

Supplementary information

Optimization of O₂ Evolution Electrocatalytic Activity via Engineered One-Pot Synthesized ZnSe/CoSe₂@N-Doped C Composite

Hyeonwook Son, Jinhyuk Baek, Shrine Maria Nithya Jeghan, Moonsu Kim^{1,}, and Gibaek Lee^{1*}*

Advanced Energy Materials Design Lab., School of Chemical Engineering, Yeungnam University,
38541 Gyeongsan, Republic of Korea

***Corresponding authors**

To whom correspondence should be addressed.

E-mail addresses: moonsu.kim@yu.ac.kr (Dr. Moonsu Kim); gibaek@ynu.ac.kr (Prof. Gibaek Lee)

Tel.: +82-53-810-2527

Fax: +82-53-810-4631

Experimental

Material Preparation

Synthesis of Zn/Co–ZIF: First, a mixture of 6 mmol of metal precursors ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 30 mL of methanol to obtain Solution A. Subsequently, 24 mmol of 2-methylimidazole in methanol, referred to as Solution B, was added to Solution A under vigorous stirring for 24 h. The resultant purple powder was collected by centrifugation, washed several times with methanol, and dried at 80 °C overnight. This protocol was repeated with different Zn/Co molar ratios to obtain different Zn/Co–ZIF compositions. The Zn/Co molar ratios were adjusted to 1:1, 1:3, 1:5, and 1:7 while maintaining a total of 6 mmol of metals.

Synthesis of ZnSe/CoSe₂@NCs. The Zn/Co–ZIF precursor was mixed with Se powder at a mass ratio of 1:2 and annealed at 600 °C for 3 h at a heating rate of 2 °C min⁻¹ in an Ar atmosphere. The final products were denoted as ZnSe/CoSe₂@NC with varying Zn/Co ratios (1:1, 1:3, 1:5, and 1:7). Moreover, single-metal samples, referred to as ZnSe@NC and CoSe₂@NC, were prepared for comparison.

Characterization

The samples were characterized through field-emission scanning electron microscopy (FE-SEM; S-4800, HITACHI) and field-emission transmission electron microscopy (FE-TEM; Titan G2 ChemiSTEM Cs Probe, FEI) with energy-dispersive spectroscopy (EDS) and selected-area electron diffraction (SAED) analysis. X-ray diffraction (XRD) was performed using a micro-powder diffractometer (DIATOME) with Cu K α radiation. Thermogravimetric analysis (TGA) was conducted from 30 to 900 °C at a heating rate of 10 °C min⁻¹ in air. X-ray photoelectron spectroscopy (XPS) was performed using an Al K α X-ray source (K-Alpha, Thermo Scientific).

Electrochemical Measurements

The electrochemical properties were assessed using an Autolab potentiostat/galvanostat (PGSTAT 302N) in a three-electrode setup with a C rod and Hg/HgO electrodes as the counter and reference electrodes, respectively. The catalyst ink was created by mixing 5 mg catalyst with 240 μL isopropyl alcohol, 240 μL deionized water, and 20 μL 5 wt% Nafion; sonicating for 30 min; and drop-casting onto a $1.0 \times 1.0 \text{ cm}^2$ C cloth. Linear sweep voltammetry (LSV) was conducted in 1 M KOH at 5 mV s^{-1} (1.1 – 1.8 V), and the reversible H_2 potential (RHE) was adjusted using the Nernst equation ($E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098$). Cyclic voltammetry (CV) was conducted at 20–100 mV s^{-1} to determine the double-layer capacitance. Stability was tested via chronopotentiometry at 10 and 100 mA cm^{-2} . Electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 100 kHz to 1 Hz at 0.68 V (vs. Hg/HgO) with an amplitude of 10 mV.

