

Supplementary Information

Trinary NiFeMn Layered Double Hydroxides as High-efficient Oxygen Evolution Catalysts

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1. Experimental Section

Preparation of binary and trinary LDHs

The NiFeMn-LDHs were synthesized via a simple co-precipitation reaction at room temperature under O₂ atmosphere. Firstly, Ni(NO₃)₂·6H₂O, Mn(NO₃)₂ and Fe(NO₃)₃·9H₂O with different molar ratios were dissolved in 250 ml DI water to form a homogeneous solution. After oxygen bubbling for 30min, another aqueous solution (60 mL) containing NaOH (0.04 M) and Na₂CO₃ (0.015 M) was added quickly with vigorous stirring. The resulting suspension was aged at room temperature for another 12 h, and oxygen was bubbled throughout the entire addition period for the oxidation of Mn²⁺. Subsequently, the product was isolated by centrifugation, washed three times with water, and then dried in an oven under 80°C overnight. The NiFe-LDH and NiMn-LDH were synthesized as the reference materials, following the same procedure.

Materials characterizations

X-ray powder diffraction patterns were recorded on an X-ray diffraction (Rigaku D/max 2500) at a scan rate of 10 (°)/min in the 2θ range from 3 to 70°. The size and morphology of the samples were characterized using a TEM system (FEI Tecnai G2 20 S Twin). The surface roughness was studied using the atomic force microscopy (AFM) software (Digital Instruments, Version 6.12). Elemental analysis was performed using a Shimadzu ICP-7500 inductively coupled plasma emission spectrometer. XPS was carried out by using a model of ESCALAB 250. The measurement of sheet resistance was performed using four point probe method in sheet resistance measurement system (RTS-8). The UV-vis diffusion reflectance

spectra were measured by UV-2600 and the Zeta Potential was obtained by Malvern Zetasizer NanoZS90.

Electrochemical measurements

The OER activities of the materials were first studied with a three-electrode system in 1 M KOH aqueous solution using an electrochemical workstation (CHI 660D, chenghua, shanghai). A saturated calomel electrode (SCE) and a platinum plate were used as the reference and the counter electrodes, respectively. To prepare the working electrode, 5 mg of catalyst, 2 mg of carbon black and 50 μL Nafion solutions were dispersed in ethanol (1 mL) with the assistance of ultrasonication for at least 1 h to form a homogeneous catalyst ink. Afterwards, the catalysts were loaded on carbon fiber paper (CFP) to achieve a mass-loading of 0.2 mg cm^{-2} . The scan rates varied from 1 to 10 mV s^{-1} for OER polarization curves. The potentiostatic stability and galvanostatic stability were measured by applying a constant potential or current density for 15 h, respectively. To further investigate the practical application, the OER activity of the NiFeMn-LDH was measured in 1 M Na_2CO_3 electrolyte at room temperature and 70°C. The ORR test was studied with a three-electrode system in 0.1 M aqueous KOH solution using a PARSTAT 2273 instrument. 5 μL of the above catalyst ink was drop-casted onto a RDE with a diameter of 5 mm and left to dry in air, yielding a catalyst loading of ~ 0.12 mg cm^{-2} . Before the start of measurement, the electrolyte was bubbled with O_2 for at least 20min. A flow of O_2 was maintained over the electrolyte during the measurement. The scan rate was 5 mV s^{-1} for ORR polarization curves.

TOF calculation

The TOF values of the materials as OER catalysts were calculated by the following equation:

$$TOF = \frac{J \times A}{4 \times F \times m}$$

Where J is the current density at overpotential of 0.3 V in A cm^{-2} , A is the area of the rotating disk electrode, F is the faraday constant (a value of 96485 C/mol), m is the number of moles of the active materials that are deposited onto the rotating disk electrode.

Electronic structure calculations

The calculations were performed within the spin-polarized density functional theory (DFT). This approach was found necessary to reduce the delocalization error of pure DFT-PBE (Perdew-Burke-Ernzerhof) and improve the description of the electronic structure of NiFeMn-LDH. Therefore we adopt a DFT+U method with U values of 5.30, 3.90, and 6.45 eV for Fe, Mn, and Ni atoms, respectively. All calculations were performed by using a standard Monkhorst-Pack grid with $1 \times 1 \times 1$ sampling mesh for bulk calculations. The cutoff energy of 400 eV and the energy change convergence criterion was set to 1×10^{-4} eV between two successive iterations.

