Electronic Supplementary Material

Three dimensional macroporous framework molybdenum disulfide-carbide heterojunction for highly efficient electrocatalytic hydrogen evolution at high current density

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Experimental section

Materials synthesis

Oxidation of Mo plates

Firstly, the cheap industrial-grade Mo plate is cleaned by diluted HCl, water, acetone and ethanol in an ultrasonic bath for 10 min. Secondly, the cleaned Mo plate is placed on a porcelain boat which is laid up in the center of a 2-inch diameter quartz tube furnace. Thirdly, a piece of clean Mo plate is placed on an empty alumina boat which is laid up in the center of a 2-inch diameter quartz tube furnace. The reaction is carried out at a temperature of 650 °C with the heating rate of 20 °C/min for 60 min in air and then cool down to the room temperature naturally.

Preparation of 3D macroporous framework MoS_2-Mo_2C heterojunction prisms

For the synthesis of 3D macroporous framework MoS_2-Mo_2C heterojunction prisms, the MoO_3/Mo plates and solid sulfur powders are placed at two separate positions in a porcelain boat with sulfur powders at the upstream side of the tube furnace. The temperature is raised to 800-1000 °C with the heating rate of 30 °C/ min, and the high purity Ar/H_2 (flow of 60 sccm and 40 sccm, respectively) is transferred to upstream and middle areas in the process. High purity methane gas (CH_4, aflow of 15 sccm) is introduced when the temperature increases to 800-1000 °C and then hold at the target temperature for 15 min. When the temperature begins to decrease, turn off CH_4, and increase Ar flow rate to vent the unreacted CH_4 gas from the quartz tube and then cool to room temperature naturally.

Electrochemical measurement

Electrochemical performance measurement is performed on an electrochemical workstation (CHI 660E). The electrochemical HER properties of each sample are measured by using a three-electrode system in the electrolyte of 1.0 mol L^{-1} KOH (pH = 14), respectively. The as-prepared MoS_2-Mo_2C/Mo samples (1.0 cm×1.0 cm) serve as the working electrodes. The saturated calomel electrode (SCE) is used as a reference electrode; a graphite rod is used as a counter electrode. All the potentials referred in the manuscript are converted to the potential versus the reversible hydrogen electrode (RHE) based on the formula: $E_{(RHE)} = E_{(SCE)} + 0.2412 + 0.059$ pH. The polarization curves are obtained by linear sweep voltammetry (LSV) in the potential range from 0 V to -0.7 V vs. RHE at a scan rate of 5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements are conducted over a frequency range from 105 Hz to 0.01 Hz. The stability is tested by cyclic voltammetry under the basic media at potentials between 0 V and -0.6 V at a scan rate of 50 mV s^{-1}. All data are collected with iR correction.

Structural characterizations

X-ray diffraction (XRD) spectra are obtained to detect the phase of samples using the D8 ADVANCE diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphology of the as-grown catalysts is characterized by scanning electron microscopy (HITACHI UHR FE-SEM SU8010). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected-area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) mapping studies are carried out on a probe-corrected transmission electron microscope operating at 200 kV (FEI Titan F20 TEM). X-ray photoelectron spectroscopy (XPS) measurements are performed by a ESCALAB 250Xi system (Thermo Fisher), equipped with a 100 W Al Kα source on a spot size of 100 μm at a 45° incident angle. The binding energy scan ranges from 0 to 1200 eV with an interval step of 1 eV, and the spectra are calibrated to carbon line of 284.8 eV.

