Supporting Information

Wang et al. 10.1073/pnas.1316792110

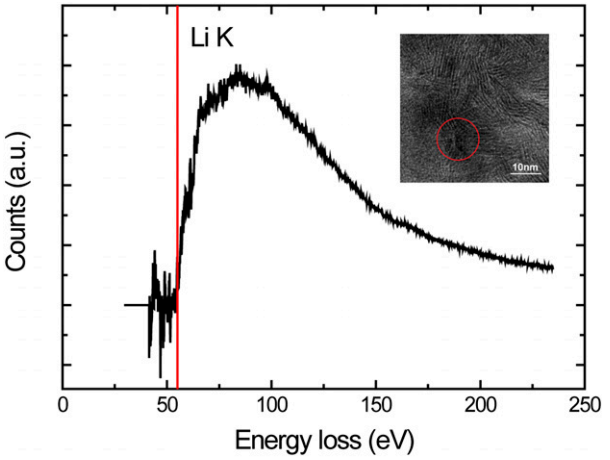

Fig. S1. Background-subtracted Li K-edge electron energy loss spectroscopy (EELS) spectrum from 1.1-V lithiation-treated MoS_2 nanofilm on MPGC after ethanol cleaning. (*Inset*) Red circle is the position where the EELS spectrum was obtained.

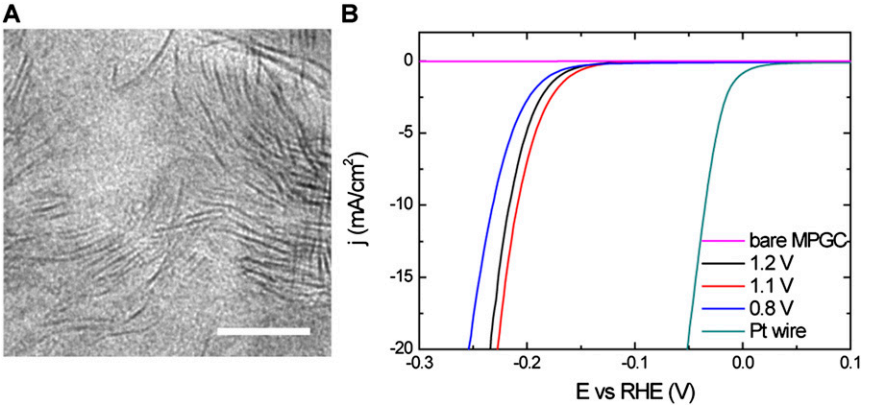

Fig. S2. Characterization of 0.8-V lithiated MoS_2. (*A*) Deep Li discharge process and the Li reaction with ethanol or water exfoliate MoS_2 which could destroy the bonds between the active material and the substrate. Scale bar,10 nm. (*B*) Polarization curves of bare MPGC electrode, Pt wire, and MoS_2 on MPGC lithiated to 1.2, 1.1, and 0.8 V vs. Li^+/Li. The 0.8-V MoS_2 shows degraded HER activity.

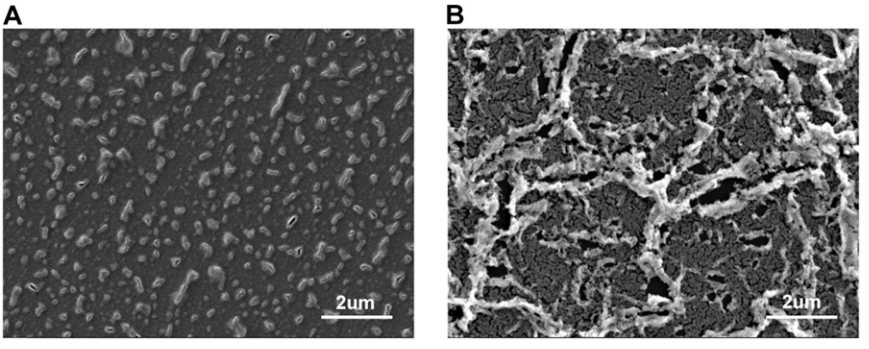

Fig. S3. SEM images of pristine and 1.1-V lithiation-treated MoS_2. *(A)* SEM image of pristine MoS_2 with pinholes formed during the sulfurization process due to the roughness of the substrate. *(B)* SEM image of 1.1-V lithiation-treated MoS_2 shows that the original pinholes were opened up during the lithiation and Li–ethanol reaction process. The nanofilm around the pinholes was easier to be peeled off but still maintain the electric contact with the substrate. Scale bar, 2 μm.

