

Li Intercalation in MoS₂: In Situ Observation of Its Dynamics and Tuning Optical and Electrical Properties

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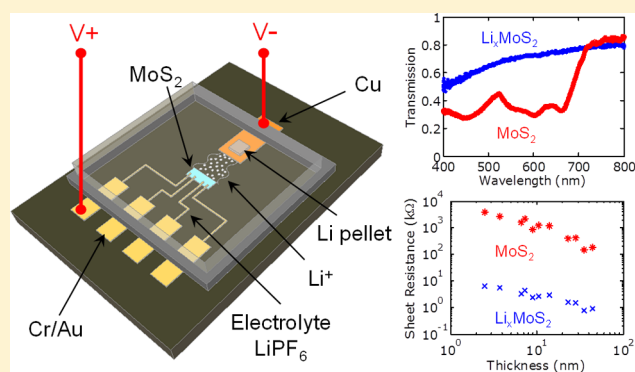
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Supporting Information

ABSTRACT: Two-dimensional layered materials like MoS₂ have shown promise for nanoelectronics and energy storage, both as monolayers and as bulk van der Waals crystals with tunable properties. Here we present a platform to tune the physical and chemical properties of nanoscale MoS₂ by electrochemically inserting a foreign species (Li⁺ ions) into their interlayer spacing. We discover substantial enhancement of light transmission (up to 90% in 4 nm thick lithiated MoS₂) and electrical conductivity (more than 200×) in ultrathin (~2–50 nm) MoS₂ nanosheets after Li intercalation due to changes in band structure that reduce absorption upon intercalation and the injection of large amounts of free carriers. We also capture the first in situ optical observations of Li intercalation in MoS₂ nanosheets, shedding light on the dynamics of the intercalation process and the associated spatial inhomogeneity and cycling-induced structural defects.

KEYWORDS: MoS₂, intercalation, lithiation, in situ, electrochemical



Molybdenum disulfide (MoS₂) is a member of a family of two-dimensional (2D) layered transition metal dichalcogenides (TMDs).¹ Because of their unique combinations of physical and chemical properties,^{2–4} as well as their 2D nature (the ability to be thinned down to monolayer), TMDs have attracted research interest in areas of nanoelectronics,⁵ optoelectronics,⁶ energy storage devices,⁷ thermoelectric devices,⁸ flexible electronics,⁹ and electrocatalysis.¹⁰ The large interlayer separation in MoS₂ (~0.65 nm) provides perfect locations to accommodate guest species such as alkali metal ions (Li⁺, Na⁺, and K⁺) through a process known as intercalation. Intercalation in layer-structured materials such as graphite and MoS₂ have been extensively studied for applications in energy storage,¹¹ liquid phase exfoliation,¹² and electrocatalysis.^{13,14} It has been reported that intercalation causes changes in the host materials' electronic structure,^{15–17} resulting in considerable variation in their optical and electrical properties.^{18–21} Similarly, intercalation in Li_xCoO₂ has demonstrated tunable thermal conductivity through intercalation-dependent phase behavior and phonon scattering.²² Large quantity of zerovalent metal intercalation has also been developed recently.^{20,23,24}

In this study, we develop a novel platform to electrochemically intercalate Li atoms into the interlayer spacing of ultrathin MoS₂ nanosheets, controllably tuning the physical and chemical properties of the material. Our electrochemical device allows in

situ characterization of both optical and electrical properties during the lithiation/delithiation process. While previous work¹⁹ focused on the effect of lithiation in MoS₂ for energy storage applications by irreversibly converting MoS₂ to Li₂S, our study emphasizes controllably and reversibly tuning the physical properties of MoS₂ films by varying Li concentration in interlayer gaps. Our work also captures the first set of in situ observations of the dynamics of the Li intercalation process in MoS₂ nanosheets. Through Raman measurement and band structure calculations, we provide possible explanations for the simultaneous enhancement of optical transmission and electrical conductivity upon lithiation, providing a path to dynamically tune the physical properties of such layered materials.

Figure 1 illustrates the sample fabrication process of our electrochemical platform, which allows us to characterize the optical and electrical properties of MoS₂ while we perform Li intercalation. We first mechanically exfoliated ultrathin MoS₂ nanosheets (~2–50 nm) onto SiO₂/Si substrates (Figure 1a). The MoS₂ thickness was determined by atomic force microscopy (AFM). We then put down metal electrodes via electron-beam (e-beam) lithography and shadow mask

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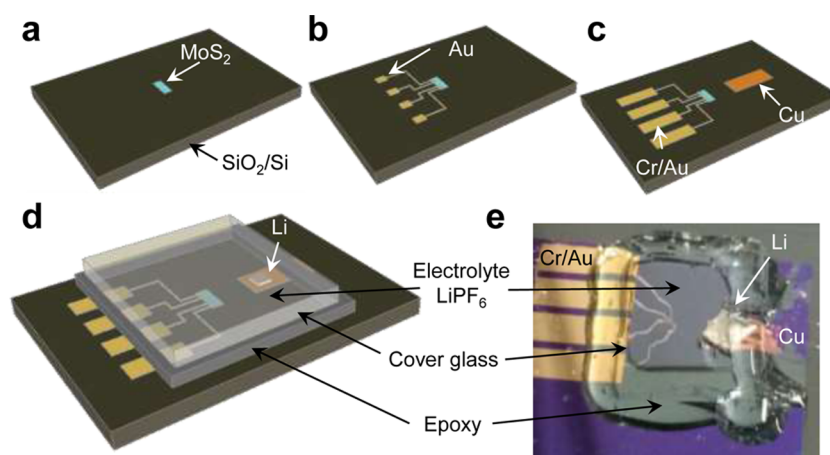


Figure 1. Schematics. (a–d) Schematics of the fabrication process of nanoscale MoS₂ device for in situ Li intercalation. (e) Optical image of an as-fabricated device. See [Methods](#) for more details of the fabrication procedures. The thin Au lines appear intentionally “wavy” in the fabricated sample to avoid contacting other bulky MoS₂ flakes (from the exfoliation step) that are present on the substrate.

