

Ni-Co LDH/M-Mo-S (M = Co, Ni and Zn) heteronanostructures as advanced

water oxidation electrode materials

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Experimental section

Materials. Cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, zinc nitrate hexahydrate, ammonium fluoride, urea, sodium molybdate dihydrate, thioacetamide and hydrochloric acid were obtained from Sigma-Aldrich.

Synthesis. The Ni-Co LDH/M-Mo-S (M = Co, Ni and Zn) hierarchical heteronanostructures with tunable morphologies on Ni foam were synthesized in two steps.

Synthesis of 1D Ni-Co LDH nanowires on Ni foam.

Before the synthesis, NF (3 cm × 5 cm) was first pretreated with 3 mol/L hydrochloric acid, ethyl alcohol and DI water by ultrasonication for about 10 min, respectively. After that, metal precursors (cobalt(II) nitrate hexahydrate (1 mmol) and nickel nitrate hexahydrate (0.5 mmol), ammonium fluoride (1 mmol) and urea (2.5 mmol) were mixed with distilled water (50 mL) to form an aqueous solution in a beaker, and the contents were stirred for about 30 min. The uniformly mixed reaction contents were poured into a Teflon-lined stainless steel autoclave (100 mL), a piece of prepared Ni foam was dipped in it, and the reaction was performed at 120 °C for duration of 6 h.

Material characterization

The composition and purity of the resulting materials was researched by X-ray powder diffraction (XRD) using an X'Pert-Pro MPD diffractometer (Netherlands PANalytical) (Cu K α radiation). The morphologies of the samples were studied by Hitachi S-4800 microscope Scanning electron microscopy (SEM) images and high-resolution transmission electron microscopy (HRTEM; JEOL 2100F) with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy spectra (XPS) were recorded using a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

Electrochemical tests

Electrochemical measurements were performed by a computer-controlled electrochemistry work station (CHI 660E) at room temperature. In a three electrode system, the resulting material was used as the working electrode, a graphite rod was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The NF was clamped by an electrode holder in an electrocatalytic reaction. Unless otherwise stated, the potential obtained by the test was converted to reversible hydrogen electrode (RHE): Evs. NHE=Evs. Ag/AgCl+0.197 (1) Evs. RHE=Evs. NHE+0.059×pH (2). In this paper, 1M Potassium hydroxide (KOH) solution was used as the electrolyte solution. Long-term stability measurements were obtained by chronopotentiometry experiments at a constant current density of 10 mA/cm² without iR compensation. Tafel curves were derived from Linear sweep voltammetry by plotting potential V against log(J). Double-layer capacitance (C_{dl}) was obtained by measuring CV curves at different scanning speeds (50-250 mV/s) in the non-faraday region. Electrochemical active surface area (ECSA) was determined based on the double-layer capacitance (C_{dl}).

DFT calculation

In this study, the Cambridge Serial Total Energy Package module of Materials Studio was used for DFT calculation. The interactions of electrons were calculated by the generalized gradient approximation functions of Perdew-Burke-Emzerh (GGA-PBE). The (003) plane optimal structures of NiOOH and Mo-NiOOH were calculated by setting a cutoff energy of 450 eV and 3×3×1 k-points grid. The structures were also optimized for energy and force convergence choosing as 2.0×10^{-5} eV/atom and 0.05 eV/Å, respectively. The vacuum space was up to 0.002 Å to eliminate periodic interactions.

