Supporting Information for

# Electrochemical Tuning of $MoS_2$ Nanoparticles on Three-Dimensional Substrate for Efficient Hydrogen Evolution

*Haotian Wang*[1,†], *Zhiyi Lu*[2,†], *Desheng Kong*[2], *Jie Sun*[2], *Thomas M. Hymel*[2], *and Yi Cui*[2,3,*]

[1]Department of Applied Physics, Stanford University, Stanford, CA 94305, USA

[2]Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

[3]Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA

†These authors contributed equally.

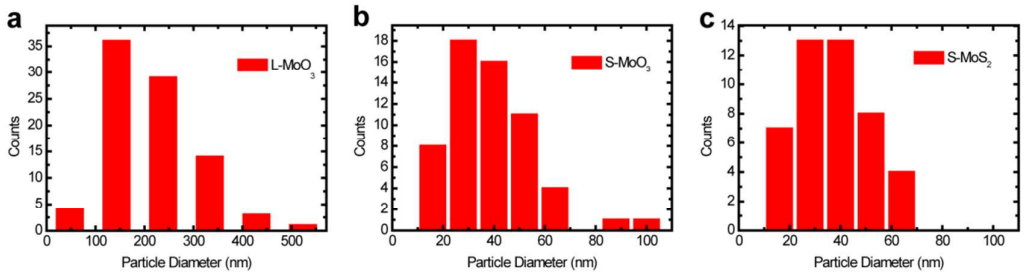


**Figure S1.** Statistical analysis of the particle size distributions of L-$MoO_3$, S-$MoO_3$, and S-$MoS_2$ respectively. The size of L-$MoO_3$ NP is ~ 200 nm, much larger than those of S-$MoO_3$ and S-$MoS_2$ which are ~ 30 nm.

*L-$MoS_2$ and S-$MoS_2$ NP surface area estimation:*

We treat the NP as a perfect sphere to simplify the calculation process. The diameters of L-$MoS_2$ and S-$MoS_2$ are 200 and 30 nm respectively. The mass loading $m_L$ and $m_S$ of the catalysts are the same. We set that the numbers of L-$MoS_2$ and S-$MoS_2$ per area on CFP are $N_L$ and $N_S$ respectively, and we can easily get the equation shown below:

$$m_L = N_L \frac{4}{3}\pi(100\ \text{nm})^3\rho,$$

$$m_S = N_S \frac{4}{3}\pi(15\ \text{nm})^3\rho,$$

$$m_L = m_S \rightarrow N_S = (\frac{100}{15})^3 N_L,$$

where $\rho$ represents the density of $MoS_2$. Then we can get the surface area ratio of S-$MoS_2$ to L-$MoS_2$ as:

$$\frac{S_S}{S_L} = \frac{N_S 4\pi(15\ \text{nm})^2}{N_L 4\pi(100\ \text{nm})^2} = \frac{100}{15} = 6.7.$$

This rough estimation agrees well with the electrochemical capacitance measurement which gives out a result of 3.6.

