

Support Information

Brush-like Co/CoSe nano-heterostructures embedded in N-doped carbon
for rechargeable Zn-air batteries

Teng Luo^a, Shengxi Lei^a, Pan Qi^a, Shuai Niu^b, Zhiwei Li^a, Hao Luo^{a,*}, and Dawei
Zhang^{a,*}

^aAnhui Province Key Laboratory of Value-Added Catalytic Conversion and Reaction
Engineering, School of Chemistry and Chemical Engineering, Hefei University of
Technology, Hefei 230009, Anhui, China.

^bCollege of Ecology, Taiyuan University of Technology, Taiyuan 030024, China.

This file includes Experimental Section, Fig.S1-S11, and Table 1.

Materials

Hexahydrate cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), nitrilotriacetic acid ($\text{C}_6\text{H}_9\text{NO}_6$), potassium hydroxide (KOH), selenium powder (Se), dicyandiamide ($\text{C}_2\text{H}_4\text{N}_4$), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), Pt/C (20 wt%), iridium dioxide (IrO_2), KB, isopropanol, ethanol, and Nafion (5%) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

1. Synthesis of various Materials

(1) Preparation of the Co-oxo framework nanowires: Firstly, 1.43 g hexahydrate cobalt chloride and 30 ml deionized water were added into a beaker. Then, 0.6 g nitrilotriacetic acid and 10 ml isopropanol were added. The beaker was placed on a magnetic stirrer and stirred for 20 minutes to ensure uniform dispersion. Subsequently, the mixed solution was transferred to a 50 ml Teflon-lined stainless autoclave solvothermal reaction under 180 °C for 6 hours. The Co-oxo framework nanowires were subsequently obtained as the precursor.

(2) Preparation of Co-NC, CoSe/Co@NC-1, CoSe/Co@NC-2, and CoSe@NC:

A quartz boat, containing 0.1 g selenium powder and 2 g dicyandiamide, was positioned upstream in a tube furnace, while a separate quartz boat containing Co-oxo framework nanowires was placed downstream. The temperatures were maintained at 800 and 1000 °C, respectively, with a calcination duration of 2 hours. The heating rate was set at 10 °C/min. This process yielded the black products, denoted as CoSe/Co@NC-1. The preparation procedure for Co@NC, CoSe/Co@NC-2, and CoSe@NC followed the same method as CoSe/Co@NC-1, with the only variation being the quantity of selenium powder utilized: 0 g, 0.2 g, and 0.6 g, respectively.

2. Material characterizations

The material phase and crystallinity were analyzed by an X-ray diffractometer (XRD, Rigaku D/MAX2500VL/PC). The morphologies of all samples were investigated by scanning electron microscope (SEM, Gemini 500) and transmission electron microscope (TEM, JEM-2100F). The nitrogen adsorption and desorption isotherms for the samples were measured using a gas adsorption analyzer (Autosorb-IQ3). The obtained curves facilitated the calculation of parameters such as specific surface area and pore size distribution. To identify the types of elements present on the surface of the samples and their chemical states, an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi) was employed.

3. Electrochemical measurements

To prepare the working electrode, initially, 5 mg synthesized sample was mixed with 1 mg KB. Subsequently, This mixture was dispersed in a solution comprising 1 mL deionized water and isopropanol in a volume ratio of 4:1, along with the addition of 20 μL Nafion (5%). The resulting black solution was then subjected to ultrasonication for 45 minutes to form a homogeneous slurry. Finally, 3 μL catalyst slurry was evenly deposited onto a polished glassy carbon surface, and the coated electrode was allowed to air-dry to form a uniformly loaded catalyst film.

The ORR and OER tests were carried out in a 0.1 M KOH solution. Prior to the experiments, oxygen was bubbled through the KOH solution for 45 minutes, utilizing a 1 M KCl-saturated calomel electrode as the reference electrode and a Pt wire as the counter electrode. Linear sweep voltammetry (LSV) was performed with a scan rate of 10 mV/s. The ORR test range extended from -0.7 to 0 V, while the OER test range covered 0 to 1.0 V. Electrochemical evaluation employed an ATA-1B rotating disk electrode (RDE) on the CHI604D electrochemical analyzer. The reversible hydrogen electrode (RHE) potential was calculated using the equation $V_{\text{RHE}} = V_{\text{SCE}} + V_{\text{SCE}}^0 + 0.0592 \times \text{pH}$, where V_{SCE}^0 is 0.2415 V at room temperature.

