

Supporting Information

For

Catalytic Activity in Lithium Treated Core-Shell

MoO_x/MoS₂ Nanowires

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S1. Lithiated MoO_x/MoS₂ Core-Shell Nanowire Synthesis

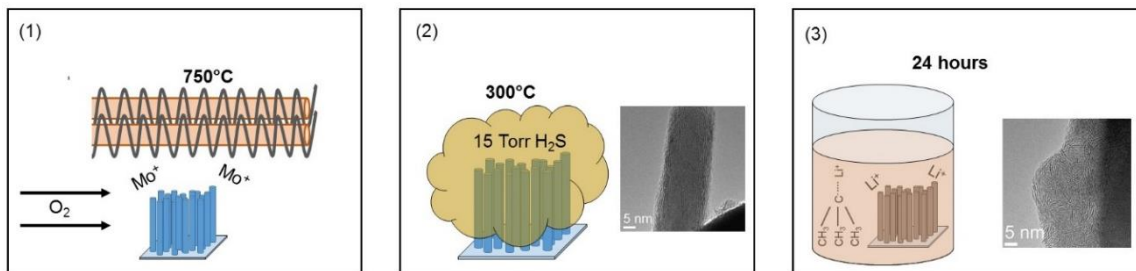


Figure S1. Schematic showing the synthesis scheme for lithiated MoO_x/MoS₂ core-shell nanowires. (1) Hot filament CVD (HFCVD) is used to deposit MoO₃ nanowire arrays on stainless steel substrate. (2) The MoO₃ nanowire array is exposed to H₂S at 300°C for 2 hours, forming an 8-10 nm MoS₂ shell on a reduced oxide (MoO_x) core. The inset shows HR-TEM of nanowire. (3) The MoO_x/MoS₂ nanowires are soaked in n-butyl lithium solution for 24 hours to allow for lithium intercalation. It is then rinsed with DI water to completely remove the lithium. Inset shows HR-TEM of intercalated MoS₂ shell.

S2. X-Ray Diffraction of MoO₃ Nanowires and Core-Shell MoO_x/MoS₂ Nanowires

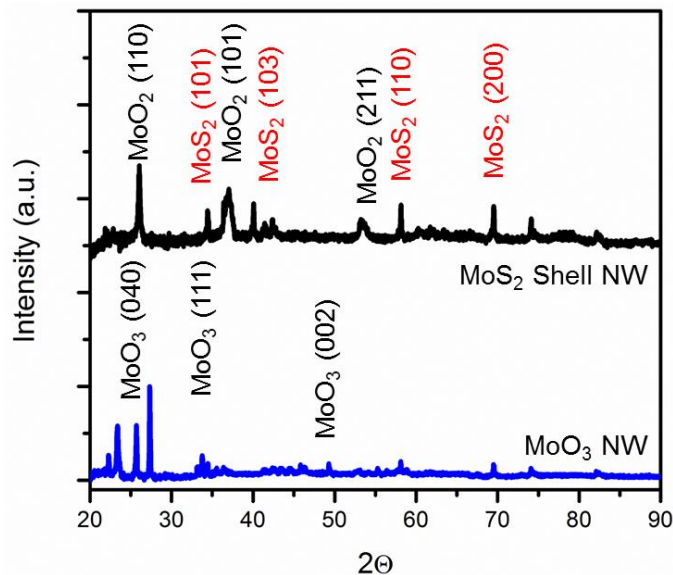


Figure S2. XRD spectra of the as synthesized MoO₃ nanowire array (blue curve), grown using HFCVD, showing orthorhombic MoO₃. After sulfurization (black curve), there is no signal from MoO₃, but instead MoO₂ (black) and MoS₂ (red). The peaks marked by asterisks correspond to metallic Aluminum, an artifact from the XRD instrument.

