

# A Comparative Study in Acidic and Alkaline Media of the Effects of pH and Crystallinity on the Hydrogen-Evolution Reaction on MoS<sub>2</sub> and MoSe<sub>2</sub>

## Supporting Information

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## Experimental

### Sample preparation

#### *a) Single crystals of MoS<sub>2</sub>*

Natural and synthetic crystals of MoS<sub>2</sub> were purchased from 2D semiconductors (El Cerrito, CA, USA) and Structure Probe Inc. (West Chester, PA). The doping and impurities of the purchased crystals were not known. To obtain crystals of uniform quality and doping, n-doped MoS<sub>2</sub> single crystals were synthesized in our laboratory by a chemical-vapor transport (CVT) technique.<sup>1</sup> Briefly, stoichiometric amounts of elemental Mo (99.99% trace metal basis, Sigma Aldrich) and S (Puratronic, 99.9995% trace metals basis, Alfa Aesar) were sealed under vacuum in a clean quartz ampule and heated to ~ 900 °C for 1 day in a furnace (Carbolite, Verder Scientific, Watertown, Wisconsin, USA). The resulting polycrystalline powder was collected. 0.92 g of the polycrystalline MoS<sub>2</sub> powder, 0.32 g of MO<sub>2</sub>Cl<sub>2</sub> (Sigma Aldrich)[MoO<sub>2</sub>Cl<sub>2</sub>?], and excess elemental S (0.104 g) were loaded and vacuum-sealed in a new quartz ampule. The ampule was then introduced into a 3-Zone furnace (Mellen, Concord, NH, USA) with the charge zone at

1170 °C and the growth zone at 1115 °C with a temperature gradient of  $\sim 2 \text{ }^\circ\text{C cm}^{-1}$  across the ampule. The growths typically lasted for 5–7 days. At the end of the growths, large crystals, typically 5-7 mm on a side, were obtained.

*b) Single crystals of MoSe<sub>2</sub>*

Single crystal samples of n-MoSe<sub>2</sub> were grown by a chemical-vapor-transport technique.<sup>2</sup> Briefly, stoichiometric amounts of elemental Mo (99.99% trace metal basis, Sigma Aldrich) and Se (99.999% trace metals basis, Aldrich) were sealed under vacuum in a clean quartz ampule and heated to  $\sim 900 \text{ }^\circ\text{C}$  for 1 day in a furnace (Carbolite, Verder Scientific, Watertown, Wisconsin, USA). The resulting polycrystalline powder was collected. 1.00 g of the polycrystalline MoSe<sub>2</sub> powder and 0.400 g of SeCl<sub>4</sub> (Sigma Aldrich) were loaded and vacuum sealed in a new quartz ampule. The ampule was then introduced into a 3-Zone furnace (Carbolite, Verder Scientific, Watertown, Wisconsin, USA) with the charge zone at 1025 °C and the growth zone at 975 °C with a temperature gradient of  $\sim 2 \text{ }^\circ\text{C cm}^{-1}$  across the ampule. The growths typically lasted for 5–7 days. At the end of the growths, large crystals, typically 5-7 mm on a side, were obtained.

*c) Polycrystalline thin films (PTF) of MoS<sub>2</sub> and MoSe<sub>2</sub>*

Magnetron sputtering was used to deposit 1-5 nm of Mo onto n<sup>+</sup> or pn<sup>+</sup> Si wafers. The sputtered samples were then loaded into a CVD chamber and sulphadized by flowing a mixture of H<sub>2</sub>S and N<sub>2</sub> at 500 °C for 20 minutes.

*d) Polycrystalline thin films of MoSe<sub>2</sub>*

Mo was deposited by e-beam evaporation on an n<sup>+</sup> Si wafer to a thickness of 5-15 nm. The evaporated samples were then loaded into a chemical-vapor deposition (CVD) chamber and selenized by flowing evaporated elemental selenium under Ar at 600°C for 20 min.

*e) Amorphous MoS<sub>x</sub>*

Amorphous MoS<sub>2</sub> was prepared as previously documented.<sup>3</sup> Briefly, 0.075 g of Na<sub>2</sub>S was dissolved in 12 mL of deionized water. A solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> was prepared by dissolving the salt in 12 mL of 0.2 M H<sub>2</sub>SO<sub>4</sub>(aq). The solutions were mixed and a black precipitate formed immediately. The precipitate was separated by centrifuging at 12,000 RPM for 30 min at 24 °C, and was subsequently washed with 15 mL of isopropanol. The solid was then sonicated in 15 mL

of isopropanol for 15-20 min, to make the suspension that was later used for preparing electrodes.

*f) Amorphous MoSe<sub>x</sub>*

Amorphous films of MoSe<sub>2</sub> were formed by an operando synthesis method.<sup>4</sup> Ammonium heptamolybdate, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O [0.40 g, 3.47 × 10<sup>-4</sup> mol, 99.98% (Sigma-Aldrich, St. Louise, MO)], was dissolved in 8 mL of a 0.20 M H<sub>2</sub>SO<sub>4</sub>(aq) that was prepared by diluting 18 M H<sub>2</sub>SO<sub>4</sub> with H<sub>2</sub>O. A separate solution was prepared by dissolving 0.10 g (8 × 10<sup>-4</sup> mol) of sodium selenide, Na<sub>2</sub>Se [99.8% (Alfa Aesar, Ward Hill, MA)], in 8 mL of H<sub>2</sub>O. The first solution of Mo was quickly poured into the second solution, and a black precipitate formed upon mixing. This mixture was agitated for 10 min with a sonicator. The suspension was then transferred to a centrifuge tube and centrifuged for 30 min at ~ 4000 rpm. A black precipitate collected at the bottom of the centrifuge tube. The supernatant liquid, which still contained some black color, was discarded. The precipitate was rinsed with 2 10 mL aliquots of 2-propanol. A final 20 mL of 2-propanol was added to the centrifuge tube, and was then subjected to sonication for 30 min. This process resulted in suspension of the black solid in the 2-propanol.

