Electronic Supplementary Information

Construction of MoO_2/MoS_2 heterojunction on carbon nanotubes as high-efficiency electrocatalysts for H_2 production

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Experimental

Materials and reagents

Chemical reagents including Molybdenum chloride ($MoCl_5$), thiourea (CH_4N_2S) and Molybdenum Trioxide (MoO_3) were analytically pure and not further processed. Carbon nanotube (CNT) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Nafion (5 wt%) was purchased from Sigma-Aldrich. Pt and glassy carbon electrodes were purchased from Tianjin Aidahengsheng Technology. Co. Ltd.

Synthesis of MoS_2@CNT

The MoS_2@CNT was synthesized by a sol-gel process according to our previous work with some modifications [1]. Firstly, 136 mg molybdenum chloride ($MoCl_5$) and 228 mg thiourea (CH_4N_2S) were mixed in a 50 mL beaker. Excessive ethanol was slowly added into the beaker and ultrasonication for 10 min to form homogenous solution, then 96 mg CNT was dispersed in the solution and ultrasonication for 30 min to form a uniform suspension. The gel-like precursor powders were obtained by drying the suspension, and transferred into a corundum boat and heated in a quartz tube furnace for 2 h under argon gas (150 sccm) flow at 500 °C. Afterwards, the product was cooled to room temperature under the protection of argon gas and samples were collected from the quartz tube. The resulting product was named MoS_2@CNT.

Synthesis of MoO_2/MoS_2@CNT

The MoO_2/MoS_2@CNT was synthesized by an evaporation crystallization and hydrogen thermal reduction method. Firstly, 70 mg the above obtained MoS_2@CNT was dispersed in 50 mL MoO_3 saturated solution and magnetically stirring for 30 min to form a uniform suspension. The black precursor powders (referred as MoO_3/MoS_2@CNT) were formed after drying and transferred to a quartz tube furnace for 2 h under Ar/H_2 (100/10 sccm) flow at 600 °C. After that, the product was cooled to room temperature under ambient Ar/H_2 and collected from the quartz tube. The

resulting product was named MoO_2/MoS_2@CNT.

Materials characterizations

The samples were characterized by field emission scanning electron microscope (FESEM, JSM-7610F), transmission electron microscope (TEM; FEI, Tecnai G2), X-ray diffraction (XRD, Bruker D8 ADVANCE with a Cu-Ka source), X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific, ESCALAB 250).

Electrochemical measurements

All electrochemical measurements were performed on a CHI 604E electrochemical workstation using a three-electrode system at room temperature. The system consists of a glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode, Pt wire electrode as counter and Ag/AgCl (3.5 M KCl) as reference electrode, respectively. For the glassy carbon (GC) electrode modified by catalysts as the working electrode, 2.0 mg of catalyst powder was ultrasonically dispersed in 500 μL 4:1 (v/v) water/ ethanol mixed solvents, combined with 30 mL Nafion solution (5 wt% Sigma-Aldrich), the mixed solution was sonicated for 30 min to form the catalyst ink. Subsequently, 5 μL of the above catalyst ink was dropped onto the polished GCE surface. The polarization curves were obtained by linear sweep voltammetry (LSV) at a scan r rate of 10 mV/s. All of the potentials were calibrated to a reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) was conducted between -0.4 and 0.1 V vs RHE at 50 mV s^{-1} to study the cycling stability. The Nyquist plots were measured with frequencies ranging from 10^{-2} to 10^{6} Hz with an AC voltage amplitude of 5 mV at an overpotential of 400 mV. The estimation of the effective active surface area of the electrocatalysts was carried out according to the literature by cyclic voltammograms with various scan rates (20-100 mV s^{-1}) in the 0.1-0.2 V vs. RHE region.

Density functional theory calculations

All calculations were conducted by Vienna Ab initio Simulation Package (VASP) based on the density functional theory (DFT). The exchange-correlation potential is described by using the generalized gradient approximation of Perdew-Burke-

Ernzerhof (GGA-PBE). The projector augmented-wave (PAW) method is employed to treat interactions between ion cores and valence electrons. The plane-wave cutoff energy was fixed to 400 eV. Given structural models were relaxed until the Hellmann-Feynman forces smaller than -0.02 eV/Å and the change in energy smaller than 10^{-5} eV was attained. During the relaxation, the Brillouin zone was represented by a Γ centered k-point grid of 3×3×1. Grimme's DFT-D3 methodology was used to describe the dispersion interactions among all the atoms in adsorption models.

