

Supporting Information

Tailoring the electronic environment of MoSe₂ via cation metal doping for enhanced alkaline hydrogen evolution reaction

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Experimental Section

Materials and Chemicals

Nickle nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 85%) were purchased from Sinopharm Chemical Reagent Co., Ltd. China. Iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), and selenium powder (Se, 99.9%) were supplied by Sigma-Aldrich. All chemical reagents were used as received without further purification.

Synthesis of NiFe@MoSe₂ nanosheets

In a typical synthesis of NiFe@MoSe₂ nanosheets, 4 mmol of Se was added to 10 ml of $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ in a separate flask and stirred continuously for about 1.5 h. Then, 2 mmol of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.02 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.02 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dispersed in 50 ml H_2O with continuous stirring to form a clear solution. After stirring, the Se solution was slowly added to the Na_2MoO_4 solution and the mixed solution was an orange-red color. Then, the reaction solutions were transferred to a Teflon-lined stainless autoclave and kept at 220 °C for 20 h for hydrothermal treatment. After natural cooling down to room temperature, the as-synthesized black precipitates were collected by centrifugation at 10000 rpm for 5 min and washed several times with D.I water, then dried in a freeze dryer for 24 h. Finally, the NiFe@MoSe₂ nanosheets were obtained. For comparison, NiCo@MoSe₂ and FeCo@MoSe₂ electrocatalysts were also synthesized by the same procedure as the preparation of NiFe@MoSe₂ nanosheets, except that the metal species were changed with $\text{Ni}^{2+}/\text{Co}^{2+}$, and $\text{Fe}^{3+}/\text{Co}^{2+}$,

respectively. The preparation of pure MoSe₂ nanosheets was the same as that of NiFe@MoSe₂ except that Ni(NO₃)₂·6H₂O and Fe(NO₃)₂·9H₂O were removed.

Materials characterization

The crystal structure was analyzed by X-ray diffraction (XRD, Bruker D8 Advance with Cu K α , $\lambda = 1.5406 \text{ \AA}$). The microstructure and morphology of the samples images were observed on a field emission scanning electron microscopy (FE-SEM) from JEOL (JSM-7800F) and a transmission electron microscopy (TEM, JEM-2100F, JEOL), respectively. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi) was employed to identify the chemical composition and electronic states of the samples, and the binding energy was calibrated against the C 1s peak energy of 284.6 eV. Raman spectra were recorded by a LaBRAM HR800 (Jobin Yvon Horiba) Raman spectrometer ($\lambda = 532 \text{ nm}$).

Electrochemical measurements

All the electrochemical measurements were performed by a CHI 760E electrochemical workstation (CHI Instruments Inc.) in N₂-purged 1.0 M KOH aqueous solution. Ag/AgCl electrode and carbon rod were used as the reference electrode and the counter electrode, respectively. The catalyst ink was prepared as follows: the electrocatalyst powders (8 mg) and 2 mg of acetylene black were dispersed into 50 μL of Nafion, 600 μL of deionized water and 350 μL of ethanol and ultrasonicated for 30 min to generate a homogeneous slurry. Then 10 μL of the resulting suspension was sprayed onto the surface of the glass carbon and dried at room temperature as the working electrode. The linear sweep voltammograms (LSVs) were measured from high potential to low

potential at a scan rate of 5 mV s⁻¹. The turnover frequency (TOF) was evaluated by the following standard equation: $TOF = J * A / 2 * F * n$. Here, J is the current density (mA cm⁻²) at an overpotential of 300 mV; A is the area of electrode; n is the moles of active metal atoms; F is the Faraday constant (96485 C mol⁻¹). The corresponding Tafel slope-
reflected reaction kinetics was calculated by the formula: $\eta = a + b \log j$ where η , b , and j represent potential, Tafel slope, and current density, respectively. By plotting graph between the potential and log (current density), Tafel slopes were obtained from the polarization curves. Electrochemical impedance spectroscopy (EIS) was tested in the frequency range of 100,000 ~0.01 Hz at the open circuit potential. The cyclic voltammetry (CV) tests were conducted in a potential range of 0.12-0.22 V (vs RHE) at a scan rate range of 20-100 mV s⁻¹ to receive the electrochemical active surface area (ECSA). The C_{dl} calculation ($C_{dl} = (j_a - j_c)/(2*v) = (j_a + |j_c|)/(2*v) = \Delta j/(2*v)$), where j_a and j_c are the anodic and cathodic voltammetric current density, respectively, and v is the scan rate. All potentials were presented with respect to the reversible hydrogen electrode (RHE) in this work: $E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + 0.059 \times \text{pH}$.