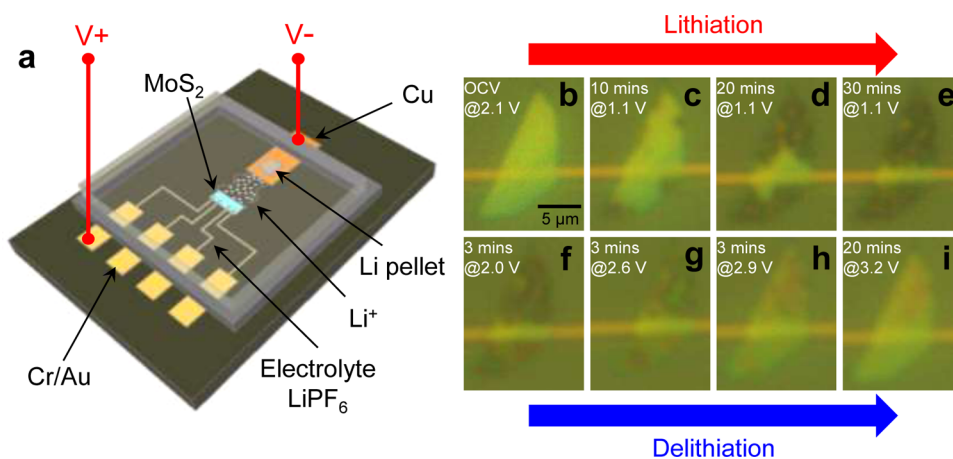


Figure 2. Direct observations of the dynamics of lithiation and delithiation process in MoS₂. (a) Experimental setup for electrochemical tuning of Li concentration in MoS₂. (b–e) Optical images of a thin (~20–35 nm) MoS₂ flake during the lithiation process. Initially, the flake had an open circuit voltage (OCV) of 2.1 V versus Li/Li⁺. When holding at voltages of 1.2 V or higher versus Li/Li⁺, no visible changes were observed even after extended periods of time. While holding at 1.1 V versus Li/Li⁺, we observed that significant amount of Li⁺ ions were intercalated into MoS₂ flake from the edges and MoS₂ underwent a 2H to 1T phase transformation. These were evident from the dark spots in the flake. (f–i) Optical images of the same flake during the delithiation process. Reversible delithiation was achieved by biasing MoS₂ flake at higher voltages versus Li/Li⁺. As the voltage was increased, Li⁺ ions moved out of the flake from the edges. At 3.2 V versus Li/Li⁺, the MoS₂ flake almost went back to its original color. The top of the flake in (f) appeared to be red instead of yellow (originally), which indicated a slightly increased thickness. This is probably due to the structural change in MoS₂ upon Li intercalation.

evaporation as shown in [Figure 1b,c](#) (see [Methods](#) for more details). To perform electrochemical intercalation, we adopted a planar nanobattery configuration ([Figure 1d](#)) where Li metal and MoS₂ nanosheets were used as counter and working electrodes, respectively. The device with electrolyte (1 M LiPF₆ in 1:1 w/w ethylene carbonate/diethyl carbonate from EMD Chemicals) was sandwiched by the top glass slide and bottom substrate and sealed with epoxy to prevent oxidation ([Figure 1e](#)). This platform allows us to carry out Li intercalation and at the same time characterize the optical and electrical properties of MoS₂ in situ. The electrochemical intercalation was performed using a SP-150 BioLogic workstation (see [Methods](#)).

With a transparent glass slide as the top seal, our electrochemical cell serves as an excellent platform to study the dynamics of Li intercalation in nanoscale MoS₂ flake. A freshly packaged MoS₂ nanosheet typically shows an open circuit voltage (OCV) between 1.8 and 2.2 V with respect to

Li/Li⁺. We carried out Li intercalation by gradually lowering the MoS₂ potential with respect to Li/Li⁺ from 2.0 to 1.0 V with steps of 0.1 V or less ([Figure 2a](#)). We avoided going below 1.0 V versus Li/Li⁺ to prevent any irreversible conversion reaction that forms Li₂S.^{7,25} [Figure 2b–i](#) depicts the first Li intercalation cycle for a typical MoS₂ nanosheet. We measured the thickness of this flake ([Figure 2b](#)) by AFM, which was ~23 nm at the bottom (green region) and ~32 nm at the top (yellow region). When we gradually lithiated this MoS₂ nanosheet by driving down its potential with respect to Li from 2.1 V (as packaged) to 1.2 V in steps of 0.1 V, we observed no significant change in the morphology and color of the flake under the optical microscope, even under extended stress time (40 min at 1.2 V versus Li/Li⁺, see [Supporting Information Figure 2](#)).

When we further lowered the MoS₂ potential to 1.1 V with respect to Li, we started to visualize the Li intercalation process under optical microscope. [Figure 2c](#) illustrates that MoS₂

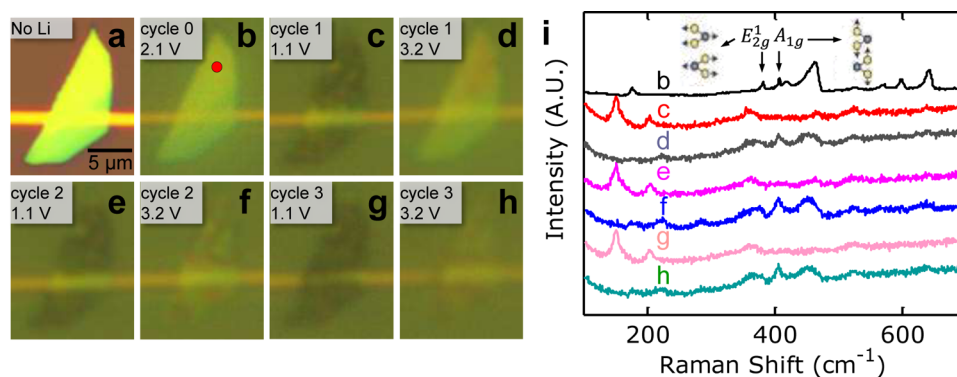


Figure 3. Cycling effects on MoS₂ nanosheet and Raman spectroscopy. (a–h) Optical reflection images of the same MoS₂ flake in Figure 2 at different cycles of Li intercalations. MoS₂ nanosheet showed progressively more structural defects as we repeatedly lithiate/delithiate the flake. These were evident from the nonuniform color change (green/yellow to red) across the flake, possibly due to an increase in interlayer thickness from Li intercalation dependent volume expansion. (i) Raman spectroscopy of the MoS₂ flake at different cycles, corresponding to (b–h) as indicated in the diagram. The red dot in (b) indicates the location of the Raman scan. The locations of first order phonon modes E_{2g}¹ (382 cm⁻¹) and A_{1g} (408 cm⁻¹) are labeled in graph. The inset shows the corresponding phonon vibration mode. After the first cycle, all Raman spectra (c–h) showed a broadening of line width of E_{2g} mode, which usually indicates high impurity scattering and structural defects. Whenever the flake is fully lithiated (c,e,g), A_{1g} peak intensity decreased significantly, suggesting the dissociation of interlayer bonding due to influx of Li⁺ ions. At the same time, peaks at ~150 and 200 cm⁻¹ started to appear, possibly due to a 2H to 1T phase transformation in MoS₂. When the flake was delithiated (b,d,f,h), A_{1g} mode reappears as interlayer bonding was restored.

