Highly Active Pd-Doped $ZnCo_2Se_4$ Spinel Nano-electrocatalysts For Synergistic Hydrogen Evolution and Methanol/Urea-Oxidation–assisted Water Splitting Validated by DFT

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2.3. Electrochemical Measurements

Electrochemical measurements were performed in a standard three-electrode configuration using 1 M KOH as the alkaline electrolyte (pH 13.6). An Ag/AgCl electrode containing saturated 3 M KCl served as the reference electrode, a platinum wire was employed as the counter electrode, and the catalyst-coated nickel foam acted as the working electrode. The in situ–prepared catalyst is denoted as $ZnPd_xCo_{2-x}Se_4(x \leq 0.08)@NF$. All electrochemical experiments were conducted at room temperature (~25 °C) using a Metrohm Autolab PGSTAT302N workstation.

Hydrogen evolution activity was evaluated by linear sweep voltammetry in 1 M KOH over a potential window from 0.00 to −0.06 V versus the reversible hydrogen electrode (RHE) at a scan rate of 10 mV/s. The open-circuit potential was first recorded to define the operational potential range for cyclic voltammetry, with the optimal alignment observed for the composition with x = 0.06. Cyclic voltammograms were collected within the non-faradaic region between −0.015 and −0.026 V at scan rates ranging from 40 to 200 mV/s.

The electrochemically active surface area of each electrode was estimated from the double-layer capacitance values extracted from the CV curves, assuming a specific capacitance of 40 μF/cm² in 1 M KOH. Electrochemical impedance spectroscopy was employed to investigate interfacial charge-transfer and mass-transport characteristics by analyzing the charge-transfer resistance (R_{ct}) at suitable applied potentials. Impedance spectrum was acquired across a frequency range of 0.01 Hz to 100 kHz. Tafel slopes were calculated from the polarization data to identify the dominant hydrogen evolution pathway, including Volmer, Volmer–Tafel, or Volmer–Heyrovsky mechanisms. Long-term stability of the optimal catalyst composition (x = 0.06) was evaluated using chronopotentiometric measurements.

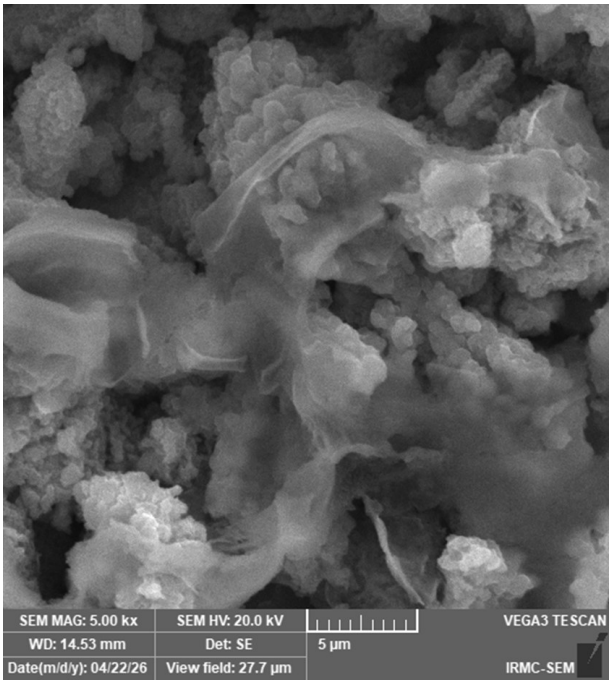

Figure S1. SEM Image of $ZnPd_xCo_{2-x}Se_4@NF$ $(x = 0.06)$ nanoelectrocatalysts states after the stability tests.

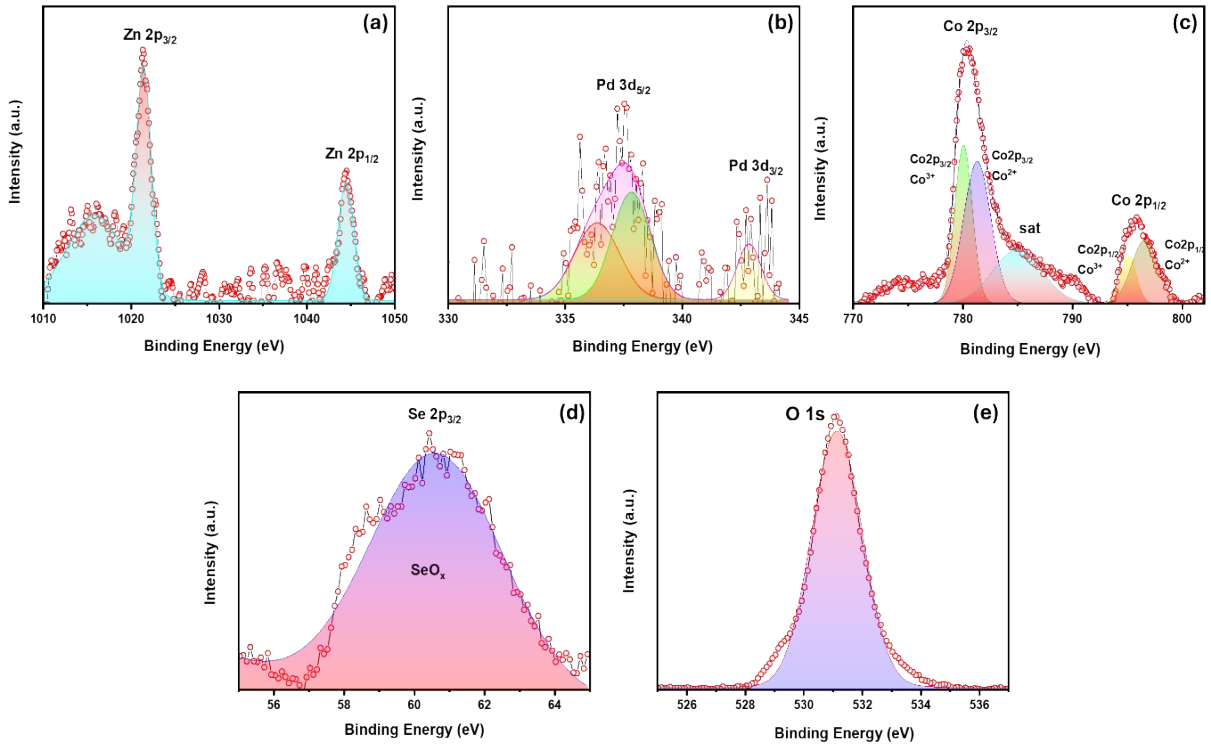

Figure S2. XPS high-resolution spectra of $ZnPd_xCo_{2-x}Se_4@NF$ $(x = 0.06)$ nanoelectrocatalysts. **(a)** Zn 2p, **(b)** Pd 3d, **(c)** Co 2p, **(d)** Se 3d, and **(e)** O 1s states after the stability tests.

Table S1. Comparison of HER performance with reported catalysts.

Electrocatalyst	HER Overpotential at 10 mA/cm^2	Electrolyte	Reference
$ReSe_2$/NiSe	111 mV	Alkaline media of pH~14	[1]
Ni_xSe_y	225 mV	1M KOH	[2]
$Fe_{0.2}Ni_{0.8}Se$	124 mV	1M KOH	[2]
$CoSe_2$/$MoSe_2$	90 mV	1M KOH	[3]
$NiSe_2$	316 mV	Alkaline media	[4]
$ZnPd_{0.06}Co_{1.94}O_4$@NF	**~64 mV**	**1M KOH**	**This work**

References

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