Electronic Supplementary Material (ESI) for ChemComm.

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: $Co(Ac)_2 \cdot 4H_2O$ 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_3O_4/CNT: Firstly, 36 mg of $Co(Ac)_2 \cdot 4H_2O$ 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 ^oC 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 ^oC for 6 h and increased the temperature to 150 ^oC for another 3 h. Co_3O_4/CNT electrocatalyst was obtained.

Synthesis of CoN/CNT: In a typical synthesis, Co_3O_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 ^oC for 2h with a slow annealing ramp of 1.5 ^oC 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 ^{o}C min^{-1} with O_2 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:

$H_2O_2\% = 2I_r/(N^*I_d + I_r)$

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-sate 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 ^{o}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 ^{o}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}).

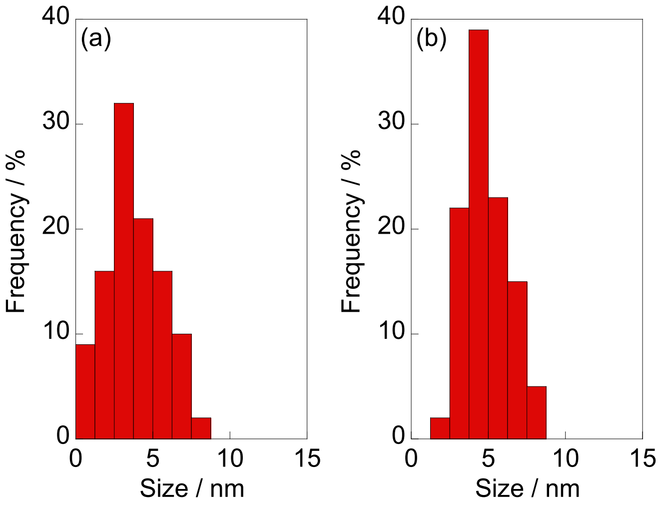


Figure S1 Histograms of particle size distributions of Co_3O_4/CNT and CoN/CNT electrocatalysts.

