2D Thin Sheet Heterostructures of MoS$_2$ on MoSe$_2$ as Efficient Electrocatalyst for Hydrogen Evolution Reaction in Wide pH Condition

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Preparation of working electrode: To prepare the Ink of MoSe$_2$-ns, MoSe$_2$-ts MoS$_2$-ns, MoS$_2$-ts, MoSe$_2$-ts@MoS$_2$-ts heterostructure. 5 mg synthesized catalyst was dispersed in 30 µL of nafion and 300 µL of Isopropanol. Here isopropanol used as a dispersing solvent and nafion function as the binder. Then for uniform dispersion whole dispersion was sonicated 30 min. 3 µL dispersion was drop casted carefully on GC electrode having diameter 3 mm which leads catalyst loading 0.63 mg/cm$^2$.

Electrochemical measurement:

Hydrogen evolution reaction were carried out in a three-electrode system. In this case calomel electrode used as a reference electrode, catalyst drop casted glassy carbon electrode as the working electrode and graphite electrode used as a counter electrode. 10 mL of different pH medium was used as electrolyte which includes 0.5 M H$_2$SO$_4$, 1 M KOH, pH~7 phosphate buffer, and 3.5 wt% saline water. All the electrochemical data was recorded in CH Instrument (CHI604E) at 25 °C. The linear-sweep voltammogram of MoSe$_2$-ns, MoSe$_2$-ts MoS$_2$-ns, MoS$_2$-ts, MoSe$_2$-ts@MoS$_2$-ts were obtained in a wide pH condition with a scan rate of 5 mV/S.

Electrochemical Impedance Spectroscopy:

Electrochemical impedance measurement was also performed in a three-electrode system. Onset potentials of different materials were chosen as the performing bias for
this measurement with the sweeping of frequency from 50 KHz to 1 Hz with a 10 mV AC dither.

**Characterization of Materials:**

Rigaku Mini Flex II diffractometer with Cu Kα radiation was utilized to monitor the powder X-ray diffraction pattern, with a scanning rate of 2° per min. Microscope version, XT Platform version, XT UI version, Modal- "APREO S" FE-SEM was used to investigate the morphology of the synthesized MoSe₂-nanostructures (MoSe₂-nanostructures), MoSe₂-tetrapods (MoSe₂-tetrapods), MoS₂-nanostructures (MoS₂-nanostructures), MoS₂-tetrapods (MoS₂-tetrapods), MoSe₂-tetrapods@MoS₂-tetrapods was investigated. EDS Analysis was carried out for these samples using the EDS attachment with FESEM which is Aztec (software), X-MaxN, NS: 77887 (Detector) of Oxford company. Raman analysis was carried out using HORIBA SCXI Raman instrument (model no LabRAM HR EVO). The detector is thermoelectrically cooled charged coupled device (CCD) detector of 576×384 pixels. Raman analysis is carried out upon excitation with 532 nm laser power. Using transmission electron microscopy (operated with a Bruker microscope) morphology and crystallinity was determined of as synthesized catalysts. XPS (X-ray photoelectron spectroscopy) computation was carried out by Omicron EA 125 source using Al Kα radiation having energy 1486.7 eV. During the course of measurement, base pressure was maintained < 10⁻⁹ mbar in the UHV.

**Calculation Method:**

Details for the calculations of mass activity is given below. The mass activity value (A/g) was calculated from the catalyst loading and the observed current density (mA/cm²geo) at a potential of -0.4 V vs. RHE.

