

## **Protruding N-doped carbon nanotubes on elongated hexagonal Co-N-C nanoplates as bifunctional oxygen electrocatalysts for Zn-air batteries**

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## 1. Supplementary experimental section

### 1.1 Chemical and electrocatalyst preparation

Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), 2-methylimidazole, ethanol and N,N-dimethylformamide (DMF) were all analytical grade and purchased from Adamas-beta, China. Cetyltrimethylammonium Bromide (CTAB) was purchased from Sigma-Aldrich. 5% Nafion was acquired from DuPont. The commercial Pt/C (20 wt%) was purchased from Hesen, Shanghai. All of the chemicals used in the experiments were analytical grade and used without further purification.

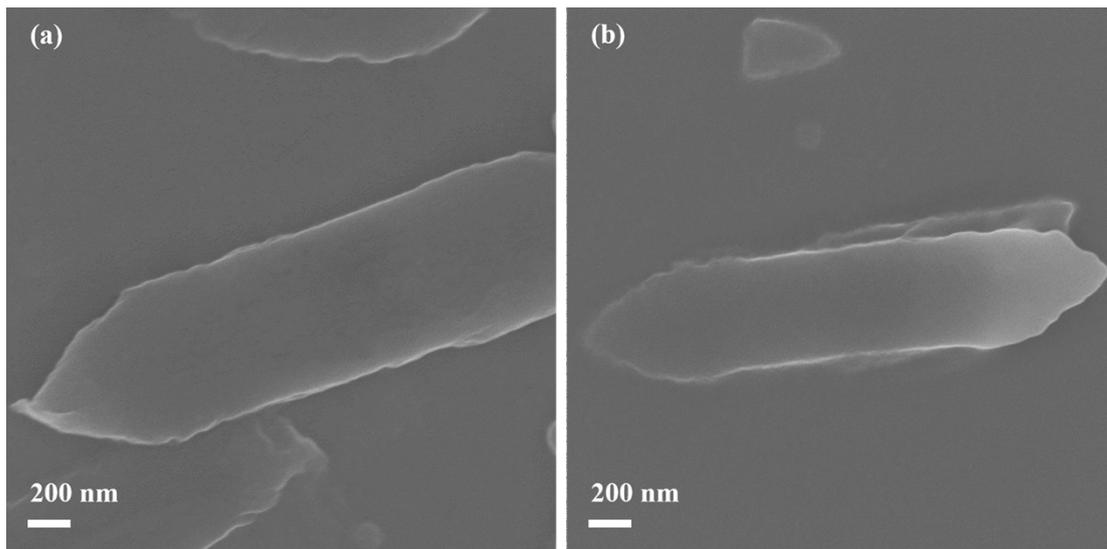
### 1.2 Preparation of other control samples

The annealing temperatures in the Co-N-C@NCNTs synthesis process were varied to prepare Co-N-C@NCNTs-800, Co-N-C@NCNTs-900 and the Co-N-C@NCNTs-1000, to determine the optimum annealing temperature. Specifically, these control samples used The as-prepared 9Co/Zn-ZIF as the precursor, calcined at 350 °C for 1.5 h and then at 800 °C (900°C, 1000°C) for 3.5 h with a temperature rise gradient of 2 °C/min under a mixed hydrogen-argon (5 %) atmosphere. After natural cooling to room temperature, the final product was obtained.