Table S1. The atomic percent of Ni-Co LDH/Ni-Mo-S

Element	Atomic %
O	56.83
S	17.08
Co	5.28
Ni	17.54
Mo	3.27
Total:	100.00

Table S2. The atomic percent of Ni-Co LDH/Co-Mo-S

Element	Atomic %
O	55.93
S	17.80
Co	15.46
Ni	6.53
Mo	4.28
Total:	100.00

Table S3. The atomic percent of Ni-Co LDH/Zn-Mo-S

Element	Atomic %
O	55.69
S	18.20
Co	5.53
Ni	6.45
Mo	4.57
Zn	9.56
Total:	100.00

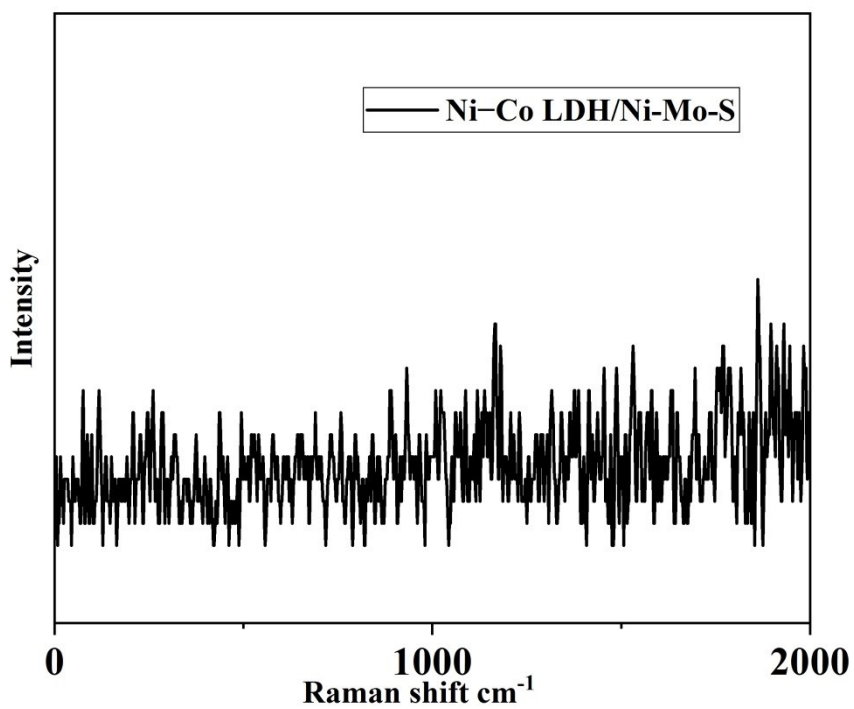


Fig. S1 Raman of the Ni-Co LDH/Co-Mo-S.

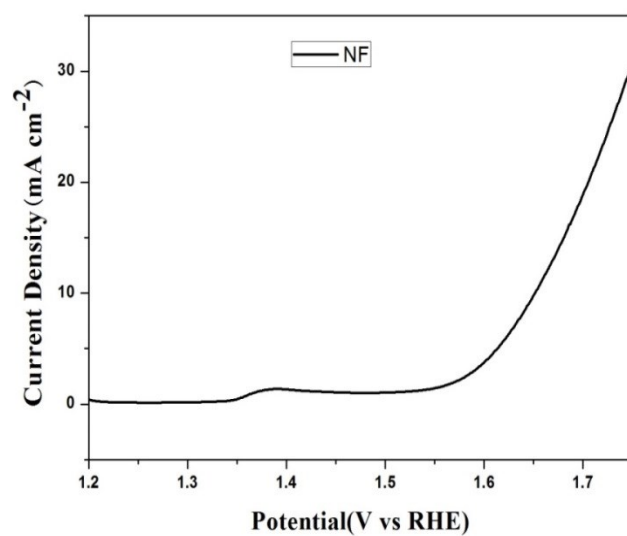


Fig. S2 Polarization curves of NF in 1.0 M KOH at a potential sweep rate of 5 mV s⁻¹.

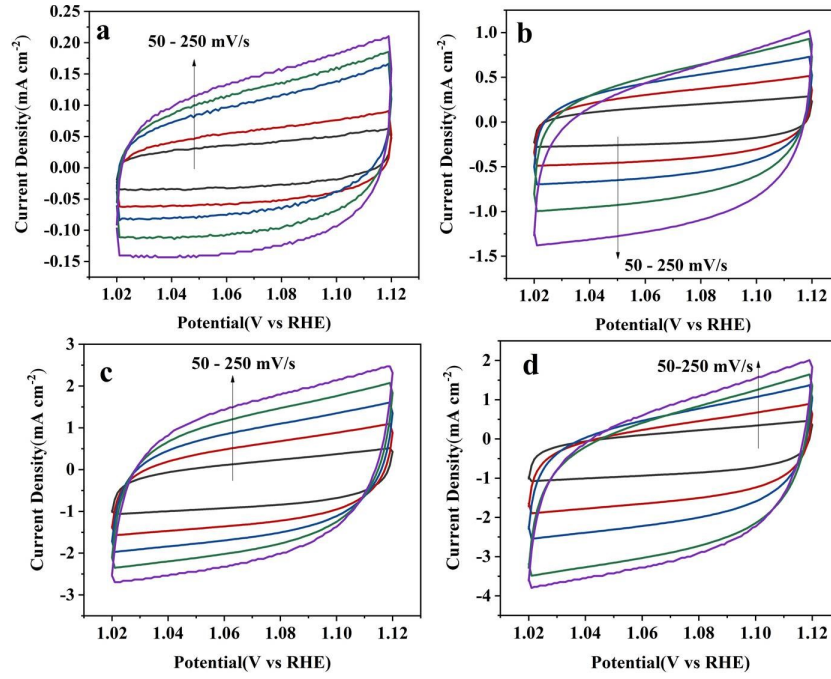


Fig.S3 CV curves with different scan rates in OER, (a) Ni-Co LDH, (b) Ni-Co LDH/Co-Mo-S (c) Ni-Co LDH/Ni-Mo-S and (d) Ni-Co LDH/Zn-Mo-S.