Figures and Table

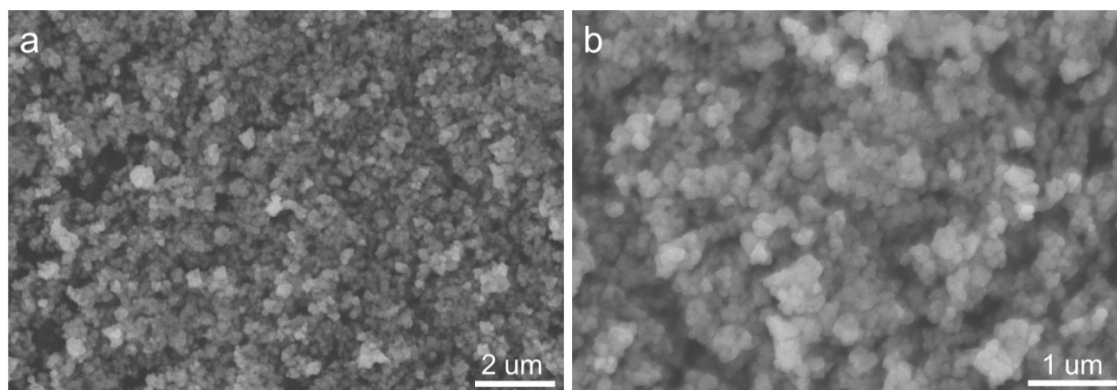


Figure S1. SEM image of the resultant MoSe₂.

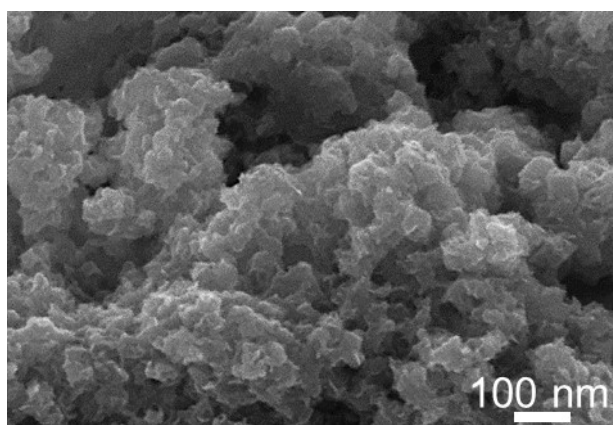


Figure S2. High-resolution SEM image of NiFe@MoSe₂.

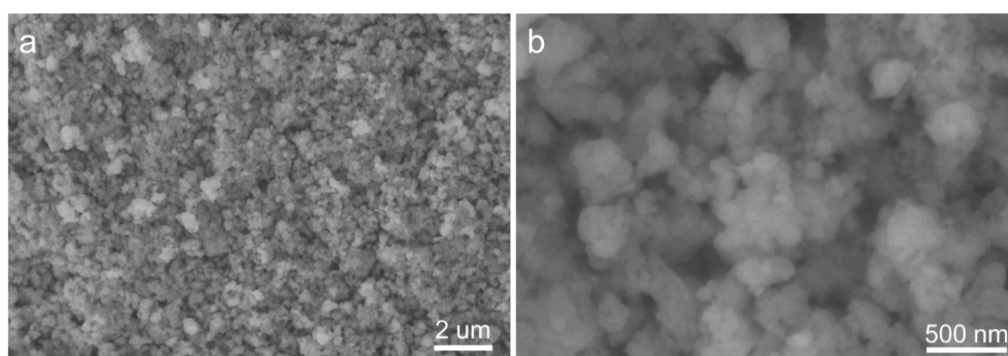


Figure S3. SEM image of the FeCo@MoSe₂ species.

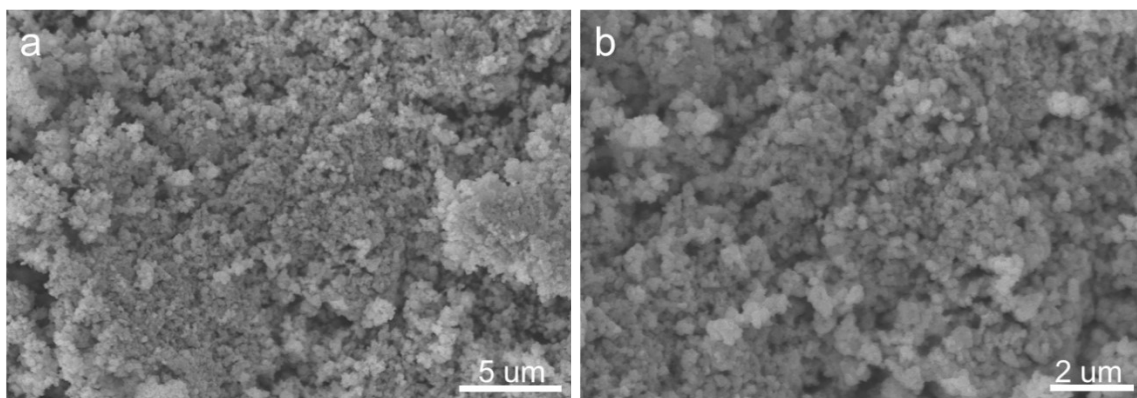


Figure S4. SEM images of the formed NiCo@MoSe₂.

