

Supporting Information

MoO₂/Ni_{0.2}Mo_{0.8}N Nanorods on Nickel Foam as High Performance Electrocatalyst for Efficient Water Oxidation

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Experimental section

Synthesis of MONMN nanorods on NF

Nickel foam of 4 cm * 6 cm purchased from Changsha Liyuan New Material Co., Ltd was first washed with deionized water and ethanol. 710 mg of H₂₄Mo₇N₆O₂₄·4H₂O and 870 mg of Ni(NO₃)·6H₂O were then dissolved in 100 ml of

deionized water and ultrasonically stirred in an ultrasonication apparatus for 15 minutes. The control ratio between Ni and Mo is ratio 1:1. The chemicals were purchased from Guangzhou Chemical Reagent Factory and were directly used without further purifying them. The mixture and the clean nickel foam were then poured into Teflon lined autoclave with 100 mL capacity. After reaction in an electric oven at 120 °C for 240 minutes, the samples were collected after cooling, washed with deionized water and dried in an electric oven of 60 °C for 12 hours. The obtained precursor was annealed in ammonia gas at 500 °C for 120 min using a scan rate of 200 sccm and rising temperature at 5 °C min⁻¹. After the furnace was naturally cooled to room temperature, the MoO₂/Ni_{0.2}Mo_{0.8}N electrocatalyst was obtained.

Sample characterization

The morphology of the MoO₂/Ni_{0.2}Mo_{0.8}N was characterized using a Technai G2 F30 and Quanta 400F for the transmission emission microscope (TEM) and scanning electron microscope (SEM) analyses, respectively. The crystal structure of the MoO₂/Ni_{0.2}Mo_{0.8}N sample were performed using the powdered form of MoO₂/Ni_{0.2}Mo_{0.8}N on a Rigaku SmartLab X at 5 °C min⁻¹ (CuK_α, λ = 1.5406 Å).

Electrochemical Measurements

The electrocatalytic tests were carried using a three-electrode system with 1.0 M KOH electrolyte on CHI 760E electrochemical work station. The MONMN catalyst is the working electrode. Both graphite rod and Ag/AgCl were the counter and reference electrodes, respectively. After subjecting the system to 100 cycle's

cyclic voltammetry (CV) cycles at 100 mV s^{-1} from 0.0 V to -1.0 vs. RHE to stabilize the curves, linear sweep voltammetry (LSV) curves were then measured at a scan rate of 1.0 mV s^{-1} . The E_{RHE} overpotential values were calculated based on $E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.059 \times \text{pH}$. Electrochemical impedance spectroscopy (EIS) was carried out between the frequency ranges of 10.0 mHz to 1.0 MHz with an AC excitation amplitude of 5 mV. The electrochemical surface area was determined by CV curves at varying scan rates from 1.0 to 8.0 mV s^{-1} . The chronoamperometry stability test was performed at different current densities of 10, 20 and 30 mA cm^{-2} for 24 hours.

The preparation of the IrO_2 coated on nickel foam ($\text{IrO}_2\text{-NF}$) was achieved by weighing 2.0 mg of commercial IrO_2 powder and ultrasonically dispersed in a 1.0 mL deionized water and 30.0 μL of 0.1% Nafion mixture. The dispersion was casted onto the nickel foam to obtain the $\text{IrO}_2\text{-NF}$ catalyst.

C_{dl} Calculation

The C_{dl} was calculated according to the following equation: $C_{\text{dl}} = |j_a - j_c|/2u$, where j_a and j_c are charging and discharging current densities and u is the scan rate.¹ The potential range of the measurements is from 0.26 to 0.34 V vs. SCE in a non-Faradaic region for the OER and the scan rates were from 1.0 to 8.0 mV s^{-1} . The difference of charging and discharging current densities at 0.01 V vs. RHE was used for calculation.

Theoretical calculations

All the calculations were performed with the ABINIT software package. Total energy calculations were performed to study the properties of MoO_2 , NiMoO_4

and $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}$ structures using the periodic density functional theory (DFT) and density functional perturbation theory (DFPT) which was implemented in ABINIT code. ABINIT stands for “Open- Source Package for Research in Electronic Structure, Simulation, and Optimization”.² *Exchange-correlation energy* was treated with the generalized gradient approximation (GGA) using the Perdew, Burke and Enzerholf (PBE) parameterization.³ In all calculations the convergence parameters were 10^{-6} eV for the energy, 0.01 eV \AA^{-1} for the forces and an energy cut-off of 500 eV. A Gaussian smearing of 0.05 eV was applied. The electron-ion interaction was modelled using the pseudo-potential generated by Van Setten, M. J., et al.,⁴ which gives very transferable norm conservation pseudo-potentials. Integrations in the reciprocal lattice were made using the k-points generation method of Monkhorst and Pack.⁵ Population analysis has been performed on the optimized structures in the ground state. Models of MoO_2 (JCPDS number #32-0671) and $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}$ (JCPDS number #29-0931) were used to simulate the samples. The models and how they have been built is outlined in the Figure S4-S6.