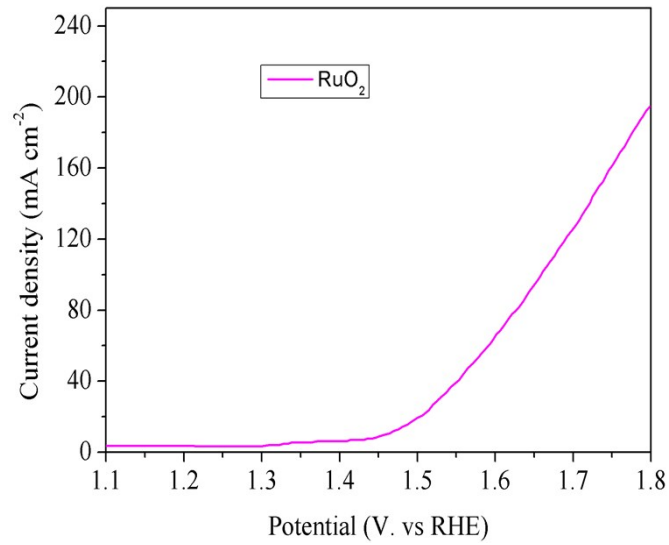


Fig. S4 Polarization curve of the RuO_2 for OER with a scan rate of 5 mV s^{-1} in 1 M KOH.

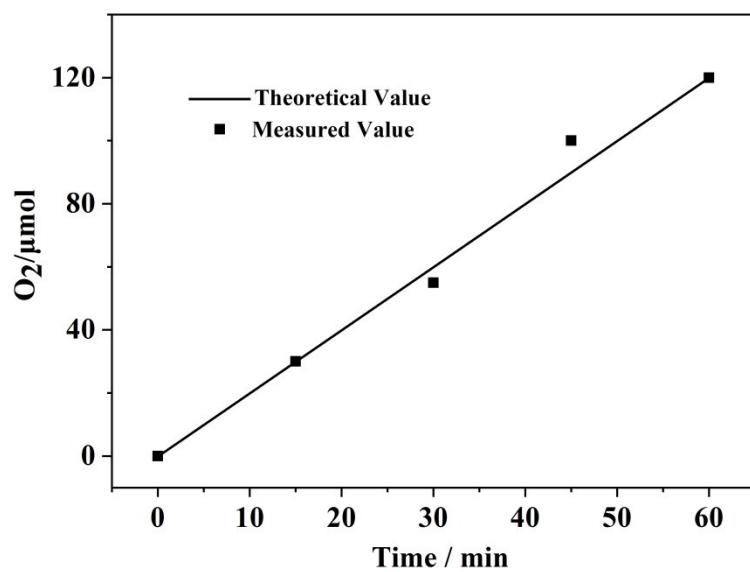


Fig. S5 Electrocatalytic efficiency of O₂ production over Ni-Co LDH/Ni-Mo-S measured for 60 min.

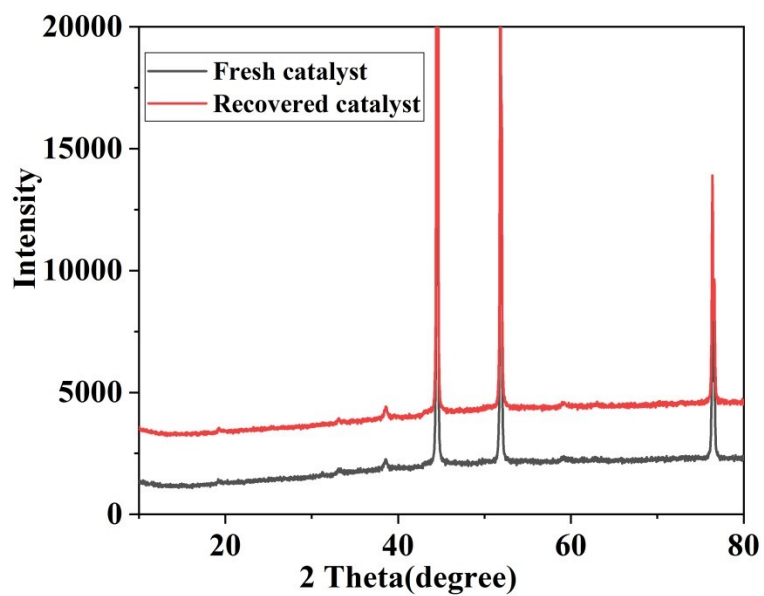


Fig. S6 XRD of the fresh and recovered Ni-Co LDH/Ni-Mo-S after reaction 15 h.