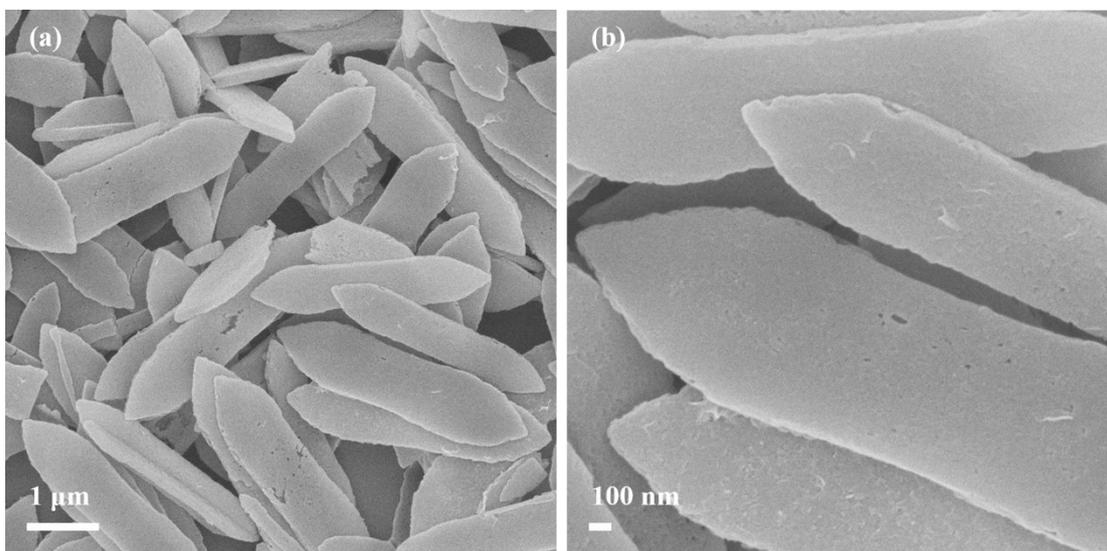
### 1.3 Electrochemical characterizations

Both ORR and OER electrochemical measurements were carried out at room temperature using a standard three-electrode system. The measurements were performed using a CHI 760E electrochemical workstation and an RRDE-3A rotating electrode stage. The 3 mm GC RDE was used as the working electrode for the ORR measurements, with a calomel electrode and a carbon rod as the reference and counter electrode respectively, and 0.1 M KOH as the electrolyte. Pure  $\text{O}_2$  was used to purge the electrolyte for at least 30 minutes to obtain an  $\text{O}_2$  saturated electrolyte before ORR measurements. In LSV measurements, the RDE speed was varied from 900 rpm to 2500 rpm, and the scan rate was 5 mV s<sup>-1</sup>. Another test was performed using RRDE, where the ring electrode voltage was set at 0.3 V. The ORR stability was tested by chronoamperometry measurements, where the RDE speed was 1600 rpm at a -0.509 V (vs. RHE). OER measurements were performed with a 3 mm GC L-type electrode as the working electrode, a glycerol electrode and a carbon rod as the reference electrode and counter electrode, respectively, and 1 M KOH as the electrolyte. Pure  $\text{O}_2$  was used to purge the electrolyte for at least 30 minutes to obtain an  $\text{O}_2$  saturated electrolyte before OER measurements. OER stability was tested by chronoamperometry measurements. For Co-N-C@NCNTs, the stability measurements were tested at a bias voltage of 1.6 V (vs. RHE) for 17 h. For  $\text{RuO}_2$ , the stability measurements were tested at a bias voltage of 1.55 V (vs. RHE) for 17 h.

