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Electronic Supplementary Material

Dual metal selenides CoSe/$MoSe_2$ heterojunction enwrapped in single-atomic-Co doped carbon for electrocatalytic water splitting

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Experimental

(1) Synthesis of Co_1Mo_2Se/Co–N–C

0.040 g (0.17 mmol) of $CoCl_2·6H_2O$, 0.058 g (0.047 mmol) of $(NH_4)_6Mo_7O_{24}$, and the g-C_3N_4@FCC slurry precursor were dissolved in 100 mL of ethanol and sonicated for 30 min until a homogeneous mixture was obtained. This solution was designated as P1 (with a molar ratio of *n*(Co)/*n*(Mo) at 1:2). In a separate vessel, 0.238 g (1 mmol) of $CoCl_2·6H_2O$ and 0.36 g (2 mmol) of 1,10-phenanthroline were dissolved in 100 mL of a mixed solvent (ethanol:water = 9:1) and stirred for 20 min to allow the coordination reaction to proceed, forming an orange-yellow transparent solution designated as P2. P1 and P2 solutions were then combined and stirred continuously for 6 h. The solvent was removed by rotary evaporation, and the resulting solid was ground into fine powder and thoroughly mixed with an excess of selenium powder. The mixture was placed in a tube furnace and heated under an argon atmosphere at a rate of 5 °C/min to 800 °C, maintained at this temperature for 2 h, and finally allowed to cool naturally to room temperature, yielding Co_1Mo_2Se/Co–N–C.

For samples with different molar ratios of *n*(Co)/*n*(Mo)Co/Mo in precursors, the P2 solution and all other synthesis conditions were kept the same, while molar ratios of *n*(Co)/*n*(Mo) in P1 were adjusted to 1:0, 1:1, and 1:3. The resulting samples were designated as CoSe/Co–N–C, Co_1Mo_1Se/Co–N–C, and Co_1Mo_3Se/Co–N–C, respectively.

(2) Synthesis of Co_1Mo_2Se/N–C

The control material Co_1Mo_2Se/N–C was synthesized using the same procedure by replacing 1,10-phenanthroline with triphenylmethane (0.488 g, 2 mmol) in P2 to suppress the formation of single atom sites.

(3) Materials characterization

Sample morphologies were studied on a scanning electron microscope (Hitachi SU8010). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) were performed on a Tecnai G2 F20. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance with the Cu Ka radiation. Raman spectra were collected using a Raman microscope (532 nm, Horiba-Jobin Yvon). X-ray photoelectron spectroscopy (XPS) was performed with the Ka radiation (Thermo Fisher). N_2 adsorption isotherms were recorded using a Micromeritics ASAP 2020.

(4) Electrochemical measurements

The electrochemical performance was evaluated with a standard three electrode system on an electrochemical workstation (CHI 760E). **Working electrode:** A mixture of 10 mg of powder samples, 200 mL of water, 360 mL of ethanol, and 40 mL of Nafion were ultrasonicated for 1 h, then 30 mL of dispersion was dropwise added onto a piece of carbon cloth (1 cm × 0.5 cm) and dried at 60 °C for 1 h. **Counter electrode:** graphite rod. **Reference electrode:** Hg/HgO electrode.

Linear sweep voltammetry (LSV) was performed for the HER from 0.3 to −0.5 V *vs*. the reversible hydrogen electrode (RHE). Cyclic voltammograms were collected between 0.425 and 0.625 V *vs*. RHE, and the scan rate varied from 50 to 500 $mV \cdot s^{-1}$. Electrochemical impedance spectroscopy (EIS) was performed at a constant bias of −0.15 V *vs*. RHE within the range of 10^{-1}–10^{5} Hz. The stability of prepared catalysts was evaluated by chronopotentiometry tests at corresponding potentials to drive an initial current density of 10 $mA \cdot cm^{-2}$.

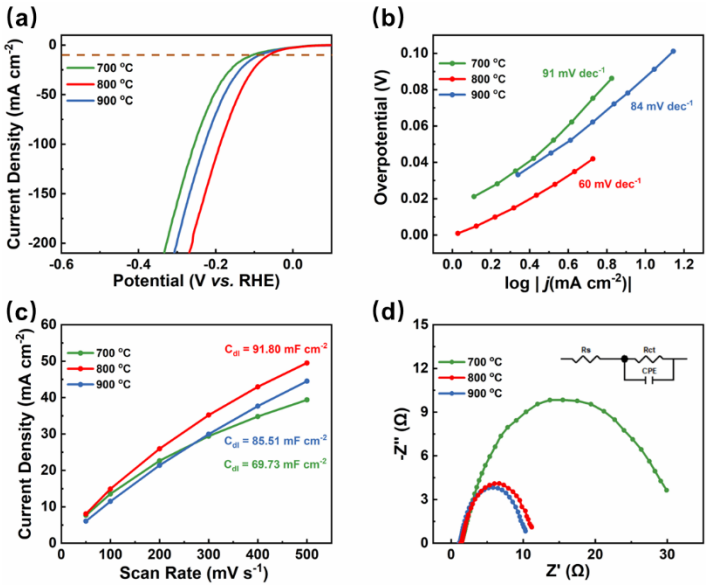

Fig. S1 HER performances for the sample in 1.0 $mol \cdot L^{-1}$ KOH at different temperatures: **(a)** LSV polarization curves; **(b)** Tafel plots; **(c)** current density–scan rate curves revealing C_{dl} values; **(d)** Nyquist plots.