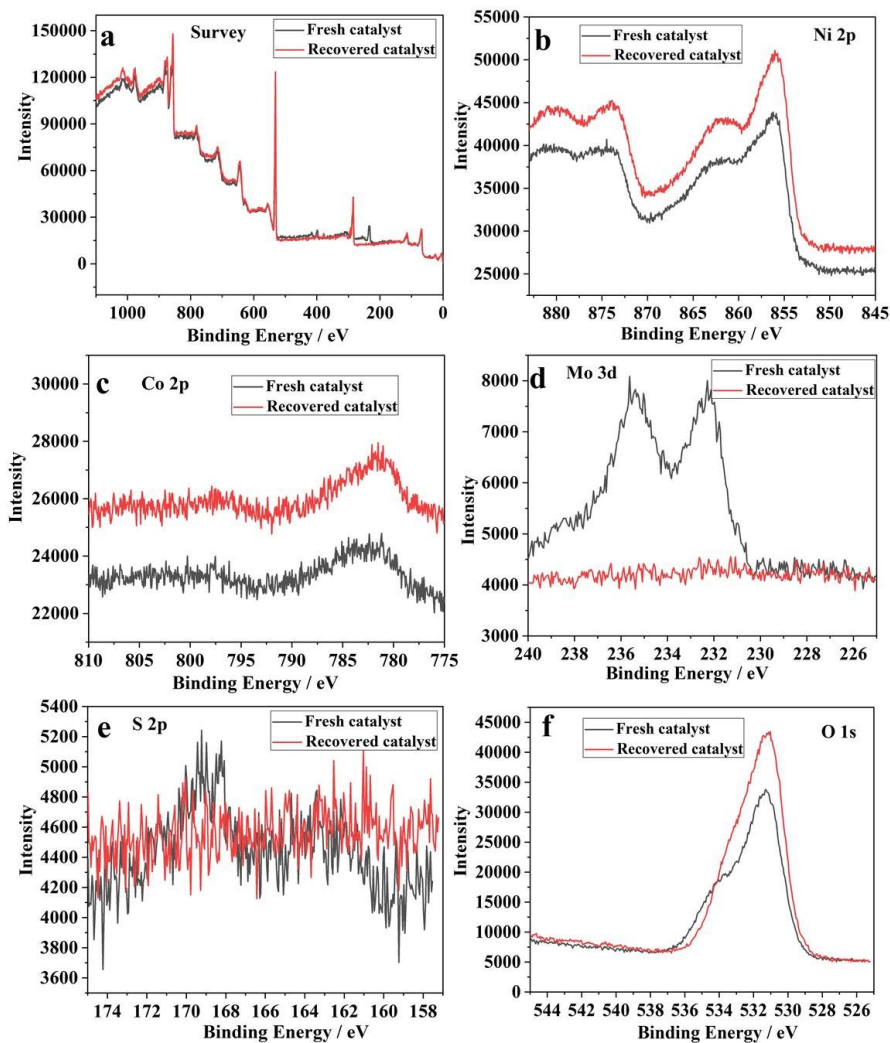


Fig. S7 XPS of the fresh and recovered Ni-Co LDH/Ni-Mo-S/NF after reaction 15 h (a) Survey, (b) Ni 2p, (c) Co 2p, (d) Mo 3d, (e) S 2p and (f) O1s.