XRD analysis shows the phase purity of the MoO₃ nanowires arrays (blue curve) as orthorhombic MoO₃ (PDF 00-001-0706), prior to exposure to H₂S. Following exposure to H₂S at 15 Torr and 300°C, XRD of the core-shell nanowires (black curve) shows that MoO₃ is no longer present, having been reduced to MoO₂ (PDF 00-002-0422), as well as other molybdenum sub oxides, shown by prominent XRD peaks from (100), (101), and (211) MoO₂ crystal planes. The MoS₂ shell shows signal which responds to 2H-MoS₂ (PDF 00-02-0132).

S3. Electron Energy Loss Spectroscopy (EELS) Analysis

Figure S3 shows the EELS analysis of the lithiated MoO_x/MoS₂ core-shell nanowires. There are clear edges for sulfur (165 eV), molybdenum (227, 392, 410 eV), and oxygen (532

eV). The inset shows the area of interest for lithium (60 eV). This curve shows a very weak signal for lithium. In searching in different areas of the nanowire, usually no lithium signal was observed, but there may be a very trace amount remaining either between the MoS₂ sheets or on the nanowire surface. EELS is a very sensitive technique, so it will detect elements in very low concentrations, but there does not seem to be a significant amount of lithium remaining in the sample to affect its catalytic performance. Minimum detection limits for lower Z elements (*i.e.* lithium) is ~0.05 at%. EELS analysis was conducted using a FEI Tecnai F20 TEM.

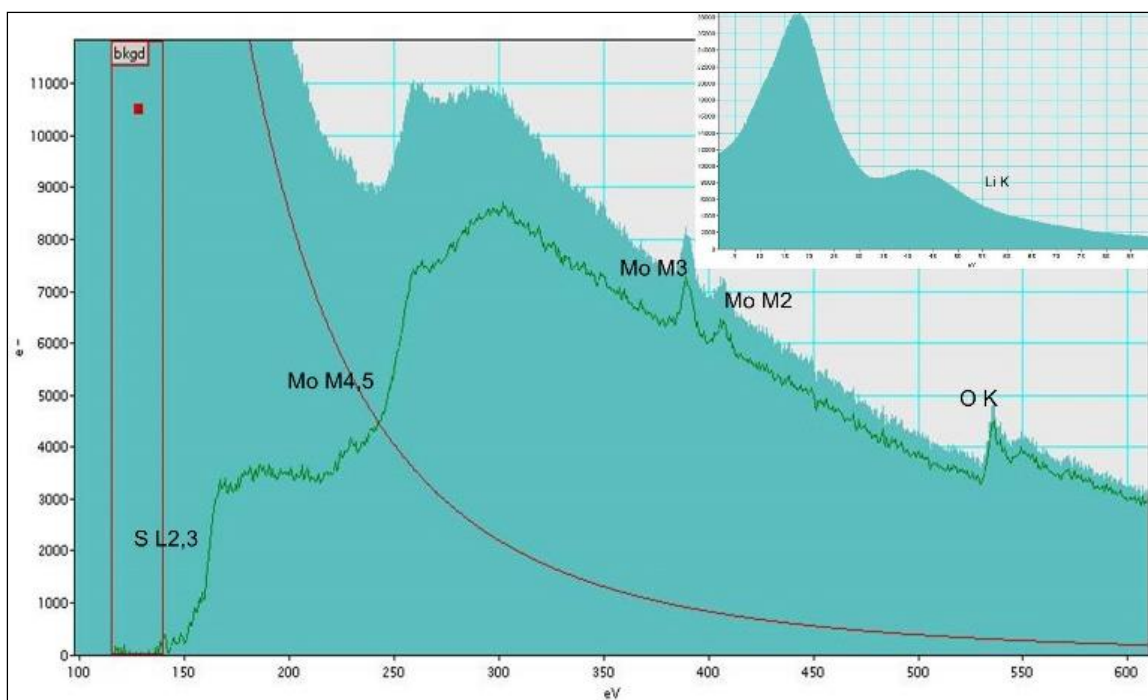


Figure S3. Electron Energy Loss Spectroscopy (EELS) for the lithiated MoS₂ nanowires. There are clear edges for sulfur, molybdenum, and oxygen. The inset shows trace signal for lithium, which is seen very rarely and confirms that almost all lithium has been removed by washing.

