

NbO_x Overlayers Protecting NiMo Alloy Electrode Realizing High-Efficient and Durable Intermittent Water Electrolysis

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Material synthesis

Synthesis of NiMo electrode :

NiMoO₄ array on nickel foam were synthesized as the precursor through a facile hydrothermal approach according to a previous report ¹. The commercial nickel foam was successively washed with ethanol, 1 M HCl aqueous solution and deionized water for several times. First, 0.25 mmol of (NH₄)₆Mo₇O₂₄ and 0.27 mmol of NH₄F were dissolved in 10 mL of deionized water, and then 20 mL of absolute ethanol was added and stirred vigorously for 1 h. Afterward, the mixture was transferred into a 45 mL Teflon-lined stainless steel autoclave, and one piece of nickel foam (1 × 3 cm²) was immersed in the mixture above. The autoclave was heated at 150 °C for 10 h. After washing with deionized water, the NiMoO₄ arrays on nickel foam were dried under vacuum at 70°C. NiMo electrodes were synthesized via treating the above NiMoO₄ array on nickel foam at 500 °C for 2 h in a reduction atmosphere (10 vol.% H₂ and 90 vol.% Ar) for 2 h.

Synthesis of NiMo/Nb electrode :

NiMo/Nb electrodes were synthesized through the electrodeposition process in a three-electrode system. To initiate the process, 10 mM of NbCl₅ was added to a 1 M KOH solution as the deposition solution. The working electrode for the process was a synthesized NiMo electrode (1 cm²), the counter electrode was a carbon rod, and the reference electrode was a calomel electrode filled with saturated KCl solution. A

current density of -50 mA cm^{-2} was applied and electrodeposition was conducted in a single cell. The content of Nb was adjusted by altering the duration of the deposition process.

Characterizations

The X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at a speed of 35° in a 2θ range of $5\text{-}50^\circ$. The Scanning electron microscopy (SEM) images were performed by GeminiSEM 450. The transmission electron microscopy (TEM) images were obtained on Hitachi-7650 with an acceleration voltage of 100 kV. The high-resolution TEM (HR-TEM), and energy-dispersive X-ray (EDX) element mapping were taken on JEOL-2100F with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra were collected on Thermo Scientific K-Alpha spectrometer. The in-suit Raman spectra were measured using an Xplora Plus confocal microprobe Raman system (HORIBA) with 1200 T grating. The excitation laser was a He-Ne laser with a wavelength of 532 nm. A $\times 50$ magnification long working distance (8 mm) objective was used and it took approximately 120 s to acquire one experimental Raman spectrum with two accumulations. The Raman frequencies were calibrated using a Si wafer (520.7 cm^{-1}) before the experiment. Electrochemical data were tested using CHI 760e workstation.

Electrochemical testing

The electrochemical performance of the synthesized electrode can be evaluated using a three-electrode system in 1 M KOH solution. The synthesized electrode material serves as the working electrode, the carbon rod is the counter electrode, and the Saturated calomel electrode is the reference electrode. A single Electrolytic cell is employed for the testing. The potential of the relative Saturated calomel electrode is then converted to the standard reversible hydrogen electrode potential formula:

$$V (\text{vs RHE}) = V (\text{vs SCE}) + 0.059 \cdot \text{pH} + 0.241.$$

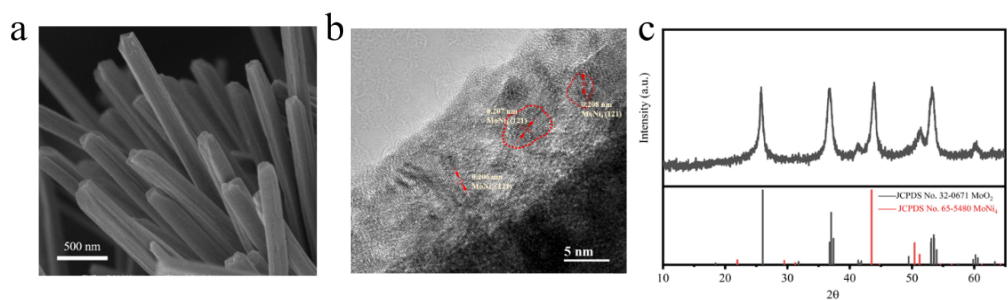


Figure S1. SEM image of NiMo electrode; (b) HR-TEM image of NiMo nanorod; (c) XRD pattern of NiMo electrode. The precursor powder obtained by hydrothermal synthesis was collected, and the treatment process was exactly the same as that of NiMo electrode. The XRD pattern was obtained from the powder sample.

