbon Fiber Films	0.1/0.1	0.8	0.73@10	185	[9]
Transition metal and nitrogen co-doped carbon	0.5 / 0.1	0.767	0.94@2	N/A	[10]
This work	**0.5 / 2**	**0.81**	**0.6@5**	**81.76**	

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