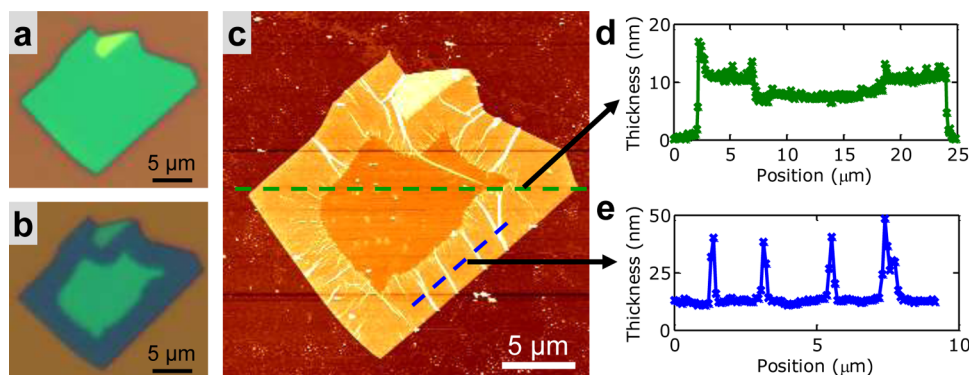


Figure 4. Strain in MoS₂ nanosheet after Li intercalation. (a,b) Optical images of a MoS₂ nanosheet before and after 2 h of chemical Li intercalation. The outer ring in (b) indicates that Li ions enter MoS₂ from the edges. The scale bars are 5 μm. (c) AFM image of the same MoS₂ nanosheet in (b) after 2 h of Li intercalation. The lithiated region showed a significant increase in thickness (~50%) due to the incoming Li ions. As a result, wrinkles were formed across the flakes due to strain built-up in the structure. (d) AFM line profile (indicated by the green dashed line) across the flake. The thickness of the flake increased from ~7.3 nm in the central un lithiated region to ~10.8 nm in the outer lithiated regions. (e) AFM line profile (indicated by the blue dashed line) across the wrinkles in the lithiated region. The height of these wrinkles ranged from 20 to 50 nm with an average of 36.7 nm.

started to turn dark brown in color from the edges after a few minutes. This color change gradually extended from the edges to the center of the flake with constant biasing at 1.1 V (Figure 2d) and finally covered up the entire MoS₂ nanosheet after 30 min (Figure 2e). Previous studies on bulk MoS₂ reported a similar plateau at ~1.1 V during Li intercalation and attributed it to a phase transition^{7,10,19,25} from 2H to 1T MoS₂. Our observation confirms that the MoS₂ flake undergoes a 2H (semiconducting) to 1T (metallic) phase transformation at ~1.1 V versus Li/Li⁺ to accommodate more Li⁺ ions in its interlayer spacing. In addition, the optical images demonstrate that Li⁺ ions (as well as the accompanying phase transition) enter MoS₂ flake from the edges and gradually diffuse toward the center of the flake. We note that in Figure 2e, MoS₂ regions under the metal electrodes remained greenish yellow in color. This was probably because the metal electrodes blocked the entry of Li⁺ ions from the edges and also acted as a clamp to prevent or slow down the phase transformation and the resulting volume expansion. We did not go below 1.0 V versus

Li/Li⁺ in the measurements to avoid the irreversible conversion reactions that form polysulfides.

Figure 2f–i shows the delithiation process of the same MoS₂ flake as we gradually increased its potential from 1.1 to 3.2 V with respect to Li/Li⁺. We could clearly visualize Li⁺ ions moving out from the MoS₂ flake edges, as MoS₂ changed back to its original color, starting from the center and finally spreading to the edges. After complete delithiation at 3.2 V for 20 min (in Figure 3i), we noticed that the bottom/thinner part of the flake completely returned to its original color before lithiation (Figure 2b), suggesting a fully reversible discharge/charge cycle with little structural changes in the thinner region. We note that this is most likely not “sample damage” in the sense of changes within the covalently bonded layers but rather changes in the spacing between layers. At the top/thicker part, the color appeared to be slightly reddish compared to the original yellow. We have observed that MoS₂ shows different color contrast at different thicknesses with all other factors (substrate, light intensity, exposure time, and lens aperture)

being the same. Our AFM measurements confirm that yellow MoS₂ are typically ~25–35 nm thick while red MoS₂ typically have a thickness of ~40–55 nm. This suggests that the color change in MoS₂ from yellow to red after one discharge/charge cycle was possibly due to an increase in MoS₂ interlayer spacing caused by intercalation. Our AFM measurements on chemically intercalated MoS₂ nanoflakes (Figure 4d) confirmed that an average of 50% increase in interlayer spacing is observed. Thus, while thinner MoS₂ might fully restore its structure upon Li intercalation (see Supporting Information Figure 4), thicker MoS₂ seems to be unable to fully recover from lithiation and tends suffer some structural changes due to the larger accumulated strain. This may explain why MoS₂ based energy storage device typically suffer significant capacity loss upon cycling, especially after the first few cycles.^{7,26,27}

We further investigated to verify if cycling causes structural changes in MoS₂ and if the yellow-to-red color change was due to cycling induced defects. Figure 3a–h shows a series of optical images of the same MoS₂ flake taken before device encapsulation with no electrolyte (Figure 3a) and at different cycles (Figure 3b–h) of Li intercalation. When fully delithiated at 3.2 V versus Li/Li⁺, we noticed that more red “bruises” start to appear on the MoS₂ nanosheet after several discharge and charge cycles of the MoS₂. After the first cycle, the top of the film showed a yellow-to-red color change most likely due to the structural changes to MoS₂ (an increase in interlayer spacing in this case) from the intercalation process. In subsequent cycles 2 and 3, more of these red spots showed up throughout the flake, suggesting accumulating changes in the MoS₂ structure upon repeated cycling.

Through the top transparent glass slide, we also performed in situ Raman spectroscopy of our MoS₂ flakes during Li intercalation. Figure 3i shows Raman spectra of MoS₂ corresponds to the cycling condition indicated in Figure 2b–h. The red spot in Figure 2b indicates where the laser spot (Horiba 633 nm He–Ne laser source) was during the measurement. Immediately after our device encapsulation and before any electrochemical intercalation, the Raman spectrum (black, top) was consistent with that of a few-layer 2H-MoS₂, which has been well studied.^{28–30} The E_{2g}¹ (in-plane optical vibration of the Mo–S bond) and A_{1g} modes (out-of-plane optical vibration of S atoms) were located at ~382 and 408 cm⁻¹, respectively. The inset illustrates the schematics of these two first-order Raman-active modes in 2H-MoS₂.