The choice to study MoS<sub>2</sub> in NaOH solution and MoSe<sub>2</sub> in KOH solution was made arbitrarily. Upon exploring the effect of changing the cation from Li, Na, and K in alkaline solution, we found a small effect of < 40 mV in the series. The pH effect on overpotential was still pronounced for MoS<sub>2</sub> in LiOH and KOH in addition to the data presented on NaOH, when compared to the overpotential in acidic media.

### **Preparation of Electrodes**

To expose fresh surfaces, the single crystals were mechanically exfoliated on both sides with Scotch tape. Ohmic contact was made to the back side of the crystal using In solder. The crystal with the back contact was then attached to one end of a Cu wire. The Cu wire was then threaded through a hollow glass tube leaving the sample outside the tube on one end. The Cu wire acted as the electrode lead. The area of the front face of the crystal, that was to be in contact with the solution, was then defined by applying epoxy (Hysol 9460, Loctite, USA) to the edges of the crystal. The rest of the crystal, the In back contact, and the exposed part of the Cu wire outside the glass tube, were all electrically isolated from the solution by applying a

continuous film of epoxy over these materials. The epoxy was allowed to cure overnight. The exposed areas of the electrodes were imaged using an optical scanner and converted to surface areas using ImageJ software. Electrode areas were typically 0.02 – 0.50 cm<sup>2</sup>.

The Si/PTF-MoS<sub>2</sub> and MoSe<sub>2</sub> electrodes were prepared by carefully cutting the as-synthesized wafer to appropriately sized pieces. Electrical contact to the Si was made by scratching In-Ga eutectic on to the back side of the Si. A Cu wire was then attached to the back side of the electrode using silver paint. The remainder of the electrode-making process was the same as that outlined for the single crystals above. Electrodes were typically of 0.5 cm<sup>2</sup> in area.

The electrodes for testing the amorphous MoS<sub>x</sub> were prepared by drop-casting the suspension of MoS<sub>x</sub> (prepared as described in the previous section) onto glassy-carbon rotating disc electrodes (RDEs) and drying the material overnight in a vacuum desiccator at 50 mbar. The geometric surface area of the RDE was ~0.2 cm<sup>2</sup>.

To prepare electrodes from the black MoSe<sub>x</sub> suspension, highly ordered pyrolytic graphite (HOPG) samples were cut into ~ 8mm x 8mm squares. The HOPG was polished for 10 min with 1200 grit SiC polishing paper on a wet polishing wheel. The polished HOPG was cleaned by sonication in isopropanol and then acetone, each for 10 min. Next, a 30 μL drop of the mixed composition suspension of Mo and Se was placed onto the polished side of a HOPG substrate. The sample was dried for 18 h at an internal pressure of < 100 mTorr in a vacuum desiccator. Electrode areas varied from 0.4 – 0.6 cm<sup>2</sup>

## **Electrochemistry**

H<sub>2</sub>SO<sub>4</sub> (99.999% trace metal basis, Sigma Aldrich) and NaOH and KOH (semiconductor grade, 99.99% trace metal basis, Sigma Aldrich) were obtained and used without further purification, to prepare solutions for the electrochemical experiments. De-ionized water ( $\rho \approx 18.2$  MΩ cm), supplied from a Barnstead Nanopure system (Thermo Scientific, Asheville, NC, USA) was used for all the experiments. The potentiostats were BioLogic SP-200 (Biologic, Grenoble, France), Autolab 302N (Autolab, Metrohm, Utrecht, the Netherlands) and Gamry REF 600 (Gamry, Warminster, PA, USA). A standard three-electrode electrochemical borosilicate glass cell was used for the experiments. A high-surface-area graphite electrode (99.9995% trace metals basis, Alfa Aesar) was used as a counter electrode, and a saturated Ag/AgCl electrode,

obtained from either CH Instruments (Austin, TX, USA) or custom-made, housed in a micro-agar-gel salt bridge, was used as the reference electrode. The saturated Ag/AgCl reference electrode in the salt bridge was calibrated against a reversible hydrogen electrode (RHE) that was freshly prepared before every experiment. For the purpose of presentation, the potentials are referenced against the relevant RHE scale using the calibration thus performed. Typically, the solution was sparged with H<sub>2</sub> before experiments, and the headspace in the cell was continuously purged with H<sub>2</sub> during the experiments, to ensure a saturation concentration of H<sub>2</sub> in the solution. The solution was continuously agitated using magnetic stirring or, in the case of amorphous MoS<sub>x</sub> on rotating-disk electrodes, by rotating the electrode at 1600 RPM.

No resistance compensation was applied to the measured current-density versus potential data.

### **Microscopy**

The optical images were obtained on an Olympus BX 51 microscope.

### **Mass Spectroscopy**

A Hiden HPR-20 QIC R&D equipped with an electron-impact ionization source and triple-filter quadrupole mass spectrometer was utilized to measure the electrocatalytic production of H<sub>2</sub> in real time. Electrolyses were conducted in a 5-port flow cell at a constant N<sub>2</sub> flow of 50 mL/min to maintain a positive pressure in the headspace. Both before and after electrolysis, a calibration gas of 500 ppm H<sub>2</sub> (Air Liquide) in N<sub>2</sub> was flowed through the cell at the same rate (50 mL/min). Once background stabilized, galvanostatic steps were applied for 6 min until signal had stabilized starting at -0.5 mA in -0.5 mA steps up to -2.0 mA. After each galvanostatic step, the electrode was allowed to return to the open-circuit potential and the mass spec signal to return to its background level.

Although in principle Faradaic efficiencies for H<sub>2</sub> production could be calculated from these data, the small size of the samples  $\sim 0.12 \text{ cm}^2 - 0.25 \text{ cm}^2$  prevented accumulation of products sufficient for reliable quantification using this method or using other methods available in our laboratory such as gas chromatography or eudiometry.