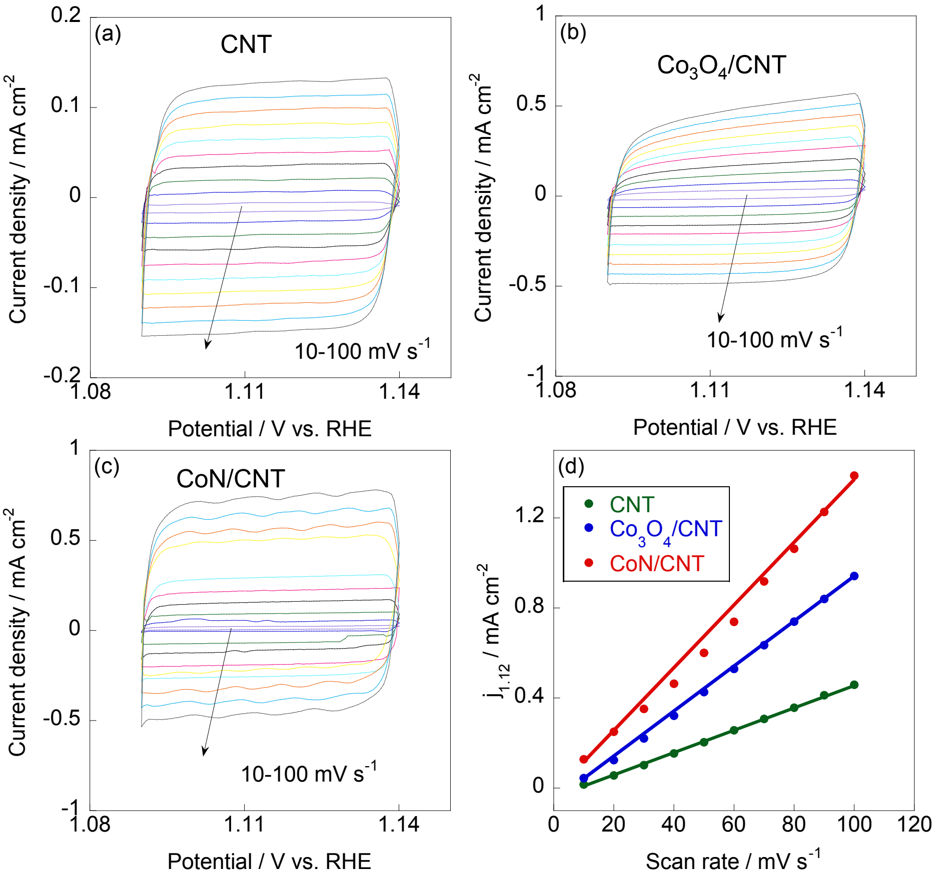


Figure S2 Cyclic voltammetry curves of CNT (a), Co_3O_4/CNT (b) and CoN/CNT (c) electrocatalysts. (d) Calculated ECSA values of CNT, Co_3O_4/CNT and CoN/CNT electrocatalysts.

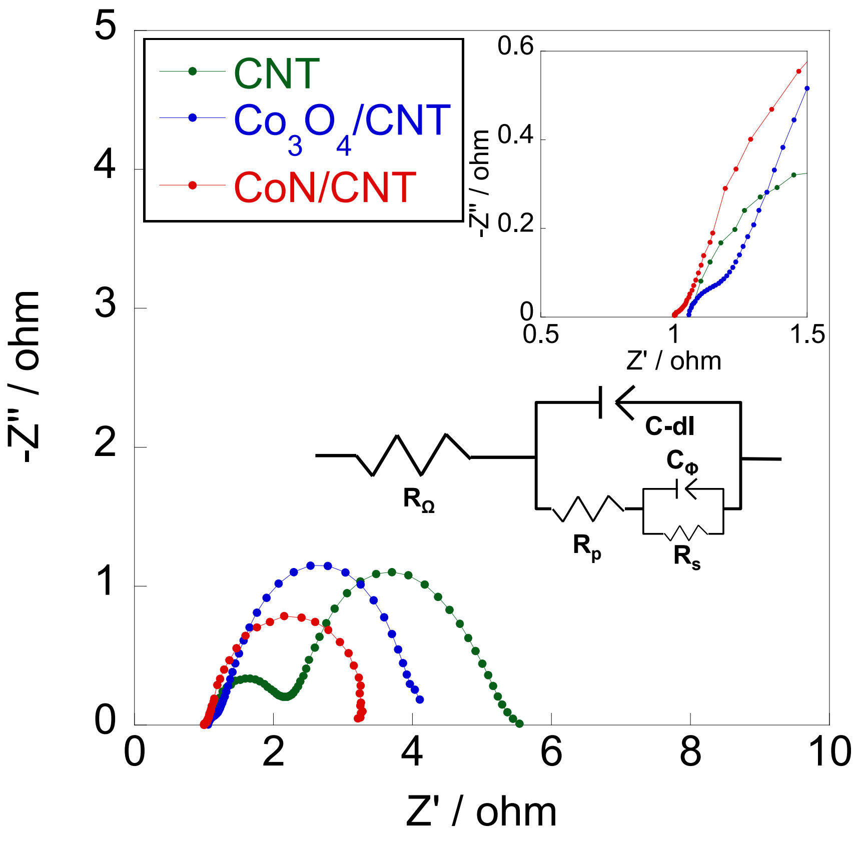


Figure S3 Electrochemical impedance spectroscopies of CNT, Co_3O_4/CNT and CoN/CNT electrocatalysts.