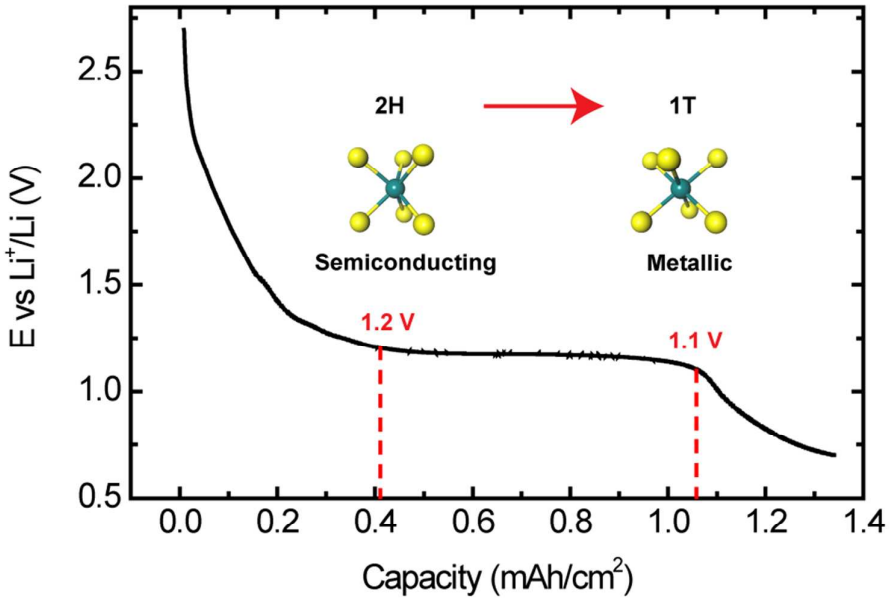


**Figure S2.** Galvanostatic discharge curve of Li electrochemical intercalation into $MoS_2$ NPs. The well-defined plateau from 1.2 to 1.1 V vs. $Li^+/Li$ represents the 2H to 1T phase transition. The atomic structure is changed from trigonal prismatic to octahedral, along with the electronic semiconducting to metallic transition. The capacity, which is 0.65 mAh/cm$^2$ as shown in the figure, of the plateau offers us the mass loading of $MoS_2$. From Ref. 10 we know that during the phase transition process the Li composition changes by about $\Delta x \approx 1$, therefore we can calculate the mass loading of $MoS_2$ to be 3.88 mg/cm$^2$, which agrees well with the measurement by microbalance.

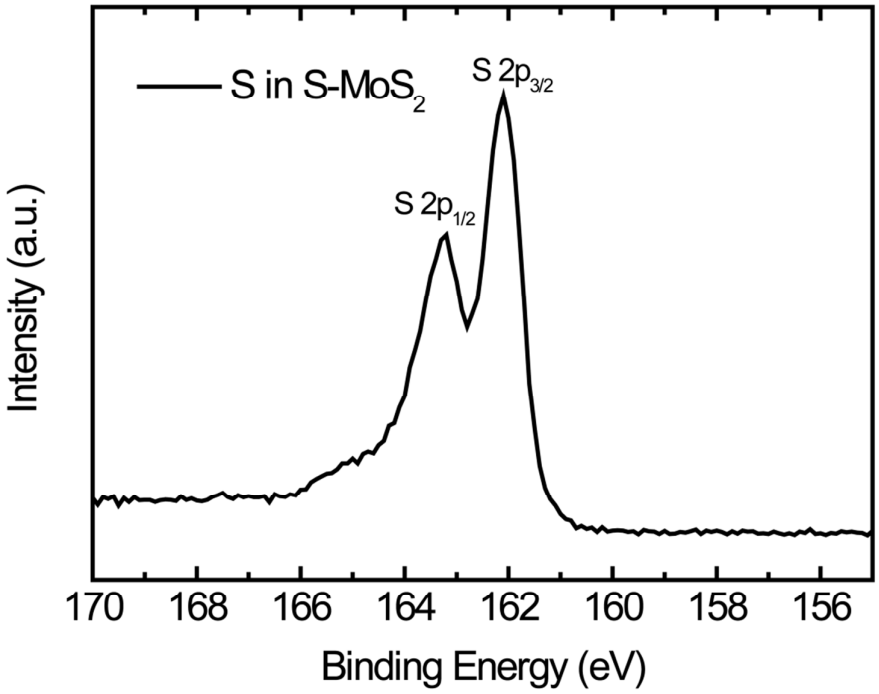


**Figure S3.** XPS spectra of S in S-$MoS_2$ catalyst. The peak positions of S $2p_{1/2}$ and $2p_{3/2}$ are 163.2 and 162.1 eV respectively.