### **X-Ray Photoelectron Spectroscopy**

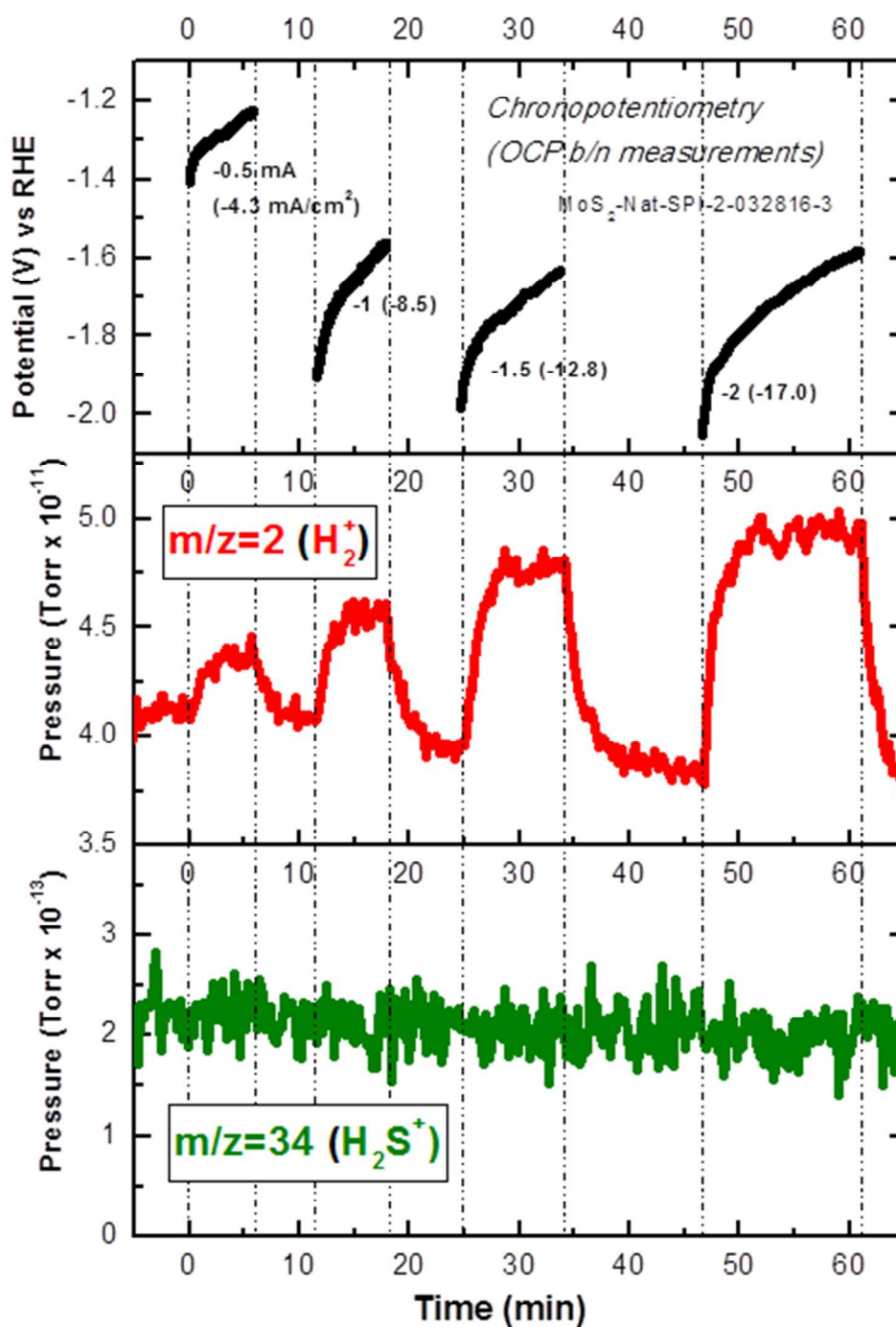
X-ray photoelectron spectroscopy (XPS) data was collected at  $\sim 5 \times 10^{-9}$  Torr using a Kratos AXIS Ultra DLD with a magnetic immersion lens that consisted of a spherical mirror and concentric hemispherical analyzers with a delay-line detector (DLD). An Al K $\alpha$  (1.486 KeV) monochromatic source was used for X-ray excitation. Ejected electrons were collected at a 90° angle from the horizontal. The CASA XPS software package v 2.3.16 was used to analyze the collected data.

