Electronic Supplementary Information (ESI)

Continuous 3D-Nanopatterned Ni-Mo Solid Solution as Free-Standing Electrocatalyst for the Hydrogen Evolution Reaction in Alkaline Medium

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In this Supplementary Information, we provide the following experimental, data, and description, which support to our main text:

Fig. S1: Schematic illustration of the fabrication procedure of the 3D Ni-Mo solid solution.

Fig. S2: TEM images of the 3D Ni-Mo solid solution.

Fig. S3: Electrochemical performances. a) Linear sweep voltammetry (LSV) curves of the 2D Ni-Mo with different composition. b) Tafel plots of the 2D Ni-Mo with different composition. c) Nyquist plots for the 2D Ni-Mo with different composition. d) Cyclic voltammetry (CV) curves of the 2D Ni-Mo. All the test were performed in 1 M KOH.

Fig. S4. Linear sweep voltammetry (LSV) curves of the 3D nanopatterned Ni-Mo with different thickness at sacn rate of 2 mV/s.

Fig. S5. Faradaic efficiency measurement of 7 μm 3D Ni-Mo showing the theoretically calculated and experimentally measured H_2 gas with time.

Fig. S6. Linear sweep voltammetry (LSV) curves of the (a) 4 μm 3D-nanopatterned Ni-Mo, and (b) 10 μm 3D-nanopatterned Ni-Mo for activation.

Fig. S7. OER polarization curves of 7 μm 3DNiMo with a scan rate of 10 mVs^{-1} in 1 M KOH.

Fig. S8. Overall water-splitting performance test of the 3D Ni-Mo with IrO_2 conducted in 1.0 M KOH. Polarization curve for overall water splitting at a scan rate of 5 mVs^{-1}.

Experimental procedures

Preparation of the 3D SU-8 template

A metal seed layer of Au (50 nm) and Cr (5 nm) was deposited on a SiO_2/Si substrate using electron-beam (e-beam) evaporator (SNTEK). The Au/Cr-deposited substrate was treated by an air plasma (CUTEMP, Femtoscience) for 2 min (50 sccm, 40 mTorr, 60 W). A 10 μm thickness of epoxy-based photopolymer film (SU-8 10, Microchem) was spin coated on the plasma-treated substrate and soft-baked on a hotplate at 95 °C for 10 min. After that a polydimethylsiloxane (PDMS) (Sylgard 184, Dow Corning) phase mask which is consisted of a square array of holes with a diameter of 480 nm, a depth of 420 nm, and a periodicity of 600 nm was placed on the photopolymer-coated substrate. The collimated 355 nm laser (Nd:YAG, Advanced Optowave) was went through the phase mask with 10.3 mJ/cm^2 of exposure dose. After that, the substrate was post-baked on the hotplate at 65 °C for 6 min. Finally, unexposed regions in the photopolymer were selectively etched by developing solution (SU-8 developer, Microchem) at room temperature for 30 min and rinsed by ethanol for 30 min.[1-5]

Preparation of the 3D Ni-Mo

A 3D Ni-Mo solid solution was deposited on the 3D SU-8 template by conventional potentiostat (VersaSTATE3, Principle-applied Research).[6-9] The electrodeposition was consisted of a three electrodes system: the seed layer under the 3D SU-8 template as a working electrode, a Pt plate as a counter electrode, and an Ag/AgCl electrode as a reference. The electrolyte was mixture of 0.3 M $NiSO_4 \cdot 6H_2O$, 0.2 M $Na_2MoO_4 \cdot 2H_2O$, and 0.3 M $Na_3C_6H_5O_7 \cdot 2H_2O$ in 90 mL of DI water. The pH value was adjusted to 10.5 using ammonia.[10] The Ni-Mo solid solution was alternatively deposited in the 3D SU-8 template with different cycles (each cycle is consisted of 5 s at -0.5 V *vs.* NHE and 5 s at 0 mA/cm^2). After the deposition of Ni-Mo, the 3D SU-8 template was etched by radical etching system (STP Compat, Muegge) and rinsed by ethanol.