S4. Crystallographic Characterization Details

XPS data were collected using a Physical Electronics VersaProbe II system with a base pressure below 1×10^{-7} Pa. A variable-size, monochromated Al $K\alpha$ x-ray source (1487 eV) was used throughout, and photoelectrons were energy sorted using a hemispherical analyzer. Samples were at room temperature. XP spectra are reported in terms of binding energy (BE) and instrument calibration was performed in accordance with ASTM procedure. The XP spectra is calibrated to the Carbon 1s peak energy of 284.5 eV. Elemental composition was determined using survey scans at pass energy of 117 eV. Pass energy of 29 eV was used for high-resolution scans to determine chemical valence state. Charge neutralization for insulating samples is accomplished by focusing low energy ions and electrons at the spot of x-ray impingement.

Raman spectroscopic analysis of the nanowire arrays was performed using a Renishaw Invia Micro Raman system with a 633 nm HeNe laser. The Raman spectrum was calibrated using single crystal Silicon at 520 cm^{-1} . FEI Tecnai F20 TEM was used for high resolution transmission electron microscopy (HR-TEM), as well as electron energy loss spectroscopy (EELS). SEM imaging was performed using FEI Quanta FEG 400 Scanning Electron Microscope.

S5. Impedance for iR Correction

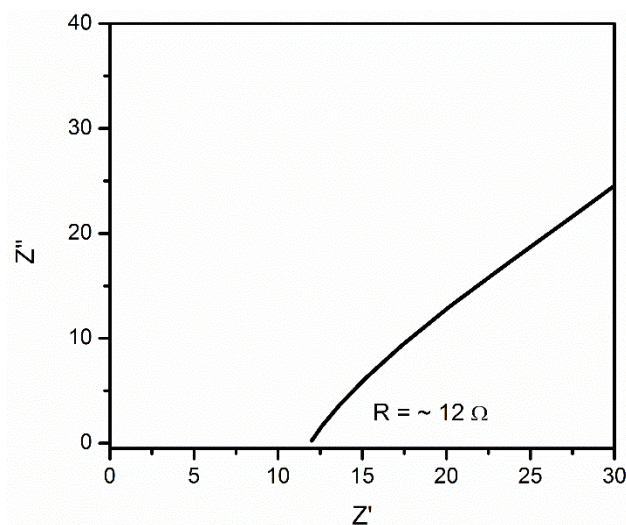


Figure S4. Nyquist plot showing the impedance of lithium intercalated MoO_x/MoS₂ core-shell nanowires dispersed on glassy carbon electrode with graphite counter, resulting in a system resistance of ~12 ohms. Used for iR correction of electrochemical data.

S6. Electrocatalytic Activity of Bulk MoS₂ Powder

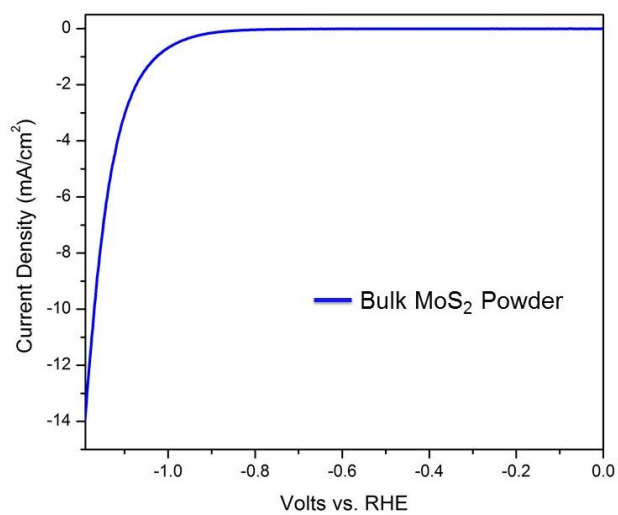


Figure S5. Linear sweep voltammogram for bulk MoS₂ powder.