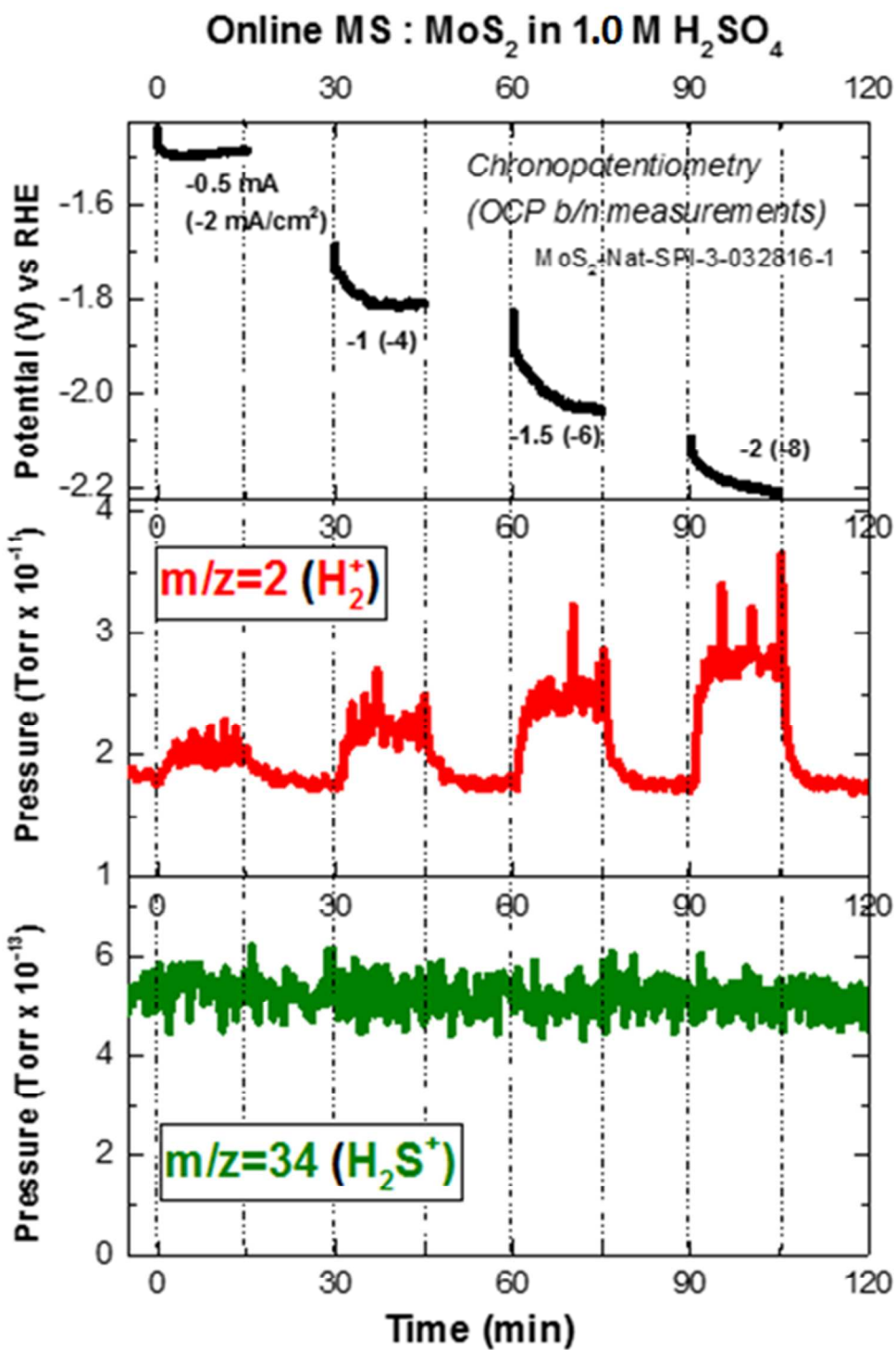
### **Tafel Analysis**

A Tafel analysis was undertaken to gain insights into the possible mechanisms of hydrogen evolution at MoSe<sub>2</sub> electrodes in acidic and alkaline media. Figure S6 shows the Tafel plot of single-crystalline MoS<sub>2</sub>, Figure S6 shows Tafel plots for polycrystalline MoSe<sub>2</sub>, and Figure S7 shows the Tafel plots for amorphous MoSe<sub>x</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub>(aq) and 1.0 M KOH(aq). For single-crystalline samples, one noticeable variation between the Tafel plots in acidic and basic media is the presence of an inflection point for the data in acid. This inflection point is not present for data collected in 1.0 M KOH(aq). The Tafel data for the polycrystalline thin film exhibited the most similarity between acidic and alkaline solutions, with the Tafel data being roughly parallel over the plotted current densities. The Tafel analysis for amorphous MoSe<sub>x</sub> showed significant variation between samples. In 1.0 M H<sub>2</sub>SO<sub>4</sub>, a linear region was observed between  $-\eta = 0.4 - 0.3$ , followed by a departure from linearity at lower  $-\eta$  values. In 1.0 M KOH(aq), the data were fit to between  $-\eta = 0.4 - 0.25$ , but extrapolating to predict an exchange-current density resulted in a low value of  $\sim 8 \cdot 10^{-7}$  A cm<sup>-2</sup> versus an exchange-current density of  $4 \cdot 10^{-3}$  A cm<sup>-2</sup> obtained from analysis of the linear region for amorphous MoSe<sub>x</sub> in H<sub>2</sub>SO<sub>4</sub>(aq).

