Supporting Information

Temperature-Induced Phase Transformation of Cobalt Selenide Optimizes Spin States for Enhanced Oxygen Electrocatalysis

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Experimental Section

Materials

Nafion perfluorinated resin solution (CAS: 31175-20-9, 5%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. Potassium hydroxide (KOH, CAS: 1310-58-3, 95%) were purchased from Shanghai Maclean Biotechnology Co., Methanol (CH_3OH, CAS: 67-65-1, 99.9%) and ethanol (CH_3CH_2OH,CAS: 64-17-5, specification: pharmaceutical grade, 99.5%) were purchased from Aladdin (Shanghai) Chemical Co., Ltd. Hexahydrate of cobalt (II) nitrate ($Co(NO_3)_2·6H_2O$, CAS: 10026-22-9, 99%) was purchased from Adamas-beta (Shanghai) Chemical Reagent Co., Ltd. 2-Methylimidazole ($C_4H_6N_2$, CAS: 693-98-1, 98%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Selenium (Se, CAS: 7782-49-2, 99.9%) was purchased from Shanghai Maclean Biotechnology Co. All chemicals and materials were utilized without further purification.

Synthesis

1. Preparation of Metal-Organic Framework ZIF-67

A solution of 2.91 g (0.5 mmol) of cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) in 80 mL of methanol (MeOH) and a solution of 3.284 g (2 mmol) of 2-methylimidazole in 80 mL of ethanol (EtOH) were prepared separately. Each solution was stirred for 30 minutes. Subsequently, the two solutions were combined and mixed uniformly. The resulting mixture was stirred at room temperature for 24 h. The product was collected by centrifugation, washed three times with ethanol, and finally dried overnight in an oven at 60 °C to afford a purple powder, designated as ZIF-67.

2. Preparation of $CoSe_2$ Precursor

A mixture of selenium powder and ZIF-67 in a mass ratio of 1:1 was thoroughly ground using an agate mortar. The resulting mixture was then transferred to a ceramic boat and placed in a tube furnace. Under an argon atmosphere, the temperature was raised to 550 °C at a heating rate of 2 °C/min and maintained for 2 h. After cooling naturally to room temperature, a black powder was obtained, denoted as the $CoSe_2$ precursor.

3. Preparation of $CoSe_2$-350

The $CoSe_2$ precursor was placed in a tube furnace and heated to 350 °C at a rate of 3 °C/min under an argon atmosphere, maintained at this temperature for 2 hours, and then allowed to cool naturally to room temperature. The resulting product was collected and designated as $CoSe_2$-350.

By setting the heating temperatures to 450 °C, 550 °C, 600 °C, and 700 °C, $CoSe_2$-450, $CoSe_2/Co_3Se_4$-550, $CoSe_2/Co_3Se_4$-600, and Co_3Se_4-700 were subsequently synthesized.

Materials Characterization:

The crystal structure of the as-synthesized material was determined by X-ray diffraction (XRD) on a BRUKER D8 ADVANCE diffractometer using CuKα radiation. The morphology was characterized by high-resolution transmission electron microscopy (HR-TEM, FEI Talos F200X) and scanning electron microscopy (SEM, SU8020). X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo Escalab 250Xi spectrometer. Thermogravimetric (TG) analysis was performed using a HITACHI STA200 thermal analyzer. The room-temperature magnetization curve was measured with a Lake Shore 8604 vibrating sample magnetometer (VSM).

Electrochemical Performance Measurement

The electrochemical measurements were conducted at room temperature using a CHI-660 electrochemical workstation.

The oxygen evolution reaction (OER) was evaluated in a 1 M KOH (pH = 14) electrolyte using a conventional three-electrode configuration. The system consisted of a Hg/HgO reference electrode (RE), a platinum plate counter electrode (CE), and a working electrode (WE). The WE was prepared as a self-supported electrode by clamping a catalyst-loaded carbon paper. The catalyst ink was formulated by ultrasonically dispersing a mixture of 10 mg catalyst and 15 μL Nafion solution (5 wt%) in 485 μL anhydrous ethanol. Subsequently, 20 μL of the resulting ink was drop-cast onto a carbon paper substrate (5 mm × 5 mm), forming a uniform thin film with a catalyst loading of approximately 1.65 mg cm^{-2}.