2. Figures

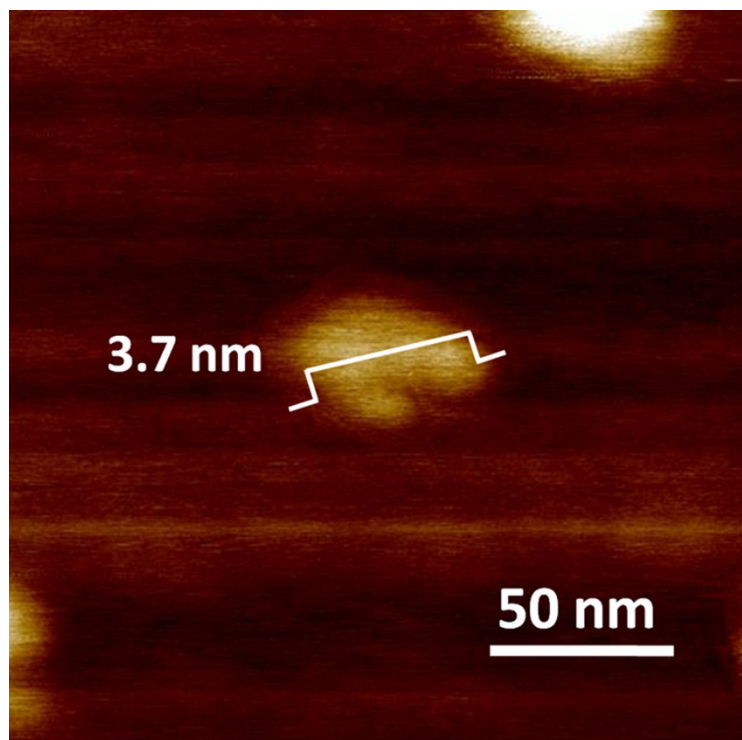


Figure S1. The AFM image of the NiFeMn-LDH, demonstrating the thin thickness.

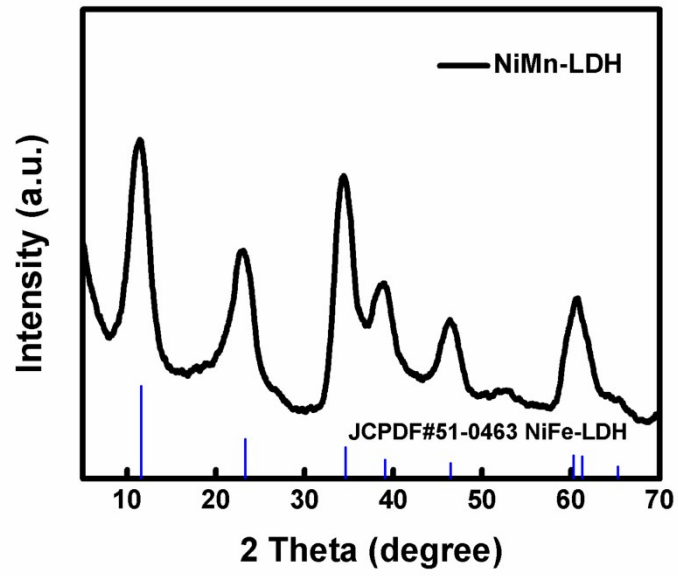


Figure S2. The XRD pattern of binary NiMn-LDH, which proved the layered structure.

