Electronic Supplementary Information

Comprehensive study on atomic layer deposition of molybdenum sulfide for electrochemical hydrogen evolution

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Ohmic potential drop (iR) correction

The ohmic drop correction was performed with the series resistances determined by the electrochemical impedance measurement. As shown in Fig. S1, all samples show similar series resistances ranged in $1 \sim 2 \Omega$. The *iR* correction for the LSV data was done with the series resistance by the equation of $\eta_{corr} = \eta_{exp} - iR$.



Fig. S1. Nyquist plots of bare CFP and MoS_x/CFP catalysts prepared in the experimental sets A and B.

Electrical Double Layer Capacitance

Generally, the electrochemically active surface area (A_e) is proportional to the double layer capacitance (C_{dl}). In order to calculate the electrical double layer capacitance, cyclic voltammetry was carried out in the range of +0.1 V ~ +0.2 V vs RHE with various scan rates of 20, 40, 60, 80, 100 mV/s. As shown in Fig. S2 and S3, the difference (Δj) between anodic and cathodic current densities were taken at 0.15 V vs RHE from the cyclic voltammograms, and then the values of Δj were plotted as a function of scan rate to obtain the slope, which corrensponds to twice the C_{dl} value. The similar data for the bare CFP can be found in the Supporting Information of Ref 19.



Fig. S2. (a-d) Cyclic voltammograms of MoS_x/CFP catalysts prepared in the experimental set A. (e) The plots of Δj – scan rate to obtain the C_{dl} values. The slope of the straight line is twice the C_{dl} value.



Fig. S3. (a-d) Cyclic voltammograms of MoS_x/CFP catalysts prepared in the experimental set B. (e) The plots of Δj – scan rate to obtain the C_{dl} values. The slope of the straight line is twice the C_{dl} value.



Fig. S4. Cross-sectional SEM image of bare CFP.



Fig. S5. (a) STEM images of MoS_x (20 cycles) on CFP. (b) EDS spectrum at the red circle in (a). Mo peak (K α :17.441 keV, L α : 2.293 keV); S peak (K α : 2.307 keV); Cu peak (K α : 8.040 keV, L α : 0.930 keV) due to the Cu TEM grid.



Fig. S6. The SAED pattern of MoS_x/CFP prepared by repeating the ALD sequence of M (4 s) – P (30 s) – D (1.5 s) – P (30 s) at 100 °C for 200 cycles.



Fig. S7. XRD pattern of the MoS_x/CFP prepared by repeating the ALD sequence of M (4s) – P (30s) – D (1.5s) – P (30s) at 100 °C for 100 cycles. The inset figure was obtained by magnifying the XRD pattern in the range of $2\Theta = 10^\circ \sim 20^\circ$.



Fig. S8. Raman spectrum of ALD-MoS $_x$ grown on CFP (532 nm laser excitation).



Fig. S9. Mo $3d_{5/2}$ binding energy (a) and turnover frequency (b) variations as a function of the ratio of S²⁻/S₂²⁻. In Fig. S9a, the binding energy was calibrated with the carbon 1s peak (284.8 eV) for this work and Ref. 19, and by using the Au $4f_{7/2}$ peak (84.0 eV) for Ref. 21. In Fig. S9b, the average TOF value at 0.2 V vs RHE was taken for the MoS_x/CFP because of the uncertainty from the mixed phase.



Fig. S10. Cathodic current density at 220 mV vs RHE (a) and electric double layer capacitance (b) variations as a function of the $Mo(CO)_6$ exposure time for the catalysts prepared in the experimental set B.