The experiments involving the zinc-air battery utilized a custom-made battery device. The device's electrolyte comprised 6 M KOH and 0.2 M $(\text{Zn}(\text{CH}_3\text{COO})_2) \cdot 2\text{H}_2\text{O}$. Typically, 8 mg catalyst was thoroughly dispersed in a solvent consisting of 60 μL Nafion (5 wt%), 200 μL isopropanol, and 740 μL deionized water through ultrasonic treatment lasting for 1 hour. Subsequently, 125 μL of the catalyst ink was evenly drop-cast onto the carbon cloth with a mass loading of 1 mg cm^{-2} . All zinc-air batteries were tested under the same experimental conditions.

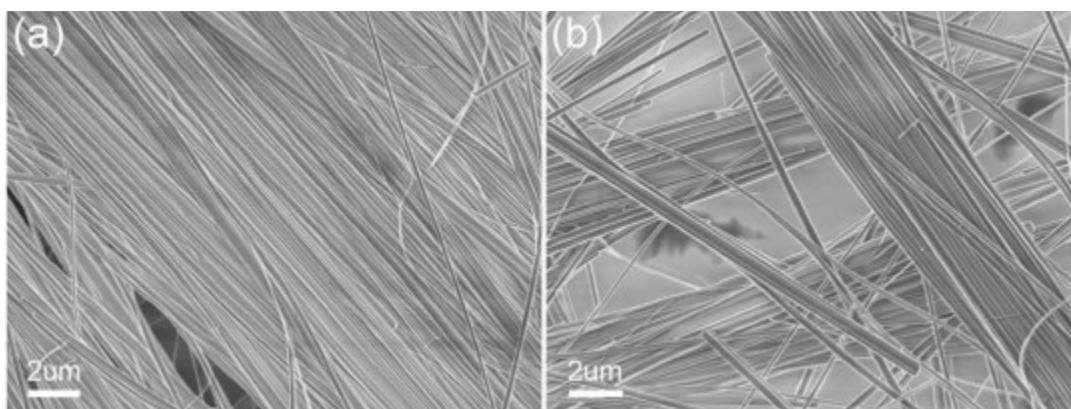


Fig. S1. (a, b) SEM images of the metal-oxo framework nanowires.

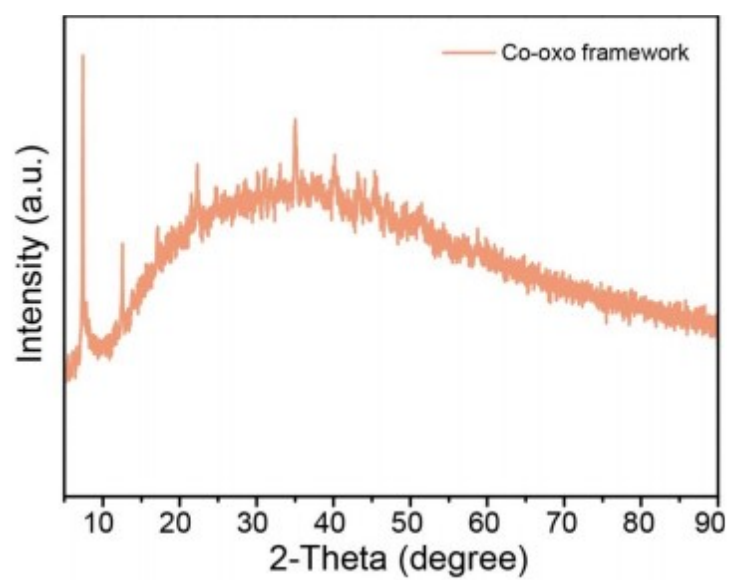


Fig. S2. X-ray diffraction curve of Co-oxo framework.