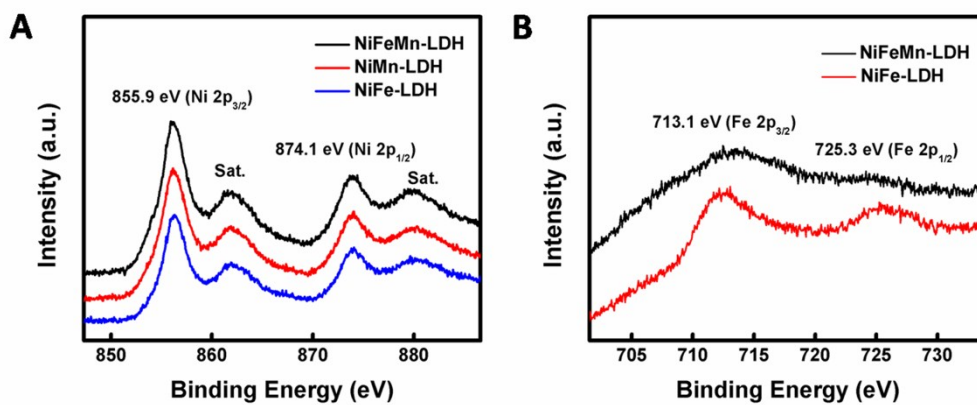


Figure S3. High-resolution XPS spectra of Ni and Fe in binary and trinary LDHs: (A), Ni 2p in NiFeMn-LDH (black line), NiMn-LDH (red line) and NiFe-LDH (blue line), respectively; (B), Fe 2p in NiFeMn-LDH (black line) and NiFe-LDH (red line), respectively.

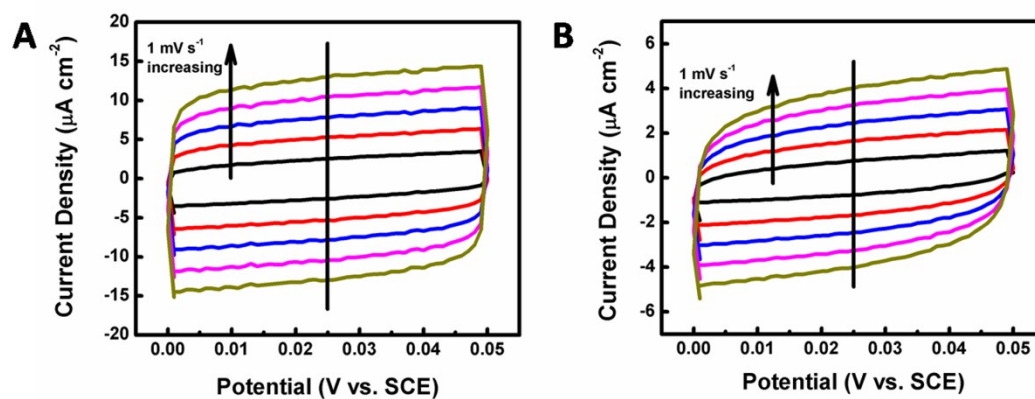


Figure S4. The electric double layer capacitance (C_{dl}) measurements of NiFeMn-LDH (A) and NiFe-LDH (B) by measuring the electric double layer current density at the non-Faradic region (0-0.05 V vs. SCE) with various scan rates.