As we began the Li intercalation process by gradually lowering the MoS₂ potential from 2.1 to 1.2 V versus Li/Li⁺, Raman signals showed almost no change because Li⁺ ion concentration in MoS₂ is relatively low before the 2H to 1T transition at ~1.1 V (see Supporting Information Figures 1 and 3). When MoS₂ was fully lithiated and transformed to the 1T phase (Figure 2c,e,g), Raman spectra were significantly different. We observed peaks at ~150 and 200 cm⁻¹, which usually indicate a 2H to 1T phase transformation in MoS₂, as reported in previous studies of chemically intercalated MoS₂ films.^{10,16,29,31} However, A_{1g} peaks, which are typically still present in the chemically intercalated MoS₂ samples, showed significantly lower intensity during lithiation as evident in curves c,e,g in Figure 2i. Supporting Information Figure 3f shows how the A_{1g} mode intensity gradually decreased during lithiation and then slowly restored to its original level during delithiation. Similar observations of the reduction and broadening of the A_{1g} phonon were reported by Chakraborty et al.³² in monolayer MoS₂ and Kiriya et al.³³ in few-layer MoS₂ at high

doping level, attributed to strong electron–phonon coupling of the A_{1g} mode. We suspect that in an electrochemical intercalation process with enough supply of electrons, Li⁺ ion concentrations in MoS₂ (theoretical maximum at Li_{x=1}MoS₂) could be significantly higher than that in a chemical intercalation process (2 h in 1.6 M *n*-butyl lithium solution at 300 K). Thus, the presence of these Li⁺ ions may have suppressed the out-of-plane S atom vibrations that contribute to A_{1g} mode (see Supporting Information Figure 5 for a comparison of Raman Spectra of MoS₂ during chemical and electrochemical intercalations). The E_{2g}¹ mode in curve b also became part of a broad peak with a large line width in all subsequent curves (c–h) after the first lithiation. This peak broadening is typically a sign of structural defects in the crystal structure, possibly due to the volume expansion in MoS₂ caused by lithiation in this case. That is why the line width of the E_{2g}¹ mode remained large even when Li⁺ ion concentration was low and MoS₂ was delithiated (Figure 2d,f,h).

In order to further investigate structural defects and strain built-up in MoS₂ from Li intercalation, we carried out AFM measurements on lithiated MoS₂ flakes. Because both the electrolyte and Li pellets are extremely reactive in air, we cannot perform AFM directly on the electrochemically intercalated devices. Instead, we immersed MoS₂ samples in *n*-butyl lithium solutions and used chemical intercalation to lithiate the flakes (see Methods for more details). Figure 4a,b shows optical images of the same MoS₂ flake before and after chemical intercalations (2 h in *n*-butyl lithium solution). The AFM image of the flake after intercalation is shown in Figure 4c. It confirms our previous observation that Li ions entered the MoS₂ van der Waals gaps from the edges and diffused toward the center, as it was evident from the outer ring of the lithiated region in Figure 4b,c. The color change in lithiated MoS₂ were due to an enhancement in optical transmission upon lithiation, which we will discuss in more details in the next section.

The dashed line profile across the flake is illustrated in Figure 4d. The MoS₂ thickness increases from 7.3 (center, unlithiated region) to 10.8 nm due to volume expansion caused by Li intercalation. There is a slight gradient of thickness from the edge (thicker) to the center (thinner) of the flake in both directions, possibly indicating the gradient of Li ion concentrations in MoS₂ from the edge (high) to the center (low). Besides the height increase due to accommodation of Li ions in the interlayer gaps, we also notice significant wrinkle formation in the lithiated region, along the entry direction of the Li ions. Because the intercalation process exerts significant strain on the MoS₂ crystal structure, the material eventually relaxes through these wrinkle formations. Similar distortion and wrinkling has been observed in the past on sodiated (Na⁺) MoS₂ films.^{34,35} The height of these wrinkles ranged from 20 to 50 nm with an average height of 36.7 nm for this 7.3 nm thick MoS₂ flake (Figure 4e). These irreversible wrinkles and strains in Li_xMoS₂ are possible reasons for the broadening of E_{2g}¹ Raman mode after the first lithiation, and for the cycling capacity loss in MoS₂. This is especially true because the intercalated Li ion concentrations are probably higher in the electrochemical intercalation process (at 1.1 V versus Li/Li⁺) than in a chemical intercalation process (2 h in 1.6 M *n*-butyl lithium solution at 300 K) and therefore would cause more strain and wrinkles.

From both electrochemical and chemical intercalations, we observed significant change in color contrast of MoS₂ upon lithiation. In order to further investigate the optical properties

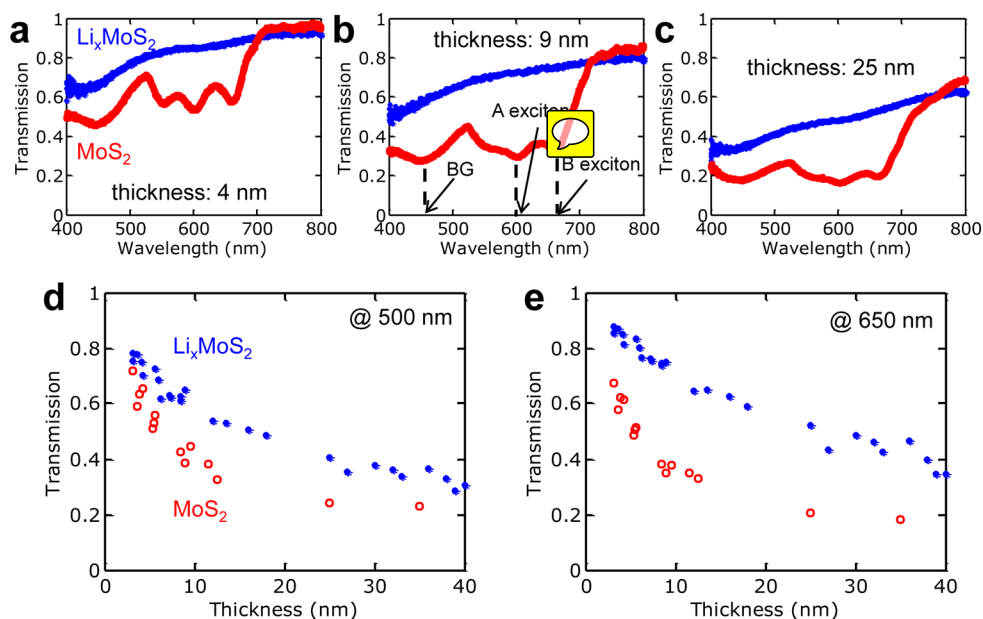


Figure 5. Optical characterizations of MoS₂ flakes upon Li intercalation. (a–c) Optical transmission spectra of MoS₂ flakes with various thicknesses (4, 9, and 25 nm) before (red) and after (blue) Li intercalations. (d,e) Thickness dependence of MoS₂ optical transmissions at 500 and 650 nm. The results showed enhancement in transmission after Li intercalation.

of MoS₂ upon Li intercalation, we performed spectral measurements (with a Nikon LV-UDM microscope) to characterize the optical transmission before and after Li intercalations. Here we exfoliated MoS₂ flakes onto quartz substrates and immersed them into 1.6 M *n*-butyl lithium solution for 2 h for chemical intercalation. The lateral dimensions of these MoS₂ flakes were typically 5–20 μm, significantly larger than the spot size of the confocal microscope.