For comparison, the HER catalytic activity was measured in a similar electrochemical testing set-up as the nanowires and nanosheets. The bulk MoS₂ shows an HER on-set potential of -0.8 V vs. RHE and a Tafel slope of 156 mV/decade, similar to 2H-MoS₂ sheets.

S7. Incremental Lithiation Experiment

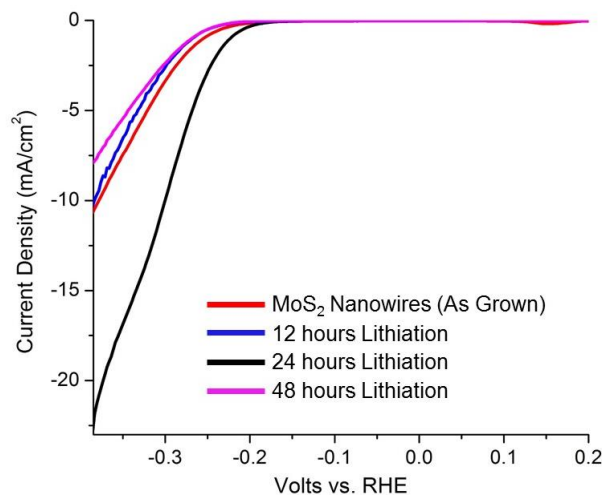


Figure S6. Linear sweep voltammograms showing the catalytic activity of MoS₂ nanowire arrays which have been incrementally lithiated.

In an attempt to better understand the lithiation mechanism, the exposure of the MoS₂ nanowires to butyl lithium was performed incrementally. After 12 hours of lithium exposure, there was no significant difference in HER catalysis from the as-grown nanowires. At 24 hours, the significantly improved catalytic activity is observed. Interestingly, when the nanowires were exposed for 48 hours, the activity was similar, if not less effective than the as-grown sample. This may be due to the complete destruction of the MoS₂ shell and active sites due to volume expansion, which has exposed the MoO_x core for corrosion, or it may simply be that the prolonged soaking and washing caused significant delamination of the nanowire array, which means there is less active material for the catalysis testing.