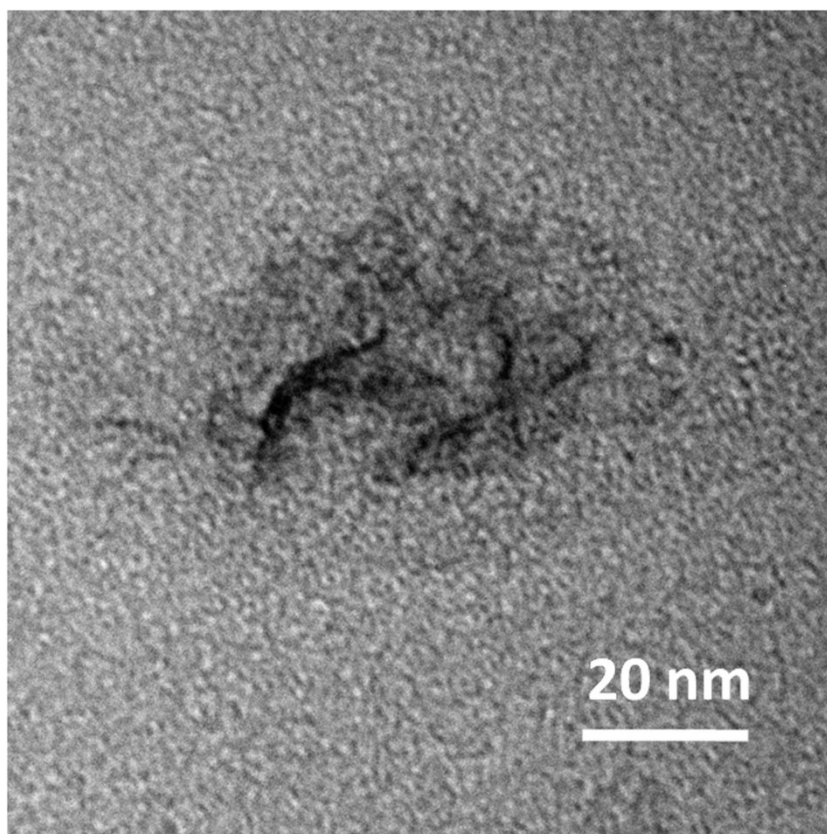


Figure S5. TEM image of the prepared NiFe-LDH nanoplate. The NiFe-LDH shows similar morphology to the NiFeMn-LDH.

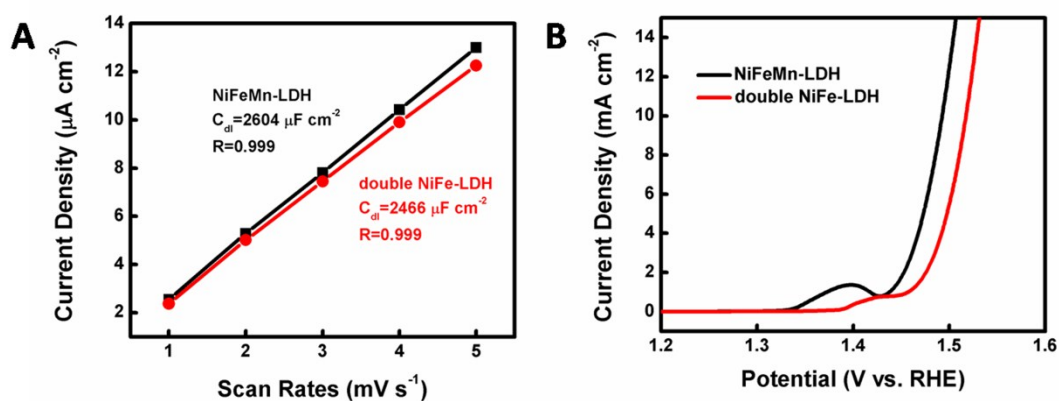


Figure S6. (A), C_{dl} comparison of NiFeMn-LDH electrode (black line) and NiFe-LDH electrode with double mass-loading (red line); (B), polarization curves of NiFeMn-LDH and double mass-loading NiFe-LDH electrodes. The results indicate that although the C_{dl} of NiFeMn-LDH and NiFe-LDH with double mass-loading are similar, the NiFeMn-LDH is still more active for OER, demonstrating the higher OER activity.

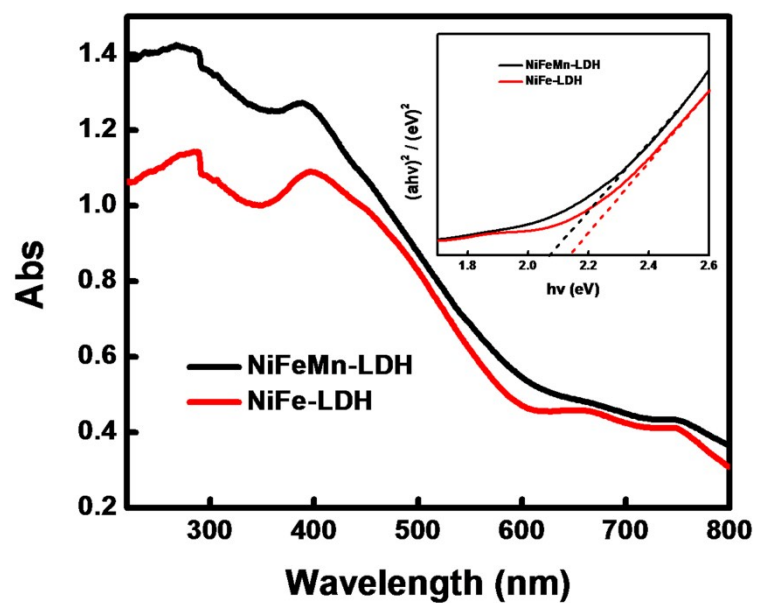


Figure S7. UV-vis diffuse reflectance spectra of NiFeMn-LDH (black line) and NiFe-LDH (red line). The inset shows their corresponding plots of $(ah\nu)^2$ vs $h\nu$ for determining the indirect band gap.