Figure 5a–c shows the transmission spectra of MoS₂ nanosheets before (red) and after (blue) 2 h of Li intercalation with initial thicknesses of 4, 9, and 25 nm, respectively. All optical transmission spectra were normalized to that of the quartz substrate that the sample sit on. We observe significant enhancement in transmission after Li intercalation at wavelengths between 400 and 700 nm, as well as slight decrease in transmission at wavelengths greater than 700 nm. This is consistent with recent observations by Wan et al.¹⁹ For the 9 nm thick MoS₂ flake, the transmission in the visible range jumped from <30% in the pristine state to >70% after Li intercalation; while thin films (<5 nm) became highly transparent (>85%) after lithiation. Examining a larger range of thicknesses in Figure 5d,e, we also observe a clear dependence of optical transmission on the sample thickness. We plot the MoS₂ transmission before and after Li intercalation versus sample thickness at 500 and 650 nm wavelengths, respectively, in Figure 5d,e. Optical transmission enhancement after lithiation is observed in all thicknesses (measured by AFM) at both wavelengths.

We attribute at least part of the MoS₂ optical transmission enhancement between 400 and 700 nm to a substantial reduction in absorption after Li intercalation. There are three distinct local minima in the transmission spectrum of 2H-MoS₂ before intercalation (red curves in Figure 5a–c) at ~455 nm (2.73 eV), 603 nm (2.03 eV), and 660 nm (1.88 eV). These are due to absorption peaks at the corresponding energies. Previous studies of MoS₂ have also reported photoluminescence (PL)

bands at around 600 and 660 nm, which were attributed to band edge transitions in the K-point.^{36,37} Figure 6a shows the schematic of the band structure of a few-layer thick 2H-MoS₂ flake at the K-point of the Brillouin zone. The A and B excitons are two exciton bands that are produced by band splitting at the K-point, possibly due to interlayer coupling.^{36–38} The absorption peaks we obtained experimentally matched well with previously reported values. The high-energy absorption peak near 2.73 eV (~455 nm) we observed is also consistent with recent optical measurements of MoS₂.^{36,39,40} While the origin of this high-energy exciton is still under debate, theoretical calculations suggest that this exciton may come from a background peak (BG) due to phonon–electron coupling^{36,39} or a transition among the nesting bands between the Γ and Λ positions of the Brillouin zone.⁴¹

After Li intercalation, the 2H-MoS₂ undergoes a phase transformation to 1T-Li_xMoS₂ lattice structure, which shows metallic behavior. Enyashin et al.⁴² used density-function theory to calculate the band structure of 1T-Li_{x=1}MoS₂, where the valence and conduction bands were overlapped at the K-point (see schematic in Figure 6b), consistent with fully metallic behavior. Without the band gap, the absorption in 1T-Li_xMoS₂ is substantially reduced, resulting in the optical transmission enhancement. We calculated the refractive indices of MoS₂ before and after Li intercalation (Figure 6c,d) from our thickness dependent transmission data (see Supporting Information). The imaginary parts of the MoS₂ refractive index became significantly less after Li intercalation, which is an indication of a decrease in light absorption of the material.²⁰

Our electrochemical device also serves as a platform to allow in situ characterization and tuning of MoS₂ electrical transport properties. Four terminal MoS₂ devices were fabricated by e-beam lithography and e-beam evaporated Cr/Au contacts (Figure 1). As shown in Figure 7a, MoS₂ nanosheets demonstrated drastic improvement in electrical sheet resistance upon Li intercalation even down to a few nanometers in thickness. Four-probe measurements showed that lithiated

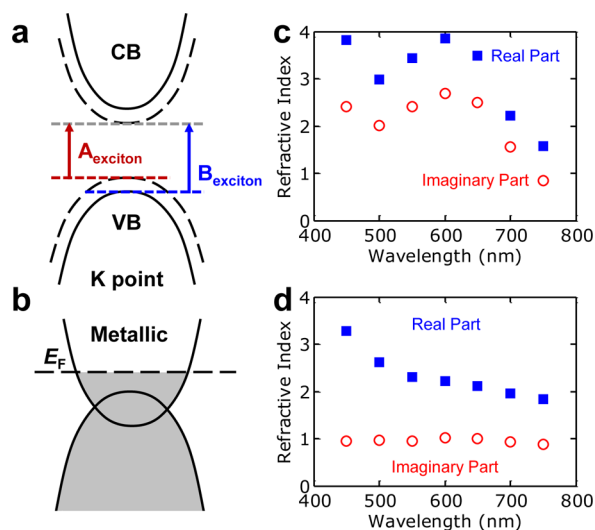


Figure 6. Reduction in absorption in MoS₂ after Li intercalation. (a) Schematic of the band structure of 2H-MoS₂ at the K-point in the Brillouin zone without Li intercalation. Optical transitions due to the A and B excitons are depicted. These transitions possibly cause absorption peaks in 2H-MoS₂, which we observe as local optical transmission minima in Figure 5a–c. (b) Schematic of the band structure of 1T-Li_{x=1}MoS₂ at the K-point in the Brillouin zone after Li intercalations. 1T-Li_{x=1}MoS₂ shows a metallic behavior as the conduction band and the valence band becomes overlapped and the Fermi level lies in an incompletely filled band. This metallic band structure with no bandgap substantially reduces the light absorption. (c,d) The refractive indices of 2H-MoS₂ and 1T-Li_{x=1}MoS₂, respectively, as functions of wavelengths were calculated from the thickness dependent optical transmission measurements. The filled blue squares are the real part while the hollow red circles are the imaginary part of the refractive indices. In 2H-MoS₂, higher values of the imaginary part at 450, 600, and 650 nm indicate higher absorption at these wavelengths, consistent with the transmission spectrum in Figure 5. In 1T-Li_{x=1}MoS₂, the imaginary part decreased significantly after Li intercalation, confirming a reduction in absorption due to the band structure change.

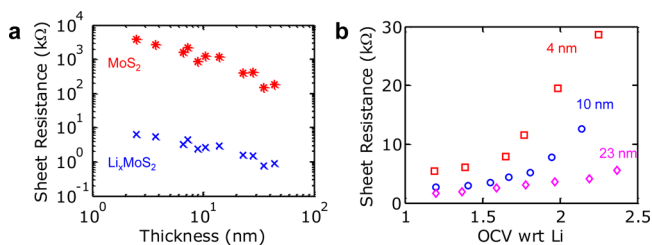


Figure 7. Electrical conductivity enhancement upon Li intercalation. (a) MoS₂ nanosheets with different thicknesses showed consistent decrease in sheet resistances by more than 100× after Li intercalation. (b) Sheet resistance of Li_xMoS₂ (with thicknesses of 4, 10, and 23 nm) are plotted as a function of their potentials versus Li/Li⁺. This indicates that we could dynamically tune the Li_xMoS₂ electrical conductivity by changing the Li⁺ ion concentration in the interlayer gaps.