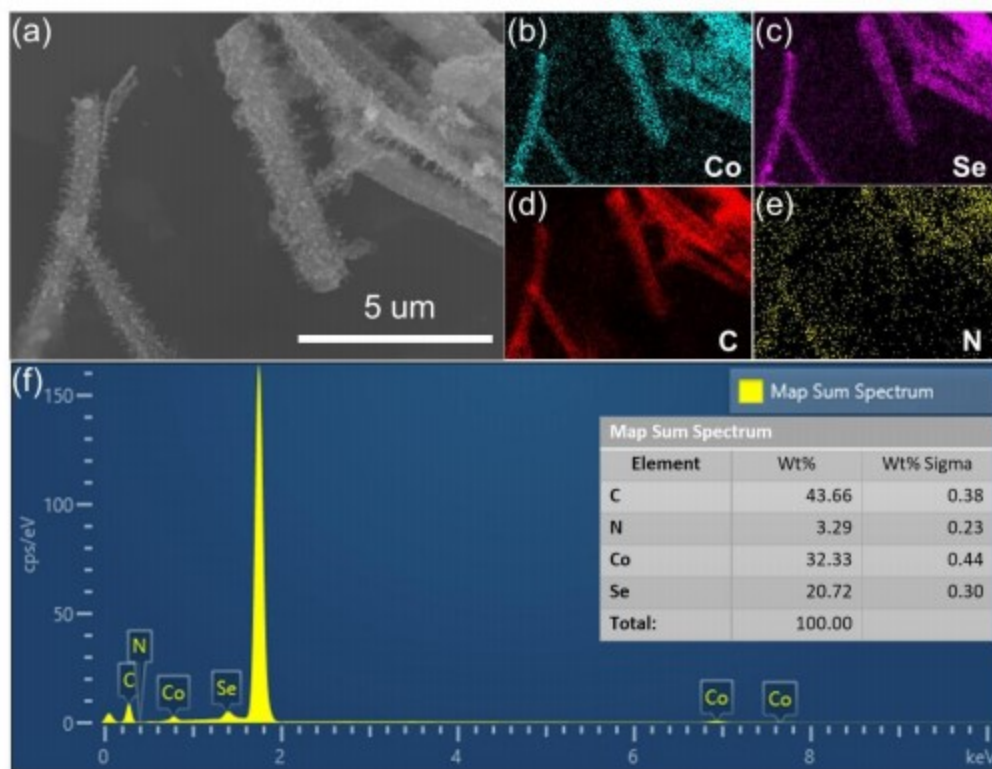


Fig. S3. SEM images and EDS element mapping of CoSe/Co@NC-1.