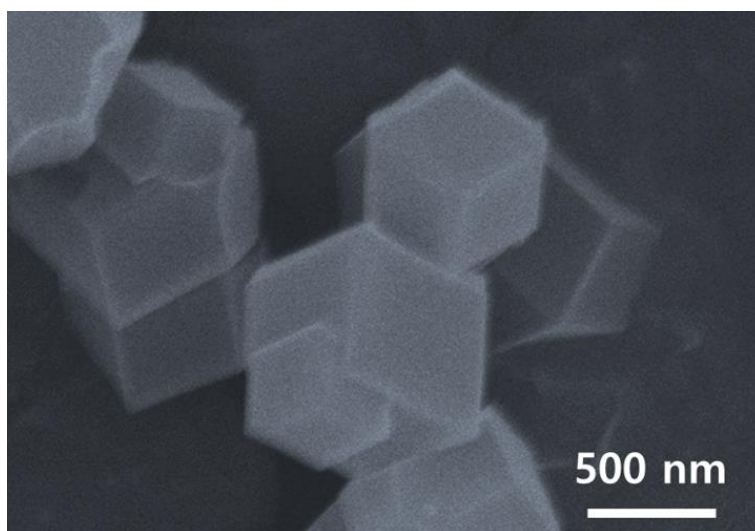


Figure S1. SEM image of Zn/Co-ZIF (1:5).

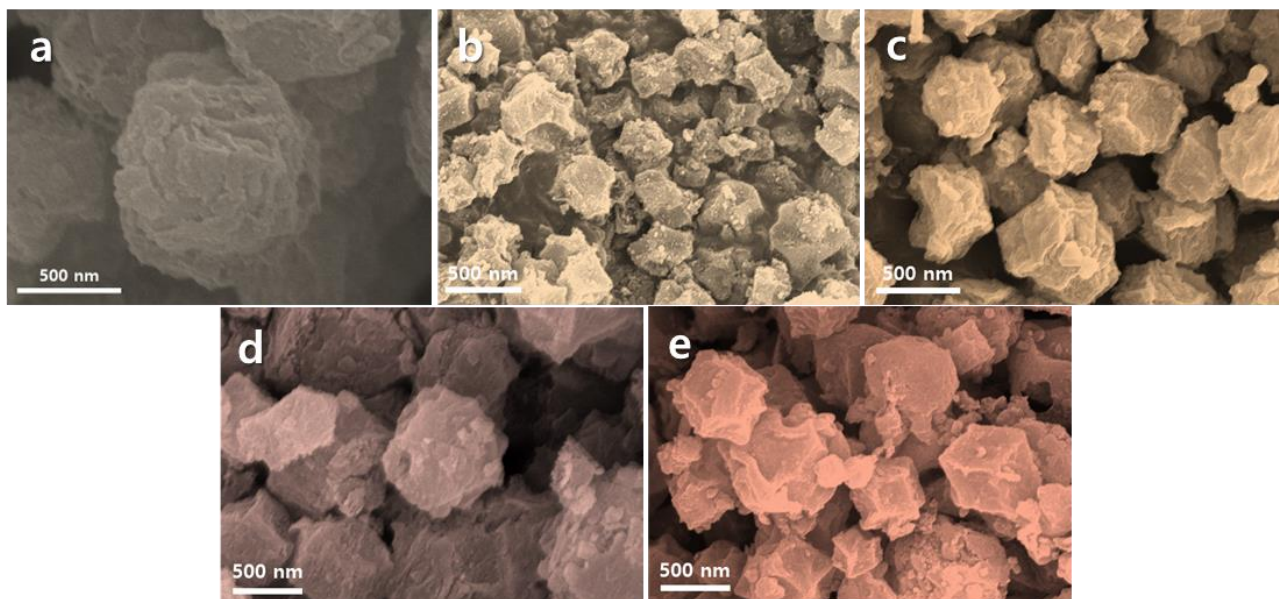


Figure S2. SEM images of (a) ZnSe@NC, (b–d) ZnSe/CoSe₂@NC (1:1, 1:3, and 1:7), and (e) CoSe₂@NC.