MoS₂ (biased at 1.2 V versus Li/Li⁺) typically exhibits over 2 orders of magnitude decrease in sheet resistance compared to pristine MoS₂, due to the high carrier density and metallic behavior caused by Li intercalation. Together with the optical transmission enhancement, this improvement in electrical sheet resistance opens up new opportunities for applications in transparent electrodes. For example, a 4 nm thick MoS₂

nanosheet exhibited optical transmission as high as 90% and showed more than 500× improvement in sheet resistance (from 2750 to 5.4 kΩ/sq.) upon Li intercalation. While this may be still short of the need for optoelectronic device applications (e.g., 90% and 10 Ω/sq. for ITO) at the moment, the large and tunable enhancement in both optical transmission and electrical conductivity through intercalation are promising and provides new opportunities in optoelectronics. Furthermore, our electrochemical platform enables dynamically tuning the MoS₂ sheet resistance in situ as a function of the Li ion concentration.

In Figure 7b, we plot the sheet resistance of Li_xMoS₂ as a function of its relative potential with respect to Li/Li⁺. We observed that the Li_xMoS₂ resistance decreased more than five times as we lowered the potential from ~2.3 to 1.2 V versus Li/Li⁺. This occurs because, as we vary the Li_xMoS₂ potential against Li/Li⁺, we are tuning the Li concentration in Li_xMoS₂ and therefore the carrier density and sheet resistance.¹⁰ We can calculate exactly how the Li concentration in Li_xMoS₂ changes as the potential in a bulk MoS₂ film, from a galvanostatic discharge curve of Li electrochemical intercalation into MoS₂ film (see Supporting Information Figure 1) and use that as a reference for our MoS₂ nanosheets. We did not lower the Li_xMoS₂ voltage to less than 1.2 V versus Li/Li⁺ in these measurements to avoid the volume expansion that may damage the electrodes or contacts. Our results suggest that Li intercalation significantly improve the MoS₂ optical transparency and electrical conductance. Similar effects have also been observed recently with Cu intercalation in Bi₂Se₃²⁰ and Li intercalation in graphite,¹⁸ making intercalation a potentially interesting technique for transparent electrode and touch screen applications.

The interlayer spacing in layered 2D materials accommodates the intercalation of large amounts of metal atoms. Our electrochemical platform enables direct observations of the reversible intercalation process in ultrathin nanosheets of 2D materials such as MoS₂, and in situ characterization of their optical and electrical properties. We provide the first evidence of the dynamics of Li intercalation in nanoscale MoS₂ flakes. Through our optical, Raman and AFM measurements, we gain better understanding of the intercalation process and the possible structural changes in MoS₂ caused by repeated Li intercalation and deintercalation. These results provide possible explanations for cycling capacity loss in MoS₂ films and shed insights on improving performance of MoS₂-based energy storage devices. Intercalation is also a powerful technique to dynamically tune the physical and chemical properties of material. Through Li intercalation, we achieve substantial improvement of MoS₂ optical transmission (up to 90% for a 4 nm flake) as well as more than 2 orders of magnitude increase in electrical conductivity for all flakes (~2–50 nm). Further investigations are under the way to study how intercalation could tune the thermal conductivity and Seebeck coefficient of Li_xMoS₂. The capability to reversibly engineer the physical and chemical properties of nanomaterials opens up exciting opportunities in optoelectronics, transparent electrodes, energy harvesting, and storage.

Methods. Sample Fabrication. Ultrathin MoS₂ flakes were exfoliated using the Scotch tape method onto a highly doped Si substrate with 90 nm of SiO₂ (Figure 1a). Inner electrodes (70 nm of Au) were patterned with e-beam lithography and deposited through e-beam evaporation (Figure 1b). Outer electrodes (1/70 nm of Cr/Au for MoS₂ and 50 nm of Cu for

Li pellet) were deposited through e-beam evaporation through a shadow mask (Figure 1c). The MoS₂ device was then transferred inside an Ar-filled glovebox, where a Li pellet is deposited onto the Cu electrode (isolated from MoS₂ electrodes). A cover glass (0.2 mm thick) was placed on top of the central region and epoxy was used to seal three sides of the glass. Because of the finite thickness of the Li pellet, a small pocket was created and fully filled with electrolyte (LiPF₆ in EC/DEC w/w = 1:1). The last (and fourth) side of the cover glass was then sealed with epoxy to isolate the electrolyte and Li pellet from the surrounding to prevent oxidations (Figure 1d,e). Care was taken to minimize the formation of gas bubbles.

Electrochemical Intercalation and Electrical Transport Measurements. Electrochemical intercalation was performed with a Biologic SP-150 potentiostat. Constant voltage charge and discharge were used to lithiate and delithiate MoS₂ nanosheets for in situ optical, Raman, and electrical measurements. Additional details were provided in the Supporting Information. Electrical transport characteristics of MoS₂ were measured with four-probe structures using a Keithley 4200-SCS parameter analyzer.

Chemical Intercalation. Samples were immersed into 1.6 M *n*-butyl lithium (Fisher Scientific) for 2 h. This was done at room temperature in an Ar-filled glovebox. After intercalation, we gently washed these samples with anhydrous hexane to remove organic residues. Samples were then sealed in an Al pouch cell within the glovebox (to slow down the oxidation of Li_xMoS₂ in air) and transferred out for further analysis (AFM, electrical, and optical measurements).

Optical Transmission Measurements. Light transmission spectra were performed by an inverted microscope (Nikon LV-UDM microscope). White light was collected by a 50× objective with a numerical aperture of 0.8 using bright field mode. Spectral range was 400–800 nm. The photodetector (Princeton Instruments Spectrometry CCD) was cooled down by liquid N₂ with exposure time of 2 s.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b02619.

Setup for in situ optical measurements, additional Raman analysis, more optical images, TEM images, additional optical transmission results, electrical data, and XPS analysis.

(PDF)

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Author Contributions

F.X., E.P., and Y.C. conceived the project. F.X. and H.W. fabricated the samples. F.X. carried out the optical microscopy, Raman spectroscopy, electrical transport, and AFM measurements. X.L. and F.X. carried out optical transmission measurements and analysis. J.S. performed TEM measurements. F.X., E.P., and Y.C. cowrote the manuscript. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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Supplementary Information

Li intercalation in MoS₂: *in-situ* observation of its dynamics and tuning optical and electrical properties