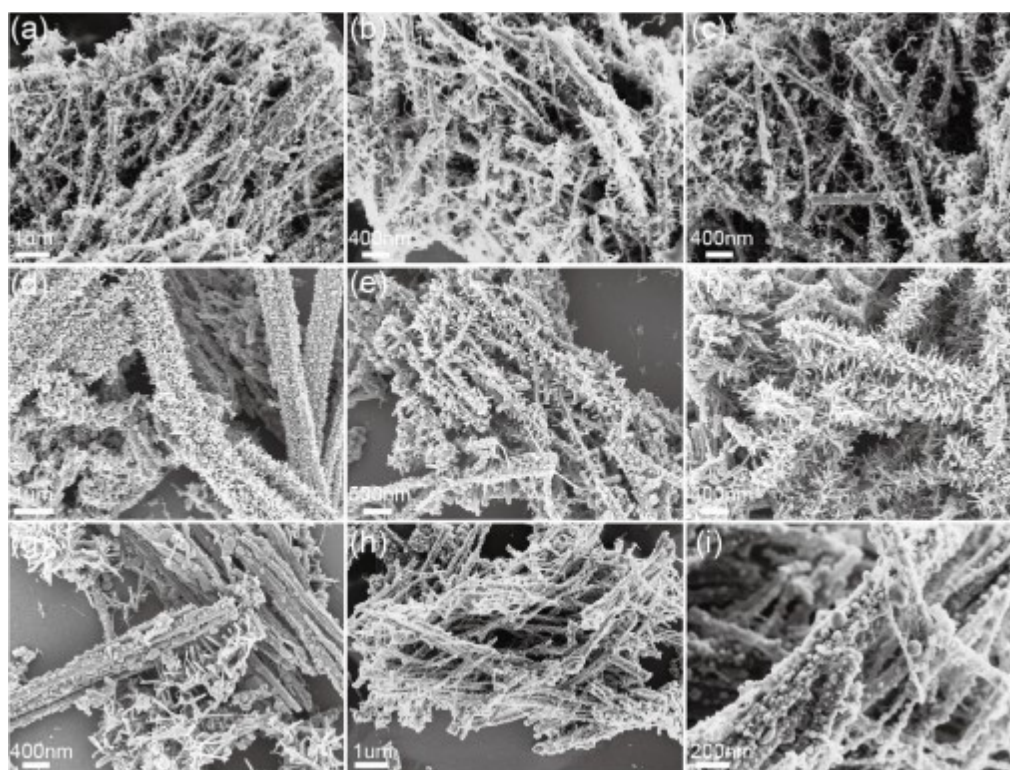


Fig. S4. (a)-(c) SEM images of Co@NC, (d)-(g) SEM images of CoSe/Co@NC-2, and (h-i) SEM images of CoSe@NC.

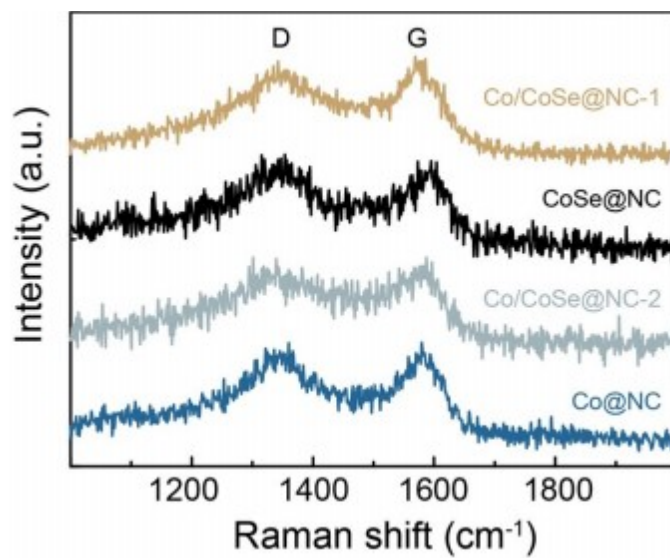


Fig. S5. Raman spectra of Co@NC, CoSe/Co@NC-1, CoSe@NC-2, and CoSe@NC.

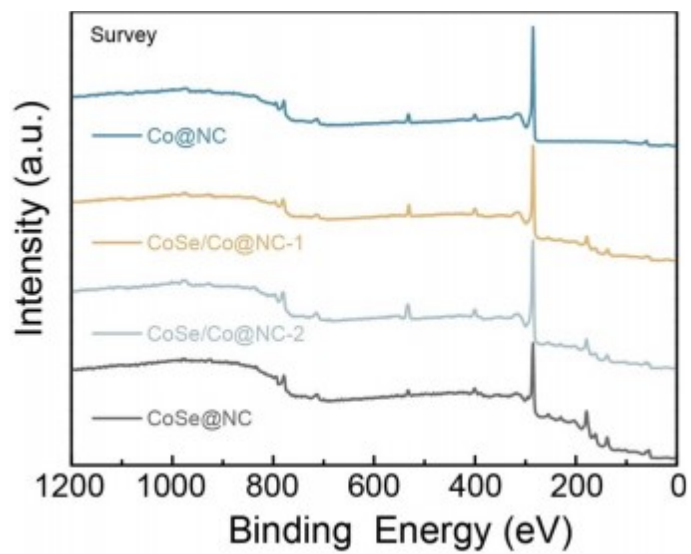


Fig. S6. XPS survey spectra of all samples.