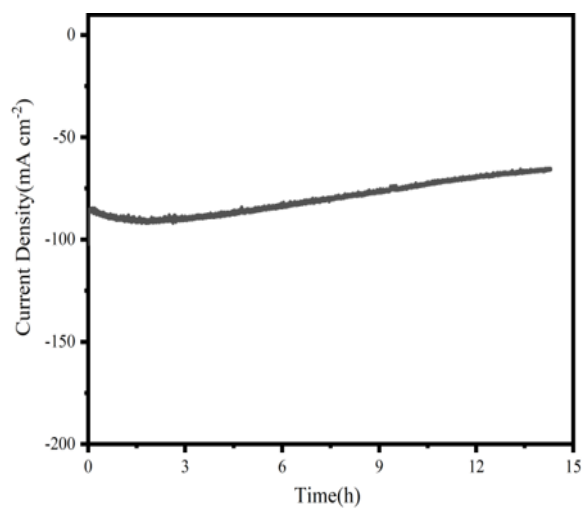


Figure S2. Long-term constant stability test of NiMo electrode.

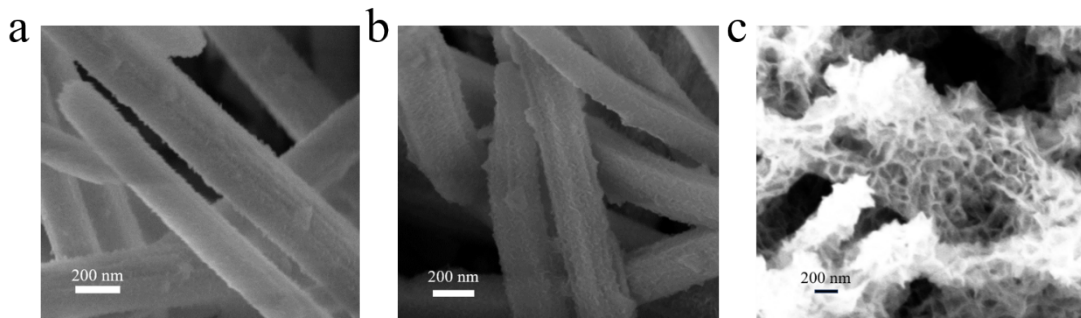


Figure S3. SEM images of NiMo electrode surface after different cycles. (a) 10 cycles; (b) 20 cycles; (c) Cycle overnight.