Linear sweep voltammetry (LSV) was employed to record the polarization curves. The measured potentials versus the Hg/HgO reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the following equation:

$$E(\text{vs.RHE}) = E(\text{vs.Hg/HgO}) + 0.0980 + 0.0591 * \text{pH} \quad (1)$$

The oxygen reduction reaction (ORR) was tested in a 0.1 M KOH (pH=13) electrolyte using a conventional three-electrode setup in a RDE workstation (PINE/AFMSRCE). The reference electrode (RE) was Ag/AgCl, the counter electrode (CE) was a platinum wire, and the working electrode was a rotating glassy carbon electrode. The catalyst ink was prepared by dispersing 6 mg of the catalyst, and 15 μL of Nafion (5 wt%) solution in 485 μL of anhydrous ethanol via ultrasonication. Then, 15 μL of the ink was drop-cast onto the surface of the glassy carbon electrode (5 mm in diameter) to form a uniform thin film with a loading of approximately 0.31 mg cm^{-2}. Polarization curves were recorded using linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1}. The following formula was used to convert the electrode potential in alkaline solution to the standard hydrogen electrode potential:

$$E(\text{vs.RHE}) = E(\text{vs.Ag/AgCl}) + 0.198 + 0.059 * \text{pH} \quad (2)$$

The zinc-air battery was tested in a 6 M KOH + 0.2 M $Zn(CH_3COO)_2$ electrolyte. The catalyst ink was prepared by ultrasonically dispersing a mixture of 3 mg catalyst, 1 mg carbon powder (CABOT BP 2000), and 15 µL Nafion solution (5 wt%) in 485 µL anhydrous ethanol. Subsequently, 50 µL of the ink was uniformly coated onto a carbon cloth substrate, serving as the cathode with a loading of approximately 0.4 mg cm^{-2}. A zinc plate was used as the anode.

Density Functional Theory calculations

Density Functional Theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP)[1, 2]. The Projector-Augmented Wave (PAW) method was adopted to evaluate electron-electron interactions, and the electron exchange-correlation effects were calculated via the revised Perdew-Burke-Ernzerhof (PBE) functional[3]. Herein, the (111) crystal plan of $CoSe_2$ and Co_3Se_4 were selected, and a vacuum layer thickness of 15 Å was set for both $CoSe_2$ (111) and Co_3Se_4 (111) surfaces to simulate the catalytic reaction interface[4,5]. The calculation parameters were set as follows: the cutoff energy was 400 eV, the k-point grid was 3×3×1, and the energy convergence criterion between electronic steps was 10^{-6} eV. The Gibbs free energy (ΔG) of each reaction intermediate was calculated using the formula:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \qquad (3)$$

where ΔE is the adsorption energy of the oxygen-containing intermediate, ΔE_{ZPE} denotes the change in zero-point vibrational energy, and ΔS is the entropy difference between the adsorbed state and the corresponding molecular state[6]. T represents temperature, which is typically set to 298 Kelvin in standard calculations. To more accurately compute the spin density of states (DOS) and band structure of the models, the DFT+U method was employed with an effective U value of 3.3 eV for cobalt (Co)[7]. All DOS calculations herein were performed using the optimized models of $CoSe_2$ and Co_3Se_4.