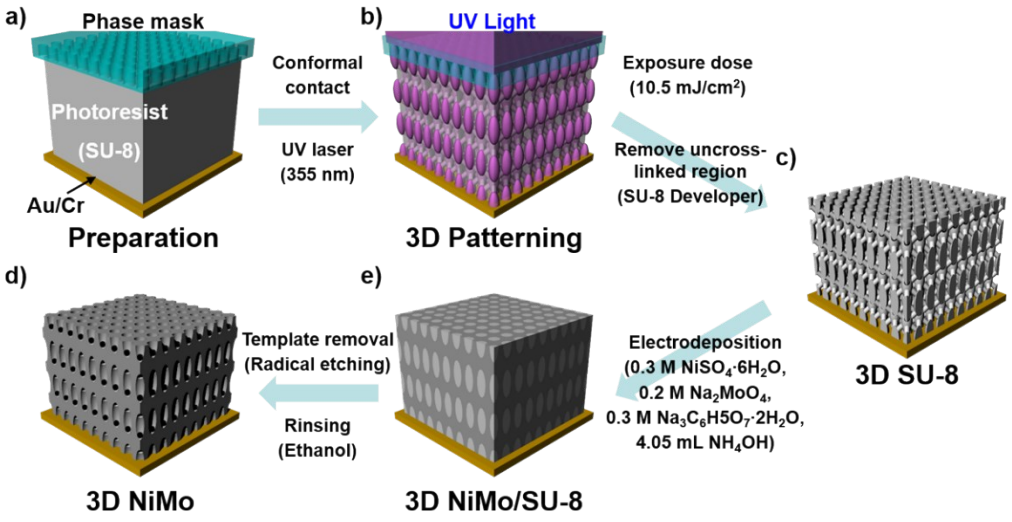


Fig. S1. Schematic illustration of the fabrication procedure of the 3D Ni-Mo solid solution.

Characterization

The microstructure analysis was conduced by field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi) and transmission electron microscope (TEM). X-ray diffraction (XRD) of the samples were performed with Cu Kα radiation (Ultima IV, Rigaku). Chemical states of the elements in the samples are confirmed by X-ray photoemission spectroscopy (XPS) (Thermo VG Scientific, K-alpha).

Electrochemical analysis

Electrochemical analyses were conducted by commercial electrochemical workstation (VersaSTAT3, Principle-applied Research). The electrochemical performances were carried out via three electrode system: as synthesized samples as a working electrodes, Pt wire as a counter electrodes, and the Hg/HgO electrodes as a reference. All electrochemical experiments was conducted in alkaline solution (1 M KOH). The evloved H_2 gas was measured using online gas chromatography system (DS Science) with thermal conductivity detector and MS-5A column. Argon gas was used as a carrier gas. The aliquots from the electrochemical cell were injected into the GC system every 2.7 mins by auto-sampling. The GC was calibrated with known concentrations of H_2 standard gas in Argon and the moles of

H_2 were calculated using the H_2 peak area. The Faradic efficiency was calculated from the total charge passed through the cell at corresponding time intervals using Faraday's law, equation

$$Faradic\ Efficiency = \frac{nF \times m}{Q}$$

Where F = Faraday's constant (96,485.33 As mol^{-1}), n = 2 for HER, m = moles of gas produced and Q = amount of charge passed.

Description to calculate turn over frequency (TOF) for H_2 of as-prepared nano-patterns

The structural data of Ni from the ICDD-PDF-4 database is used.

Density of NiMo = 6.3 g·cm^{-3}. Average size of NiMo nanoparticle (determined from the Scherrer equation) = 14 nm. The shapes of the nanoparticles are approximated to spherical.

Total volume of NiMo particles present on the electrode

$= (1 \times 10^{-5}) / 6.3 = 1.6 \times 10^{-6}\ cm^3$

Total number of NiMo nanoparticles present on the electrode

$= (1.6 \times 10^{-6}) / [(4/3)\cdot(\pi)\cdot(r^3)]$

$= (1.6 \times 10^{-6}) / [4.18 \times (7 \times 10^{-7})^3]$

$= 1.17 \times 10^{12}$ particles

Surface area of one NiMo nanoparticle

$= (4)\cdot(\pi)\cdot(r^2)$

$= 0.6 \times 10^{-15}\ m^2$

Total surface area of all NiMo the nanoparticles present

$= (1.17 \times 10^{11}) \times (7.9 \times 10^{-15}) = 9.2 \times 10^{-4}\ m^2$

The area of per unit cells of NiMo = $7.4 \times 10^{-19}\ m^2$

There are six Ni atoms in this cell.

Total number of Ni atoms presents

$= [6 / (7.4 \times 10^{-19}] \times (9.2 \times 10^{-4})$

$= 7.5 \times 10^{15}$ atoms

After dividing effective atoms by total number of particles, we can get turn over frequency at particular potentials.