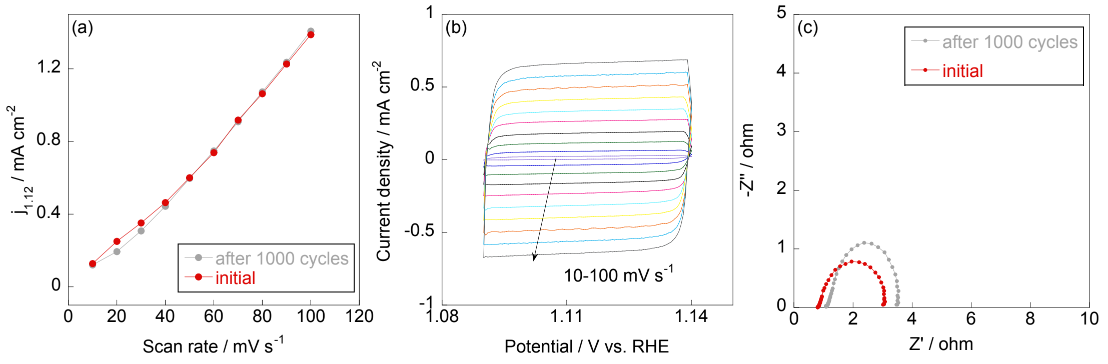


Figure S4 ECSAs (a), CV curves (b) and electrochemical impedance spectroscopies (c) of CoN/CNT before and after durability test.

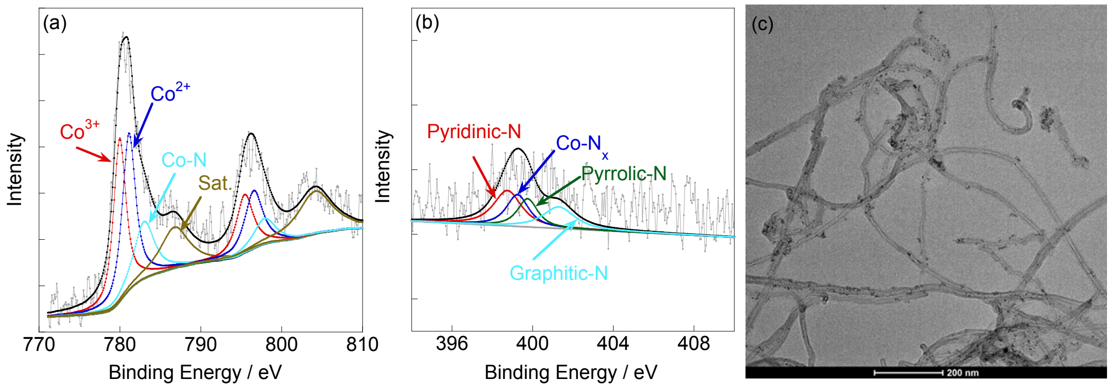


Figure S5 Deconvoluted Co2p (a) and N1s (b) peaks of CoN/CNT after durability test. (c)TEM images of CoN/CNT after durability test.

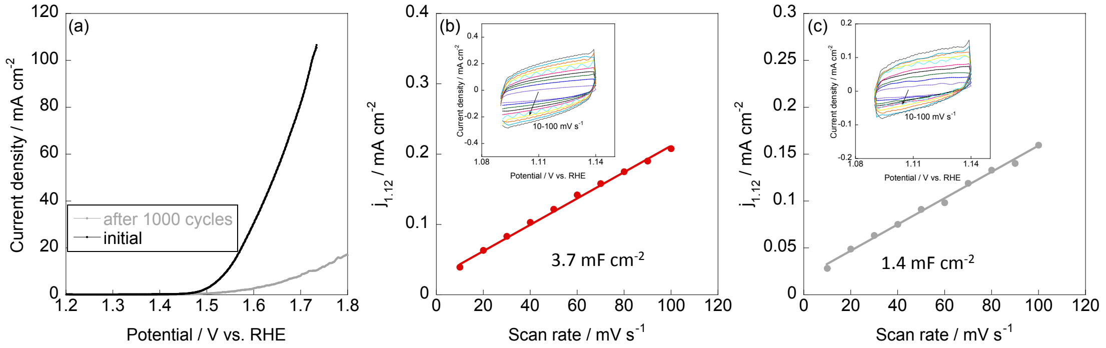
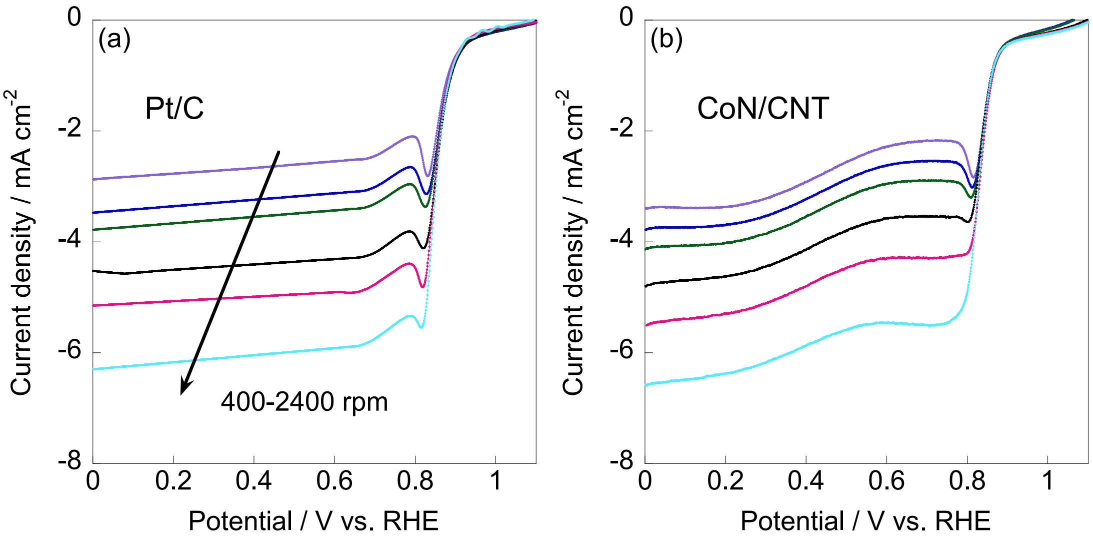