### **Supplementary Figures**

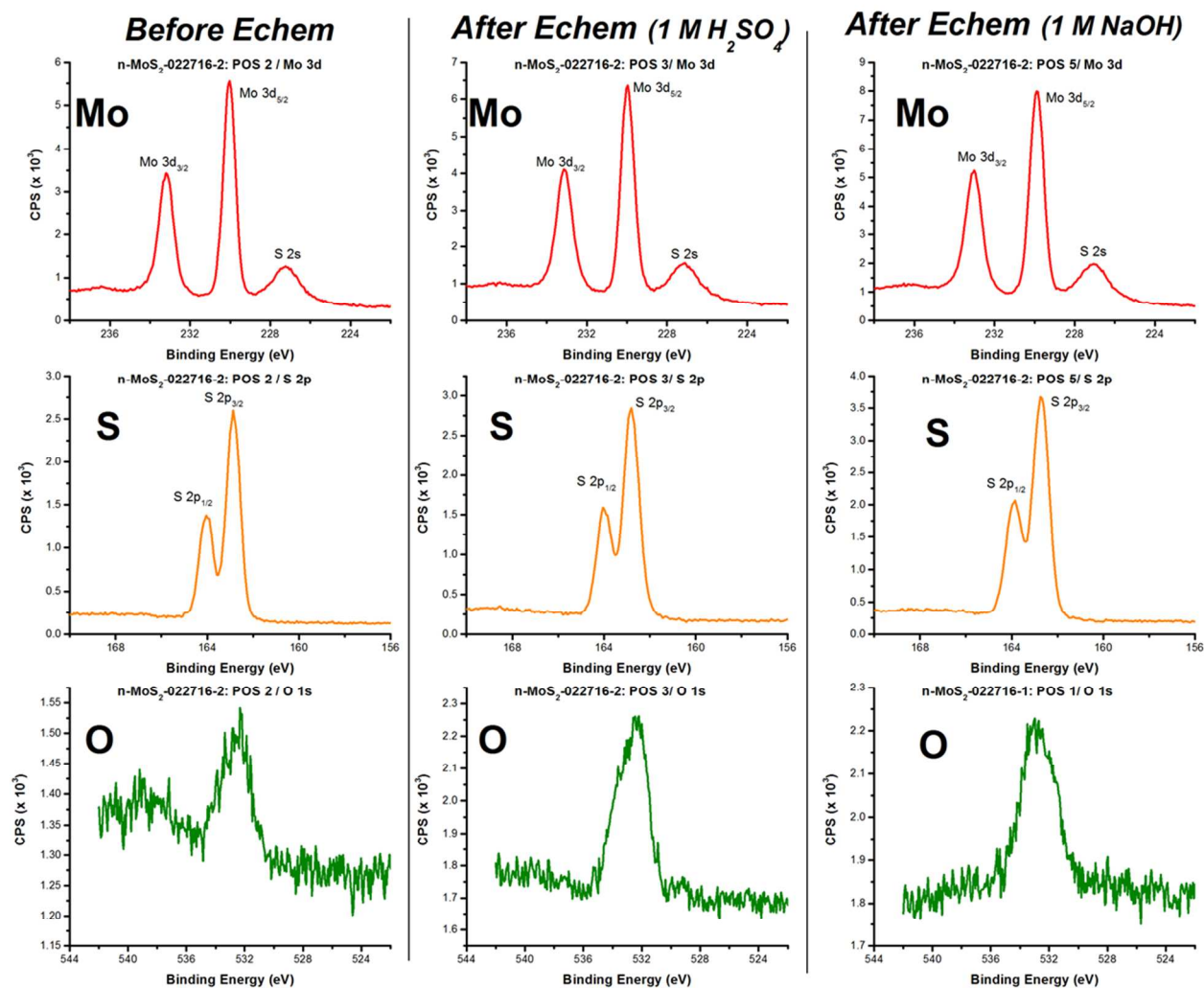
# Online MS : MoS<sub>2</sub> in 1.0 M NaOH



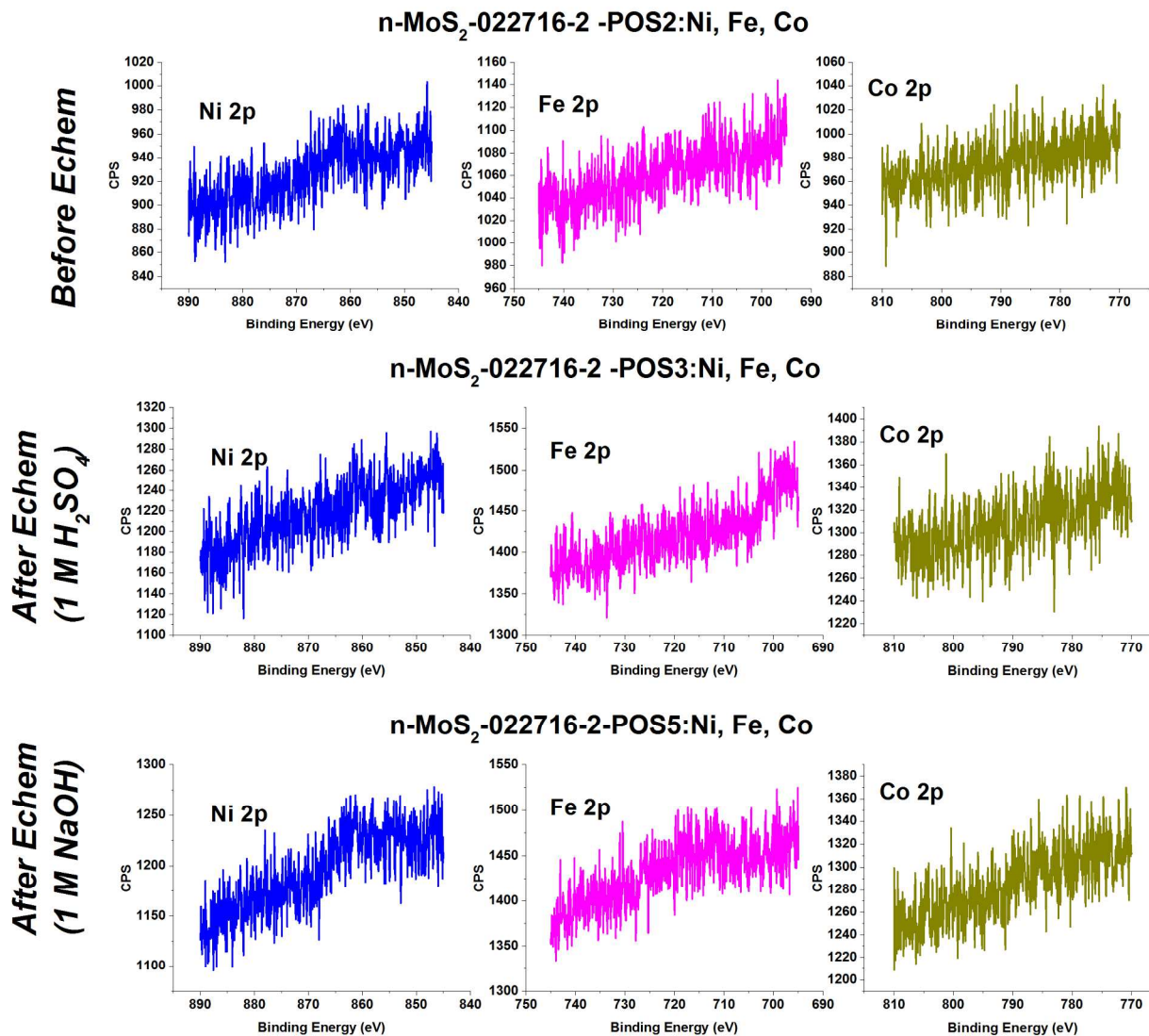


**Figure S1.** Online mass spectrometry and chronopotentiometry during hydrogen evolution on n-MoS<sub>2</sub> in base (top) and acid (bottom).

