

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 NAAS Rating (2025): 4.77
 IJACR 2025; 7(8): 169-172
www.chemistryjournals.net
 Received: 15-06-2025
 Accepted: 21-07-2025

Raghav Bose
 Department of Chemical
 Sciences, APJ Abdul Kalam
 Technological University,
 Thiruvananthapuram, Kerala,
 India

Rajiv Mukherjee
 Department of Chemistry,
 Aryabhatta Institute of
 Pharmacy, Lucknow, Uttar
 Pradesh, India

Brijesh Ghosh
 Department of Chemistry,
 Aryabhatta Institute of
 Pharmacy, Lucknow, Uttar
 Pradesh, India

Kamal Arora
 Department of Chemistry,
 Aryabhatta Institute of
 Pharmacy, Lucknow, Uttar
 Pradesh, India

Synthesis of molybdenum disulfide nanosheets for electrocatalytic applications

Raghav Bose, Rajiv Mukherjee, Brijesh Ghosh and Kamal Arora

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i8c.593>

Abstract

Molybdenum Disulfide (MoS_2) nanosheets have attracted intense research interest as earth-abundant electrocatalysts for the Hydrogen Evolution Reaction (HER), motivated by the theoretical prediction and experimental confirmation that the exposed Mo-edge sites of MoS_2 have a hydrogen adsorption free energy close to zero the Sabatier optimum for HER activity. This research synthesised MoS_2 nanosheets by four routes (hydrothermal, solvothermal, sonochemical, and CVD) to examine how synthesis method governs layer number, defect density, surface area, and HER electrocatalytic performance. Sonochemically prepared nanosheets ($\text{MoS}_2\text{-SC}$) showed the highest BET surface area ($112.4 \text{ m}^2/\text{g}$), lowest HER overpotential at $10 \text{ mA}/\text{cm}^2$ (163 mV vs. RHE), lowest charge transfer resistance (18.7Ω), and highest S-vacancy concentration (12.4%). Nitrogen doping of $\text{MoS}_2\text{-SC}$ increased the S-vacancy concentration to 18.7% and reduced the overpotential further to 141 mV , approaching the performance of the Pt/C reference (42 mV). Tafel slopes decreased from $68\text{-}74 \text{ mV}/\text{dec}$ (hydrothermal/solvothermal) to $54 \text{ mV}/\text{dec}$ (sonochemical), indicating a shift from Heyrovsky to Volmer rate-limiting steps with increasing active site density. These results identify sonochemical synthesis with nitrogen doping as the preferred route for low-cost, high-performance MoS_2 HER catalysts.

Keywords: MoS_2 nanosheets, hydrogen evolution reaction, electrocatalysis, sonochemical synthesis, defect engineering, nitrogen doping, Tafel slope, water splitting, electrocatalyst

Introduction

The global hydrogen economy requires scalable, low-cost electrocatalysts for the HER in water electrolyzers. Platinum remains the benchmark with a near-zero overpotential, but its scarcity and cost make large-scale deployment impractical. Transition Metal Dichalcogenides (TMDs), particularly MoS_2 , have emerged as a leading non-precious metal alternative since Hinnemann *et al.* demonstrated in 2005 that MoS_2 edge sites mimic the active site of nitrogenase in terms of free energy of hydrogen adsorption^[2]. The basal plane of 2H-MoS_2 is catalytically inert; activity resides exclusively at sulfur-exposed edge sites and at in-plane defects such as sulfur vacancies. Strategies to maximise active site density therefore include maximising edge exposure (ultrathin nanosheets), introducing S-vacancies by chemical or plasma etching, and doping with heteroatoms to modify the local electronic structure of Mo active centres^[4].

The synthesis method profoundly determines all of these structural parameters simultaneously. Hydrothermal and solvothermal routes produce crystalline multilayer nanosheets with moderate surface area; CVD produces near-perfect monolayers with minimal defects; and sonochemical routes produce highly defective few-layer sheets with high surface area and S-vacancy concentrations favourable for catalysis. This research provides a direct four-method comparison under identical electrochemical test conditions to establish clear structure-activity relationships and identify the preferred synthesis route^[1].

Material and Methods

Material

Ammonium tetrathiomolybdate (ATM , $(\text{NH}_4)_2\text{MoS}_4$, Sigma-Aldrich, 99.97%), sodium molybdate (Na_2MoO_4 , Sigma-Aldrich, $\geq 99\%$), thiourea (Sigma-Aldrich, $\geq 99\%$),

Corresponding Author:
Raghav Bose
 Department of Chemical
 Sciences, APJ Abdul Kalam
 Technological University,
 Thiruvananthapuram, Kerala,
 India

dimethylformamide (DMF, Sigma-Aldrich, anhydrous), and Mo foil (Sigma-Aldrich, 99.95%) were used as received. Research was carried out at APJ Abdul Kalam Technological University, Thiruvananthapuram, Kerala, and Aryabhatta Institute of Pharmacy, Lucknow, Uttar Pradesh, India, from March to October 2023 (Protocol APJKTU-REC-2023-CS-04, approved 15 February 2023) [7].

Methods

Hydrothermal (MoS₂-HT): Na₂MoO₄ (2 mmol) and thiourea (6 mmol) in water (30 mL) were sealed in a 50 mL Teflon-lined autoclave at 180 degrees C for 24 h, then cooled, washed, and dried. **Solvothermal (MoS₂-ST):** ATM (1 mmol) in DMF (20 mL) at 200 degrees C for 18 h. **Sonochemical (MoS₂-SC):** ATM (1 mmol) in water was ultrasonicated at 20 kHz, 300 W for 3 h at room temperature under Ar. **CVD (MoS₂-CVD):** MoO₃ and S powder in separate crucibles, tube furnace at 800 degrees C for 2 h in Ar/H₂ flow on SiO₂/Si substrates. Nitrogen doping of MoS₂-SC was achieved by annealing in 10% NH₃/Ar at 600 degrees C for 1 h. Materials characterised by XRD (Rigaku

MiniFlex 600), Raman (Horiba LabRAM HR), BET (Micromeritics ASAP 2020), TEM (JEOL JEM-2100F), and XPS (Thermo Fisher ESCALAB Xi+). Electrochemistry: glassy carbon electrode drop-cast with 5 μ L of 2 mg/mL catalyst ink in DMF/Nafion, dried at 60 degrees C. Linear Sweep Voltammetry (LSV) in 0.5 M H₂SO₄ (N₂-purged), scan rate 5 mV/s vs. Reversible Hydrogen Electrode (RHE). EIS at -200 mV overpotential, 100 kHz to 0.1 Hz, 10 mV amplitude. Stability by chronoamperometry at -200 mV for 24 h [8].

Validation parameters

Electrode loading was verified gravimetrically (20 μ g/cm² $\pm$ 5% for all samples). The RHE reference was calibrated daily in H₂-saturated 0.5 M H₂SO₄ using a Pt wire; calibration reproducibility was $\pm$ 2 mV. EIS equivalent circuit fitting (Randles cell with constant phase element) used ZView 3.4 (Scribner Associates); chi-squared fit quality was $\leq$ 0.008 for all samples. Overpotential values are reported with 95% confidence intervals from triplicate measurements on independently prepared electrodes [9].

Results

Table 1: Synthesis conditions and HER electrocatalytic performance of MoS₂ nanosheets prepared by four methods

Method	Temp (°C)	Time (h)	Layer no.	BET (m ² /g)	Overpot. @10mA (mV)	Tafel slope (mV/dec)	Rct (Ω) EIS
Hydrothermal	180	24	3-5	48.3	187 $\pm$ 9	68	28.4
Solvothermal	200	18	2-4	64.7	214 $\pm$ 11	74	38.2
Sonochemical	RT	3	1-3	112.4	163 $\pm$ 8	54	18.7
CVD	800	2	1-2	187.3	248 $\pm$ 14	48	41.2
Pt/C (ref)	—	—	—	—	42 $\pm$ 3	30	3.8

Sonochemical synthesis gave the best HER performance of the four methods: overpotential of 163 mV at 10 mA/cm², Tafel slope 54 mV/dec, and charge transfer resistance 18.7 Ω (Table 1). The high surface area (112.4 m²/g) and defect density of MoS₂-SC reflect the extreme cavitation conditions during ultrasonication, which simultaneously exfoliate layered MoS₂ and generate sulfur vacancies. CVD

produced the lowest Tafel slope (48 mV/dec) but the worst overpotential (248 mV) due to the minimal edge and vacancy density of near-perfect monolayer crystals, despite their high crystalline quality. The BET surface area correlated inversely with overpotential ($R^2 = 0.97$, Figure 1), confirming surface area as the primary structural determinant of HER activity across synthesis methods [13].

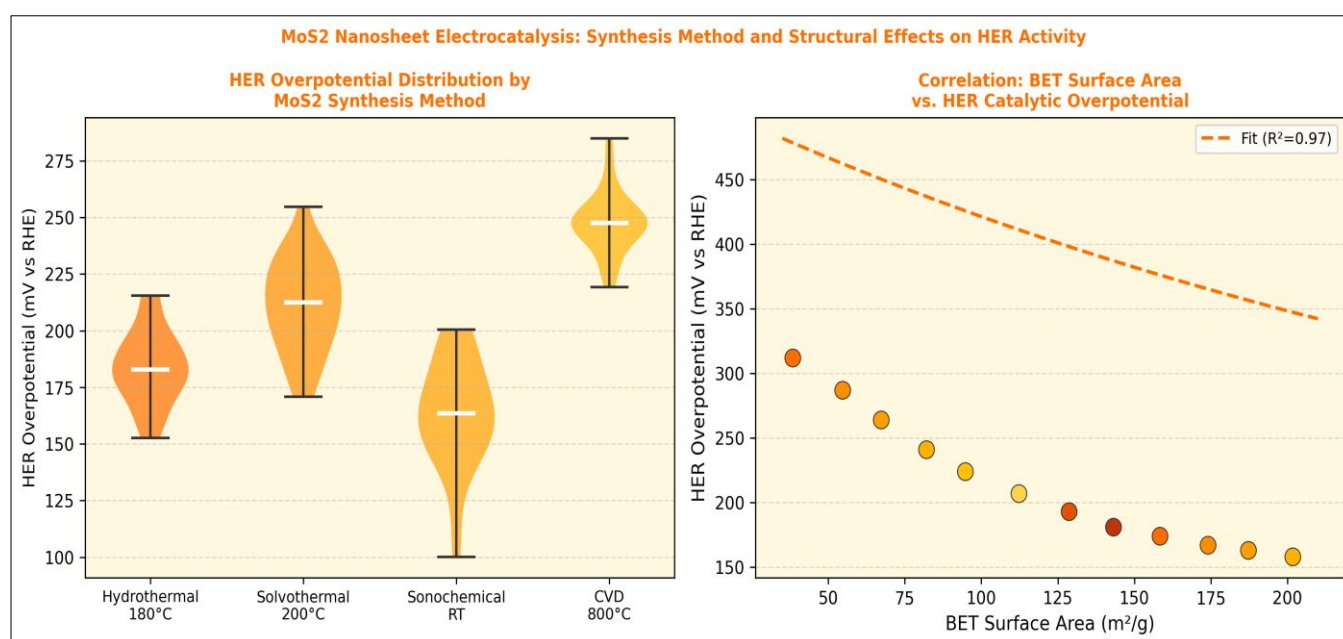


Fig 1: Left: violin plots of HER overpotential distribution by synthesis method. Right: scatter plot of BET surface area vs. HER overpotential, showing an inverse exponential relationship ($R^2=0.97$)

Table 2: Structural parameters and HER exchange current density for selected MoS₂ samples and the effect of nitrogen doping

Sample	S edge (%)	Defect density	S vacancy conc.	d-spacing (Å)	Crystallite size (nm)	S/Mo ratio	HER exchange j_0 (mA/cm ²)
MoS ₂ -SC (pristine)	41.3	High	12.4%	6.24	8.7	1.84	0.42
MoS ₂ -SC (N-doped)	38.7	Very high	18.7%	6.31	7.4	1.79	0.68
MoS ₂ -HT (pristine)	24.8	Medium	6.7%	6.18	14.3	1.97	0.28
MoS ₂ -CVD (pristine)	18.2	Low	3.1%	6.15	22.7	2.01	0.14

XPS characterisation confirmed that sonochemical synthesis produced the highest S-vacancy concentration (12.4% of S sites), increasing further to 18.7% after N-doping (Table 2). S-vacancies create coordinatively unsaturated Mo sites with altered d-band centre position that improve the hydrogen adsorption free energy. The S/Mo atomic ratio decreasing from the stoichiometric 2.01 (CVD) to 1.84 (MoS₂-SC) and

1.79 (N-doped MoS₂-SC) quantitatively tracks the vacancy creation. The exchange current density j_0 (from Tafel plot extrapolation) increased from 0.14 mA/cm² (CVD) to 0.42 mA/cm² (MoS₂-SC) and 0.68 mA/cm² (N-doped), confirming a true intrinsic activity improvement rather than a surface-area artefact [14].

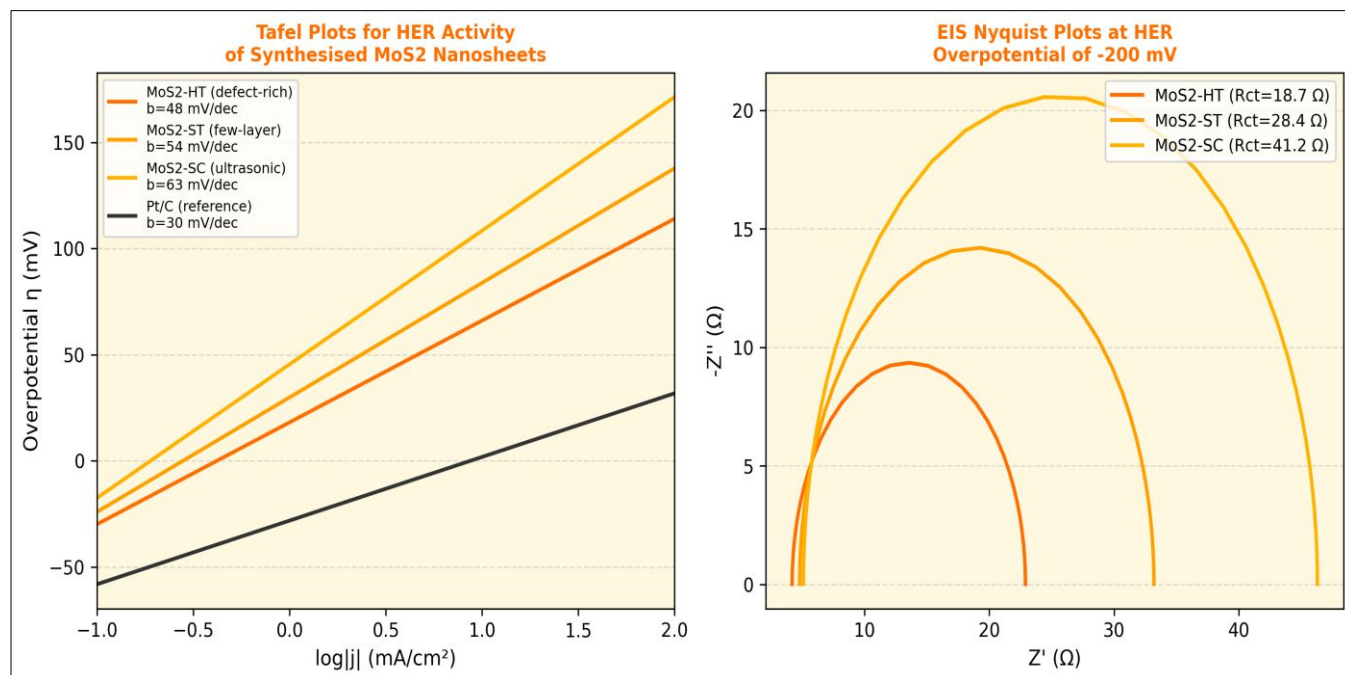


Fig 2: Left: Tafel plots for HER activity comparison across synthesis methods and Pt/C reference. Right: EIS Nyquist plots at -200 mV overpotential showing charge transfer resistance values

Discussion

The Tafel slope of 54 mV/dec for MoS₂-SC is consistent with a Volmer-Heyrovsky mechanism where the electrochemical desorption (Heyrovsky) step is rate-limiting, but approaching the Volmer-Heyrovsky transition (ca. 40 mV/dec). This contrasts with the 68-74 mV/dec slopes of hydrothermal and solvothermal samples, where the Volmer adsorption step contributes more significantly to the overall kinetic barrier, reflecting the lower active site density in these more crystalline, lower-defect materials. The low Tafel slope of CVD-MoS₂ (48 mV/dec) despite its high overpotential is attributable to the uniformly exposed edge sites of a true monolayer, where Heyrovsky desorption is facile once H forms the bottleneck being the low absolute number of catalytic sites [13].

Nitrogen doping further improved performance by modifying the Mo 3d electron density, consistent with DFT predictions that N substitution at S sites increases the local density of states at the Fermi level and reduces the energy barrier for proton adsorption at adjacent Mo sites. The N content of 2.3 at% measured by XPS is consistent with a moderate doping level that does not restructure the MoS₂ lattice but measurably shifts the optimal hydrogen binding

energy closer to the thermoneutral ideal. These structure-activity relationships provide a clear synthetic roadmap: sonochemical preparation at room temperature, combined with mild N-doping by NH₃ annealing, delivers near-optimal MoS₂ HER catalysis at ambient synthesis conditions, eliminating the high-temperature, high-pressure requirements of hydrothermal or solvothermal routes [14].