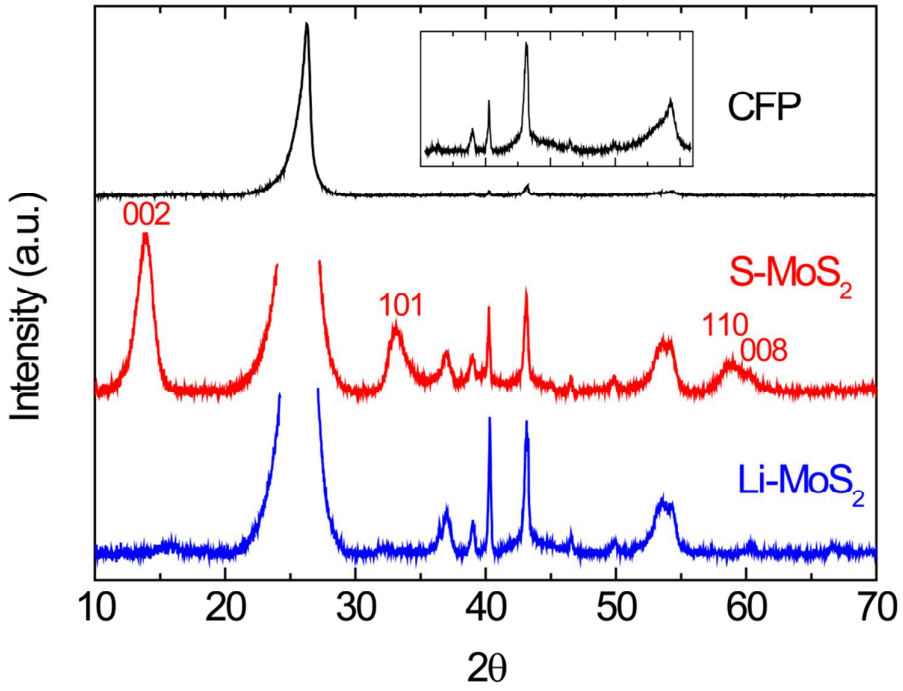


**Figure S4.** X-ray diffraction spectra of the substrate background, S-$MoS_2$, and Li-$MoS_2$. CFP has a very strong peak which is truncated for amplification of other peaks. The additional small peaks of CFP are zoomed in as shown by the inset. Distinguished peaks of $MoS_2$ are marked in the spectrum of S-$MoS_2$. However, after the lithiation and exfoliation processes those peaks disappear in Li-$MoS_2$ spectrum.

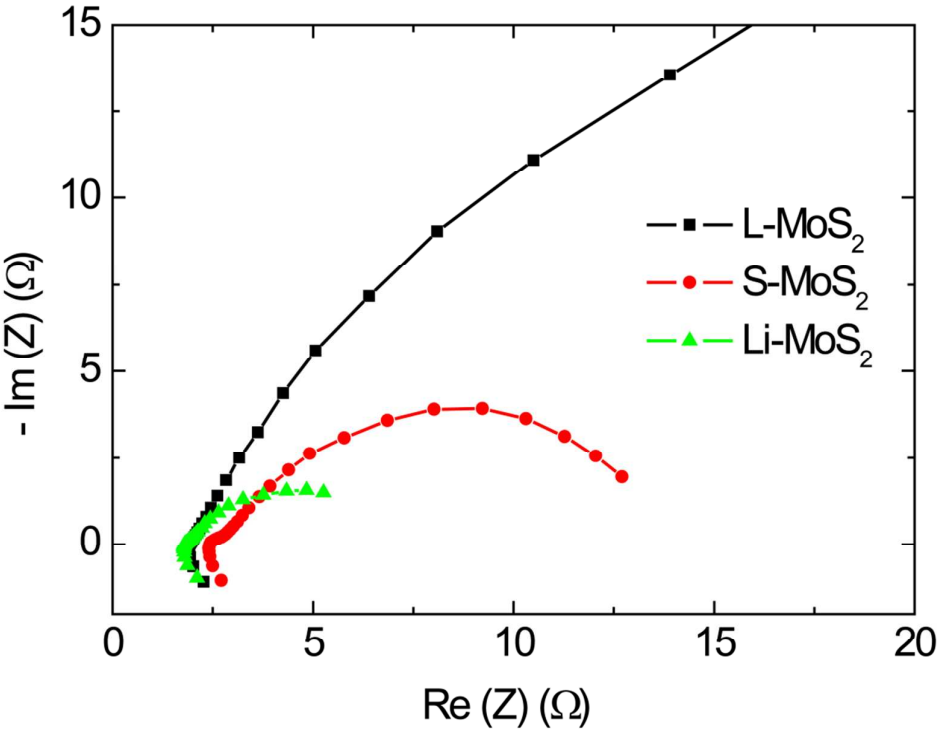


**Figure S5.** Nyquist plots of impedance spectroscopy analysis of the electrochemical cells setup, where L-$MoS_2$, S-$MoS_2$, and Li-$MoS_2$ were used as working electrodes. The series resistances are 1.92 Ω for L-$MoS_2$, 2.43 Ω for S-$MoS_2$, and 1.80 Ω for Li-$MoS_2$ respectively. The series resistance primarily comes from wiring and the electrolyte, while the resistance of $MoS_2$ NPs is negligible.