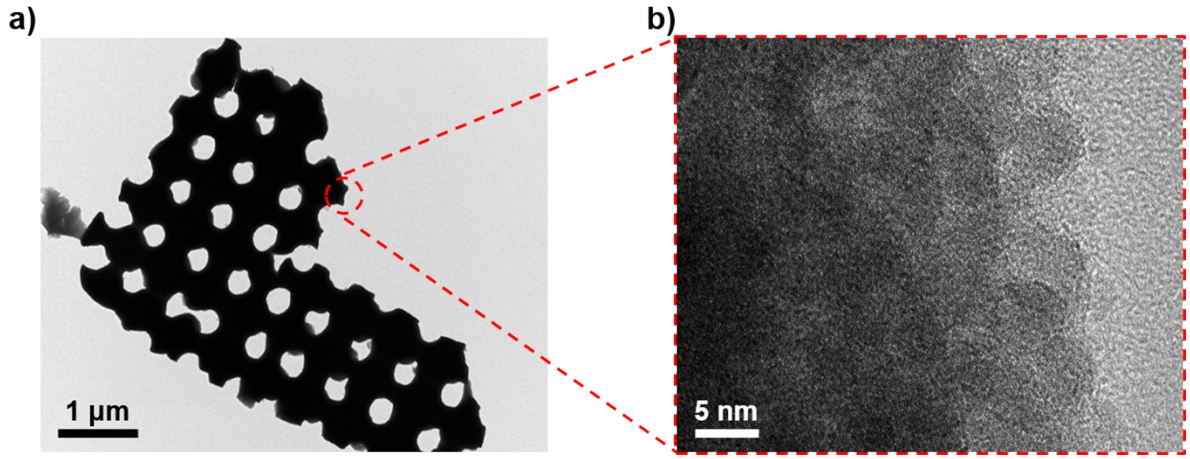
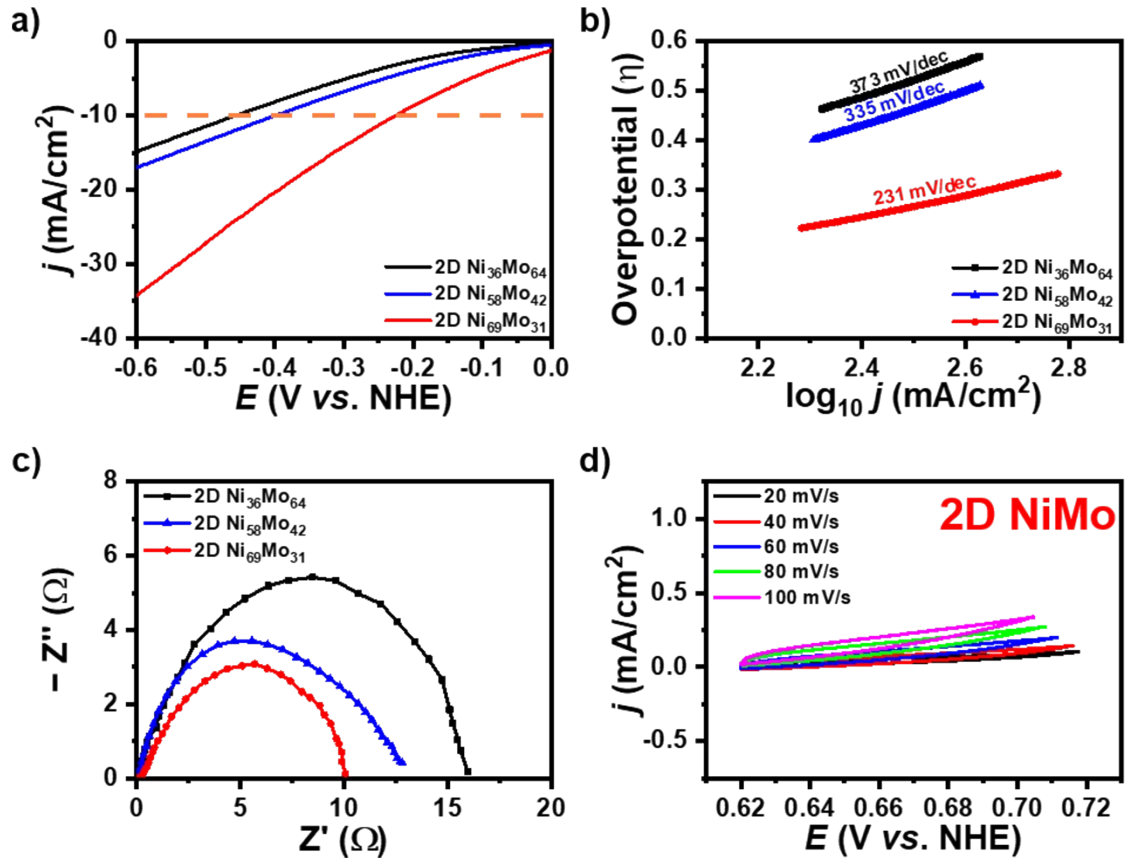


Fig. S2. TEM image of 3D Ni-Mo.