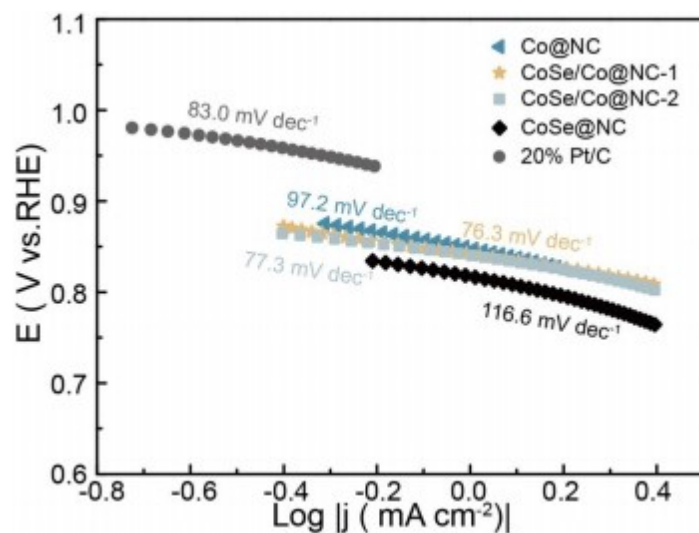


Fig. S7. Tafel slope curves for the corresponding ORR.

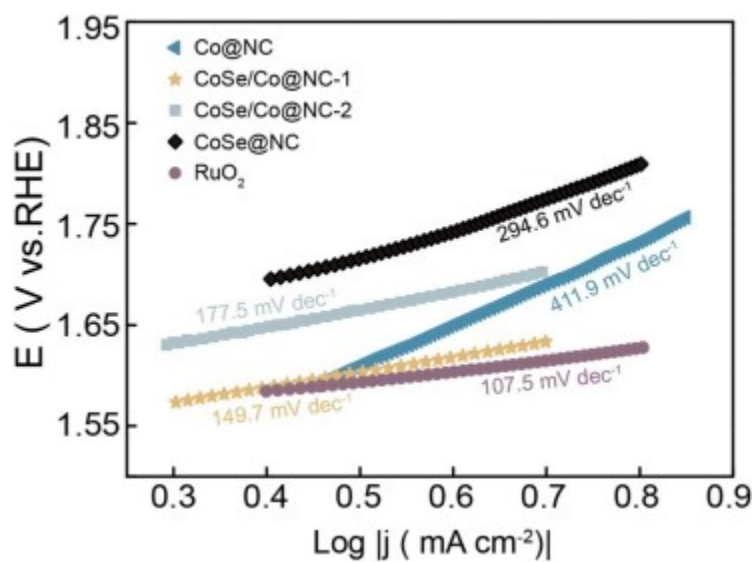


Fig. S8. Tafel slope curves for the corresponding OER.



Fig. S9. The homemade zinc-air battery device and the optical photo of open circuit voltage about precious metal 20% Pt+IrO₂ catalyst.

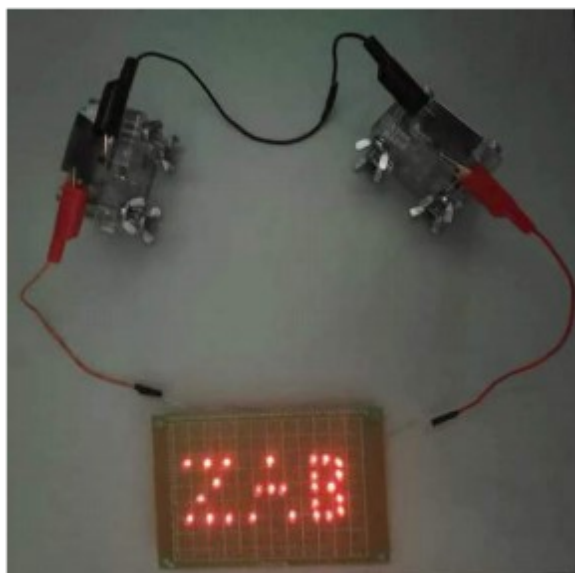


Fig. S10. LED light with the word "ZAB" lit by zinc-air batteries assembled by CoSe/Co@NC-1.