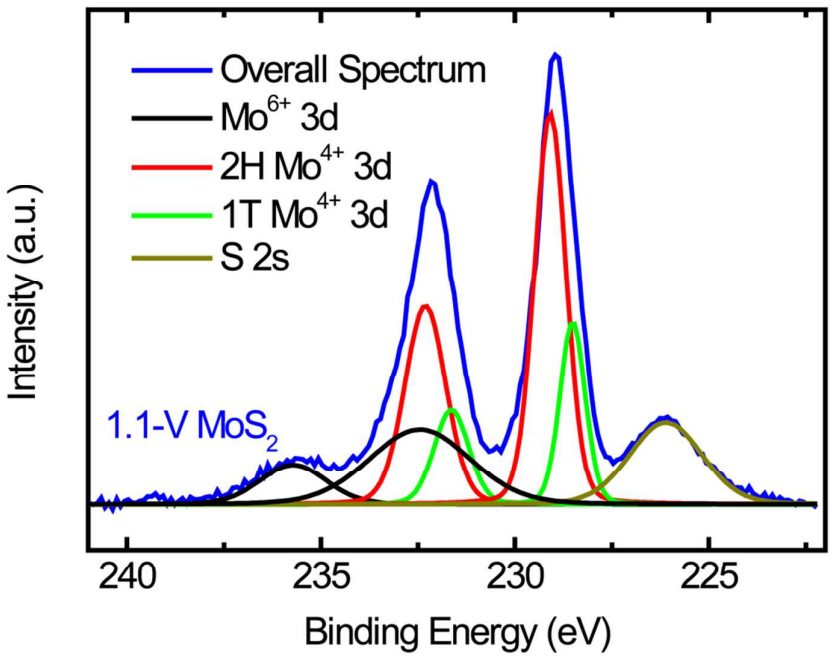


**Figure S6.** XPS spectrum of the 1.1-V $MoS_2$ sample. The broad Mo regions in 1.1-V $MoS_2$ spectrum is deconvoluted into red and green peaks, corresponding to 2H $MoS_2$ and 1T $MoS_2$ respectively. The ratio of $MoS_2$ 2H to 1T phase is estimated to be 2.67 by the Mo $3d_{5/2}$ peak intensities.

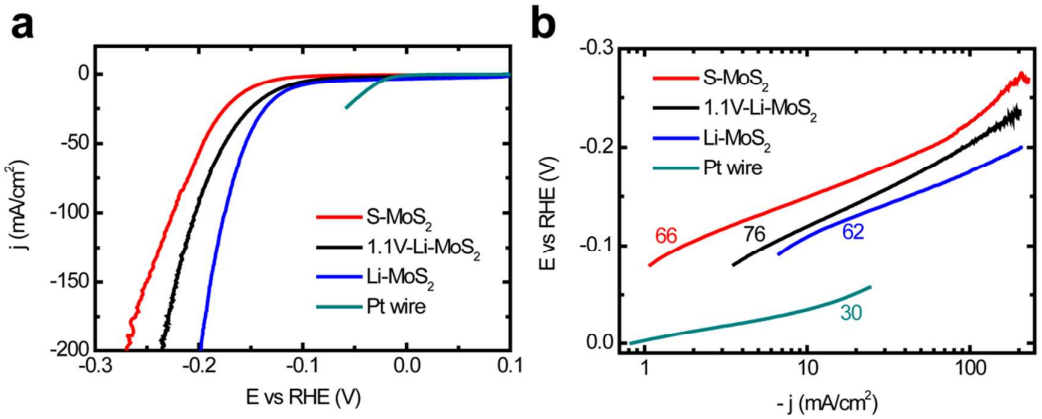


**Figure S7.** Comparison of HER performances of S-$MoS_2$, 1.1-V $MoS_2$, and Li-$MoS_2$ catalysts. (a) Polarization curves of S-$MoS_2$, 1.1-V $MoS_2$, Li-$MoS_2$, and Pt wire. 1.1-V $MoS_2$ shows an improved HER activity than that of S-$MoS_2$ due to the formation of 1T phase $MoS_2$ and increased surface area. The performance of Li-$MoS_2$ is further enhanced as the percentage of 1T phase is increased from 1.1-V $MoS_2$. (b) Tafel plots of S-$MoS_2$, 1.1-V $MoS_2$, Li-$MoS_2$, and Pt wire.