Figure S6 OER performances (a) and double layer capacitances (b, c) of commercial IrO_2 before and after durability test.



Figurer S7 ORR curves of commercial Pt/C and CoN/CNT with different rotation speeds tested in 1 M KOH electrolyte.

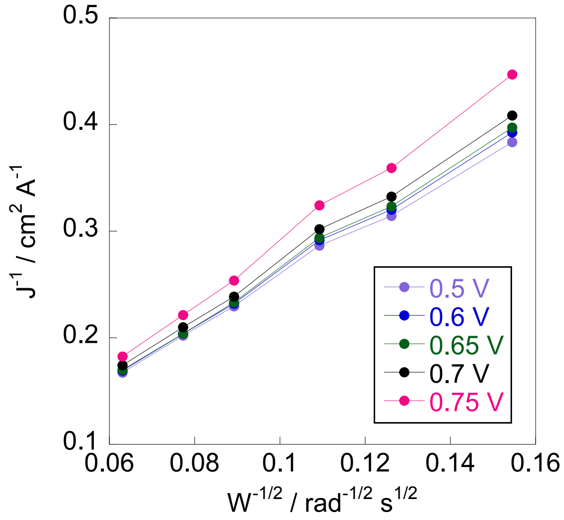
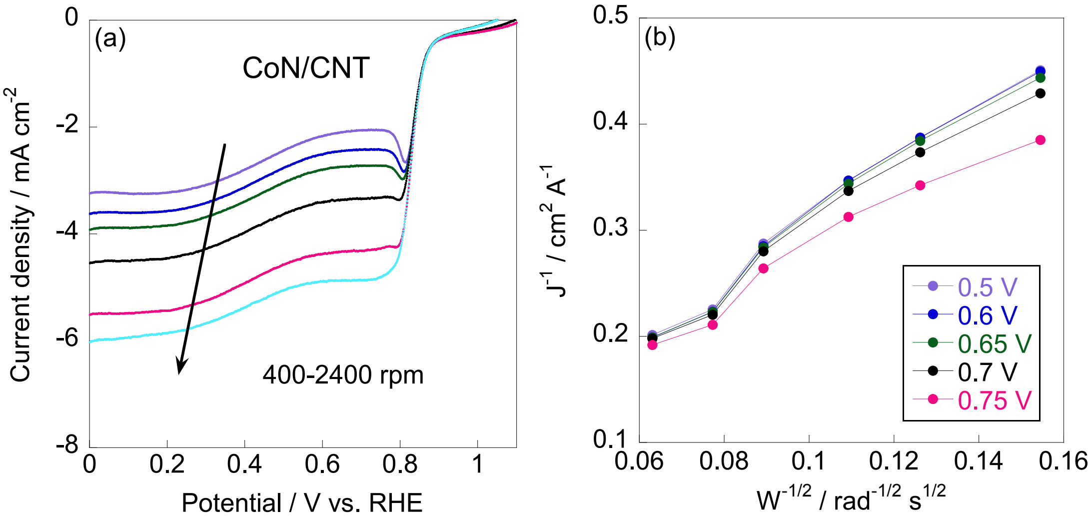


Figure S8 Calculated number of involved electrons of Pt/C at various potentials.