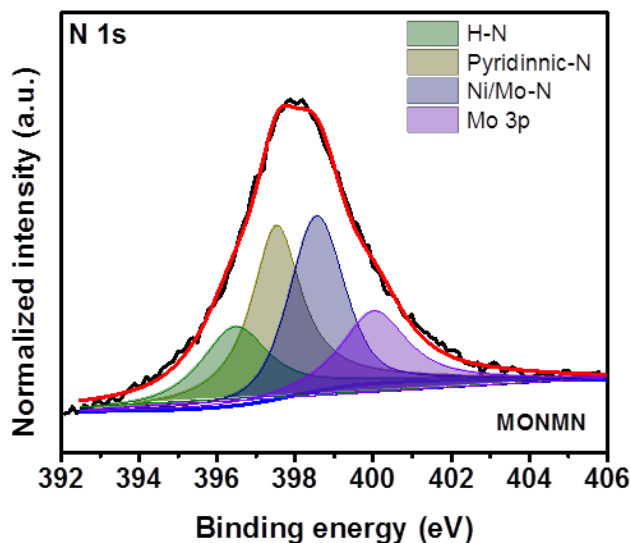


Figure S1. N 1s XPS spectra of MONMN catalyst.

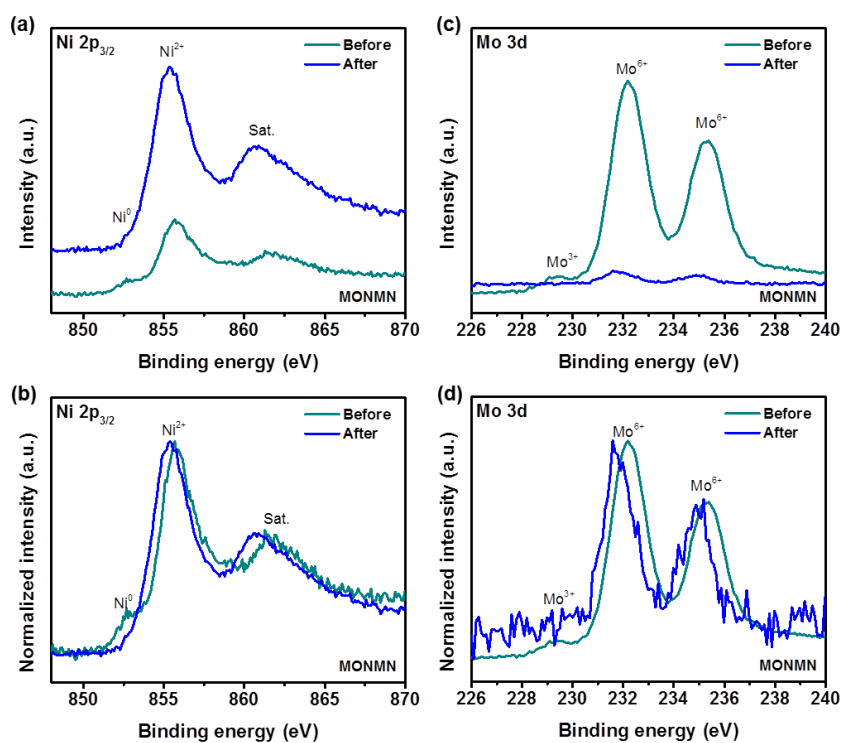


Figure S2. (a) Ni $2p_{3/2}$ and (b) normalized Ni $2p_{3/2}$ XPS spectra of MONMN catalyst before and after OER stability test. (c) Mo 3d and (d) normalized Mo 3d XPS spectra of MONMN catalyst before and after OER stability test.

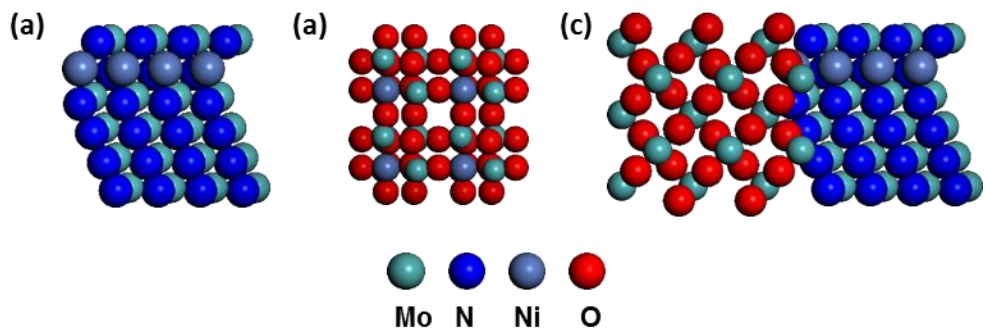


Figure S3. Structural models of (a) MoO₂, (b) Ni_{0.2}Mo_{0.8}N, and (c) MONMN.