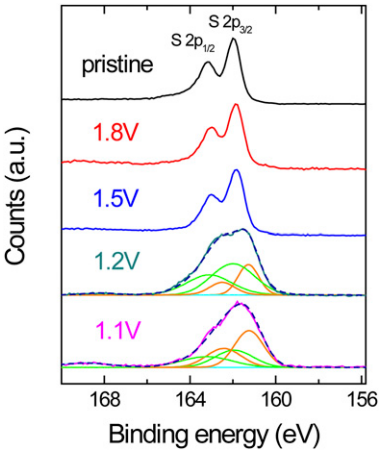

Fig. S4. XPS spectra of pristine and Li electrochemically intercalated MoS_2. S $2p_{1/2}$ and $2p_{3/2}$ peaks of pristine MoS_2 are located at 163.1 and 162.0 eV, respectively. The peaks have no obvious shift when MoS_2 is discharged to 1.8 and 1.5 V vs. Li^+/Li. Additional peaks emerge when 2H (green line) to 1T (orange line) MoS_2 phase transition happens. The 1T S $2p_{1/2}$ and $2p_{3/2}$ peaks are shifted toward 0.8 eV lower binding energies.

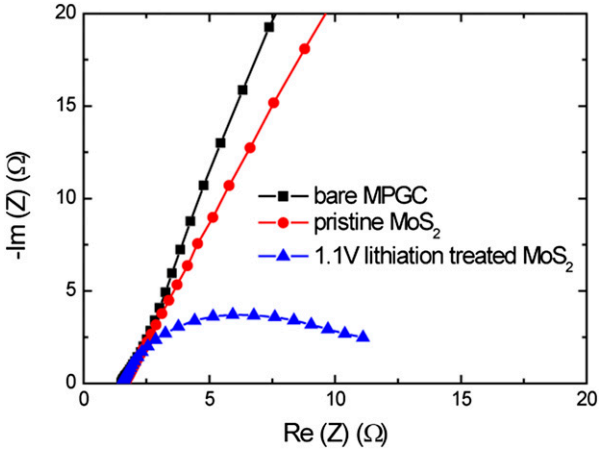

Fig. S5. Nyquist plots of impedance spectroscopy analysis of the electrochemical cells setup, where 1-cm^2 bare MPGC and pristine and 1.1-V lithiation-treated MoS_2 nanofilms on it were used as working electrodes. The measurement was performed at −0.2 V vs. RHE. The series resistances are 1.51 Ω for MPGC electrode, 1.68 Ω for MoS_2 electrode, and 1.53 Ω for 1.1-V lithiation-treated MoS_2. The series resistance primarily comes from wiring and the electrolyte, whereas the resistance of MoS_2 nanofilm is negligible.

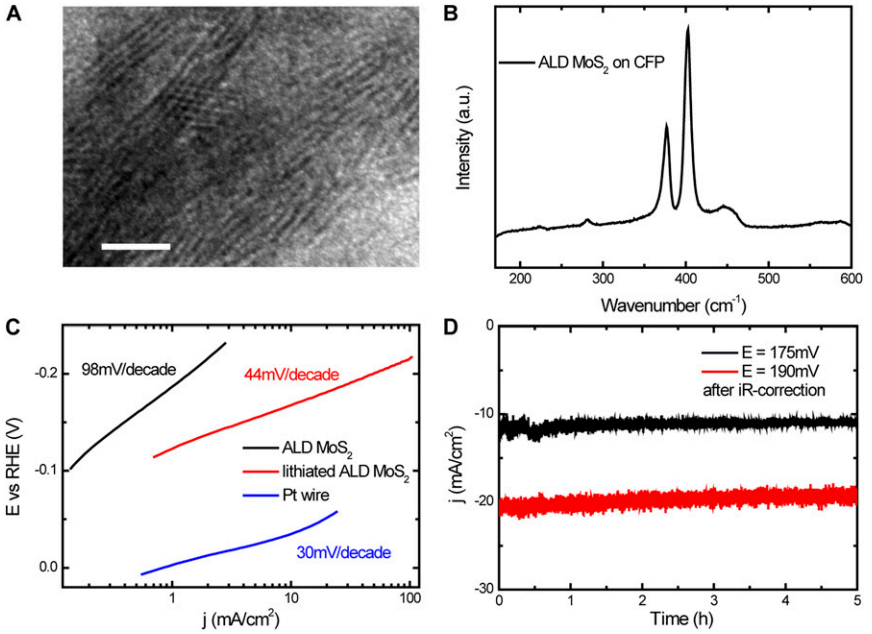

Fig. S6. Characterizations of ALD MoS_2 and lithiated ALD MoS_2. (*A*) TEM image of ALD MoS_2 synthesized on SiO_2–Si substrate for sample preparation. The surface is covered by the edges, showing the same structure with MoS_2 converted from Mo illustrated in Fig. 2. Scale bar, 5 nm. (*B*) Raman spectrum of ALD MoS_2 on CFP. *(C)* Tafel plots of pristine and lithiated ALD MoS_2 on CFP and Pt wire, with Tafel slopes of 98, 44, and 30 mV per decade, respectively. *(D)* Stable cathodic currents around 10 and 20 mA/cm^2 were observed for at least 5 h when constant voltages at 175 and 190 mV vs. RHE (iR-corrected) were applied on 0.7-V lithiation-treated ALD MoS_2 catalyst on CFP.