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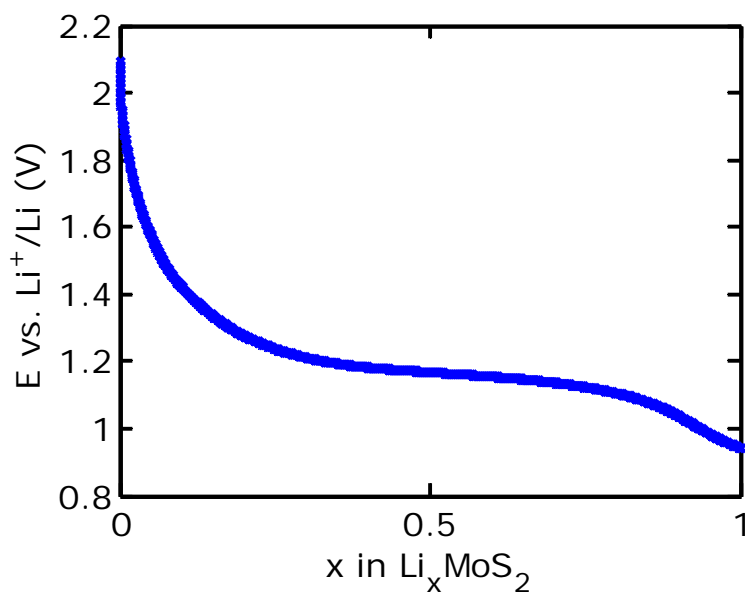
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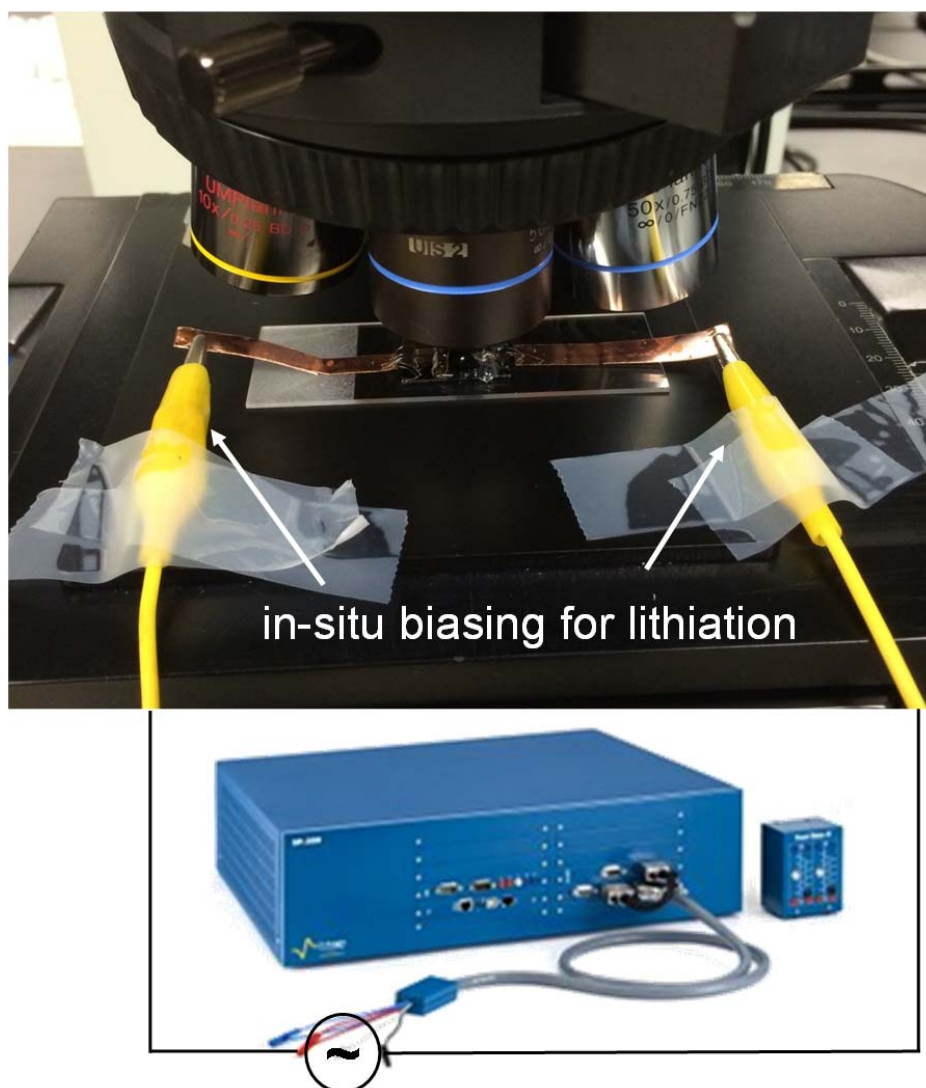
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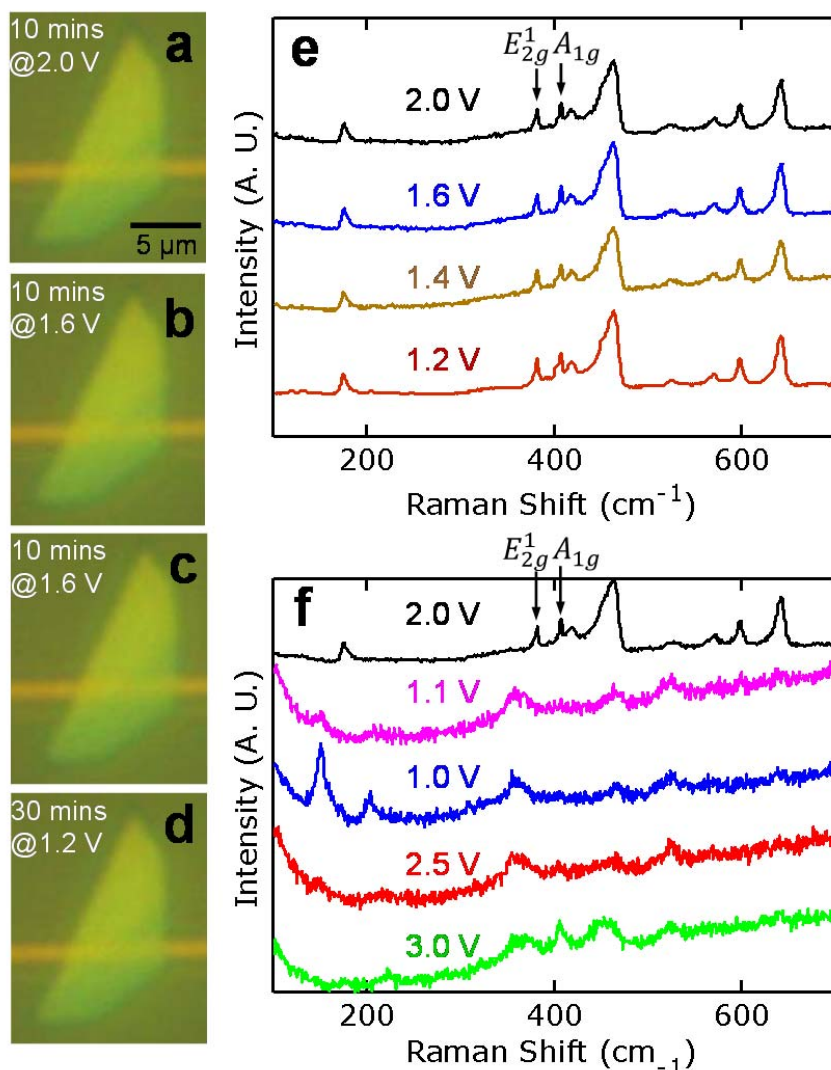
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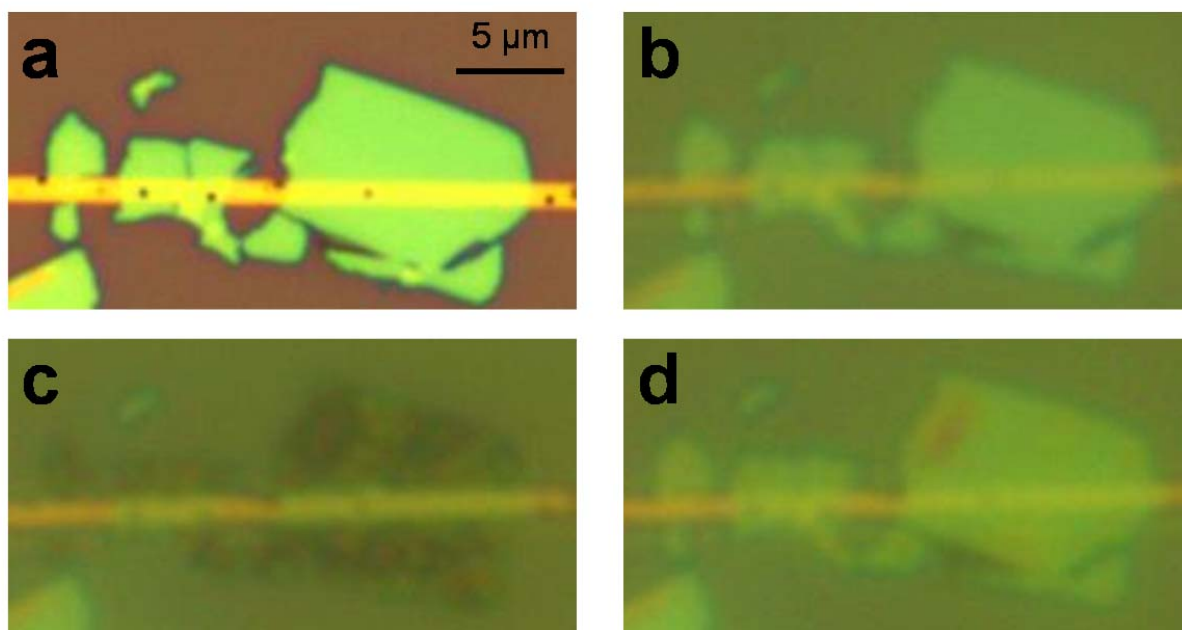
Supplementary Figure 1. Galvanostatic discharge curve of the Li intercalation process in MoS_2 . During the initial lithiation process, MoS_2 potential vs. Li/Li^+ gradually decreases as more Li^+ ions enter the interlayer spacing. We observe a voltage plateau at ~ 1.2 V due to the 2H to 1T phase transformation. From the constant current measurement, we can calculate the exact amount of Li ions that are intercalated into MoS_2 and thus the Li concentration in Li_xMoS_2 as a function of the potential.



