Supplementary Information for

Advanced Zinc Air Batteries Based on High Performance Hybrid Electrocatalysts

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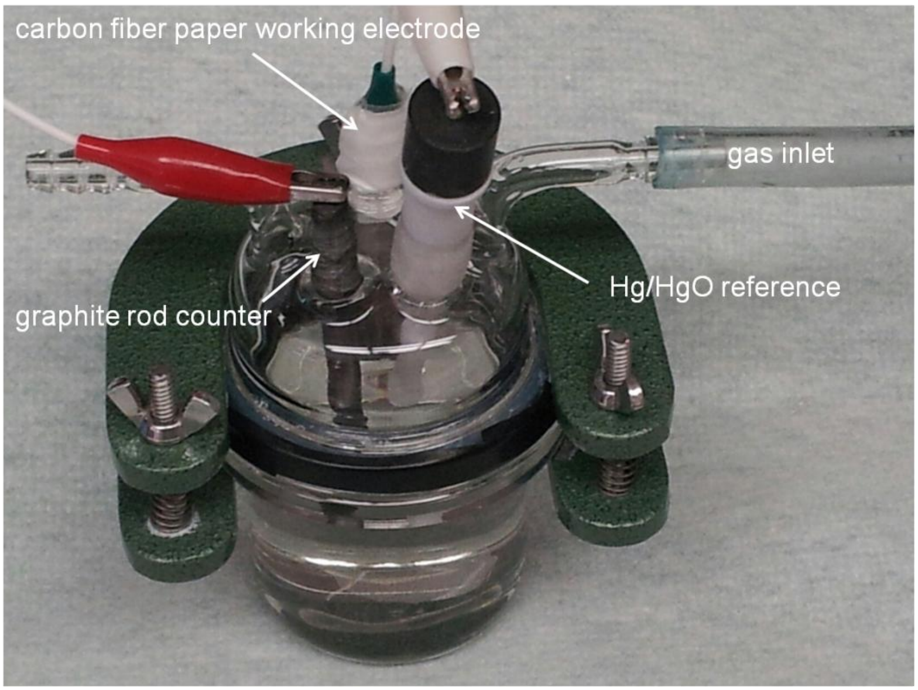
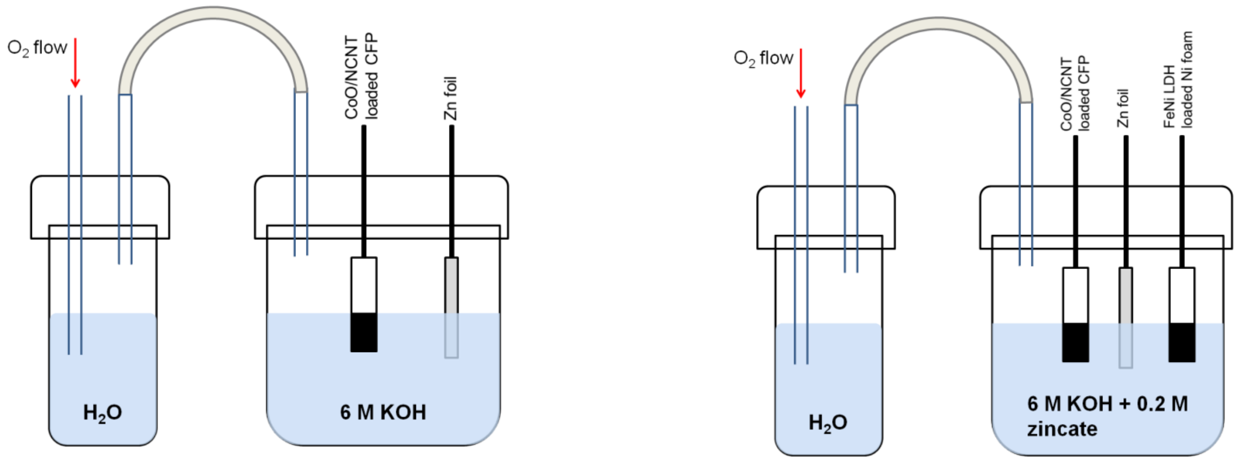
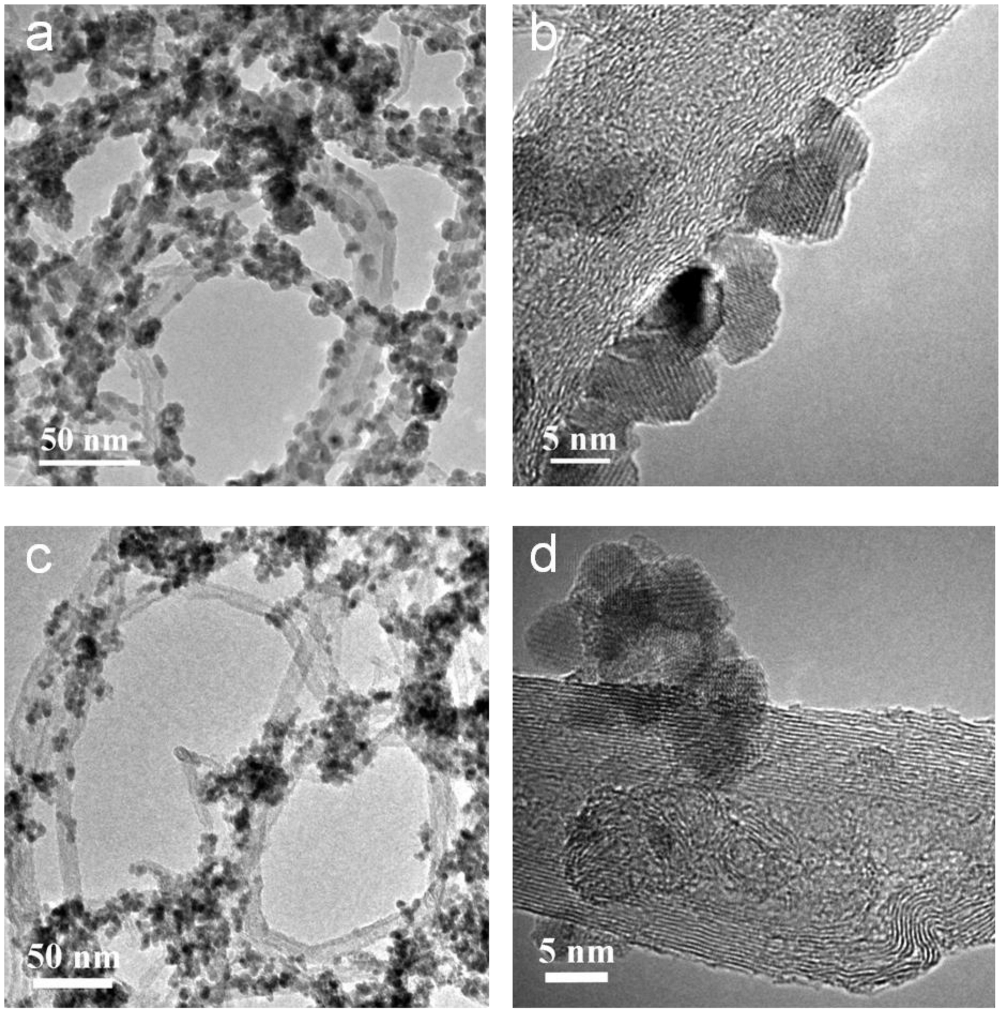


