Supporting information

for

Ultrafine cobalt nitride nanoparticles supported on carbon nanotubes as efficient electrocatalyst for rechargeable Zinc-air batteries

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Experimental section

Materials: Co(Ac)$_2$·4H$_2$O was purchased from Shanghai Macklin Biochemical Co. Ltd. Multi-walled carbon nanotubes were purchased from Nanjing XFNANO Co. Ltd. N,N-dimethylformamide (DMF), potassium hydroxide (KOH) and ethyl alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. Commercial Pt/C, commercial IrO$_2$, graphite rod (99.9995%), glassy carbon electrode (GCE), and Hg/HgO electrode were supplied from Alfa Aesar. Nafion solution was obtained from Sigma-Aldrich. De-ionized water was obtained from an ultra-pure purification system (Milli-Q, resistivity ≥ 18.5 MΩ). All chemicals were used as received without further purification.

Synthesis of Co$_3$O$_4$/CNT: Firstly, 36 mg of Co(Ac)$_2$·4H$_2$O and 40 mg of CNT were dissolved in a mixture containing 8 mL of de-ionized water, 120 mL of ethyl alcohol and 2.4 mL of ammonia. The resultant mixture was heated up to 80 °C in three-necked flask under N$_2$ atmosphere with vigorous magnetic stirring for 20 h to form a homogeneous solution. The resultant solution was centrifuged three times using ethyl alcohol. Then the powder was dried at 70 °C for 6 h and increased the temperature to 150 °C for another 3 h. Co$_3$O$_4$/CNT electrocatalyst was obtained.

Synthesis of CoN/CNT: In a typical synthesis, Co$_3$O$_4$/CNT was put into a porcelain boat and was subsequently subjected to a nitriding procedure under NH$_3$ atmosphere (5 vol.% in argon) at 750 °C for 2h with a slow annealing ramp of 1.5 °C min$^{-1}$. Finally, the product was filtered by repeatedly washing
with de-ionized water and dried overnight to obtain CoN/CNT electrocatalyst.

**Material characterization:** Thermal decomposition property was studied by thermogravimetric (TGA, STA 449 F3, Germany) with a heating rate of 10 °C min⁻¹ with O₂ atmosphere. Typical elements were detected by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The morphologies and particle size of CoN/CNT were analyzed by a high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2) equipped with an energy-dispersive X-ray spectroscope (EDS, EDAX Apollo XP, USA).

**Electrochemical measurements**

**Oxygen evolution reaction (OER) test:** All electrochemical measurement was performed at room temperature on Gamry in a conventional three-electrode system. A catalyst-coated carbon paper (1 cm×1 cm) with 1 mg of catalyst was used as the working electrode. Hg/HgO electrode was used as reference electrode. A graphite rod was used as the counter electrode. All electrochemical properties were measured in 1 M KOH electrolyte. The polarization curves were measured at the scan rate of 5 mV s⁻¹. CV was carried out between 1.09 and 1.14 V vs. RHE at various sweep rates ranging from 10 to 100 mV s⁻¹ to investigate the electrochemical double-layer capacitances. The electrochemical impedance spectroscopy (EIS) measurements of samples were performed over the frequency range from 1 MHz to 0.01 Hz with an applied perturbation voltage of 10 mV as the excitation AC amplitude and DC voltage biased at a anodic overpotential at 10
mA cm\(^{-2}\). Before all electrochemical measures, the electrolyte was degassed by bubbling pure O\(_2\) for 0.5 h to meet the criteria for practical application.

**Oxygen reduction reaction (ORR) test:** All electrochemical measurement was performed at room temperature on Gamry in a conventional three-electrode system. A catalyst-coated mirror-polished rotation disk electrode (4mm diameter) was used as the working electrode. Hg/HgO electrode was used as reference electrode. A graphite rod was used as the counter electrode. As for the prescription of the ink, 2 mg of the catalyst was dispersed in the mixture of de-ionized water (780 μL), isopropanol (200 μL) and Nafion solution (20 μL). Then a homogenous catalyst ink was obtained by an ultrasonic disperse dispose for 1 h. 18 μL of the ink was dropped onto the RDE. Linear sweep voltammetry (LSV) was performed in O\(_2\)-saturated 1 M KOH with a scan rate of 5 mV s\(^{-1}\) with rotation rate of 1600 rpm. To calculate the average number of electrons transferred (n), the working electrode was scanned at the rate of 5 mV s\(^{-1}\) by various electrode rotating rates (400, 600, 800, 1200, 1600 and 2400 rpm), using the Koutecky-Levich (K-L) equation in the potential range of 0.5-0.75 V vs. RHE. The hydrogen peroxide yield could be calculated by the following equation:

\[
\text{H}_2\text{O}_2\% = \frac{2I_r}{(N*I_d+I_r)}
\]

Where \(I_r\) and \(I_d\) represent ring and disc current density, respectively. N is the collection efficiency (N=0.4).