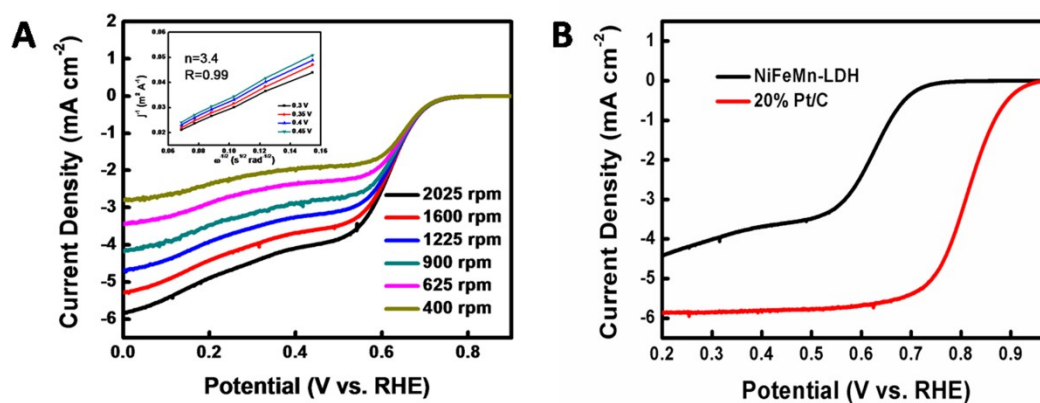


Figure S8. Electrochemical ORR performance of NiFeMn-LDH: (A), ORR polarization curves of NiFeMn-LDH at different rotation rates, the inset in the corresponding K-L plots at different potentials, indicating the reasonable selectivity of the NiFeMn-LDH catalyst; (B), performance comparison of NiFeMn-LDH and 20% Pt/C benchmark with a rotating rate of 1600 rpm at a scan rate of 5 mV s^{-1} .

Table S1. The ICPAES results of the as-prepared NiFeMn-LDH, NiFe-LDH and NiMn-LDH.

| Sample | starting metal ratios | Ni | Fe | Mn | metal ratios in product |
|------------|-----------------------|-------|-------|-------|-------------------------|
| NiFeMn-LDH | 3:1:0.5 | 34.73 | 11.91 | 6.612 | 2.92:1:0.55 |
| NiFe-LDH | 3:1 | 39.72 | 13.55 | NA | 2.93:1 |
| NiMn-LDH | 3:1 | 44.04 | NA | 13.69 | 3.21:1 |

Table S2. The TOF value of the NiFeMn-LDH, NiFe-LDH, NiMn-LDH and 20% Ir/C calculated at η of 300 mV.

| Sample | NiFeMn-LDH | NiFe-LDH | NiMn-LDH | 20% Ir/C |
|------------------------|------------|----------|----------|----------|
| TOF (s ⁻¹) | 0.03837 | 0.00416 | 0.00024 | 0.02121 |

Table S3. Comparison of NiFeMn-LDH with the previous reported LDHs and high-performance OER catalysts.

| Sample | Electrolyte | Overpotential at 10 mA cm ⁻² (mV) | Ref |
|-----------------------------------|--------------------------|--|-----------|
| NiFeMn-LDH | 1 M KOH | 262 | This work |
| CoMn-LDH | 1 M KOH | 324 | 9 |
| NiFe-LDH/CNT | 1 M KOH | ~240 | 14 |
| ZnCo-LDH | 0.1 M KOH | ~480 | 29 |
| Double perovskite | 0.1 M KOH | ~290 | 32 |
| Co(PO ₃) ₂ | 0.1 M phosphate (pH≈6.4) | ~440 | 34 |
| Amorphous metal oxides | 0.1 M KOH | ~260 (5 mA cm ⁻²) | 36 |
| NiCo binary oxide | 1 M NaOH | 325 | 37 |