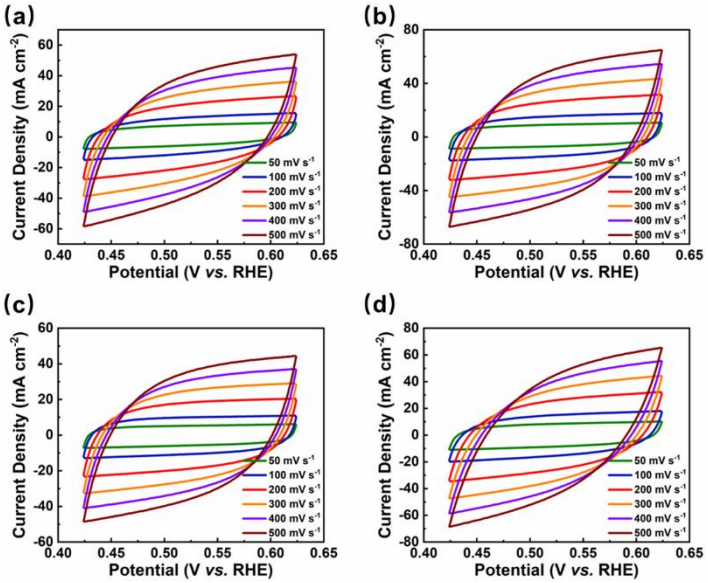

Fig. S2 CV spectra of **(a)** Co_1Mo_1Se/Co–N–C, **(b)** Co_1Mo_2Se/Co–N–C, **(c)** Co_1Mo_3Se/Co–N–C, and **(d)** CoSe/Co–N–C with various scan rates in 1.0 $mol \cdot L^{-1}$ KOH.

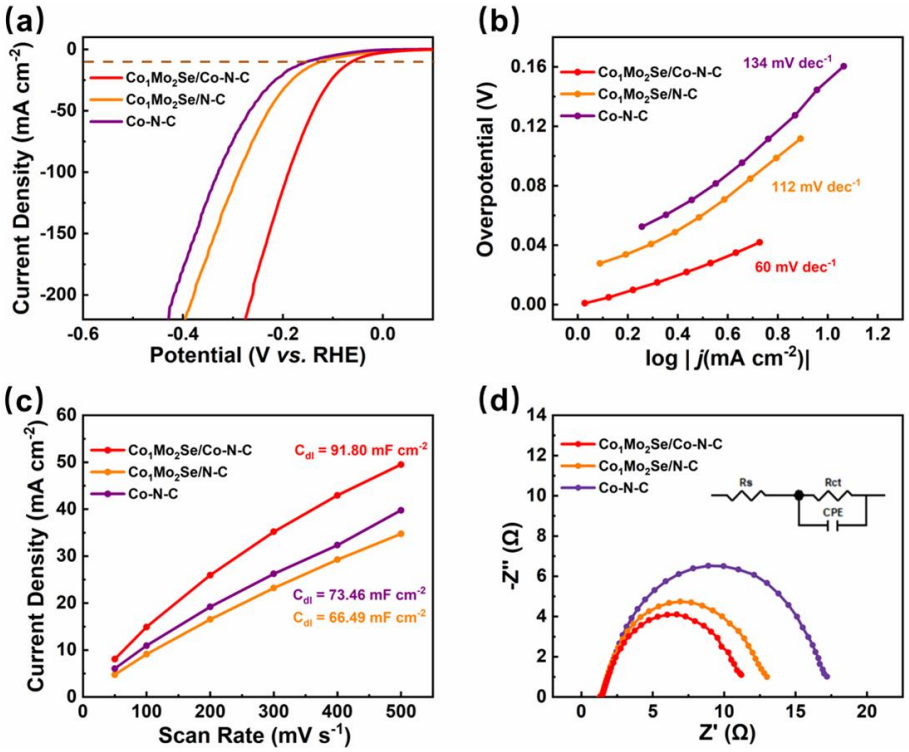

Fig. S3 HER activities for samples in 1.0 mol·L^{-1} KOH: **(a)** LSV polarization curves, **(b)** Tafel plots; **(c)** current density–scan rate curves revealing C_{dl} values; **(d)** Nyquist plots.