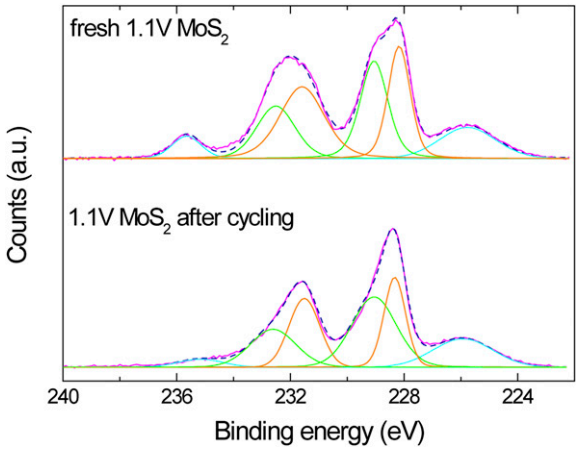

Fig. S7. XPS spectra of 1.1-V lithiated MoS_2 before and after electrochemical cycling in acid environment. The ratios of 2H to 1T MoS_2 before and after cycling are 0.86 and 0.78, showing no obvious change. The 1T phase MoS_2 is stable during the hydrogen evolution process.

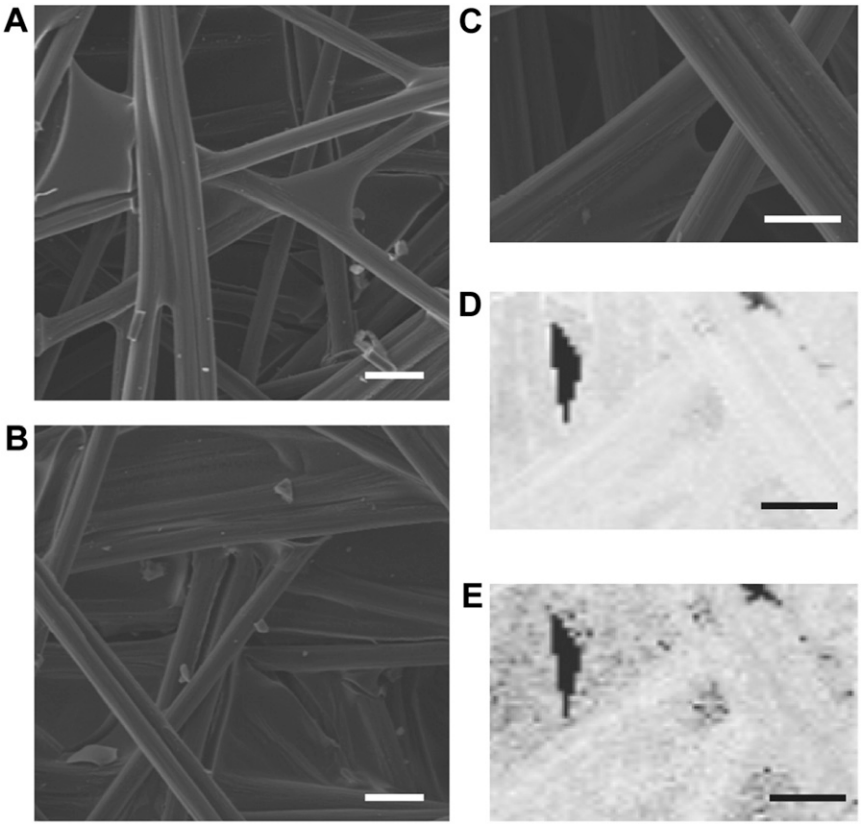

Fig. S8. Auger element mapping of ALD MoO_3 on CFP. (*A*) SEM image of CFP. (*B* and *C*) SEM images of ALD MoO_3 on CFP. (*D* and *E*) Auger electron microscopy element mapping at the same area in (*C*) for O and Mo, respectively. (*A* and *B*) Scale bar, 20 μ m. (*C*–*E*) Scale bar, 10 μ m.

Table S1. Inductively coupled plasma mass spectroscopy results of lithiation-treated MoS_2 on CFP after different processes

Materials	Li:Mo atomic ratio, %
1. MoS_2 on CFP after lithiation process	287.0
2. Lithiated MoS_2 on CFP after ethanol cleaning	16.5
3. Lithiation-treated MoS_2 after 1,000 cycles	8.6

MoS_2 was synthesized on carbon fiber paper and lithiated to 0.7 V vs. Li^+/Li. Sample 1 was prepared after the catalyst was discharged to 0.7 V and washed in diethyl carbonate in the glovebox to remove the electrolyte. Sample 2 was made after the lithiated MoS_2 was washed by ethanol. Sample 3 was taken after 1,000 CV cycles in H_2SO_4.