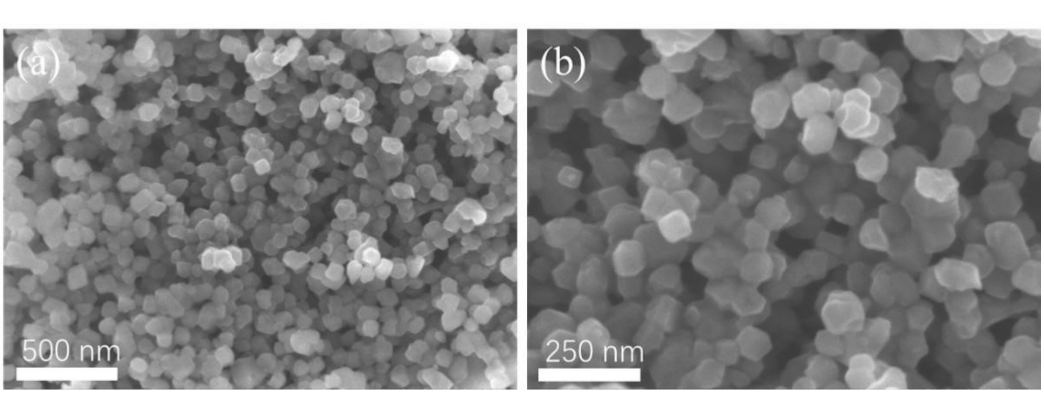

Fig. S1 SEM image of ZIF-67

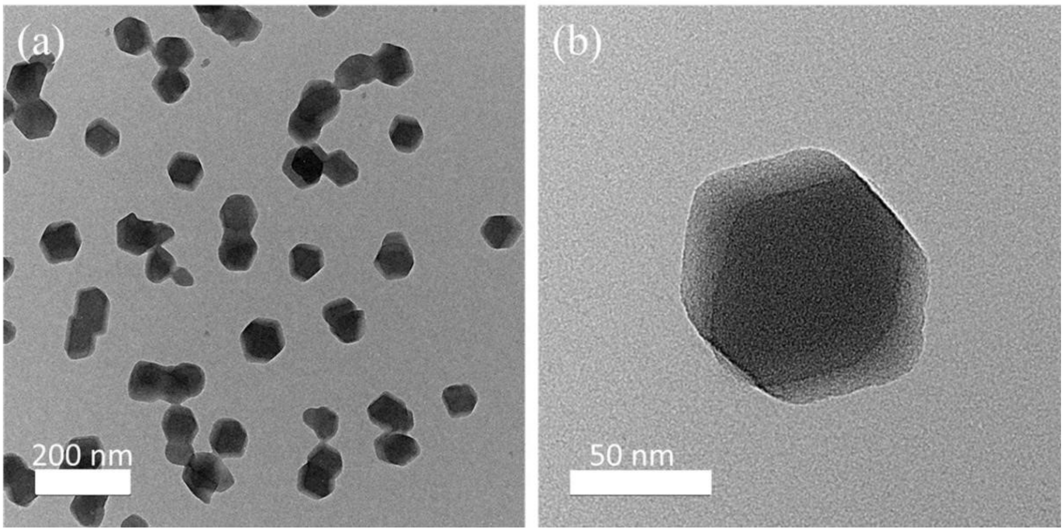

Fig. S2 TEM image of ZIF-67

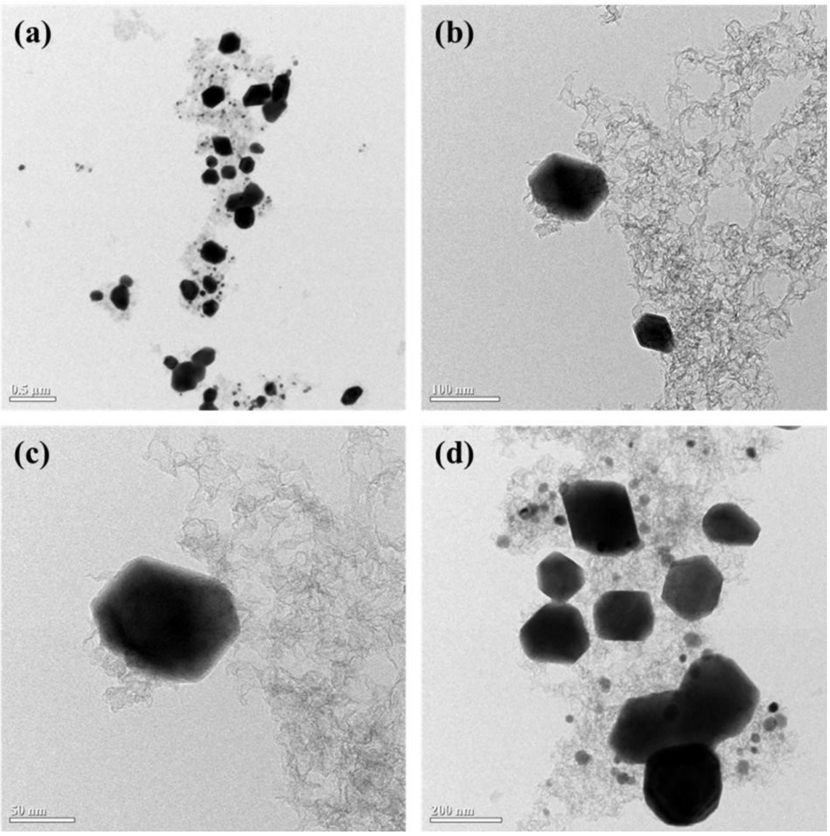

Fig. S3 TEM image of Co_3Se_4

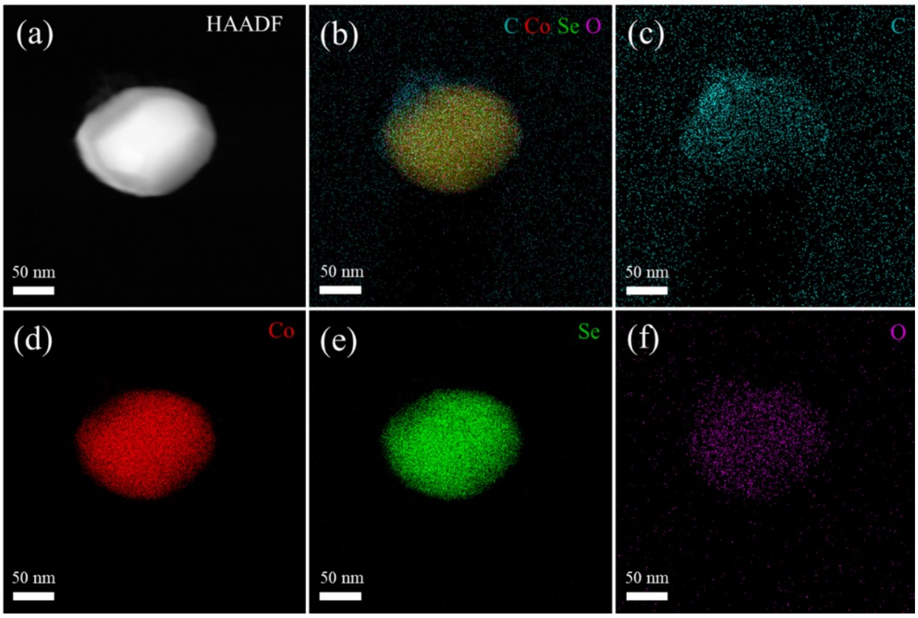

Fig. S4 (a) HAADF image of Co_3Se_4, (b-f) STEM-EDX mapping of C, Co, Se, and O in Co_3Se_4.

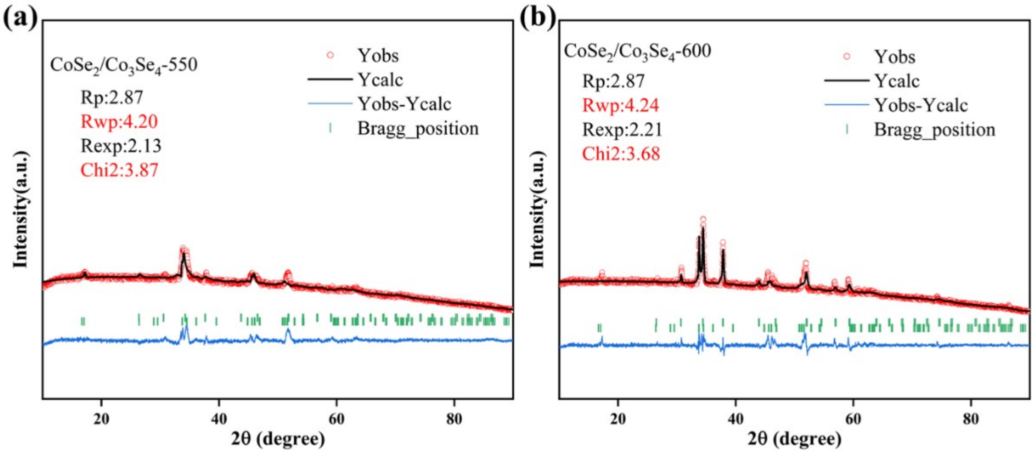

Fig. S5 Rietveld-refined XRD profile of (a) $CoSe_2/Co_3Se_4$-550 and (b) $CoSe_2/Co_3Se_4$-600 using Fullprof software.

Fig. S6 (a) The error values associated with the refined results of Fig. S5, obtained from Fullprof software. The corresponding XRD refinement error values, including R_p, R_{wp} and R_{exp} are all date below 10, the Chi^2 below 4, indicating the reliability of the refined results, (b) Content of $CoSe_2$ and Co_3Se_4 in samples.

