Supporting Information for

Interlaced NiS₂-MoS₂ Nanoflake-Nanowires as Efficient Hydrogen Evolution Electrocatalysts in Basic Solutions

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Experimental

Synthesis of NiMoO₄ nanowires (NWs). Typically, Ti foils in rectangular shape of 1.5 cm \times 4 cm were cleaned by diluted HCl solution, ethanol and pure water under ultrasonication for several minutes respectively. Then, the clean Ti foil substrates were placed within a sealed Teflon reactor (50 mL), containing 30 ml of homogeneous solution of Ni(NO₃)₂·6H₂O (1.5 mmol) and Na₂MoO₄·2H₂O (1.5 mmol). The mixture was kept in an oven at 150 °C for 6 h. Then, the Ti substrates uniformly covered with as-synthesized NiMoO₄ NWs were rinsed

with pure water and dried at 60 °C in a vacuum oven overnight.

Synthesis of NiS_2 - MoS_2 NWs. In a typical procedure, a home-built CVD reactor consisting of a 1-inch diameter fused silica tube equipped with pressure and gas flow controls placed in a single-zone tube furnace, an alumina combustion boat containing 1 g of powdered sulfur was placed outside of the tube furnace upstream of the prepared Ti foil with NiMoO₄ NWs. The reactor was evacuated and flushed three times with argon before it was back filled to the set-point pressure of 770 Torr under an argon flow of 125 sccm and heated to 300 °C at a rising rate of 2 °C/min. The combustion boat was pushed 1.5 cm into the furnace using a magnet and lasted for 60 min, where the sulfur powder first evaporated and then reacted with NiMoO₄ NWs to form NiS₂-MoS₂, then the furnace was cooled naturally under an argon flow.

*Synthesis of nanostructured NiS*₂, *MoS*₂ and *Ni-Mo-S*. The synthesis of nanostructured MoS₂ and Ni-Mo-S is according to previous literature with modulation.^{S1} Sodium molybdate dihydrate (Na₂MoO₄·2H₂O), nickel sulfate hexahydrate (NiSO₄·6H₂O) and L-Cys (C₃H₇NO₂S) were used as Mo, Ni and S sources, respectively. Briefly, aqueous solution of Na₂MoO₄·2H₂O (25 mM, 10 ml), NiSO₄·6H₂O (25 mM, 10 ml) and L-Cys (132 mM, 20 ml) were mixed together and transferred to a 50-ml Teflon-lined stainless autoclave with Ti foil substrates and then heated at 200 °C for 24 hours. For nanostructured NiS₂,^{S2} 30 ml of aqueous solution containing 1.454g Ni(NO₃)₂·6H₂O and 1.442g hexamethylenetetramine (HMT) was poured into 50-ml Teflon-lined stainless autoclave with Ti foil substrates and reacted at 100 °C for 10 h in order to obtain Ni(OH)₂. Then, the CVD process to synthesis NiS₂ is similar to the synthesis of NiS₂-MoS₂ NWs.

Characterization. The as-synthesized samples were characterized by field-emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). Powder X-ray diffraction (PXRD) data were obtained by X-ray diffraction (2θ range: 10-80°, $\lambda = 0.15418$ nm) with Cu-K α radiation (Bruker SMART APEX (II)-CCD, Germany). X-ray photoelectron spectroscopy (XPS) was carried out under ultrahigh vacuum (< 10⁻⁶ Pa) on a Perkin-Elmer PHI 5000C ESCA system (Perkin-Elmer, USA). All calibrations were done with contaminant carbon as a reference (C1s = 284.6 eV). Raman spectra were performed using a Renishaw inVia Raman Microscope (UK). N₂ adsorption-desorption isotherms were measured with a Micromeritics Tristar 3020 analyzer (Micromeritics, USA). Before the measurements, the sample was degassed in vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the surface areas from the data in the range of pressure (P/P₀) from 0.05 to 0.2.

Electrochemical Characterization. Electrochemical measurements (LSV, stability, EIS) were carried out in a CHI660D electrochemical workstation (CHI Instruments Inc., USA) with a three-electrode configuration at 25 ± 1 °C, where the active materials, a coiled Pt wire and an Ag/AgCl electrode served as the working, counter and reference electrodes, respectively. 1 M KOH aqueous solution was used as the electrolyte, which was deaerated with high-purity argon prior to and throughout all the measurements. The linear sweep voltammetry (LSV) was carried out under scan rate of 5 mV·s⁻¹. Electrochemical impedance spectroscopy (EIS) experiments were performed with frequencies ranging from 100 kHz to 0.01 Hz.

Capacitance measurements and comparison of electrochemically active surface areas. The electrochemically active surface areas was estimated by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammograms (CVs). The potential window of CVs was 0.1~0.2 V vs RHE, and the scan rates were 5, 10, 20 and 40 mV·s⁻¹. The double layer capacitances (C_{dl}) of various samples were estimated by plotting the $\Delta J = J_a - J_c$ against the CV scan rates, where the slope was twice C_{dl} , which can be used to represent the electrochemical active surface area.

Supporting Figures and Tables



Fig. S1 N_2 sorption isotherms of (a) NiMoO₄ nanowires and (b) NiS₂-MoS₂ hetero-nanowires.



Fig. S2 Element mapping of the synthesized NiS₂-MoS₂ hetero-nanowires.



Fig. S3 The synthesized NiS_2 -MoS₂ hetero-nanowires on different substrates: (a-c) nickel foam, (d-f) carbon cloth.



Fig. S4 XRD pattern (blue curve) and fitting data (red curve) using DIFFRAC TOPAS software for NiS₂-MoS₂ hetero-nanowires.



Fig. S5 Raman spectrum of the NiS_2 -MoS₂ hetero-nanowires.



Fig. S6 Morphology of nanostructured MoS_2 , NiS_2 and Ni-Mo-S composite by methods in previous literatures.



Fig. S7 Polarization curves of NiS_2 -MoS $_2$ with and without IR-correction.



Fig. S8 SEM images of NiS_2 -MoS₂ hetero-nanowires after electrochemical stability test.



Fig. S9 (a-d) Cyclic voltammetry curves at various scan rates of (a) NiS₂-MoS₂, (b) MoS₂, (c) NiS₂, and (d) Ni-Mo-S, in the region of 0.1 - 0.2 V vs RHE. (e) Charging current density differences ($\Delta J = Ja - Jc$) plotted against scan rates of NiS₂-MoS₂, MoS₂, NiS₂ and Ni-Mo-S. The linear slope, equivalent to twice the double-layer capacitance, C_{dl} , was used to represent the ECSA.

Table S1

| Electrocatalysts | Electrolyte | μ (mV) | Tafel Slope (mV/dec) | Literature |
|--|--------------------------------------|--------|-------------------------|------------|
| NiS ₂ /GS | 1M NaOH | 110 | 80 | S2 |
| Ni ₃ S ₂ @Ni | 1M KOH | ~80 | 110 | S3 |
| MoS ₂ /Ni ₃ S ₂ | 1M KOH | 50 | 83 | S4 |
| Co-S/CP/CNT | 1M KOH | - | 131 | S5 |
| Co ₉ S ₈ @MoS ₂ | 0.5 M H ₂ SO ₄ | 64 | 110 | S6 |
| CoS ₂ @MoS ₂ | 0.5 M H ₂ SO ₄ | 44 | 57.3 | S7 |

Table S1. Comparison of HER activity of the NiS_2 -MoS2 hetero-nanowires with recentlyreported metal sulfide catalysts.

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