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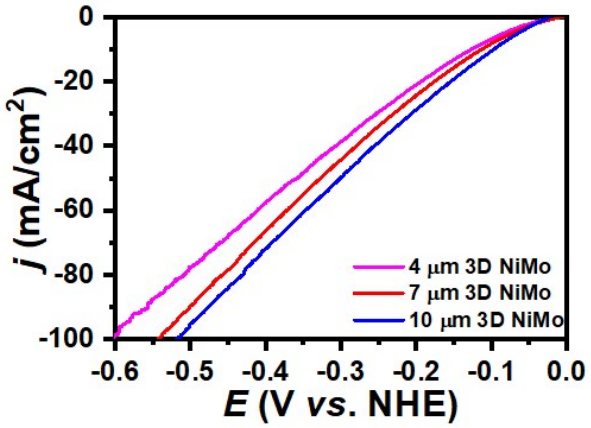
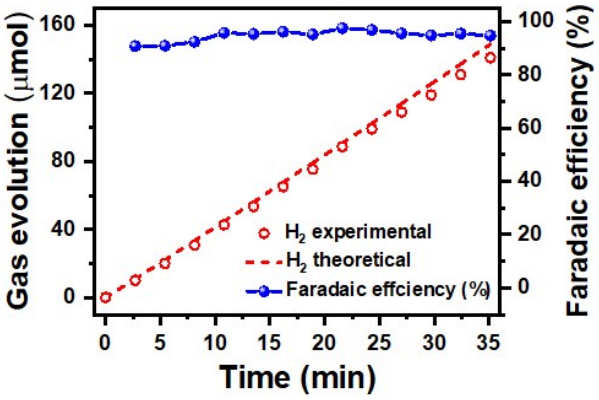


Fig. S4. Linear sweep voltammetry (LSV) curves of the 3D nanopatterned Ni-Mo with different thickness at sacn rate of 2 mV/s.



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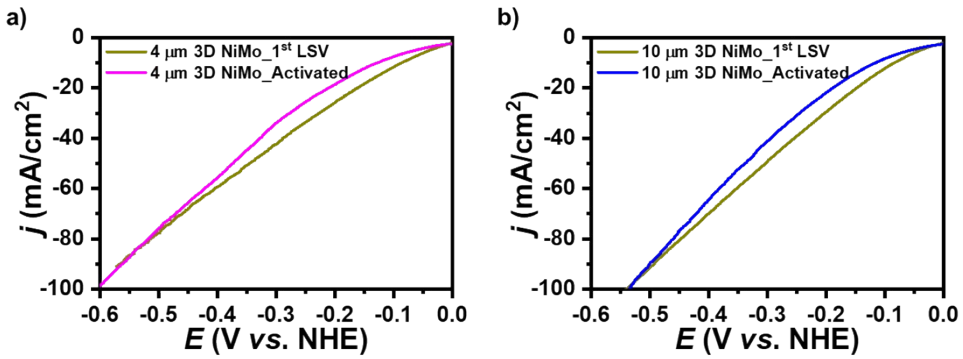

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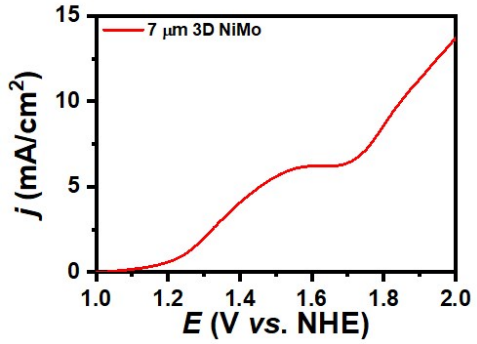

Fig. S7. OER polarization curves of 7 μm 3DNiMo with a scan rate of 10 mVs^{-1} in 1 M KOH.

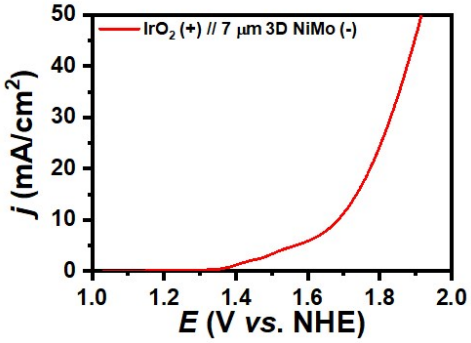

Fig. S8. Overall water-splitting performance test of the 3D Ni-Mo with IrO_2 conducted in 1.0 M KOH. Polarization curve for overall water splitting at a scan rate of 5 mVs^{-1}.

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