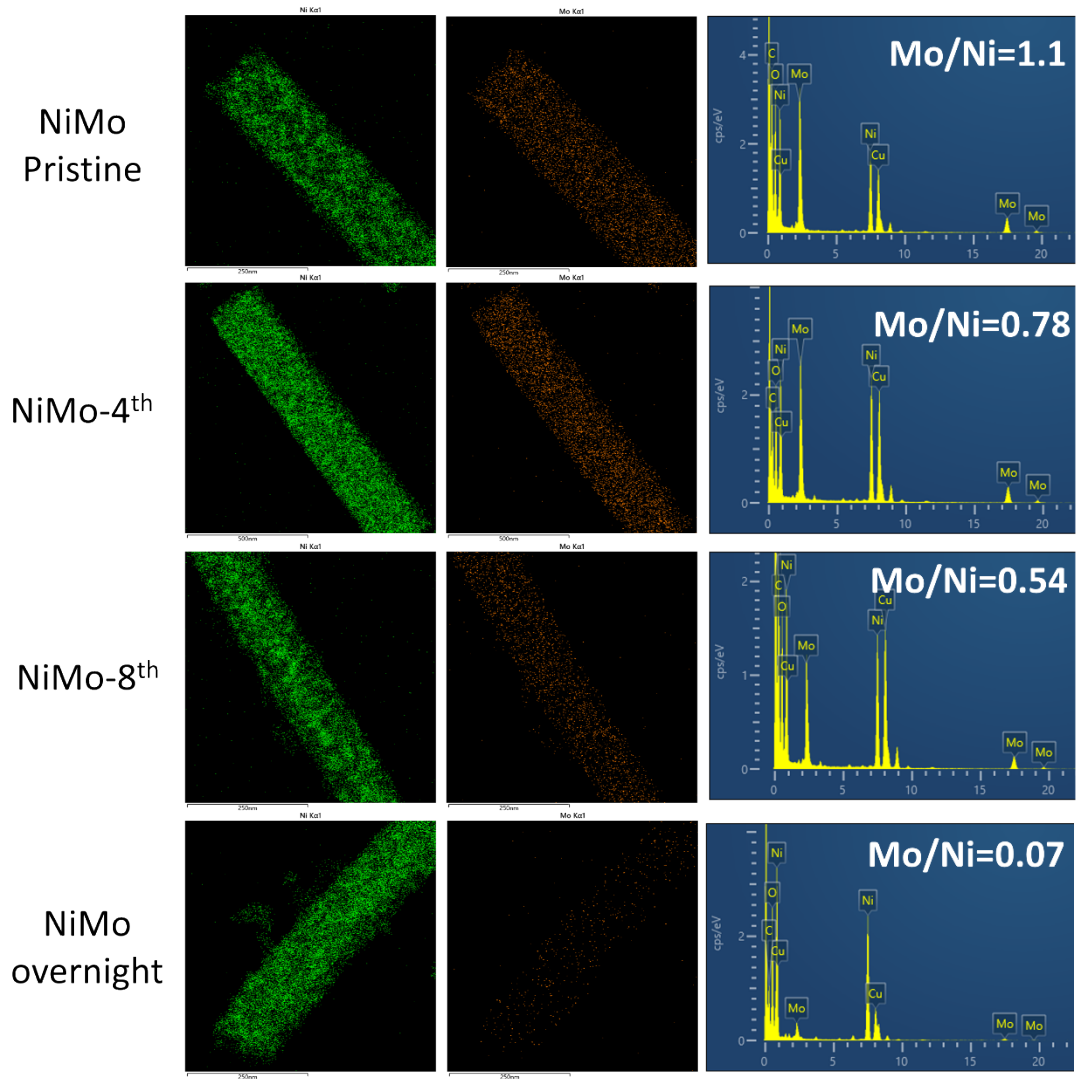


Figure S4. Mapping and EDS of NiMo electrode at different HER periods.

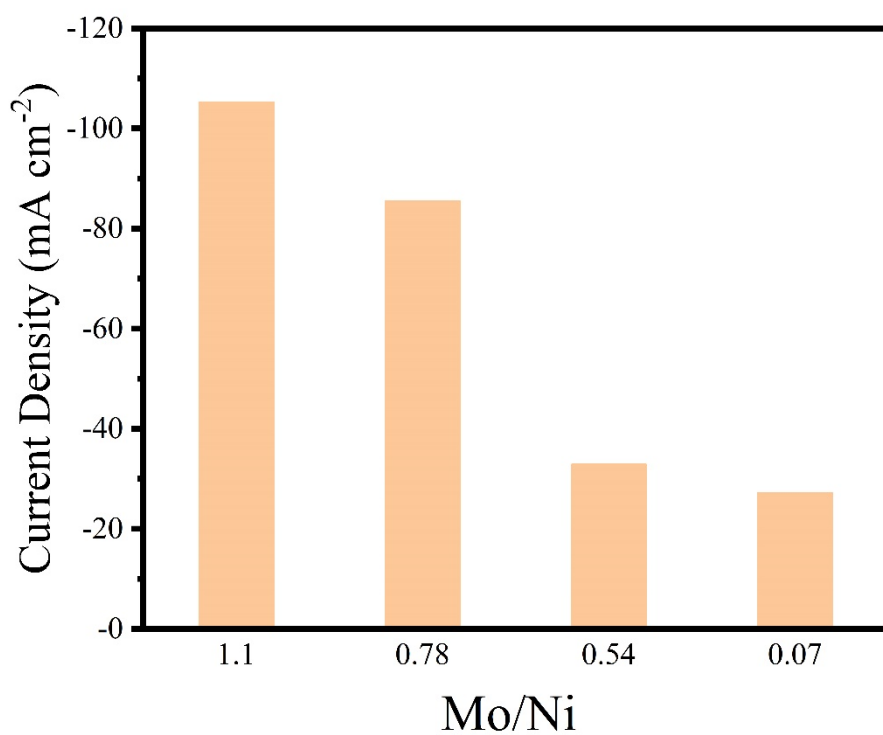


Figure S5. The HER performance at -0.2 V vs RHE of NiMo electrodes with different ratio of Mo/Ni.

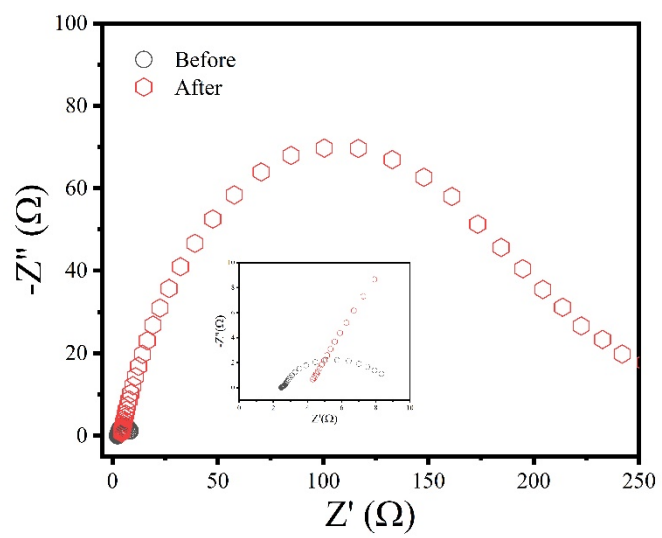


Figure S6. EIS of NiMo electrodes before and after the reaction.