Figurer 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.

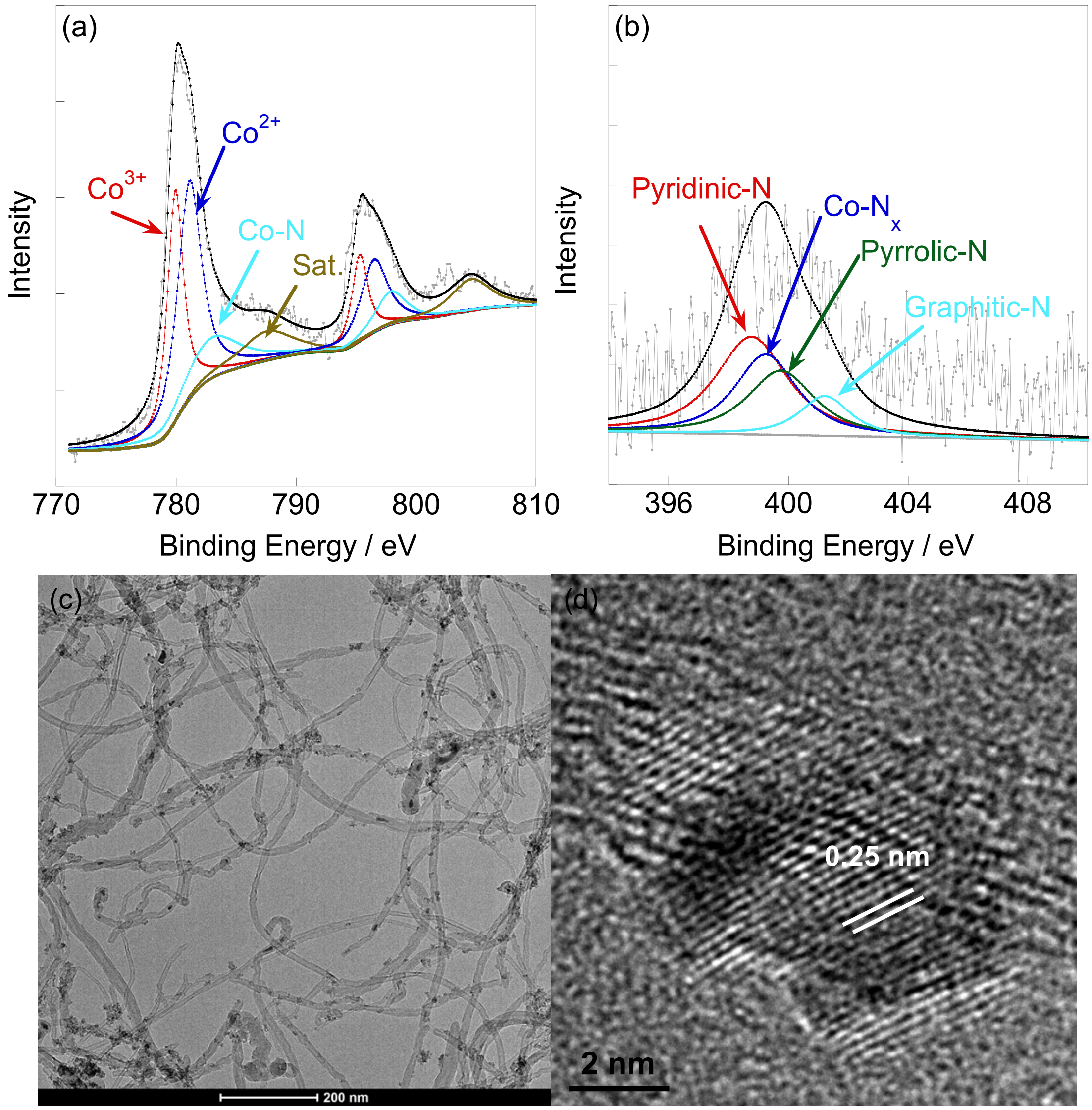


Figure S10 Deconvoluted Co2p (a) and N1s (b) peaks of CoN/CNT after durability test. TEM (c) and HR-TEM (d) images of CoN/CNT after durability test.