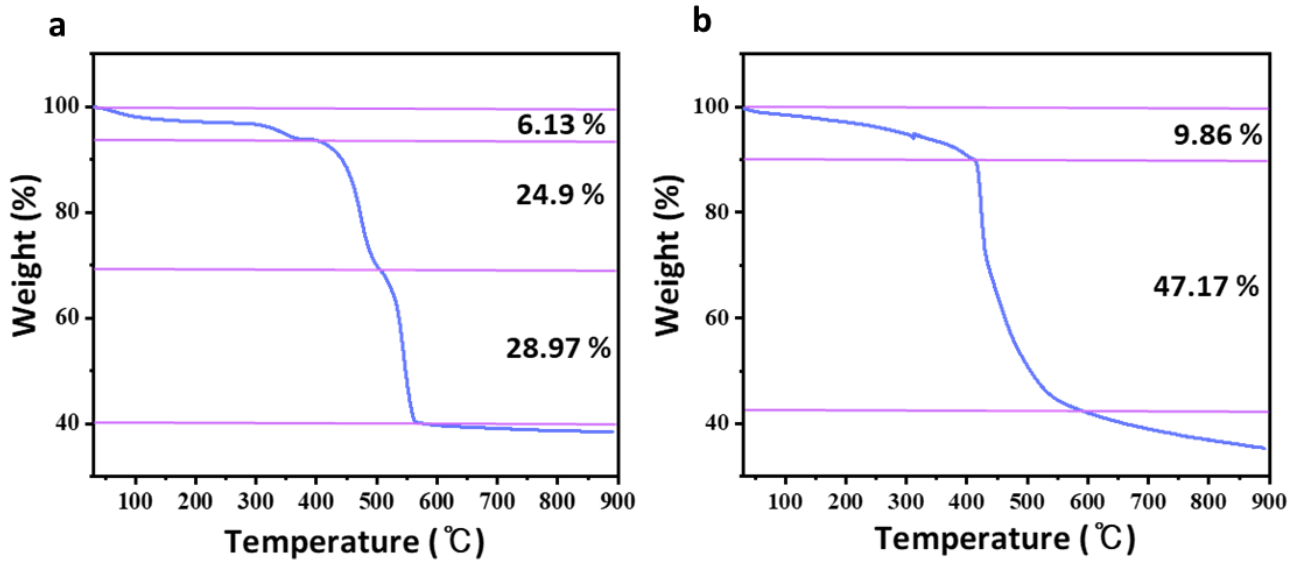


Figure S3. TGA profiles of (a) CoSe₂@NC and (b) ZnSe@NC.

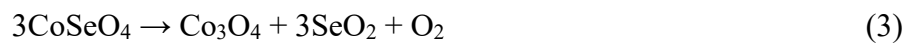
In the initial stage, from room temperature to 400 °C, a weight loss of 7.49% is noted owing to the evaporation of water molecules and formation and subsequent sublimation of SeO₂, as described in Equation (1):



In the second stage at 400–550 °C, rapid weight loss occurs corresponding to the combustion of the N-doped C matrix, as represented by Equation (2):



In the final stage at >550 °C, the oxidation of Zn and Co occurs, as depicted in Equations (3) and (4), respectively:



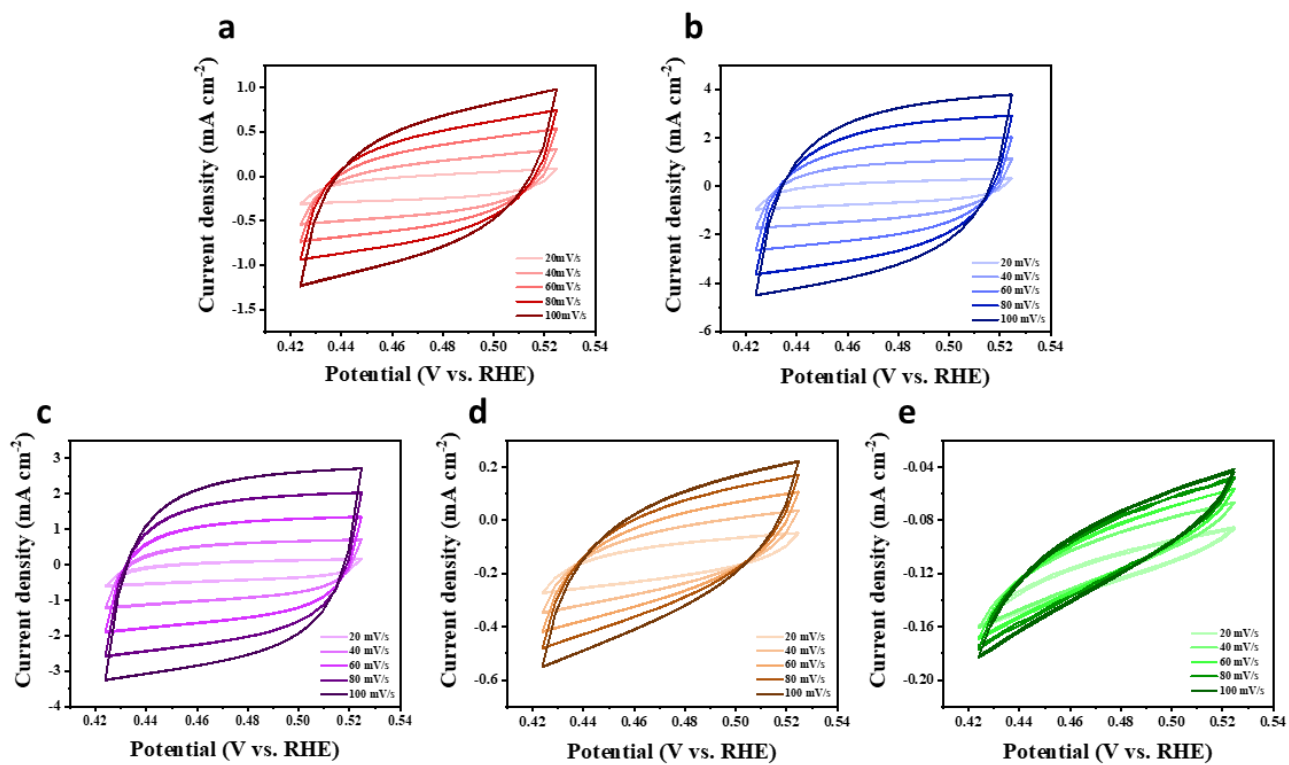


Figure S4. CV profiles of (a–d) ZnSe/CoSe₂@NC (1:1, 1:3, 1:5, and 1:7) and (e) CoSe₂@NC at different scan rates of 20–100 mV s⁻¹.

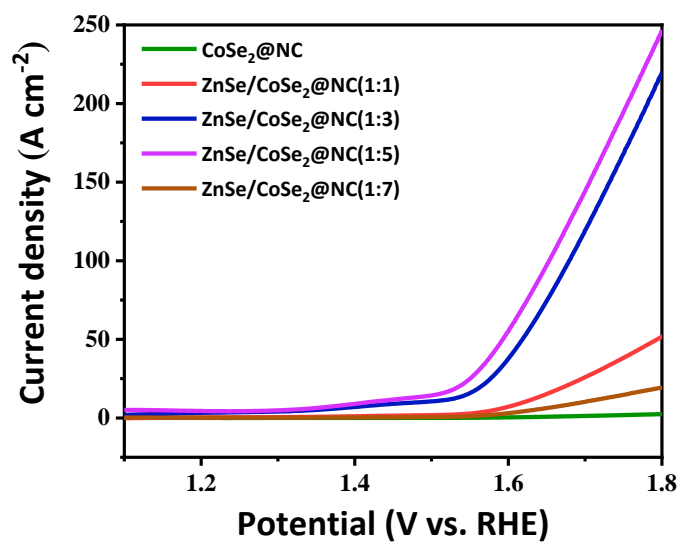


Figure S5. LSV curves representing electrocatalytic OER performance ZnSe@CoSe₂/NC (1:0, 1:1, 1:3, 1:5, 1:7, and 0:1) normalized by the ECSA.