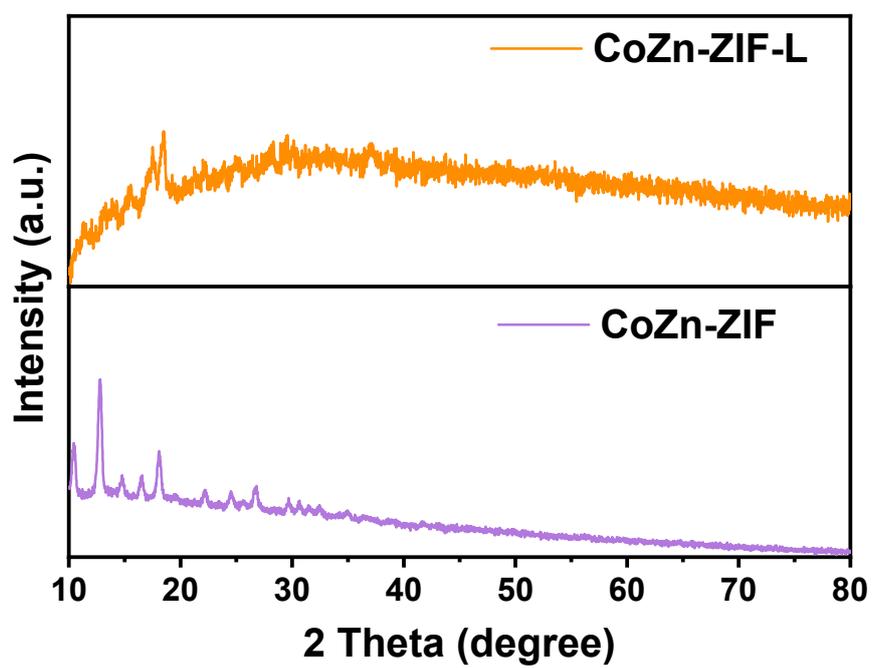
## 2. Supplementary figures



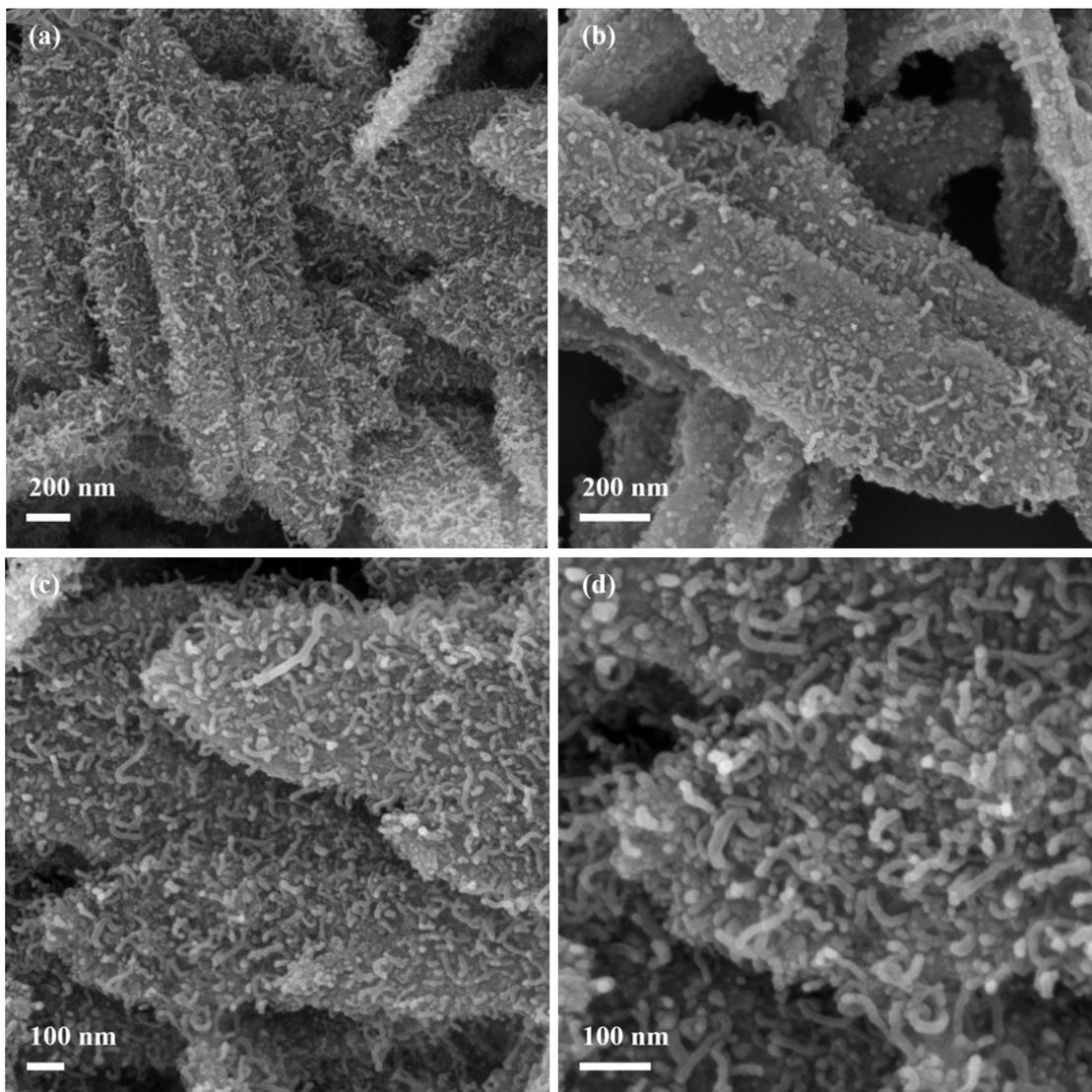
**Figure S1.** (a,b) SEM of CoZn-ZIF-L.