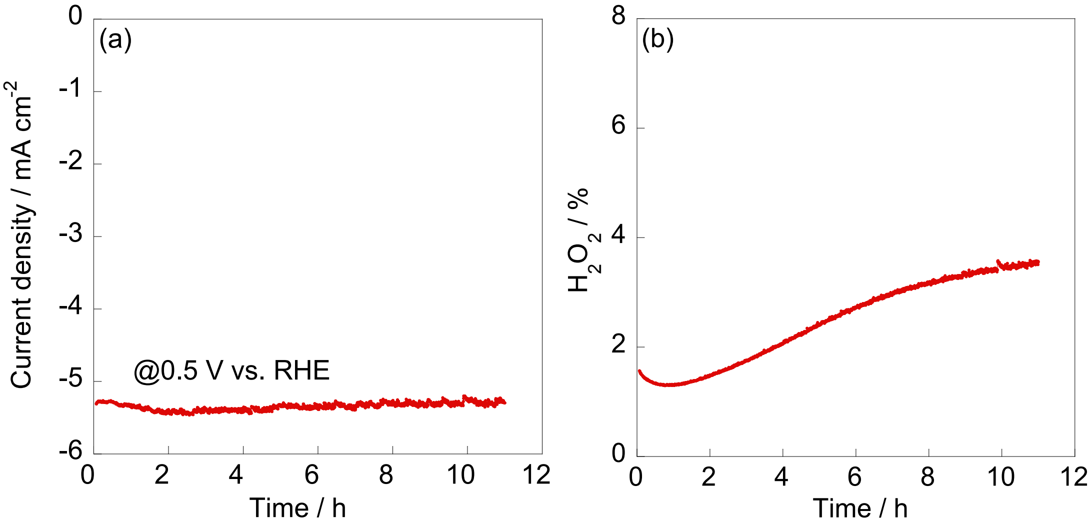
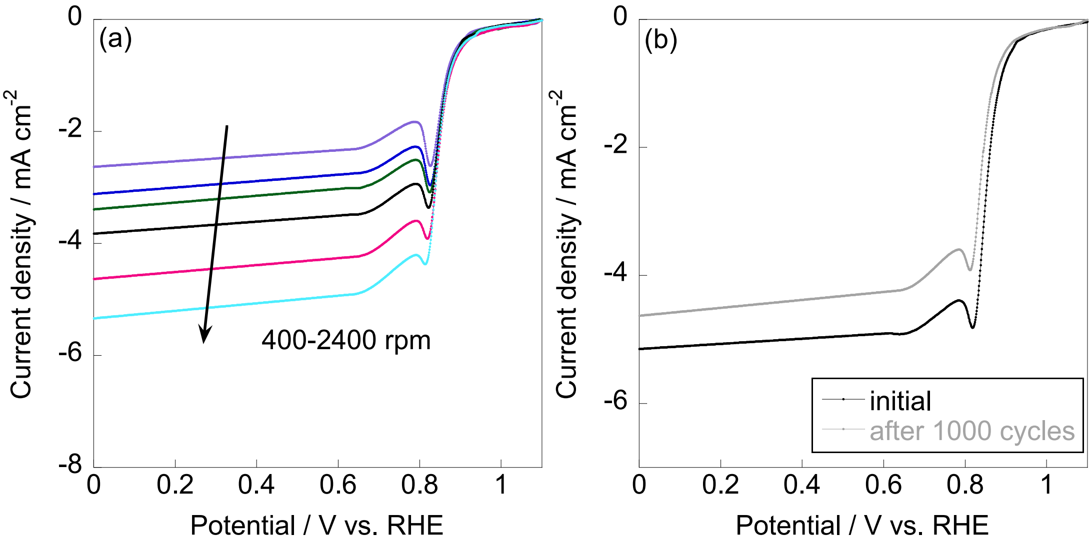


Figure S11 (a) Chronoamperometric test of CoN/CNT at 0.5 V vs. RHE and (b) relative H_2O_2 generation.



Figurer 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.

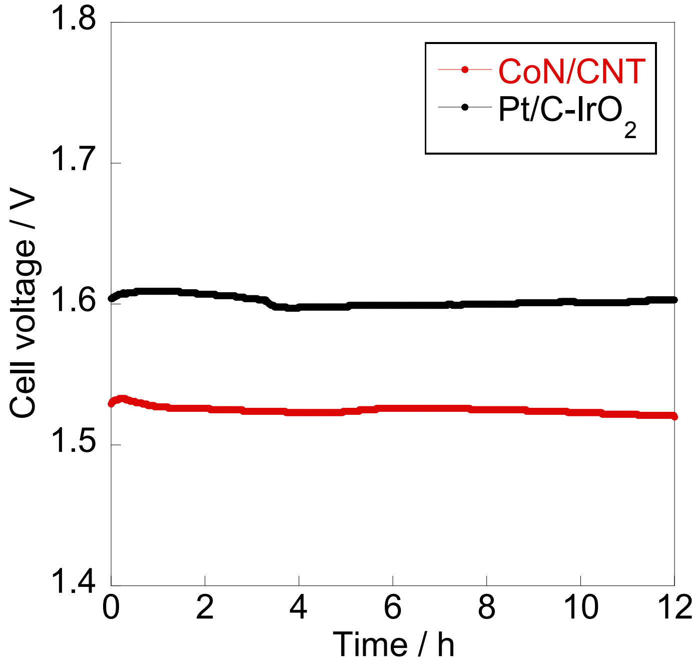


Figure S13 Stability test of open circuit voltages (OCVs) of ZABs fabricated from Pt/C-IrO_2 (black line) and CoN/CNT (red line) as air electrodes, respectively.

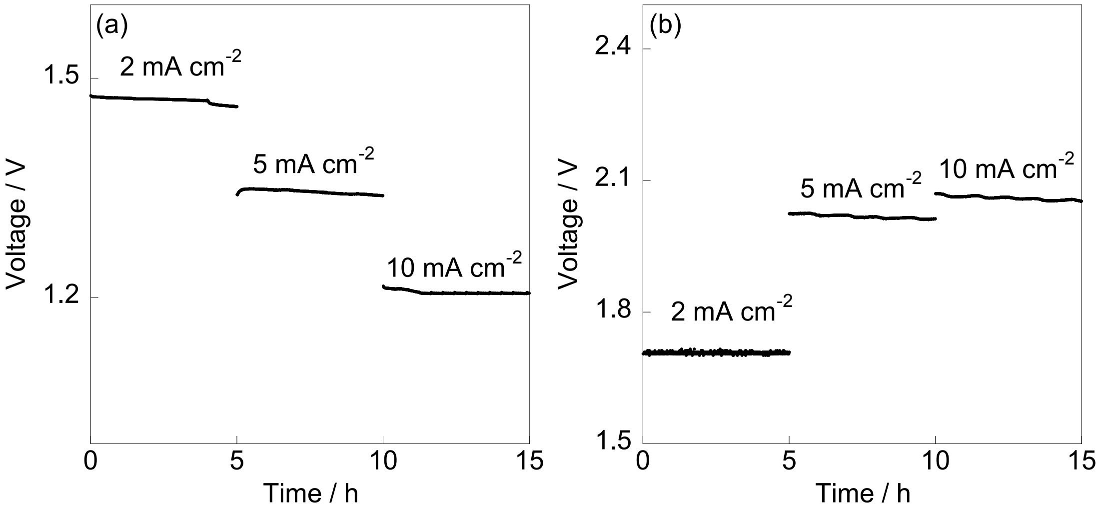


Figure S14 Galvanostatic discharge (a) and charge (b) curves of CoN/CNT at different current densities.