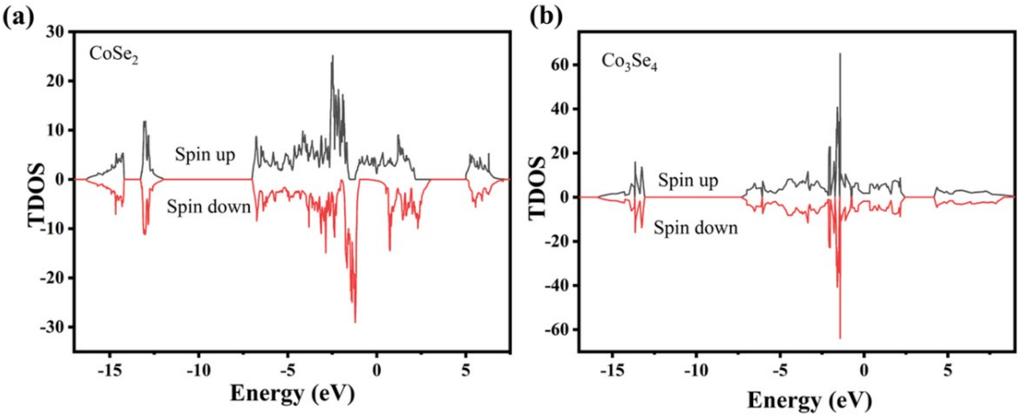

Fig. S7 TDOS of (a) $CoSe_2$ and (b) Co_3Se_4

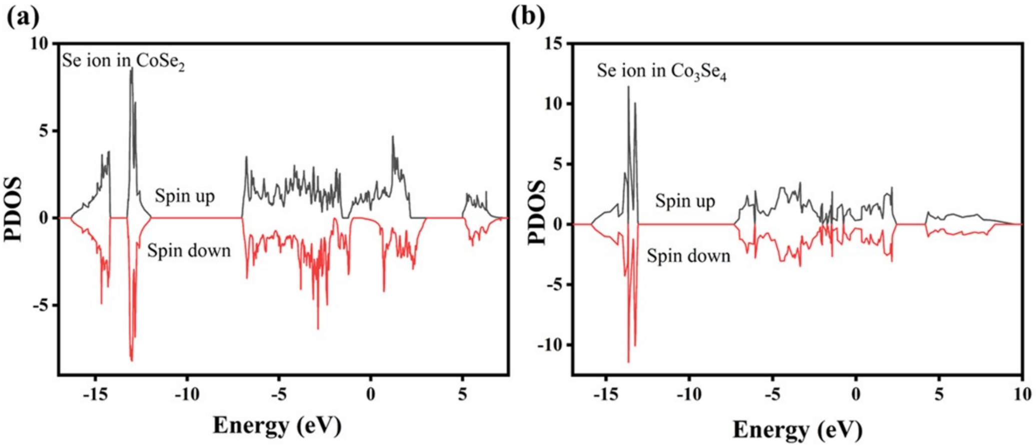

Fig. S8 PDOS of Se ion in (a) $CoSe_2$ and (b) Co_3Se_4,

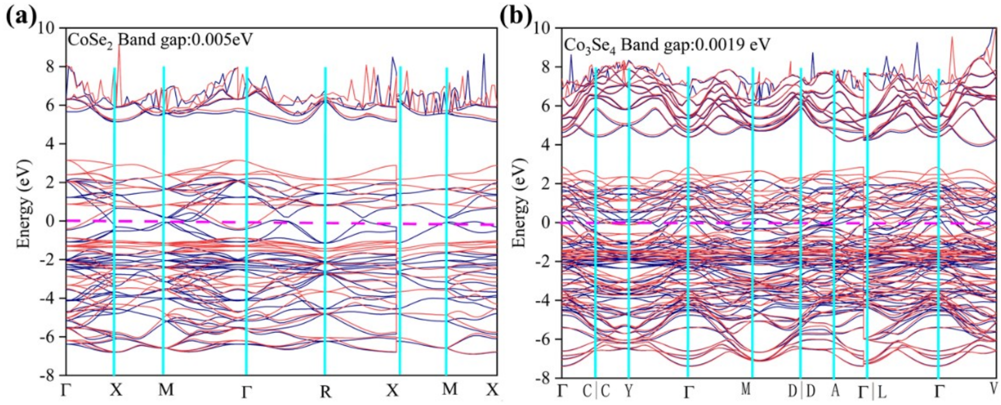

Fig. S9 Calculated band structures of (a) $CoSe_2$ and (b) Co_3Se_4.

References

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