Mass activity = observed current density at a fixed potential / catalyst loading

Specific activity = observed current at a fixed potential / electrochemically active surface area
Figure S1: PXRD of (a) MoSe$_2$-ns and MoSe$_2$-ts, and (b) MoS$_2$-ns and MoS$_2$-ts respectively.
Figure S2: Raman spectra of (a) MoS$_2$-ns and MoS$_2$-ts, and (b) MoSe$_2$-ns and MoSe$_2$-ts respectively.
Figure S3: XPS spectra of MoS$_2$-ts and MoSe$_2$-ts, respectively (a) Survey XPS spectrum of MoS$_2$-ts, high resolution XPS spectrum of (b) Mo 3d, (c) S 2p (d) Survey XPS spectrum of MoSe$_2$-ts, high resolution XPS spectrum of (e) Mo 3d, (f) Se 3d.
Figure S4: FESEM and TEM images (a), (b), of MoS$_2$-ns respectively and (c), (d) of MoS$_2$-ts respectively.
Figure S5: FESEM and TEM images (a), (b), of MoSe$_2$-ns respectively and (c), (d) of MoSe$_2$-ts respectively.
Figure S6: EDS mapping and EDS spectra of the as-synthesized MoS$_2$-ts
Figure S7: EDS mapping and EDS spectra of the as-synthesized MoSe$_2$-ts
Figure S8: EDS mapping and EDS spectra of the as-synthesized MoSe$_2$-ts@MoS$_2$-ts heterostructure.
Figure S9: Comparative polarization curves of MoS$_2$-ts and ns (a) and MoSe$_2$-ts and ns (b).
Figure S10: Comparative polarization curves of MoS$_2$-ts MoSe$_2$-ts and MoS$_2$@MoSe$_2$ in different pH conditions (a) pH-7 buffer, (b) 3.5% saline water, (c) 1 M KOH and, (d) comparative polarization curve of MoS$_2$@MoSe$_2$-heterostructure and MoS$_2$@MoSe$_2$-PM (physical mixture).
Figure S11: Cyclic voltammetry curves of (a) MoSe₂-ts, (b) MoS₂-ts, (c) MoSe₂-ts@MoS₂-ts recorded in 0.5 M H₂SO₄ at scan rates of 40, 80, 120, 160 and 200 mV/s and Plot of (c) capacitive current at 0.3605 V vs. RHE with scan rate.
Figure S12: Cyclic voltammetry curves of (a, b, c) MoSe\textsubscript{2}-ts@MoS\textsubscript{2}-ts-a, b, d recorded in 0.5 M H\textsubscript{2}SO\textsubscript{4} at scan rates of 40, 80, 120, 160 and 200 mV/s and Plot of (d) capacitive current at 0.3605 V vs. RHE with scan rate.
Figure S13: (a) Chronoamperometric study for 24 h, (b) 1000 cycle consecutive run of MoSe$_2$-ts@MoS$_2$-ts to study the stability.
Figure S14: FESEM image of MoS$_2$@MoSe$_2$ after electrocatalysis.
Figure S15: EDS line mapping of the as-synthesized MoSe$_2$-ts@MoS$_2$-ts after electrocatalysis.
Table S1: Data Comparison for electrocatalytic activity of different reported catalysts, closely relating to the present work.

<table>
<thead>
<tr>
<th>S. N.</th>
<th>Electrocatalyst</th>
<th>Electrode reaction</th>
<th>Electrolyte</th>
<th>Potential (RHE) at 10 mA/cm² Current</th>
<th>Tafel slope</th>
<th>Reference</th>
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<tr>
<td>1</td>
<td>SWCNTs/MoSe₂</td>
<td>HER</td>
<td>0.5 M H₂SO₄</td>
<td>-100 mV</td>
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<td>38</td>
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<td>CoSe₂/MoSe₂</td>
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<td>1 M KOH</td>
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<td>3</td>
<td>Superstructured MoS₂ and Graphitic Nanocarbon Hybrid</td>
<td>HER</td>
<td>0.5 M H₂SO₄</td>
<td>-195 mV (over potential)</td>
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<td>NiCo₂O₄@MoS₂</td>
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<td>Doped-MoSe₂ Nanoflakes/3d Metal Oxide–Hydr(Oxy)Oxides</td>
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<td>MoS₂/CoSe₂</td>
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<td>MoS₂/NiCoS Heterostructures</td>
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<td>186 mV</td>
<td>71</td>
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This work
References:


