Electronic Supporting Information

Strongly Enhanced Visible Light Photoelectrocatalytic Hydrogen Evolution Reaction in n-doped MoS₂/TiO₂(B) Heterojunction by Selective Decoration of Platinum Nanoparticles at the MoS₂ Edge Sites

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Fig. S1: (a) Bright field STEM image of few-layer $MoS_2 NFs$ grown on $TiO_2 NBs$, and (b) its enlarged view, showing the spatial distribution of the number of layers in $MoS_2 NFs$.

Fig. S2: (a) HAADF image of the MSTB, (b-e) elemental map of Ti, O, Mo and S, respectively. (f) The resulting mapping image, and (g) the corresponding EDS spectrum (rectangular region) depicting the atomic percentage of each element present in the system. (h) The EDS spectrum for $Pt@MoS_2/TiO_2$ HS.





Fig. S3: (a) HAADF image of few-layer MoS_2 nanoflower edges, and (b-c) elemental map of S and Mo, respectively. (d) The resulting mapping image, and (e) the corresponding EDS spectrum depicting the atomic weight percentage of each element present in the system.



Fig. S4: XRD patterns of (a) few-layer $MoS_2 NFs$, (b) TB, (c) MSTB, and (d) PMSTB.



Fig. S5: XPS core level spectra for (a) Ti 2p in TB, (b) Pt 4f in PMSTB, (c,d) Mo 3d in MSTB and PMSTB, respectively, fitted with the Shirley baseline. The symbols represent the experimental data and the solid lines correspond to the Gaussian fits. The identity of each fitted peak is denoted with corresponding charge states in the respective cases.



Fig. S6: Raman spectra of MSTB before and after the PEC reaction, showing the high structural stability of the catalyst.



Fig. S7: Nyquist plots of (a) pristine MoS_2 and (b) $Pt@MoS_2$ HS, under dark and light conditions. Note that the symbols represent experimental data, while the solid lines are simulation using the Randle's circuit (shown as (c)) to estimate the characteristic charge-transfer resistance (R_{ct}).

S1.1 Photocurrent response of pristine MoS₂ and its HSs

To evaluate the photo action of the composite catalysts, photocurrent versus time (I-t) measurement is performed under visible light irradiation (at a fixed bias of 5 V) for pristine MoS_2 , MSTB and PMSTB HSs and the results are shown in Fig. S8. When light is turned ON, the current rises to a high value for all three samples, clearly indicating the high photoresponse and charge separation under illumination. When the light is turned OFF, the current swiftly reduces to the

minimum value (dark current), as expected for a semiconductor. The pristine MoS₂ and MoS₂ based HSs exhibit good visible light photoresponse, as evident from Fig. S8. It is noteworthy that the dark current, as well as the photocurrent, is higher in MSTB as compared to that of MS. The enhanced dark current may be attributed to the heavy S-doping in TiO₂ in the course of in-situ MoS₂ growth on it, facilitating the increased charge carrier density. The enhanced photocurrent is due to the photoexcitation of both the S-doped TiO₂ and narrow bandgap MoS₂ and their easy interfacial charge transfer inhibiting the recombination possibility. After the Pt NP decoration over MSTB, both the dark as well as photocurrent is increased further. The presence of Pt NPs can serve as advantageous metallic current collector nodes to facilitate lower resistance transport pathways of photo-excited electrons from TiO₂ and MoS₂ domains to Pt NPs (see Fig. 10(b)), improving the overall conductivity. This is also consistent with the very low charge transfer resistance (27 Ω in dark and 14 Ω in light) and very high exchange current density (0.182 mA/cm² in dark and 0.296 mA/cm² in light) for PMSTB.



Fig. S8: Time-dependent photocurrent response of MS, MSTB, and PMSTB under visible light illumination.

S1.2 Effect of scan rate on the LSV polarization curves

To investigate the effect of scan rate on the polarization curves as well as the overpotential (at -10 mA/cm²), we have recorded linear sweep voltammograms (LSV) of each sample at different scan rates of 2, 5, 10 mV/s, as shown in Fig. S9. Fig. S9(a) shows the comparison of polarization curves of MS and MSTB at various scan rates under the dark condition and the corresponding overpotential values are tabulated in Table S1. As shown in Table S1, the overpotential reduces by merely ~1% when the scan rate increased from 2 mV/s to 10 mV/s. Fig. S9(b) shows the comparison of polarization curves of PMS, PTB, PMSTB and Pt/C at various scan rates under the dark condition and the corresponding overpotential values are tabulated is only ~1% for high scan rate (10 mV/s). This is also the case for PMSTB under light illumination, as shown in Fig. S9(b). Thus, the results are nearly independent of the scan rates up to 10 mV/s. Considering the above fact, we have carried out all our experiments at 5 mV/s scan rate.



Fig. S9: LSV polarization curves in dark condition for (a) MS and MSTB, (b) PMS, PTB, PMSTB and Pt/C at various scan rates (2, 5, 10 mV/s). Polarization curves for PMSTB under light condition is also shown in (b).

Catalyst code	Overpotential @ -10 mA/cm ²					
	[(mV) V RHE]					
	SR=2 mV/s		SR=5 mV/s		SR=10 mV/s	
	dark	light	dark	light	dark	light
	10.0		40.5		40.1	
MS	-426	-	-425	-	-421	-
MSTB	-338	-	-336	-	-333	-
PMS	-148	-	-147	-	-147	-
РТВ	-113	-	-113	-	-112	-
PMSTB	-98	-74	-97	-74	-97	-73
Pt/C	-106	-	-106	-	-105	-

Table S1: Comparison of the overpotential of various catalysts at different scan rates (SR).

S1.3 Evidence of H₂ evolution and its quantification by gas chromatography

The H₂ generation during the electrocatalytic reaction was detected and quantified by a thermal conductivity detector (TCD) of Thermo Trace GC- 1110 gas chromatogram equipped with a hayesep D and molecular sieve column. Argon was used as a carrier gas with a flow rate of 20 mL/min. To quantify the H₂ gas, chronoamperometry was performed for 3 samples (PMS, PTB, and PMSTB) using Pt/C as a counter electrode at -0.32V *vs*. Ag/AgCl (or -0.123 V *vs*. RHE) for 10 min. After 10 min, 250 μ L gas was collected from the headspace of the electrochemical cell and injected into the gas chromatogram.



Fig. S10: Gas chromatography of PMSTB for characterization of retention times and qualitative composition showing the evidence of H_2 and N_2 gas.

It is confirmed from Fig. S10 that the gas produced in electrocatalysis is H_2 only. As the electrochemical cell is N_2 saturated, it is also detected as an additional gas. The amount of H_2 gas produced in 10 min of chronoamperometry for PMS, PTB, and PMSTB is shown in Fig. S11. It is clear that the amount of H_2 is highest for PMSTB as compared to the other samples, which is fully consistent with the respective polarization curves shown in Fig. 8(b). Finally, we provide a video (as supporting information) showing the release of gas bubbles during catalytic reaction, which confirms the release of H_2 gas.



Fig. S11: Quantification of H₂ produced in electrocatalysis for various catalysts collected after 10 min.