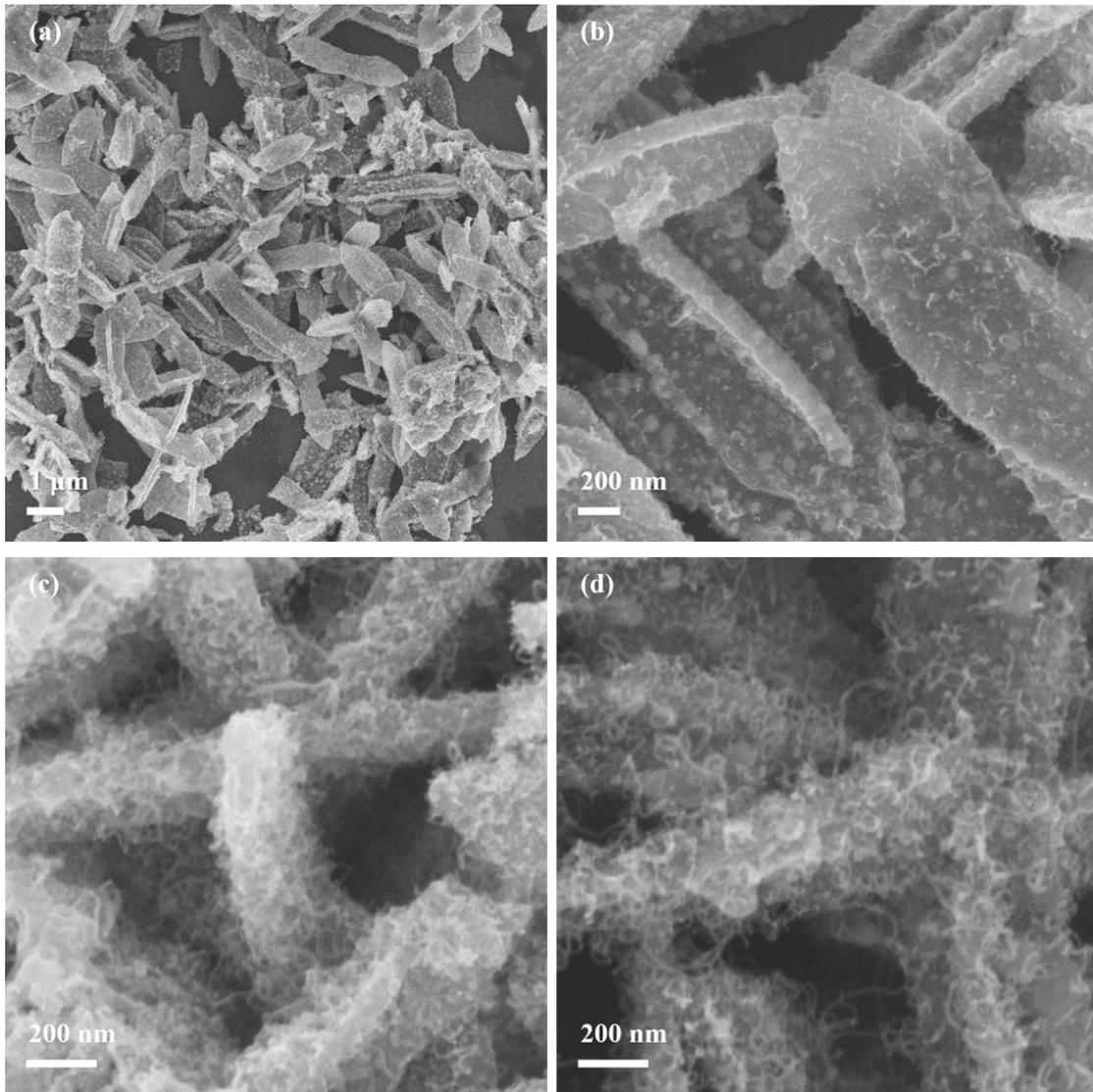
**Figure S2.** (a,b) SEM of CoZn-ZIF-67.