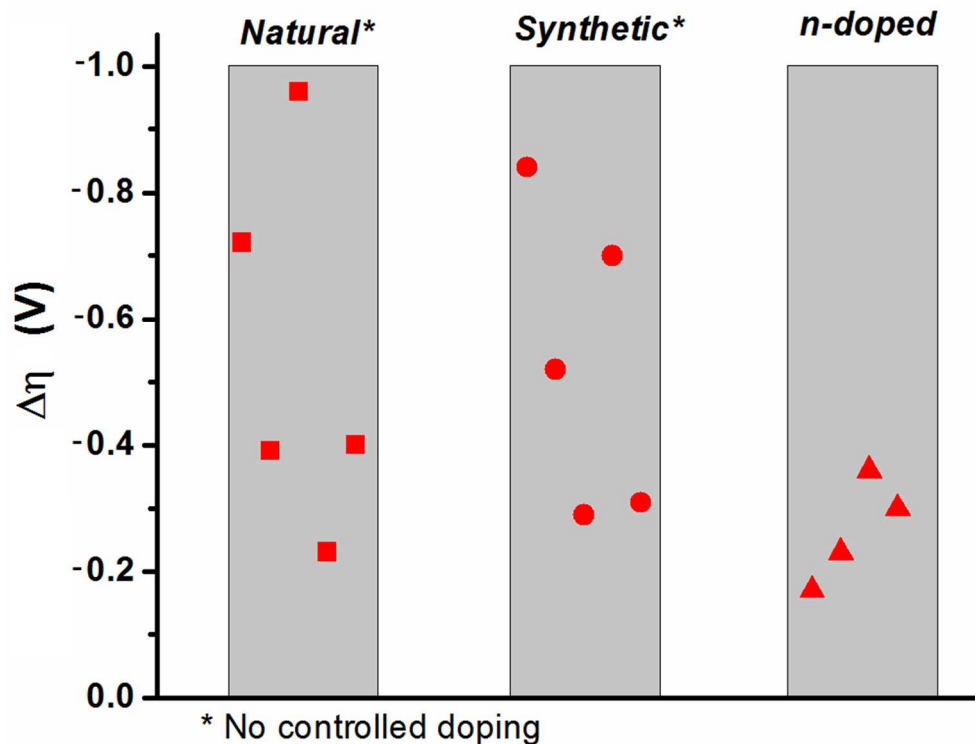




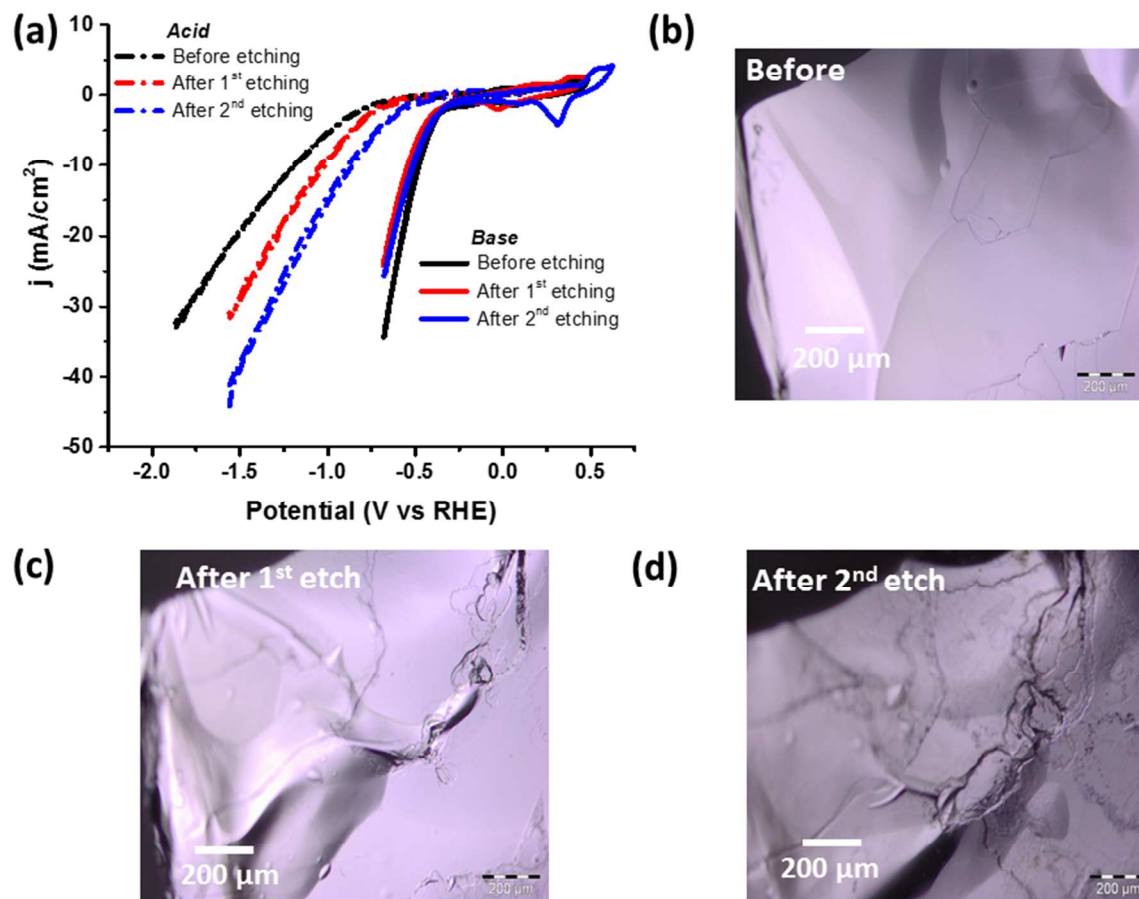
**Figure S2.** X-ray photoelectron spectroscopy of n-MoS<sub>2</sub> single crystals before (left column) and after electrocatalysis in 1.0 M H<sub>2</sub>SO<sub>4</sub> (center column) or 1.0 M NaOH (right column).