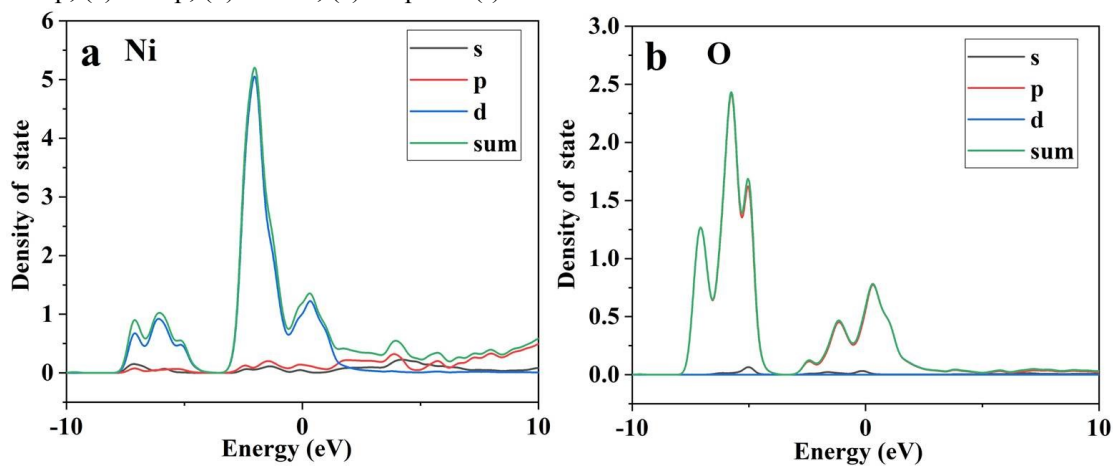


Fig. S8 Calculated density of states for Ni and O in NiOOH.

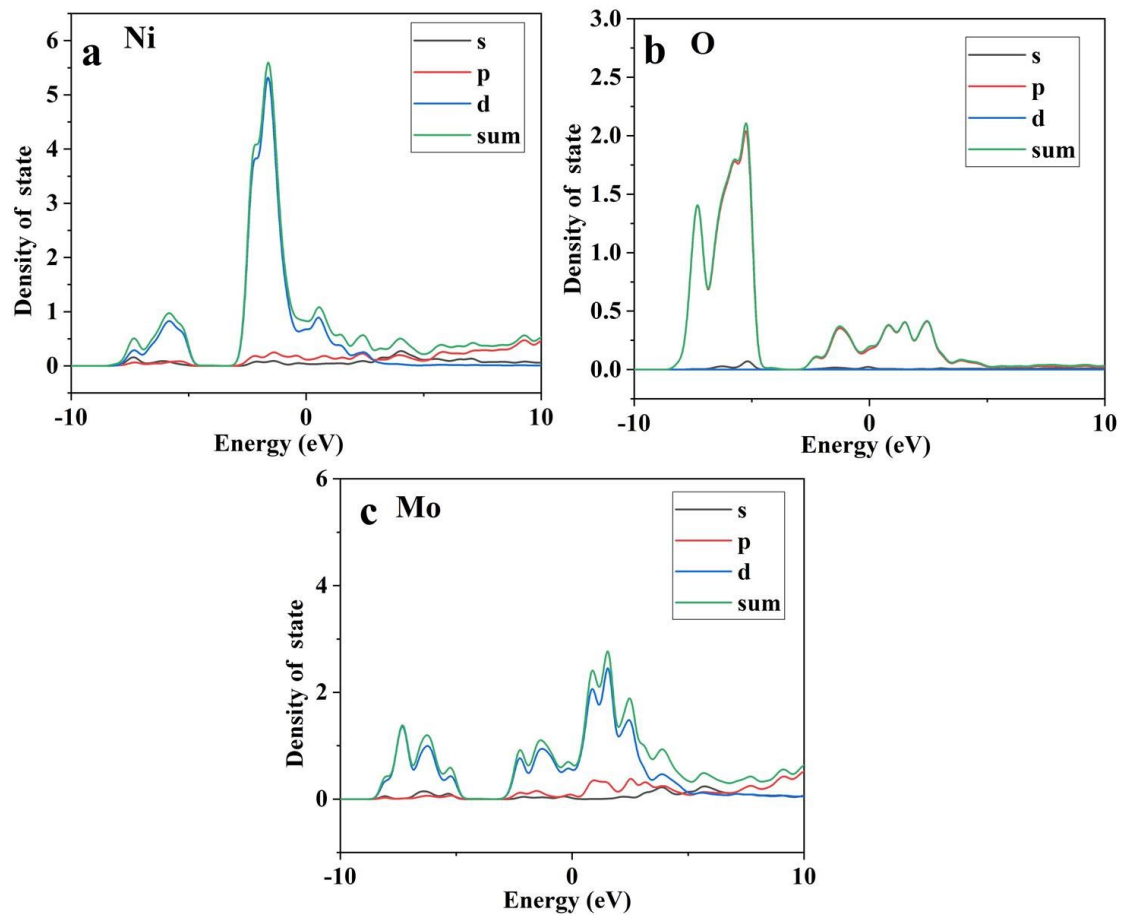


Fig. S9 Calculated density of states for Ni , O and Mo in Mo-NiOOH.