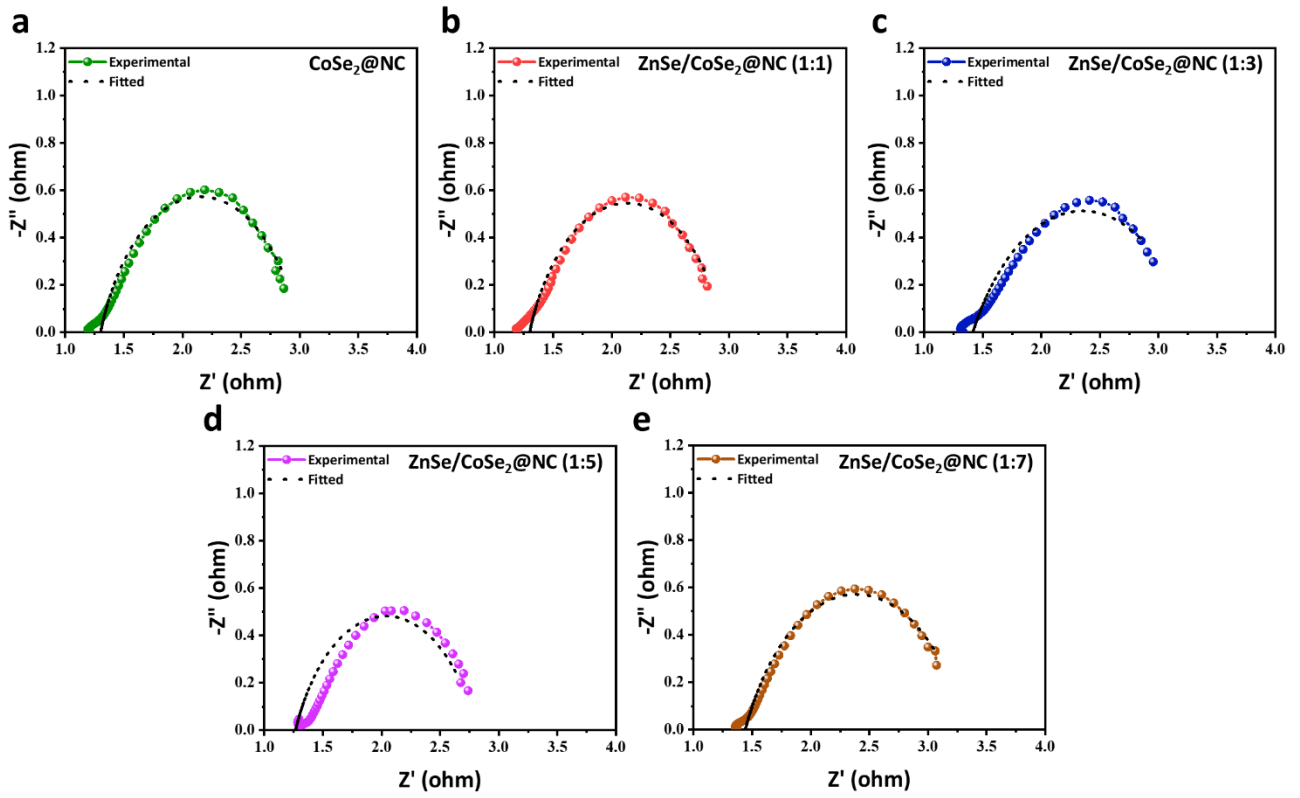


Figure S6. Comparing actual with fitted Nyquist plot of the samples. (a) $\text{CoSe}_2@NC$, $\text{ZnSe}/\text{CoSe}_2@NC$ (b) 1:1, (c) 1:3, (d) 1:5, and (e) 1:7.

Table S1. Comparing the electrolyte resistance (R_s) and charge transfer resistance (R_{ct}) of the samples.

	Electrolyte resistance (R_s)	Charge transfer resistance (R_{ct})
CoSe₂@NC	1.265	1.664
ZnSe/CoSe₂@NC (1:1)	1.3	1.709
ZnSe/CoSe₂@NC (1:3)	1.414	1.874
ZnSe/CoSe₂@NC (1:5)	1.299	1.547
ZnSe/CoSe₂@NC (1:7)	1.441	1.890

Table S2. Comparing the concentration of Se in the electrolyte before and after 48 h stability test.

	Se concentration (ppm)
Fresh electrolyte (1 M KOH)	0
Spent electrolyte (after 48 h at 100 mA cm⁻²)	4.558