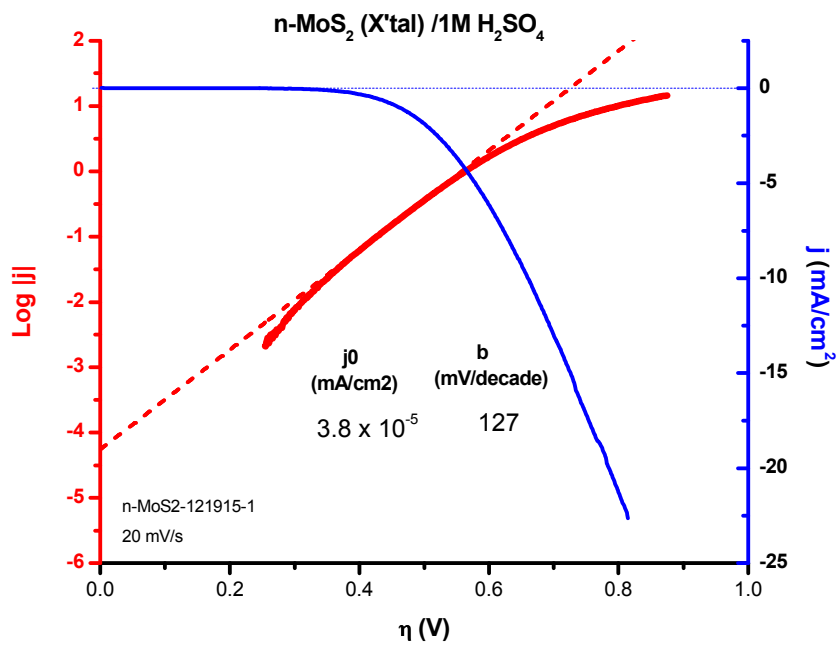
**Figure S3.** MoS<sub>2</sub> Single crystals (synthetic, n-doped). No Ni, Fe or Co 2p signals were detected after electrochemistry in either acid or base.



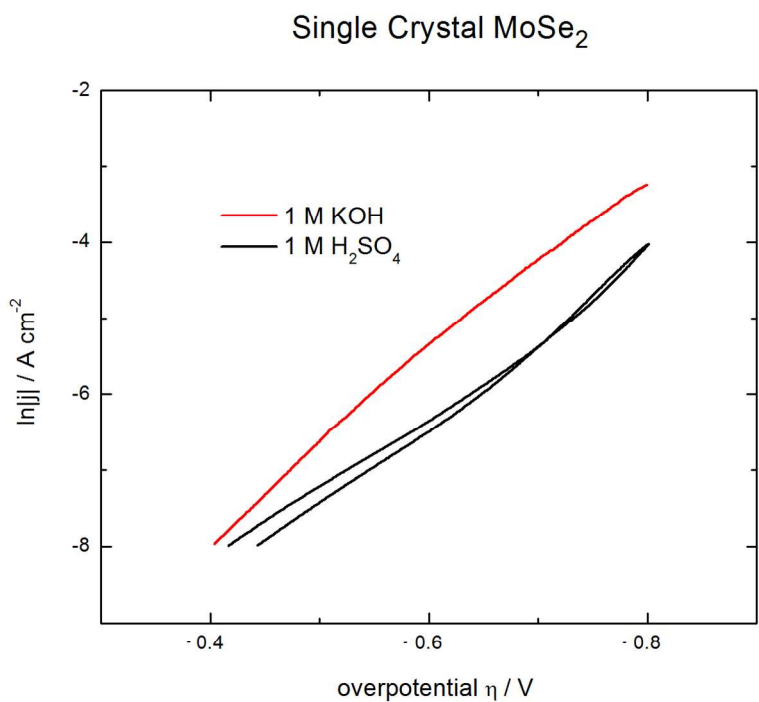
**Figure S4.**  $\Delta\eta$  for single crystal MoS<sub>2</sub> samples from a variety of sources. Note the natural and undoped synthetic single crystals have larger variations in  $\Delta\eta$  than for single crystal samples grown under conditions where doping is controlled. ( $\Delta\eta = \eta_{\text{Acid}} - \eta_{\text{Base}}$  where  $\eta_{\text{Acid}}$  is the overpotential required to drive H<sub>2</sub> evolution at a current density of -10 mA cm<sup>-2</sup> for samples in contact with 1.0 M H<sub>2</sub>SO<sub>4</sub>(aq), and  $\eta_{\text{Base}}$  is the overpotential required to drive H<sub>2</sub> evolution at a current density of -10 mA cm<sup>-2</sup> for samples in contact with 1.0 M NaOH(aq) or 1.0 M KOH(aq).)