S8. Capacitance Measurements

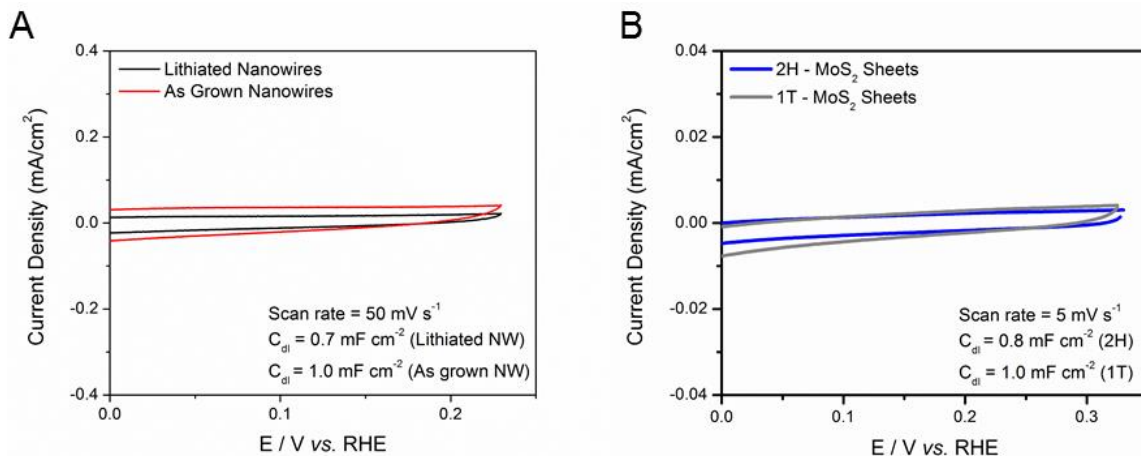


Figure S7. A) Cyclic voltammograms of the MoO_x/MoS₂ core/shell nanowires as grown (red curve) and after lithiation (black curve) dispersed on glassy carbon electrodes. B) Cyclic voltammograms of 2H-MoS₂ (blue curve) and 1T-MoS₂ (gray curve) 2D sheets dispersed on glassy carbon electrode.

Table S1. Calculation of Double Layer Capacitance (C_{dl})

Catalyst	Double Layer Capacitance (mF/cm ²)
As Grown Nanowires	1.0
Lithiated Nanowires	0.7
2H-MoS ₂ Sheets	0.8
1T-MoS ₂ Sheets	1.0

Analysis of cyclic voltammetry shows that the double layer capacitance, C_{dl}, of the nanowire system does not significantly change following the lithium exfoliation; it can be concluded that the wetted surface area of the nanowires does not change. This demonstrates that the resulting improved catalysis is due to exposure of catalytic sites, not an increase in actual surface area. For comparison, the double layer capacitance of the 2H and 1T-MoS₂ sheets are shown (Figure S7B). Both sheets have similar wetted surface area; since the sheets and nanowires

are scanned at different scan rates (5 mV/s and 50 mV/s respectively), the wetted surface areas cannot necessarily be compared between Figure S7A and Figure S7B.

S9. Annealing of Nanowires and Nanosheets

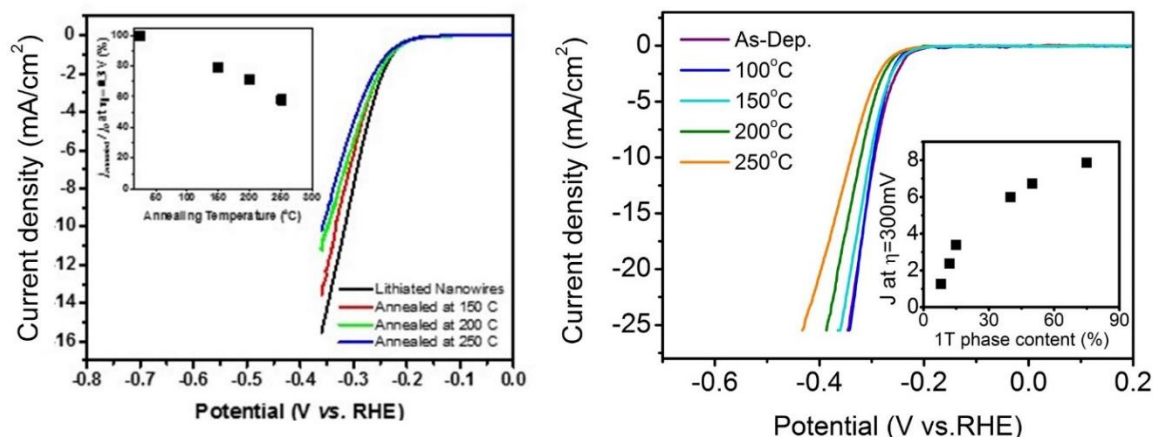


Figure S8. Linear voltammograms showing HER activity following annealing at various temperatures for lithiated MoO_x/MoS₂ nanowires (left figure) and lithiated nanosheets (right figure).

For the nanowire annealing, there is no shift in the HER on-set potential after annealing for 1 hour at 150°, 200°, and 250°C and insignificant change in the current density at -0.35 V vs. RHE. Contrarily, the annealing of the exfoliated 1T-MoS₂ sheets leads to the phase transformation to semiconducting 2H-MoS₂. The HER on-set potential decreases as the annealing temperature is increased, and also the current diminishes dramatically, as can be seen in the figure in-set.