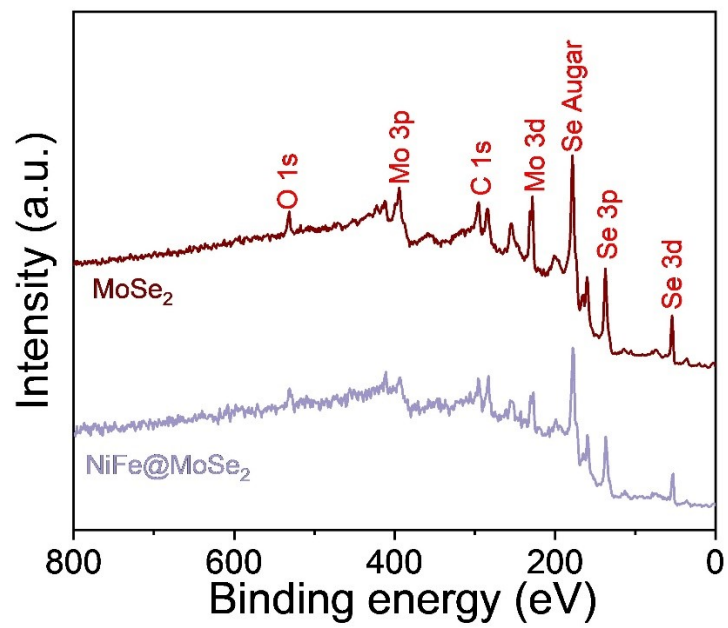


Figure S5. XPS survey spectrum of NiFe@MoSe₂.

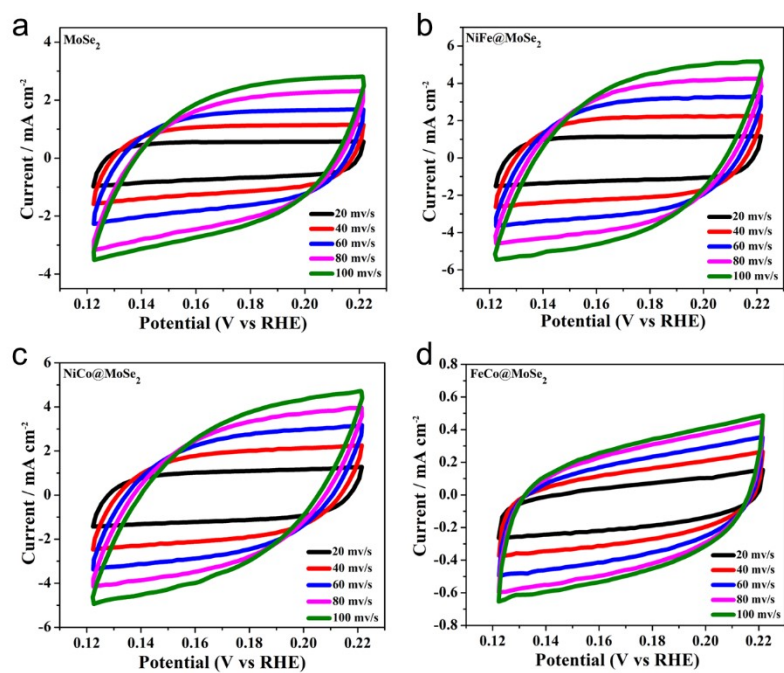


Figure S6. CV curves of the synthesized catalysts in the non-Faradaic region (0.12 – 0.22 V vs. RHE) obtained at different scanning rates. (a) MoSe₂, (b) NiFe@MoSe₂, (c) NiCo@MoSe₂, and (d) FeCo@MoSe₂.

Table S1. HER performance comparison between the as-synthesized NiFe@MoSe₂ and representative nonprecious catalysts reported previously.

Catalyst	Overpotential / mV (10 mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	Ref.
NiFe@MoSe ₂	146	79	This work
Co _{0.5} Mo _{0.5} S	181	N/A	<i>ACS Appl. Energy Mater.</i> 2022, 5, 10396–10401.
Ni-Co ₃ S ₄	262	81.2	<i>ACS Appl. Nano Mater.</i> 2022, 5, 7, 9901–9909.
Co ₉ S ₈ /Cu ₂ S/CF	165	80.2	<i>ACS Appl. Interface Mater.</i> 2021, 13, 9865–9874.
MnCo-CH@NiFe-OH	177	97.8	<i>Appl. Catal. B: Environ.</i> 2021, 292, 120160.
MoO ₂ NPs@N-C NSs/NF	160	92.9	<i>Energy Fuels</i> 2020, 34, 9050–9057.
Co _{1.11} Te ₂ /C	178	77.3	<i>Appl. Catal. B: Environ.</i> 2019, 244, 568-575.
CoPS@NPS-C	191	106	<i>J. Mater. Chem. A</i> 2018, 6:10433–10440.
Cu _{0.3} Co _{2.7} P/NC	220	122	<i>Adv. Energy Mater.</i> 2017, 7, 1601555.
NiFeOF	253	96	<i>ACS Catal.</i> 2017, 7, 8406-8412.