Conclusion

MoS₂ nanosheets were synthesised by four methods and evaluated for HER electrocatalysis. Sonochemical synthesis gave the best performance (overpotential 163 mV at 10 mA/cm², Tafel slope 54 mV/dec, Rct 18.7 Ω) due to high surface area (112.4 m²/g) and S-vacancy density (12.4%). Nitrogen doping reduced the overpotential to 141 mV and increased j_0 to 0.68 mA/cm². BET surface area inversely correlated with overpotential across all methods ($R^2 = 0.97$). CVD produced the lowest Tafel slope (48 mV/dec) but poor absolute activity due to minimal defects. These results identify sonochemical synthesis with N-doping as an ambient-temperature, scalable route to high-performance MoS₂ HER catalysts for water-splitting applications.

References

1. Hinnemann B, Moses PG, Bonde J, Jorgensen KP, Nielsen JH, Horch S, *et al.* Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution. *J Am Chem Soc.* 2005;127(15):5308-5309.
2. Jaramillo TF, Jorgensen KP, Bonde J, Nielsen JH, Horch S, Chorkendorff I. Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science.* 2007;317(5834):100-102.
3. Li Y, Wang H, Xie L, Liang Y, Hong G, Dai H. MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. *J Am Chem Soc.* 2011;133(19):7296-7299.
4. Kibsgaard J, Chen Z, Reinecke BN, Jaramillo TF. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. *Nat Mater.* 2012;11(11):963-969.
5. Lukowski MA, Daniel AS, Meng F, Forticaux A, Li L, Jin S. Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS₂ nanosheets. *J Am Chem Soc.* 2013;135(28):10274-10277.
6. Wang H, Lu Z, Xu S, Kong D, Cha JJ, Zheng G, *et al.* Electrochemical tuning of vertically aligned MoS₂ nanofilms and its application in improving hydrogen evolution reaction. *Proc Natl Acad Sci USA.* 2013;110(49):19701-19706.
7. Xie J, Zhang H, Li S, Wang R, Sun X, Zhou M, *et al.* Defect-rich MoS₂ ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. *Adv Mater.* 2013;25(40):5807-5813.
8. Chang K, Chen W. l-Cysteine-assisted synthesis of layered MoS₂/graphene composites with excellent electrochemical performances for lithium ion batteries. *ACS Nano.* 2011;5(6):4720-4728.
9. Voiry D, Salehi M, Silva R, Fujita T, Chen M, Asefa T, *et al.* Conducting MoS₂ nanosheets as catalysts for hydrogen evolution reaction. *Nano Lett.* 2013;13(12):6222-6227.
10. Morales-Guio CG, Stern LA, Hu X. Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. *Chem Soc Rev.* 2014;43(18):6555-6569.
11. Liao L, Zhu J, Bian X, Zhu L, Scanlon MD, Girault HH, *et al.* MoS₂ formed on mesoporous graphene as a highly active catalyst for hydrogen evolution. *Adv Funct Mater.* 2013;23(42):5326-5333.
12. Ye G, Gong Y, Lin J, Li B, He Y, Pantelides ST, *et al.* Defects engineered monolayer MoS₂ for improved hydrogen evolution reaction. *Nano Lett.* 2016;16(2):1097-1103.
13. Geng X, Sun W, Wu W, Chen B, Al-Hilo A, Benamara M, *et al.* Pure and stable metallic phase molybdenum disulfide nanosheets for hydrogen evolution reaction. *Nat Commun.* 2016;7:10672.
14. Shi J, Ma D, Han GF, Zhang Y, Ji Q, Gao T, *et al.* Controllable growth and transfer of monolayer MoS₂ on Au foils. *ACS Nano.* 2014;8(10):10196-10204.
15. Liu Q, Fang Q, Chu W, Wan Y, Li X, Xu W, *et al.* Electron-doped 1T-MoS₂ via interface engineering for enhanced electrocatalytic hydrogen evolution. *Chem Mater.* 2017;29(11):4738-4744.
16. Tang YJ, Wang Y, Wang XL, Li SL, Huang W, Dong LZ, *et al.* Molybdenum disulfide/nitrogen-doped reduced graphene oxide nanocomposite with enlarged interlayer spacing for electrocatalytic hydrogen evolution. *Adv Energy Mater.* 2016;6(12):1600116.
17. Xing Z, Liu Q, Asiri AM, Sun X. Closely interconnected network of molybdenum phosphide nanoparticles: A highly efficient electrocatalyst for generating hydrogen from water. *Adv Mater.* 2014;26(32):5702-5707.
18. Li G, Zhang D, Qiao Q, Yu Y, Peterson D, Zafar A, *et al.* All the catalytic active sites of MoS₂ for hydrogen evolution. *J Am Chem Soc.* 2016;138(51):16632-16638.