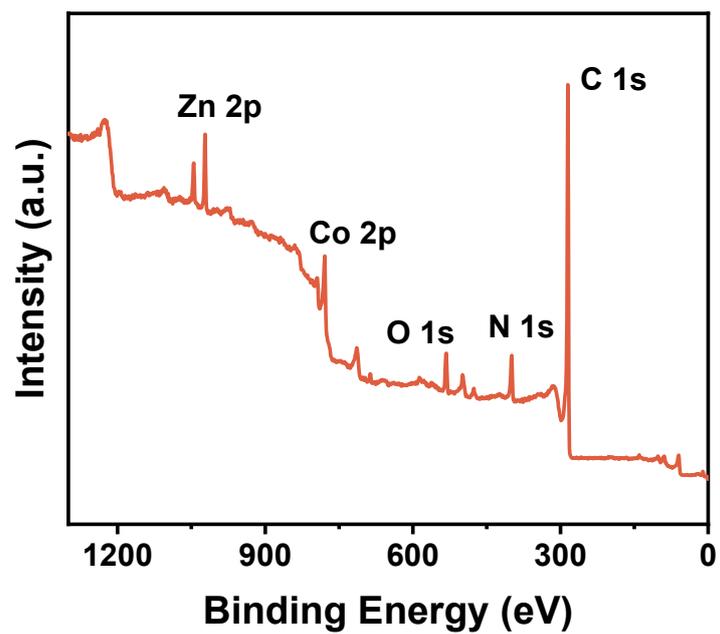
**Figure S3.** XRD pattern of CoZn-ZIF-L and CoZn-ZIF.



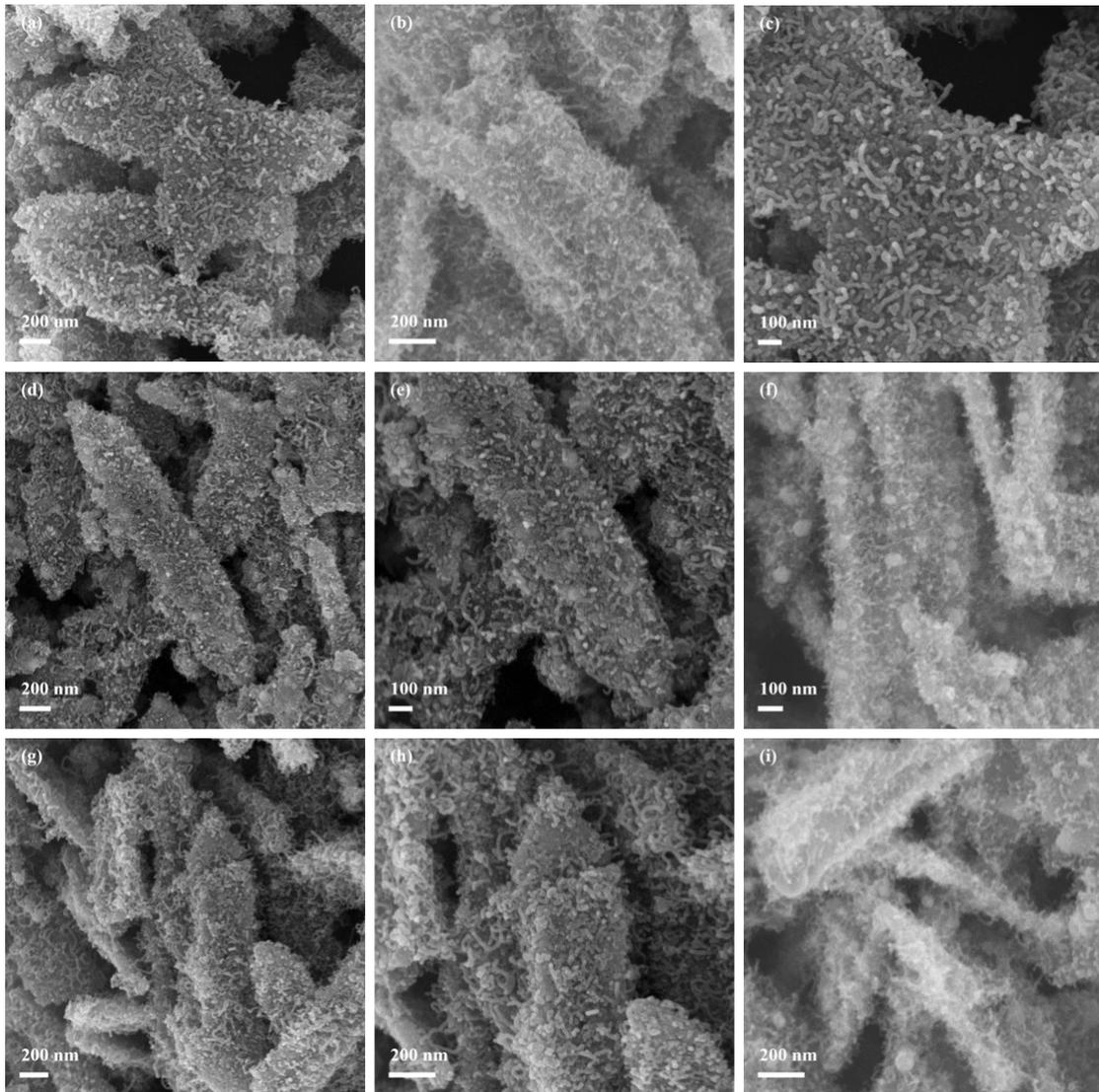
**Figure S4.** SEM of Co-N-C@NCNTs.



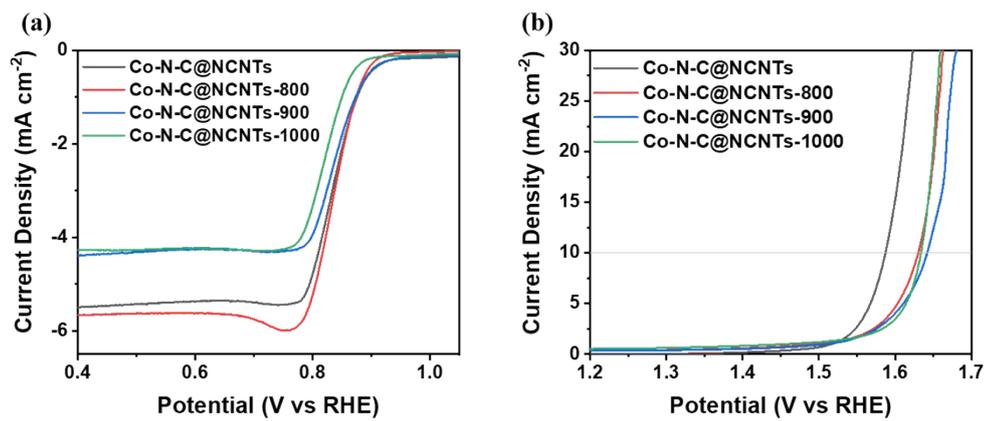
**Figure S5.** (a,b) SEM of Co-N-C@NCNTs(Co). (c,d) SEM of Co-N-C@NCNTs(2Co/Zn).



**Figure S6.** XPS survey spectra of Co-N-C@NCNTs.



**Figure S7.** (a-c) SEM of Co-N-C@NCNTs-800. (d-f) SEM of Co-N-C@NCNTs-900. (g-i) SEM of Co-N-C@NCNTs-1000.



**Figure S8.** (a) LSV curves of ORR activities. (b) LSV curves of OER activities.