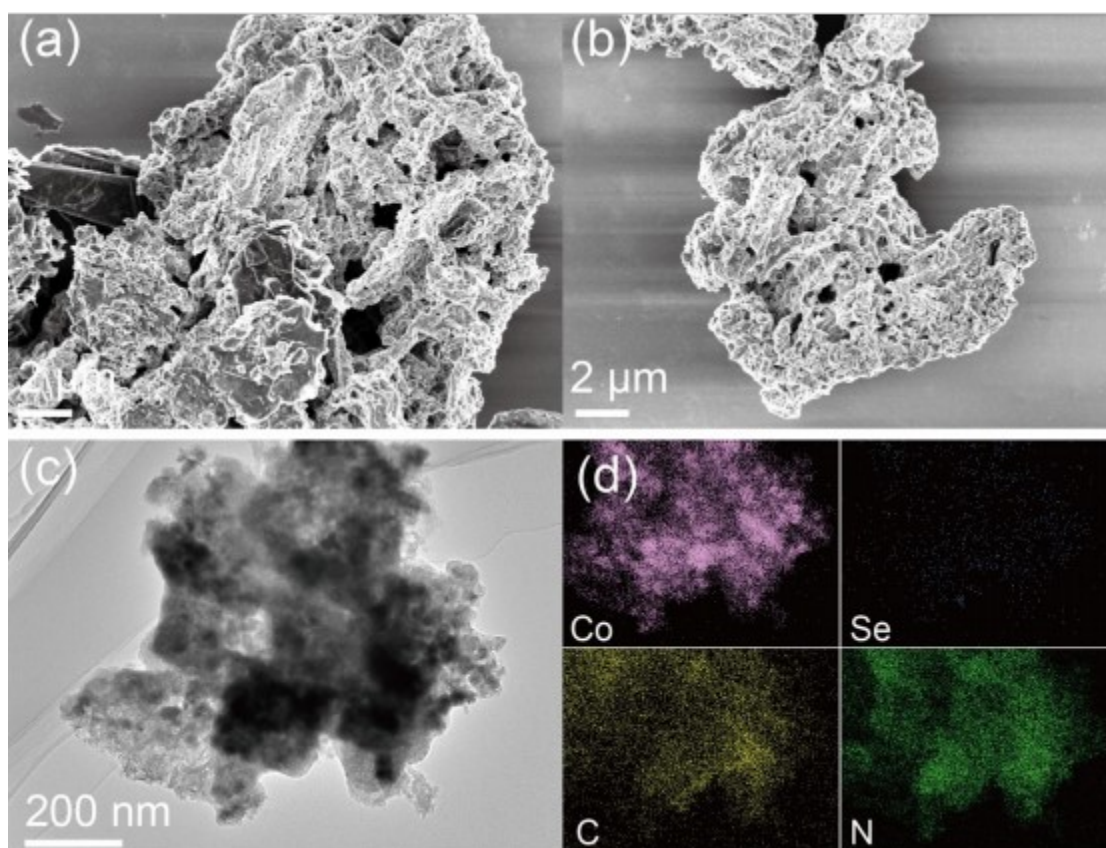


Fig. S11. SEM and HRTEM images of CoSe/Co@NC-1 after 2850 cycles at 2.0 mA cm⁻² in Zn-air batteries.

Table S1. Zn-air batteries' performance comparison for CoSe/Co@NC-1 with reported analogs catalysts.

Sample	Discharge power density (mWcm ⁻²)	Cycling stability	Reference
Co/N-C@NiCo ₂ O ₄ -500	176	100h	Energy Fuels 2023, 37, 11319-11331
Ag-Fe-N-C	211	100h	J. Alloys Compd. 2023, 967,171673
CoNP@FeNC-0.05	104.4	500h	Nano-Micro Lett., 2022, 14, 162
NSC/Co ₉ S ₈ -200	176	120h	Nano Energy, 2022, 92, 106750
CoSe ₂ @NC@NCNFs	126.8	240cycles	Chin. J. Chem. 2024, 42, 397-405
CoSe/NC	154	170 h	Chem. Commun., 2023,59,5898-5901
FeCo-NC@Co ₂ P-NC	159.3	140 h	J. Alloys Compd. 2023, 939,168679
CoSe/Co@NC-1	215	475 h (2850 cycles)	This work