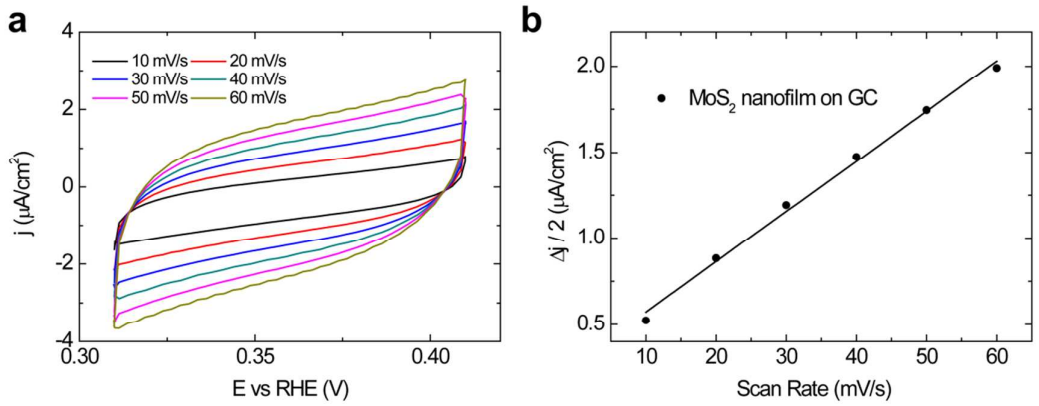


**Figure S8.** Electrochemical double layer capacitance measurement of $MoS_2$ nanofilm on flat glassy carbon substrate. (a) Electrochemical cyclic voltammogram of $MoS_2$ nanofilm at different potential scanning rates. The scan rates are 10, 20, 30, 40, 50, 60 mV/s respectively, due to the much smaller surface area compared with Li-$MoS_2$. The selected potential range where no faradic current was observed is 0.31 to 0.41 V *vs.* RHE. (b) Linear fitting of the capacitive currents of the catalysts *vs.* scan rates. The calculated double layer capacitance is 29 μF/cm$^2$. From Ref. 8 we know that the density of HER active sites in $MoS_2$ nanofilm is $5.37 \times 10^{14}$ sites/cm$^2$. Therefore, the density of the active sites in Li-$MoS_2$ sample is $5.37 \times 10^{14}$ sites/cm$^2$ $\times$ 345000 / $29 = 6.4 \times 10^{18}$ sites/cm$^2$. At 200 mV overpotential we get 200 mA/cm$^2$ cathodic current, by which the TOF is calculated as follows:

$$\text{TOF (at 200 mV)} = \frac{0.2\ \text{A/cm}^2}{1.6 \times 10^{-19}\ \text{C/e}^- \times 2\ \text{e}^-/\text{H}_2 \times 6.4 \times 10^{18}\ \text{sites/cm}^2} = 0.1\ \text{H}_2/\text{s per site.}$$

| Catalyst | Mass Loading | Tafel Slope | j @ - 200 mV vs RHE |
|---|---|---|---|
| Li-$MoS_2$ (current work) | ~ 3.4 mg/cm$^2$ | 62 mV/decade | 200 mA/cm$^2$ |
| 1T $MoS_2$ nanosheets[36] | 0.05 mg/cm$^2$ | 40 mV/decade | 7 mA/cm$^2$ |
| Exfoliated 1T $MoS_2$[28] | N/A | 43 mV/decade | 21 mA/cm$^2$ |
| $MoS_2$ NPs on graphene[17] | 1 mg/cm$^2$ | 41 mV/decade | 43 mA/cm$^2$ |
| Double-gyroid $MoS_2$[26] | 0.06 mg/cm$^2$ | 50 mV/decade | 4 mA/cm$^2$ |
| Amorphous $MoS_2$[22] | N/A | 40 mV/decade | 15 mA/cm$^2$ |
| $MoS_2$ sponges[27] | N/A | 185 mV/decade | 71 mA/cm$^2$ |

**Table S1.** The mass loadings, Tafel slopes, and the cathodic currents at 200 mV overpotential of different $MoS_2$ catalysts.