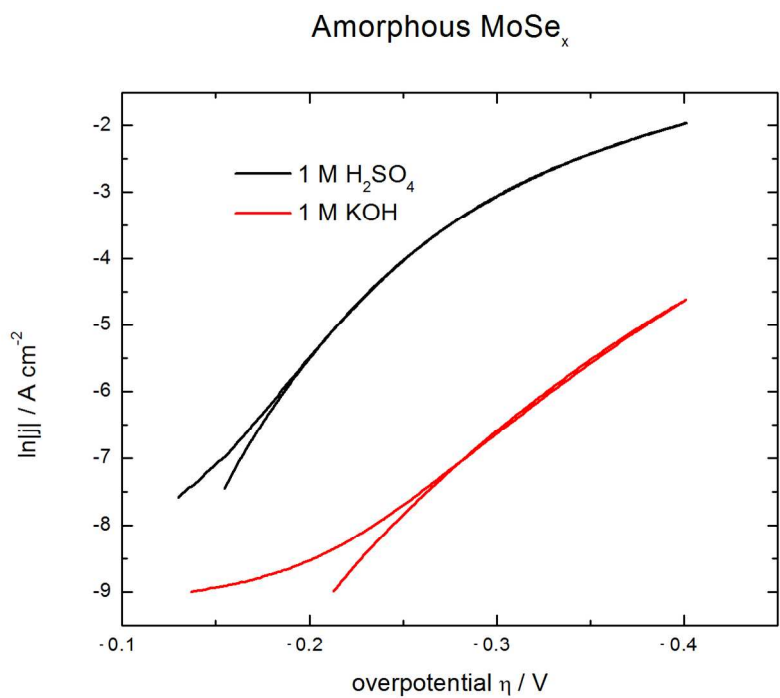
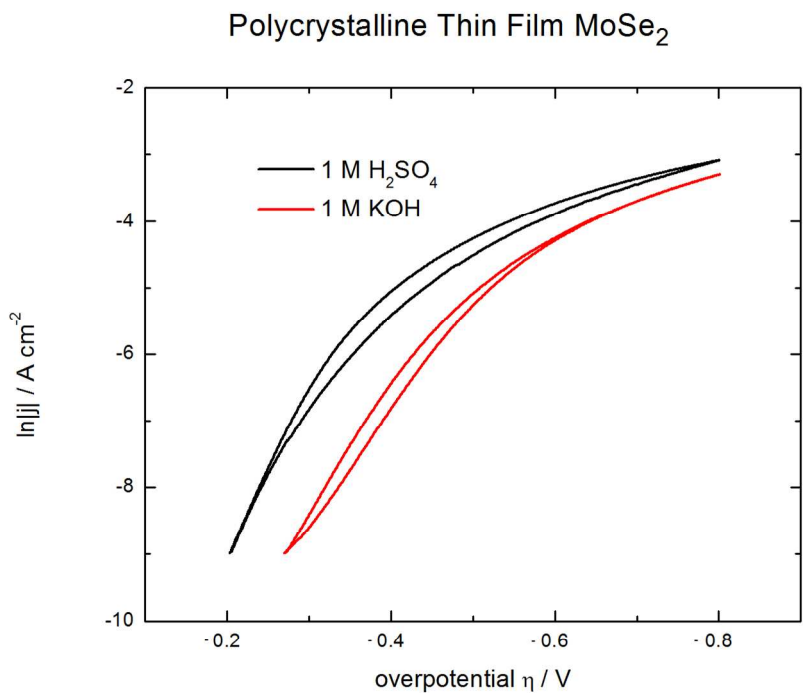


**Figure S5.** (a) Cyclic voltammograms obtained in acid (0.10 M H<sub>2</sub>SO<sub>4</sub>(aq)) and base (1.0 M NaOH(aq)) before and after each electrochemical etching step of a natural single crystal MoS<sub>2</sub>. Scan rate: 50 mV s<sup>-1</sup>. Figure 2 in the main text is plotted using these data. (b)–(d) optical images of the same area of the electrode before and after the etching process.



**Figure S6.** Tafel plot for single-crystalline n-MoS<sub>2</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub>(aq).





**Figure S7.** (top) Tafel plot of single crystal MoSe<sub>2</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub>(aq) and 1.0 M KOH(aq). (middle) Tafel plot of polycrystalline thin film MoSe<sub>2</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub>(aq) and 1.0 M KOH(aq). (bottom) Tafel plot of amorphous MoSe<sub>x</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub>(aq) and 1.0 M KOH(aq).

## References

- (1) Baglio, J.; Kamieniecki, E.; DeCola, N.; Struck, C.; Marzik, J.; Dwight, K.; Wold, A. Growth and Characterization of n-WS<sub>2</sub> and Niobium-doped p-WS<sub>2</sub> Single Crystals. *J. Solid State Chem.* **1983**, *49*, 166-179.
- (2) (a) Kline, G.; Kam, K.; Canfield, D.; Parkinson, B. A. Efficient and Stable Photoelectrochemical Cells Constructed with WSe<sub>2</sub> and MoSe<sub>2</sub> Photoanodes. *Solar Energy Mater.* **1981**, *4* (3), 301-308; (b) McKone, J. R.; Pieterick, A. P.; Gray, H. B.; Lewis, N. S. Hydrogen Evolution from Pt/Ru-Coated p-Type WSe<sub>2</sub> Photocathodes. *J. Am. Chem. Soc.* **2013**, *135* (1), 223-231; (c) J. Baglio, E. K., N. DeCola, C. Struck, J. Marzik, K. Dwight, A. Wold, Growth and Characterization of n-WS<sub>2</sub> and Niobium-Doped p-WS<sub>2</sub> Single Crystals. *J. Solid State Chem.* **1983**, *49*, 166-179; (d) C. Koval, J. O. Preparation and Electrochemical Characterization of WSe<sub>2</sub> Electrodes having a wide Range of Doping Densities. *J. Electroanal. Chem.* **1987**, *234*, 133-143.
- (3) Benck, J. D.; Chen, Z.; Kuritzky, L. Y.; Forman, A. J.; Jaramillo, T. F. Amorphous Molybdenum Sulfide Catalysts for Electrochemical Hydrogen Production: Insights into the Origin of their Catalytic Activity. *ACS Catal.* **2012**, *2*, 1916-1923.
- (4) Saadi, F. H.; Carim, A. I.; Velazquez, J. M.; Baricuatro, J. H.; McCrory, C. C. L.; Soriaga, M. P.; Lewis, N. S. Operando Synthesis of Macroporous Molybdenum Diselenide Films for Electrocatalysis of the Hydrogen-Evolution Reaction. *ACS Catal.* **2014**, *4* (9), 2866-2873.