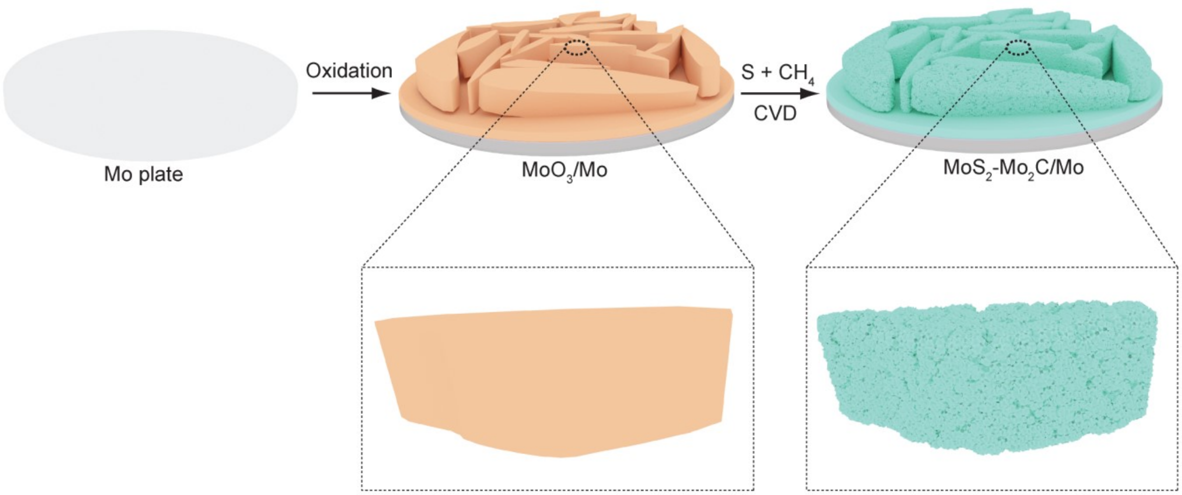

Figure S1. The schematic illustration of the synthetic process of 3D macroporous framework MoS_2-Mo_2C heterojunction electrode.

Figure S2. Optical photograph of MoS_2-Mo_2C/Mo electrodes.

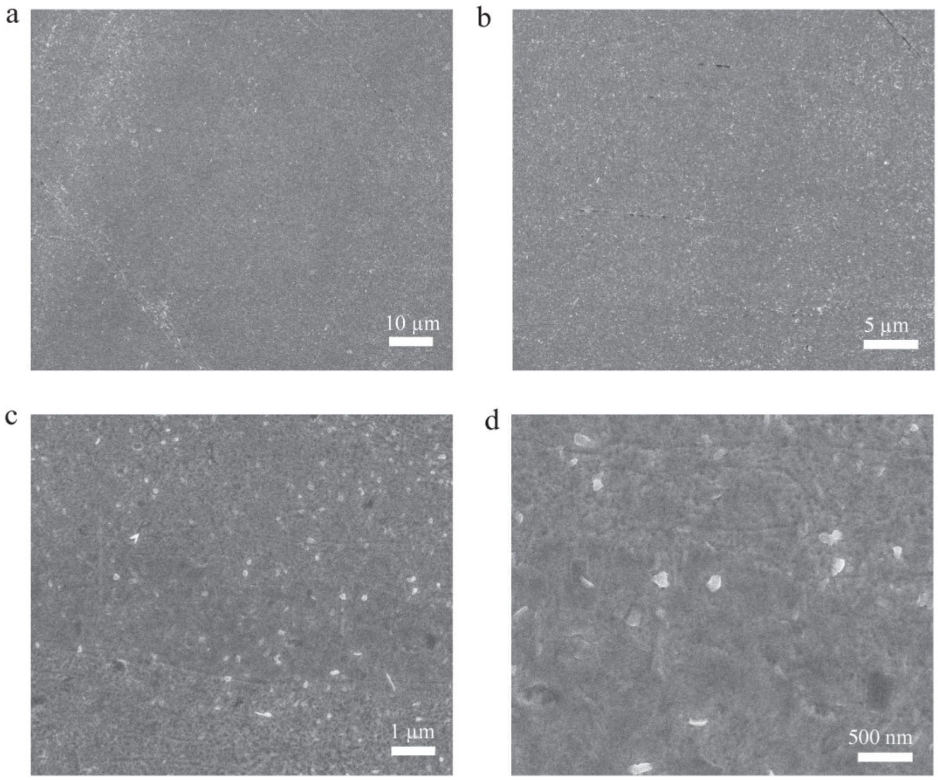

Figure S3. SEM images of prinstine Mo plate with different magnifications.

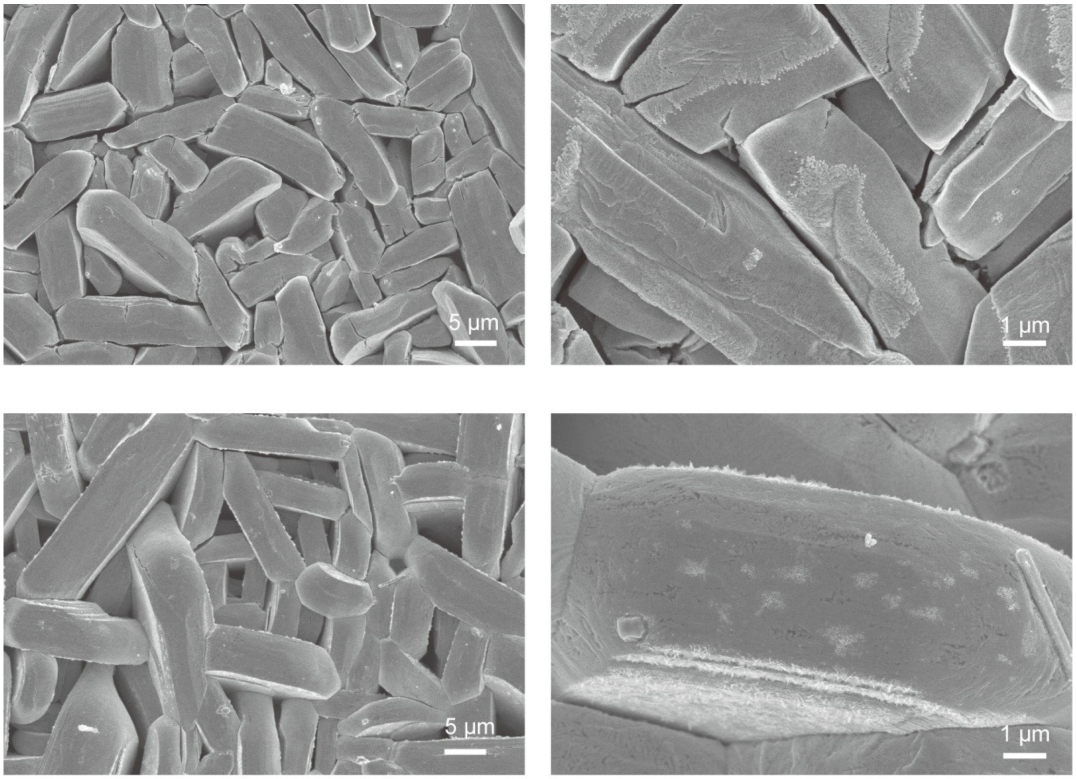

Figure S4. SEM images of MoO_3 with different magnifications.

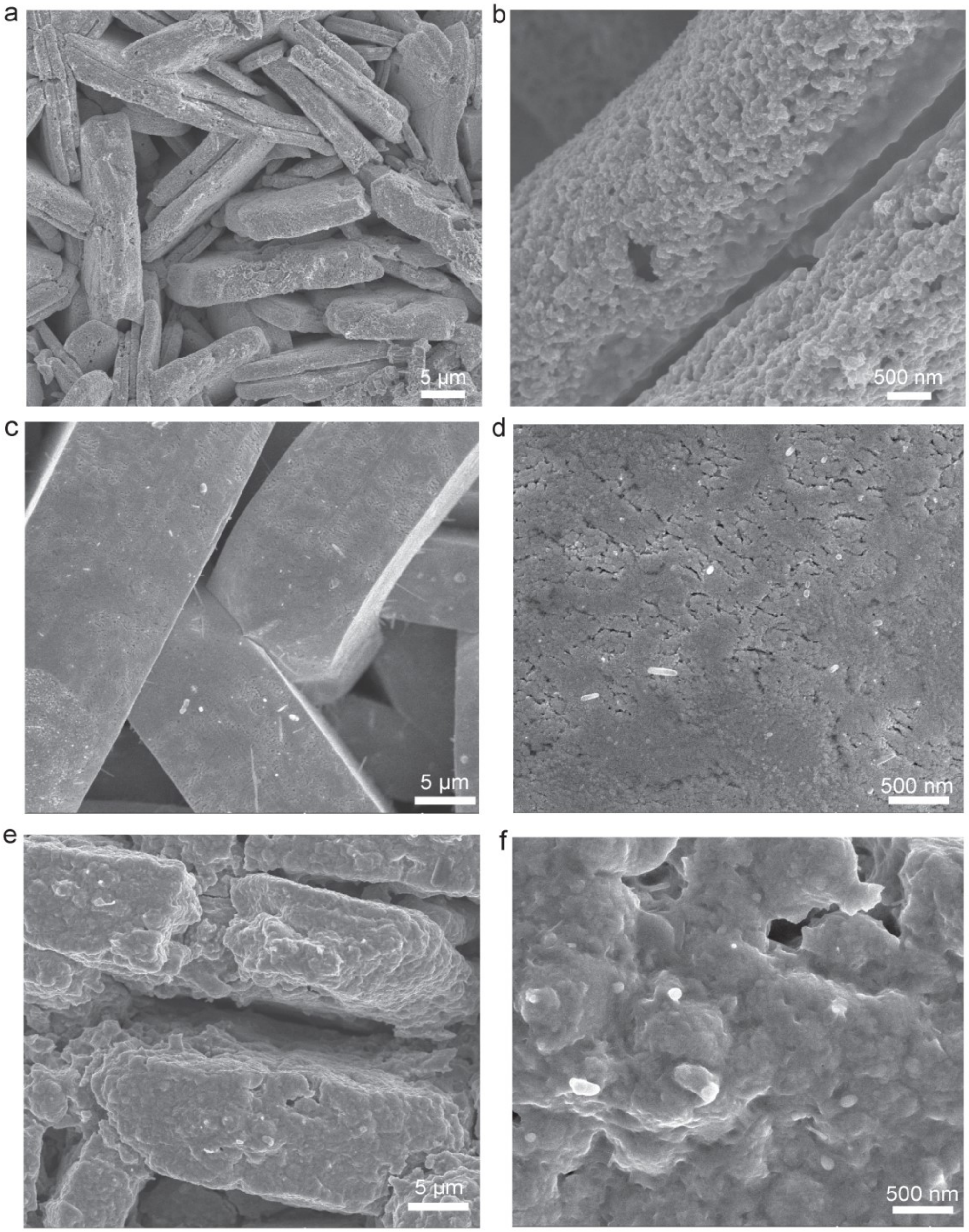

Figure S5. SEM images of (a, b) MoS_2-Mo_2C, (c, d) MoS_2 and (e, f) Mo_2C with different magnifications.