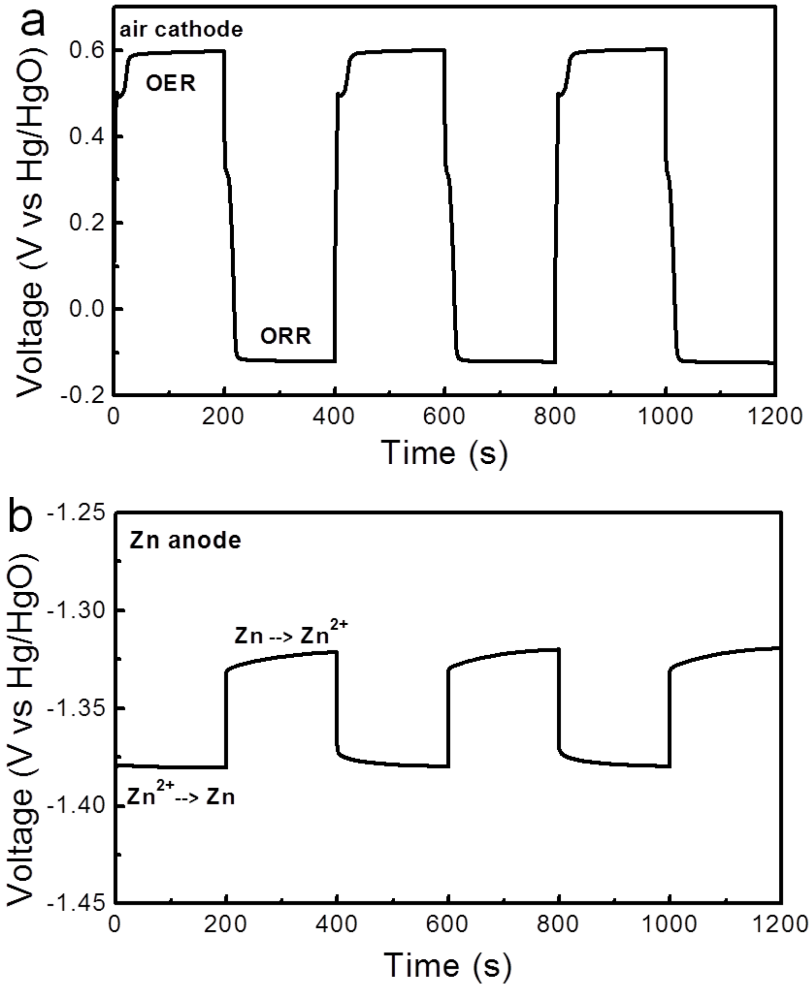
Supplementary Figure S1. Photo of our home-built electrochemical cell for the ORR and OER measurements. The three electrode system consists of an Hg/HgO reference electrode (filled with 6 M KOH), a graphite rod counter electrode and electrocatalyst loaded carbon fiber paper as the working electrode. The cell has a gas inlet that allows continuous O_2 purge when needed for ORR.