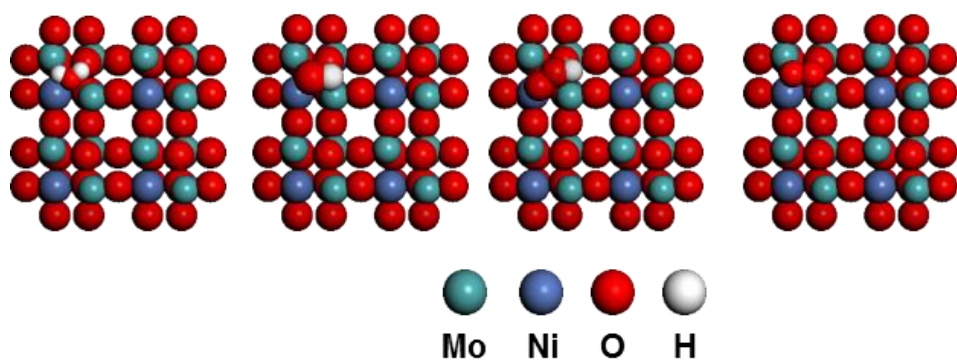


Figure S4. Structural models of MoO₂ with the general alkaline OER 4e⁻ path that mainly consists of the adsorption of OH*, O* and OOH*.

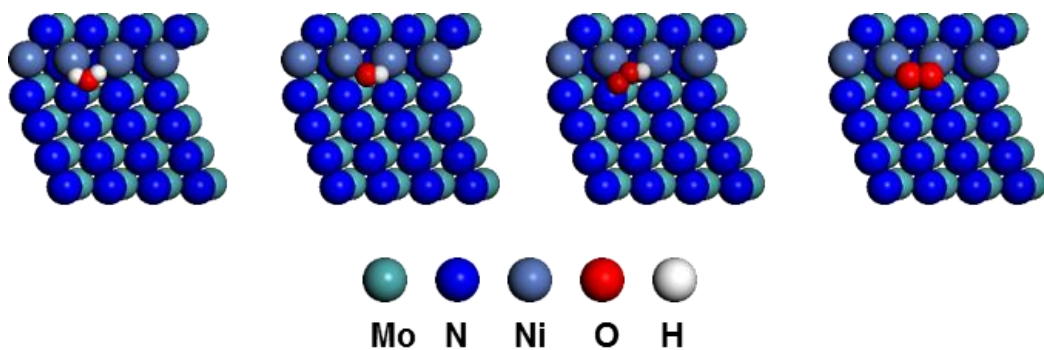


Figure S5. Structural models of Ni_{0.2}Mo_{0.8}N with the general alkaline OER 4e⁻ path that mainly consists of the adsorption of OH*, O* and OOH*.

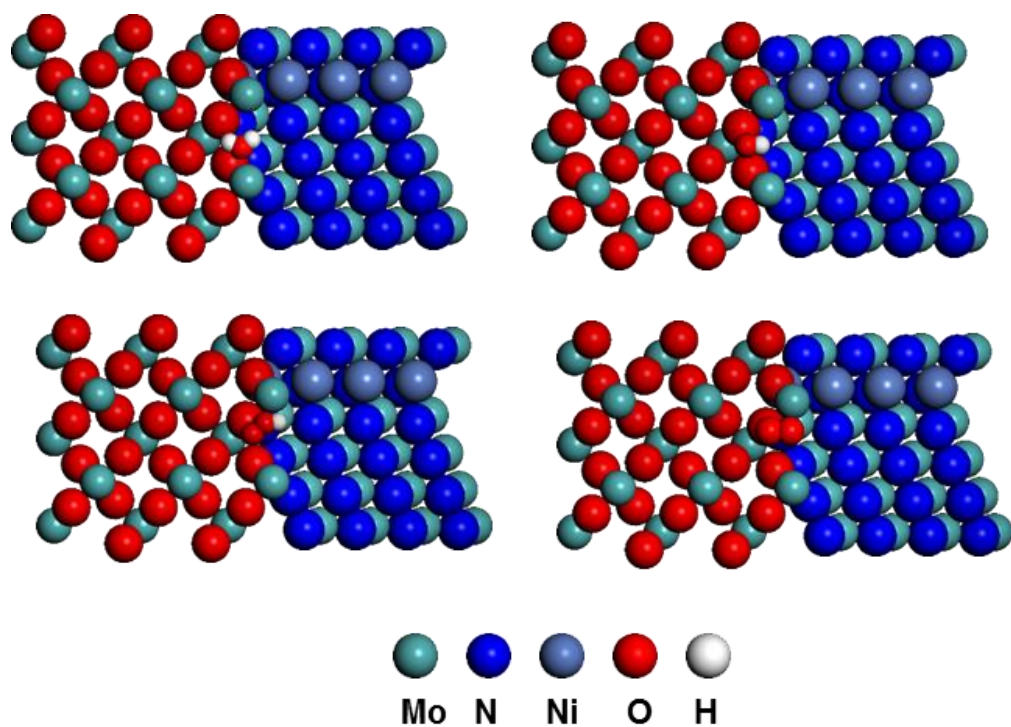


Figure S6. Structural models of MONMN with the general alkaline OER $4e^-$ path that mainly consists of the adsorption of OH^* , O^* and OOH^* .

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