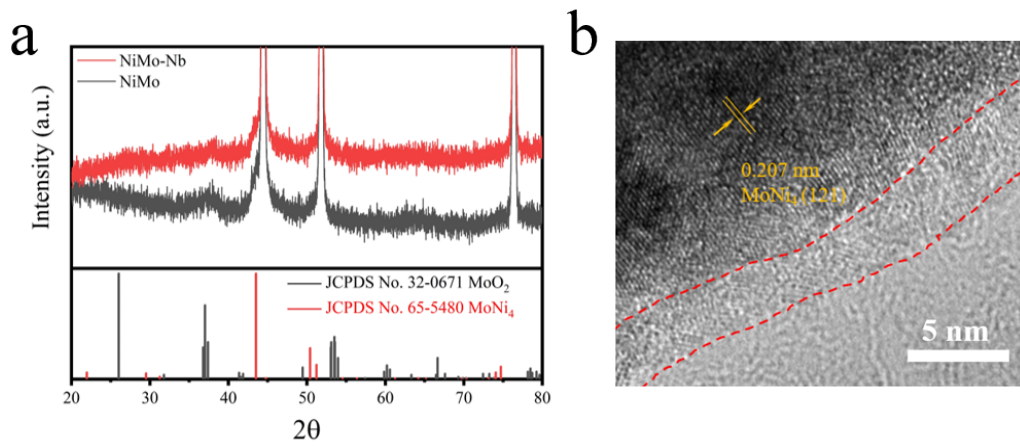


Figure S7. (a) XRD pattern and (b) HR-TEM of NiMo/Nb electrode.

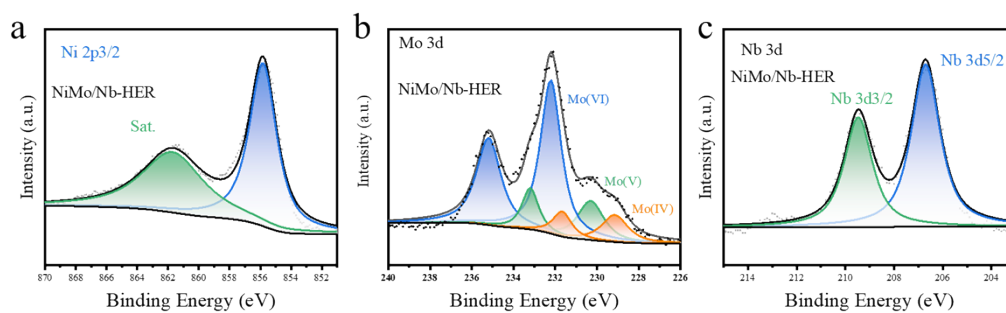


Figure S8. High-resolution (a) Ni 2p (b) Mo 3d and (c) Nb 3d XPS spectrum of NiMo/Nb after HER test.

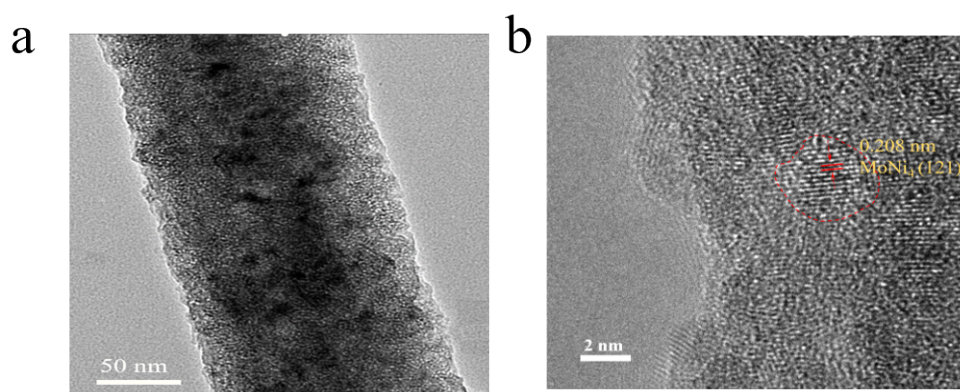


Figure S9. (a) TEM image and (b) HR-TEM image of NiMo/Nb after intermittent HER stability test.

1. W. K. Han, X. P. Li, L. N. Lu, T. Ouyang, K. Xiao and Z. Q. Liu, Partial S substitution activates NiMoO(4) for efficient and stable electrocatalytic urea oxidation, *Chem Commun (Camb)*, 2020, **56**, 11038-11041.