The adsorption energy (ΔE_{*H}) of H is calculated by: $\Delta E_{*H}=E_{*H}-E_{*}-1/2E_{H2}$, where E_{*H}, E_{*}, and E_{H2} are the energies of hydrogen adsorbed on catalyst, isolated catalyst, and hydrogen gas molecule, respectively.

The catalytic activity for HER could be evaluated by the hydrogen adsorption free energy of ΔG_{H*}: $\Delta G_{H*} = \Delta E_{*H} - \Delta E_{ZPE} - T\Delta S_{H}$, Where ΔE_{ZPE} is the zero-point energy change between the adsorbed state of the catalyst and gas phase state. ΔS_{H} is the difference in entropy and T is taken as 298.15 K.

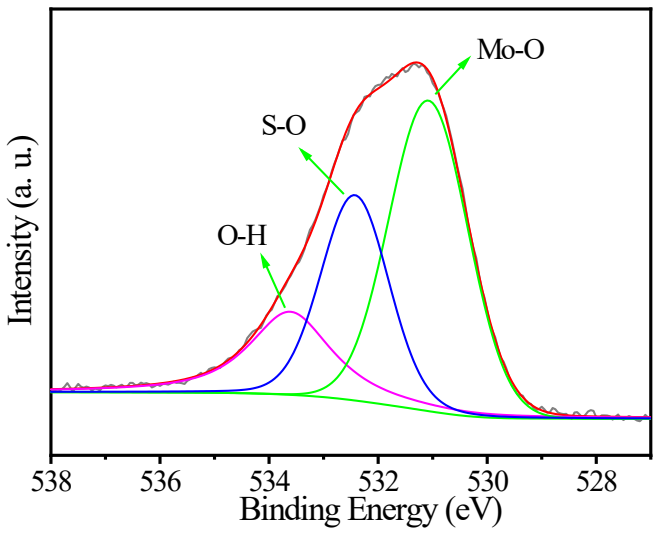

Fig. S1. High resolution XPS spectrum of O 1s of MoO_2/MoS_2@CNT.

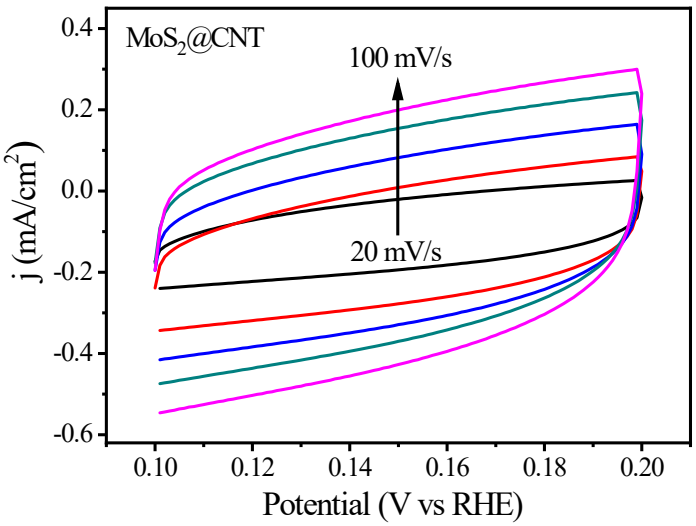

Fig. S2. (a, b) Electrochemical cyclic voltammogram of MoS_2@CNT at different potential scanning rates. The scan rates are 20, 40, 60, 80 and 100 mV/s. The selected potential range where no faradic current was observed is 0.10 to 0.2 V vs RHE.

