## Supporting Information for Phase Selective Hydrothermal Synthesis of 1T MoS<sub>2</sub> and Janus 1T MoSSe for Hydrogen Evolution Reaction

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<sup>a</sup> Schematic description of the solvothermal synthesis procedure followed for the preparation of 1T-MoSSe. The molar concentration of the precursors and the parameters for solvothermal reaction (time and temperature) dictate the selective 1T phase growth of MoSSe.

Scheme 1 describes the solvothermal synthesis to produce 1T phase of MoSSe. The growth of metastable 1T-MoSSe is highly sensitive to reaction parameters in the solvothermal process. Key factors, including precursor molar concentrations, solvent composition, reaction temperature (200 °C), and duration (24 hours), were optimized to selectively stabilize the 1T phase over the thermodynamically stable 2H phase. Precise precursor ratios ensured sufficient molybdenum, sulfur, and selenium availability, while an NMP-based solvent mixture stabilized precursors and facilitated Mo<sup>6+</sup> reduction, aided by hydrazine hydrate. Optimal thermal and temporal conditions promoted the 1T phase while avoiding decomposition or 2H phase formation. The resulting 1T-MoSSe demonstrated metallic conductivity and abundant active sites, ideal for electro-catalytic applications like HER.



**Fig. S1.** The FESEM-EDX data of the MoSSe sample showing the presence of Mo, S and Se inside the material. The insets depicts the elemental mapping of (a) all the elements, (b) Se, (c) Mo, and (d) S with the molar ratio of Se: Mo: S = 33: 29: 38 %. The inset (e) shows the area which was chosen for the FESEM-EDX investigations.



Fig. S2. (a - c) TEM images of 1T-MoSSe.



**Fig. S3.** LSV curves and their respective overpotentials at 10 mA/cm<sup>2</sup> for 1T-MoSSe catalyst for different batches 1, 2, and 3, respectively.



Fig. S4. Chronoamperometry graph of 1T-MoSSe at -0.6 V for 5 h.

## **Computational Method**

All the calculations were adopted within the context of periodic boundary conditions by density functional theory (DFT) methods as implemented in Vienna Ab initio Simulation Package (VASP) code with the generalized gradient approximation (GGA)-based Perdew-Burke-Ernzerhof (PBE) functional.<sup>1-3</sup> Self-consistent field (SCF) calculations were performed with the force and energy tolerance of 0.02 eV Å<sup>-1</sup> and 10<sup>-5</sup> eV, respectively. The atomic structures were visualized by the VESTA code.<sup>4</sup> To investigate the HER activity for 2H-MoS<sub>2</sub>, 1T-MoS<sub>2</sub>, MoSSe, and MoSeS, a 3 X 3 MoS<sub>2</sub> monolayer supercell systems were built from experimental bulk lattice constants. This supercell is optimized and used for further calculations. The k-points and cutoff energy were set as  $3 \times 3 \times 1$  and 450 eV. The Gibbs free energy ( $\Delta G_H$ ) of hydrogen adsorption on each surface can be calculated by:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H,$$

In which  $\Delta E_H$  is the chemisorption energy of the H atom on the surface.  $\Delta E_{ZPE}$  and  $\Delta S_H$  are the difference in zero-point energy and entropy between gas phase and the adsorbed state,

respectively. In our calculation for the H adsorption on the surfaces,  $\Delta E_{ZPE} - T\Delta S_H$  value is considered to be 0.25 eV according to the previous calculation of MoS<sub>2</sub>.<sup>5</sup>

**Table S1:** The values of the Bond lengths and bond angles derived from the DFT Results for all the materials in two different conditions (with and without Hydrogen Adsorption).

Material	2H-MoS <sub>2</sub>		1T-MoS <sub>2</sub>		1T-MoSSe		1T-MoSeS	
Bond length with 'H' atom	1.41 Å		1.35 Å		1.36 Å		1.49 Å (Se)	
Conditions	Without H	With H	Without H	With H	Without H	With H	Without H	With H
Mo (1) – S (1) Bond Length	2.41 Å	2.39 Å	2.43 Å	2.45 Å	2.41 Å	2.43 Å	2.57 Å (Se)	2.53 Å (Se)
S (1) – Mo (2) Bond Length	2.41 Å	2.39 Å	2.43 Å	2.45 Å	2.41 Å	2.43 Å	2.57 Å (Se)	2.53 Å (Se)
Mo (2) – S (2) Bond Length	2.41 Å	2.42 Å	2.43 Å	2.52 Å	2.57 Å (Se)	2.65 Å (Se)	2.41 Å	2.52 Å
S (2) – Mo (1) Bond Length	2.41 Å	2.42 Å	2.43 Å	2.52 Å	2.57 Å (Se)	2.65 Å (Se)	2.41 Å	2.52 Å
Mo (1) – S(1) – Mo(2) Angle	82.55 °	82.98 °	82.55 °	99.83 °	82.57 °	101.27 °	76.40 ° (Se)	96.16 ° (Se)
Mo (2) – S(2) – Mo(1) Angle	82.55 °	81.69 °	82.55 °	95.89 °	76.40 ° (Se)	89.98 ° (Se)	82.58 °	96.34 °

(Se) – Bond with Se

## References

- 1 G. Kresse, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 2 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.
- 3 P. E. Blöchl, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 50, 17953–17979.
- 4 K. Momma and F. Izumi, J. Appl. Cryst., 2008, 41, 653-658.
- 5 Q. Tang and D.-E. Jiang, ACS Catal., 2016, 6, 4953–4961.