Supplementary Figure S2. Schematics of our home-built electrochemical cells for the measurements of primary (left) and rechargeable (right) Zn-air batteries. For primary cells, a two-electrode configuration was used by pairing CoO/N-CNT loaded on carbon paper electrode (1 cm^2, catalyst loading 1 mg) with a Zn foil in 6 M KOH. For rechargeable cells, a three-electrode configuration was used with CoO/N-CNT loaded on carbon paper electrode (1 cm^2, catalyst loading 1 mg) for discharge, NiFe LDH loaded on a Ni foam (1 cm^2, catalyst loading ~5 mg) for charge, and a Zn foil anode in 6 M KOH and 0.2 M zinc acetate dissolved to form zincate. For both of them, the oxygen flow was humidified by passing through a separate liquid water container before entering the cell. Such beaker-type cells are not suitable for practical applications, but they are easy to construct, modify and dissemble. They serve the purpose of testing Zn-air batteries' electrochemical performance.



Supplementary Figure S3. TEM images of (a,b) as-made CoO/N-CNT and (c,d) CoO/N-CNT after charge-discharge cycling. In (c-d), it can be clearly observed that CoO nanocrystals are detached from CNT supports and aggregated. Covalent coupling between CoO nanocrystals and CNTs were likely destroyed during the charging step. Such morphology change was accompanied by a large ORR activity loss in the hybrid catalyst. This result prompted us to pursue the tri-electrode configuration for rechargeable Zn air battery.



Supplementary Figure S4. Alternating oxidation and reduction of (a) the air cathode and (b) the Zn anode at a current density of 20 mA/cm^2. Based on above data, the voltage polarization observed in Figure 5b of the main text was mainly contributed by the air cathode side (sum of ORR and OER overpotentials). Polarization on the Zn anode was negligible.

Supplementary Table S1: A survey of primary Zn-air batteries with several key parameters extracted from the literature.

ORR catalyst used	Zn electrode/ electrolyte	Current Density @ *V* = 1.0 V (mA/cm^2)	Peak Power Density (mW/cm^2)	Reference
CoO/N-CNT	Zn foil/6M KOH	197	265	This work
Graphene supported Mn_3O_4 nanoparticles	Zn powders/no mention of electrolyte	70	120	*Energy Environ. Sci.* **2011**, 4, 4148
Ketjenblack carbon supported amorphous MnO_x	Zn powders/6M KOH	120	190	*Nano Lett.* **2011**, 11, 5362
N-doped carbon nanotubes	Zn plate/6M KOH	50	75	*Electrochim. Acta* **2011**, 56, 5080
Fe, Co and N precursors pyrolyzed with carbon	Zn plate/6M KOH	150	232	*J. Power Sources* **2011**, 196, 3673.

Supplementary Table S2: A survey of rechargeable Zn-air batteries with several key parameters extracted from the literature.

Air catalyst Used	Cycling conditions and stability	Voltage polarization @ *j* = 20 mA/cm^2 (V)	Reference
Tri-electrode: CoO/N-CNT + NiFe LDH	20-50 mA/cm^2, 4-20 h per cycle period for >200 h: negligible voltage change at the end	0.70	This work
MnO_2 nanotube and carbon nanotube composite	~8 mA/cm^2, 600 s per cycle periods for 50 cycles: polarization increased ~0.4 V at the end	1.5	*Electrochim. Acta* **2012**, 69, 295-300
$LaNiO_3$ supported on N-doped carbon nanotubes	~17.6 mA/cm^2, 600 s per cycle period for 75 cycles: polarization increased 0.1~0.2 V at the end	~1.2	*Nano Lett.* **2011**, 11, 5362–5366
Tri-electrode: MnO_2 + stainless steel	5-15mA/cm^2, 24-30 h per cycle period for ~120 hrs: negligible voltage change at the end	>0.9	*ECS Trans. 2011, 28 25-34*