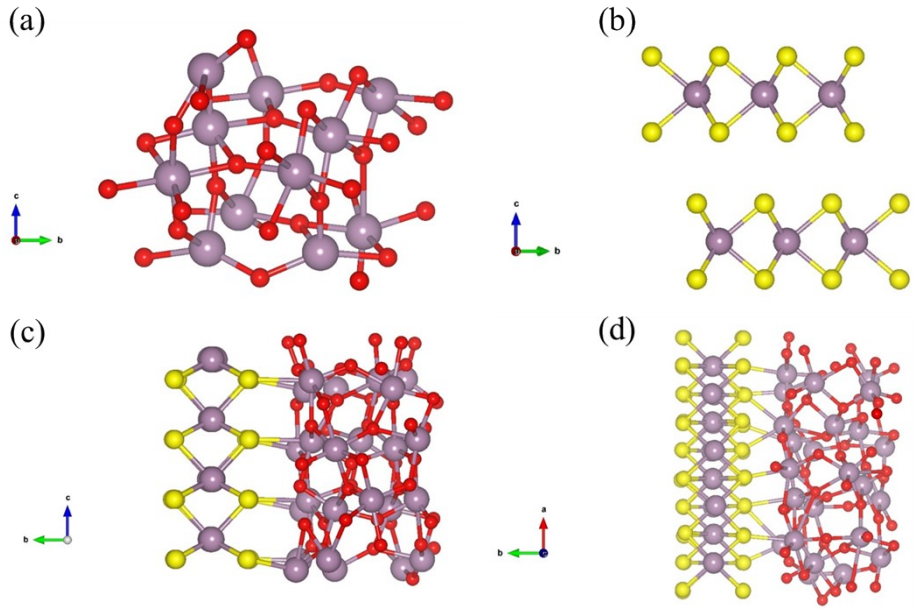

Fig. S3. Geometry-optimized models of MoO_2, MoS_2 and MoO_2/MoS_2 heterostructure. (a) MoO_2 (-211); (b) MoS_2 (002); (c) MoO_2/MoS_2 heterostructure (layer-side views); (d) MoO_2/MoS_2 heterostructure (layer-top views). The atoms in red lilac, yellow and red colors represent Mo, S, and O element, respectively.

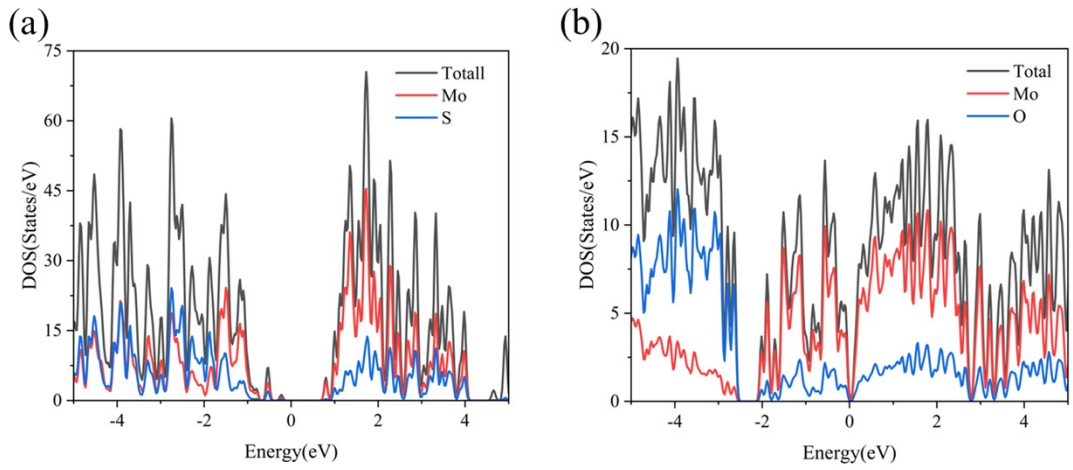

Fig. S4. Total density of states for MoS_2 (a) and MoO_2 (b).

Table S1. Comparison of electrocatalytic performance in acidic media for $MoO_2/MoSe_2$@CNT with other MoS_2-based and MoO_2-based electrocatalysts.

catalyst	η(mV) for j=10 mA cm^{-2}	Tafel slope (mV dec^{-1})	References
MoS_2	-330	110	Electrochim. Acta, 2019, 300, 45-52.
MoS_2	-330.8	101.1	ACS Appl. Energy Mater., 2019, 2, 5799-5808.
MoO_2	-477	192	ACS Appl. Nano Mater. 2023, 6, 13926-13934.
MoO_2	-233	123	Nanotechnology, 28, 465404.
MoS_2/MoO_2/MF	-154	52.1	Int. J. Hydrogen Energ., 2020, 45, 17422-17433.
MoS_2-MoO_2/CW	-148	86.7	ACS Appl. Nano Mater. 2022, 5, 8175-8183.
MoS_2/MoO_2	-380	113	Mater. Res. Lett., 2019, 7, 275-281.
$MoO_2/MoSe_2$	-167	68	Nanotechnology, 28, 465404.
SnS_2/MoS_2	-240	65	Electrochim. Acta, 2019, 300, 45-52.
MoS_2@Bi_2Se_3	-208	57	J. Catal., 2020, 381, 590-598
MoO_2/MoS_2@CNT	-158	70	This work

MF: Mo foil

CW: carbonized wood

CNT: carbon nanotubes

References

[1] Xianpei Ren, Qingbo Wei, Fei Wu, Yonghua Wang, Liangjun Zhao, CNT/VS_2-MoS_2 with multi-interface structure for improved hydrogen evolution reaction, *Chem. Commun.*, 2021, **57**, 2531-2534.