**Zinc-air battery performance:** The Zn-air battery performance was tested in
home-made electrochemical cell. Like a traditional liquid rechargeable zinc-air
battery, it was constituted by electrolyte (6 M KOH with 0.2 M Zn(Ac)$_2$), the
current collectors (nickel foam), a polished zinc plate and a catalyst layer
coated gas diffusion electrode. To prepare the air-electrode, 1 mg of
CoN/CNT was dispersed in 2 mL of ethanol and 20 μL of Nafion solution.
After 1 h ultrasonic treatment, all of the ink was sprayed onto a carbon paper
(1 cm×1 cm) (loading: 1 mg cm$^{-2}$). As a meaningful comparison, the battery
using commercial Pt/C and commercial IrO$_2$ (loading: 0.285 mg cm$^{-2}$) mixture
catalyst was fabricated through the same method.

**All-solid-state zinc air battery test:** To get the polymer electrolyte, 1 g of
poly(vinyl alcohol) (PVA) was dissolved in 10 mL of DI water and then heated
to 95 °C for 2 h. Then 1 mL of mixture of 18 M KOH and 0.6 M zinc acetate
was added and stirred at 95 °C for 10 min. The film was obtained by pouring
the resulting goop onto a glass plate and scraping with a spatula (400 μm).
The resultant film was stored in refrigerator overnight. And then the film was
soaked in the mixture of 18 M KOH with 0.6 M zinc acetate for 12 h. To
assemble the battery, PVA film was placed between zinc foil and air-cathode.
Nickel foam was used as current collector. The catalyst loading on carbon
paper was controlled to 1 mg cm$^{-2}$).
Figure S1 Histograms of particle size distributions of Co$_3$O$_4$/CNT and CoN/CNT electrocatalysts.

Figure S2 Cyclic voltammetry curves of CNT (a), Co$_3$O$_4$/CNT (b) and CoN/CNT (c) electrocatalysts. (d) Calculated ECSA values of CNT, Co$_3$O$_4$/CNT and CoN/CNT electrocatalysts.
**Figure S3** Electrochemical impedance spectroscopies of CNT, Co$_3$O$_4$/CNT and CoN/CNT electrocatalysts.

**Figure S4** ECSAs (a), CV curves (b) and electrochemical impedance spectroscopies (c) of CoN/CNT before and after durability test.
**Figure S5** Deconvoluted Co2p (a) and N1s (b) peaks of CoN/CNT after durability test. (c) TEM images of CoN/CNT after durability test.

**Figure S6** OER performances (a) and double layer capacitances (b, c) of commercial IrO2 before and after durability test.

**Figure S7** ORR curves of commercial Pt/C and CoN/CNT with different rotation speeds tested in 1 M KOH electrolyte.
Figure S8 Calculated number of involved electrons of Pt/C at various potentials.

Figure S9 (a) ORR curves of CoN/CNT with different rotation speeds tested in 1 M KOH electrolyte after 1000 potential cycles. (b) Calculated number of involved electrons of CoN/CNT after 1000 potential cycles at various potentials.
Figure S10 Deconvoluted Co2p (a) and N1s (b) peaks of CoN/CNT after durability test. TEM (c) and HR-TEM (d) images of CoN/CNT after durability test.
Figure S11 (a) Chronoamperometric test of CoN/CNT at 0.5 V vs. RHE and (b) relative H$_2$O$_2$ generation.

Figure S12 (a) ORR curves of commercial Pt/C with different rotation speeds tested in 1 M KOH electrolyte after 1000 potential cycles. (b) ORR curves of commercial Pt/C before and after 1000 potential cycles.
**Figure S13** Stability test of open circuit voltages (OCVs) of ZABs fabricated from Pt/C-IrO$_2$ (black line) and CoN/CNT (red line) as air electrodes, respectively.

**Figure S14** Galvanostatic discharge (a) and charge (b) curves of CoN/CNT at different current densities.