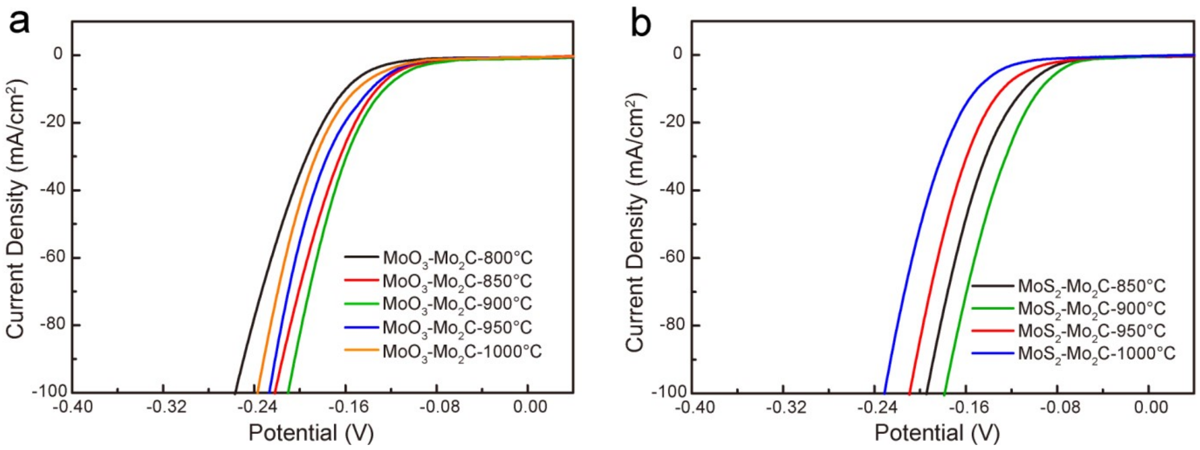

Figure S6. The polarization curves of electrocatalysts synthesized and tested under various conditions: (a) Mo plates are oxidized in air at 650 °C followed by carbonization in $CH_4/H_2/Ar$ at 800, 850, 900, 950 and 1000 °C, respectively. (b) The sulfurization temperature of MoO_3/Mo is 700 °C, and then carbonized at 850 ~ 1000 °C. It's apparent that carbonization temperature of MoO_3 and MoS_2 has effect on the HER performance of the as-prepared electrode.

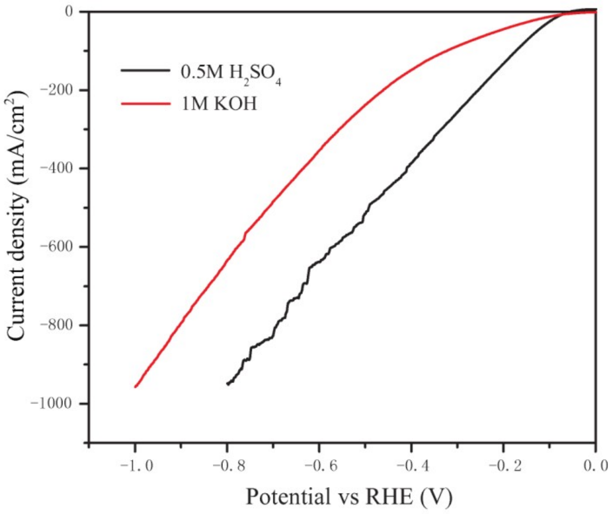

Figure S7. The LSV plots of Pt foil.

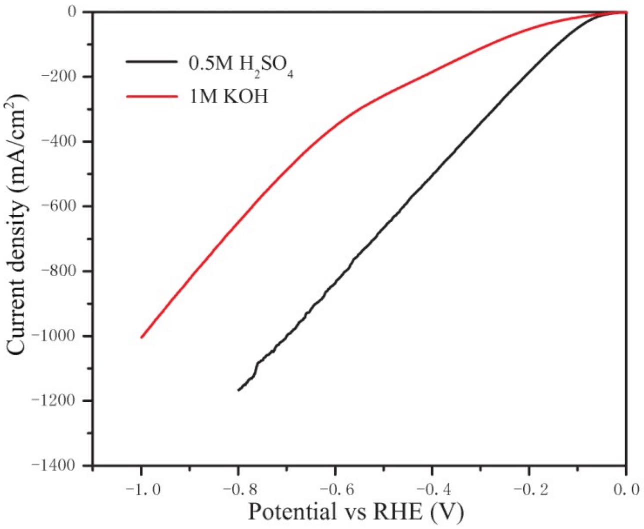

Figure S8. The LSV plots of Pt mesh.

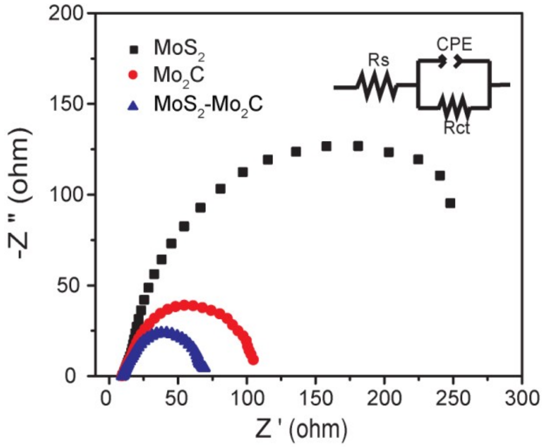

Figure S9. EIS Nyquist plots of Mo_2C, MoS_2 and MoS_2-Mo_2C electrocatalysts.

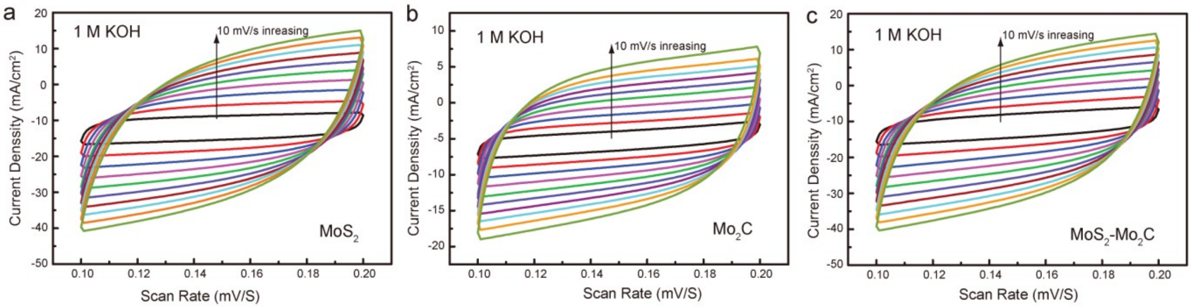

Figure S10. Electrochemical cyclic voltammogram (CV) tests on Mo_2C, MoS_2, and MoS_2-Mo_2C with different rates from 10 to 100 mV/s in the potential range of 0.1 ~ 0.2 V in 1 M KOH.

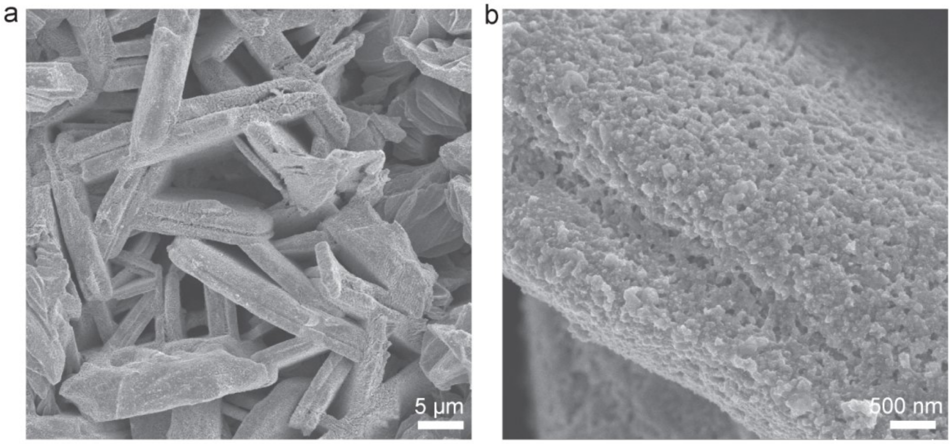

Figure S11. SEM images of the MoS_2-Mo_2C sample after stability test.

Tables S1. A comparison of the HER activity of the MoS_2-Mo_2C catalyst in this work with previously reported data and our tested data of Pt-based catalysts in KOH solution.

Catalysts	Electrolyte	Potential @ 1000 mA cm^{-2} (mV),	Reference
MoS_2-Mo_2C	KOH	446	This work
Pt/C	KOH	709	This work
Pt foil	KOH	998	This work
Pt mesh	KOH	973	This work
20 wt% Pt/C	KOH	415	22
Pt mesh	KOH	950	22
Pt foil	KOH	1180	22
Pt foil	KOH	822	20
Pt/C/Nafion	KOH	900	20

Table S2. The comparison of the HER activity of Mo-based electrocatalysts measured in 1 M KOH electrolyte.

Catalysts	η_{onset} (mV)	η_{10} (mV)	Reference
MoS_2-Mo_2C	**~0**	**56**	**This work**
NiO@1T-MoS_2	~0	46	Nat. Commun. 2019, 10, 982
C–MoS_2	~0	45	Nat. Commun. 2019, 10, 1217
MoS_2/Co_9S_8/Ni_3S_2/Ni	~20	113	J. Am. Chem. Soc. 2019
Ni/Mo_2C-NCNFs	29	143	Adv. Energy Mater. 2019, 9, 1803185
Mo_2N-Mo_2C/HGr	18	154	Adv. Mater. 2018, 30, 1704156
N-Mo_2C NSs	69	140	ACS Nano 2017, 11, 12509
Co-Mo_2C	25	118	Adv. Funct. Mater. 2016, 26, 5590