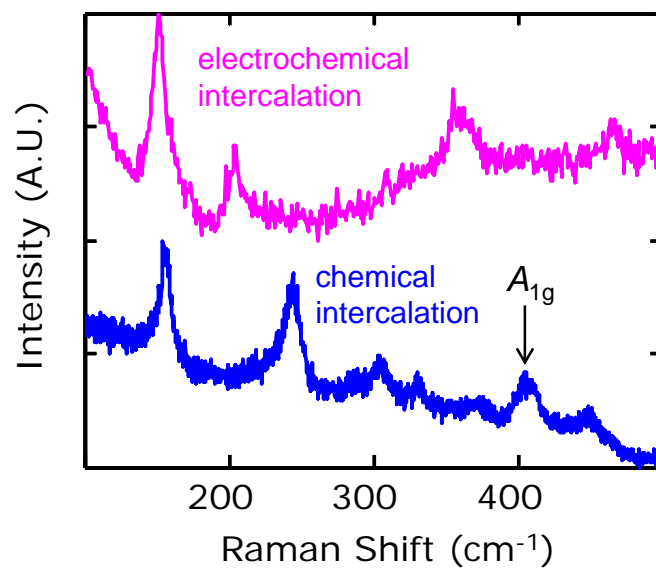
Supplementary Figure 2. Setup for *in-situ* optical and Raman measurement. Schematics of the experimental setup for *in-situ* optical and Raman measurement during the lithiation process.



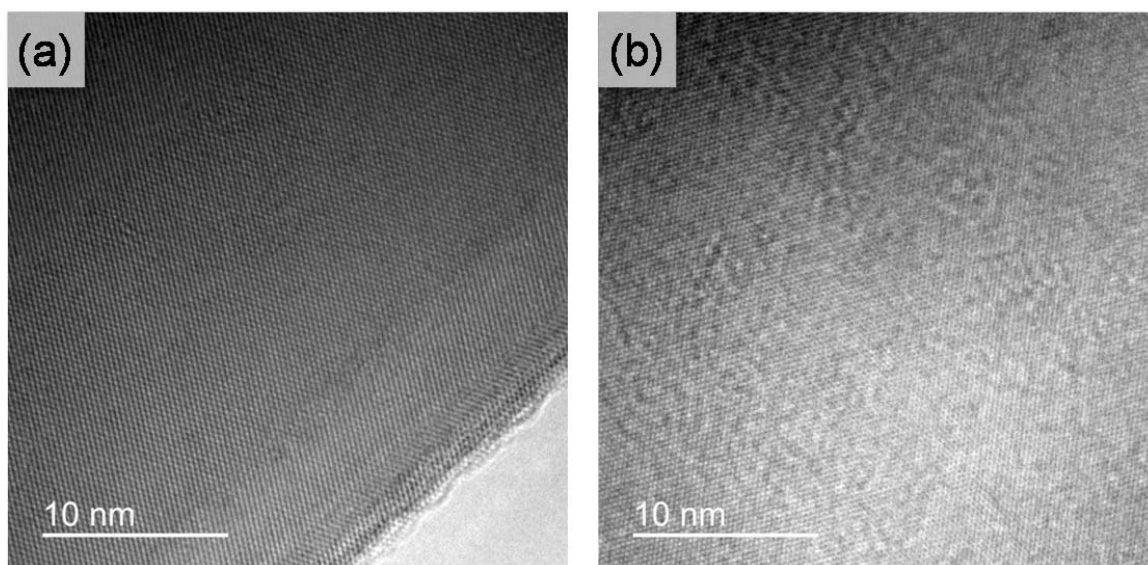
Supplementary Figure 3. More optical images of MoS₂ during lithiation. (a-d) Optical images of MoS₂ at 2.0, 1.6, 1.4 and 1.2 V vs. vs. Li/Li⁺, respectively. No discernable changes in the optical images before the phase transformation at 1.1 V. The scale bar is 5 μm. (e) Raman Spectra of MoS₂ at 2.0, 1.6, 1.4 and 1.2 V vs. vs. Li/Li⁺ during Li intercalation. (f) the top black curve is the reference spectrum at 2.0 V before lithiation. The other four curves from top to bottom are Raman spectra of the flake when it was lithiated to 1.1 V and 1.0 V and then delithiated to 2.5 V and 3.0 V, respectively. We could see the 2H to 1T phase transition as peaks at (150 and 200 cm⁻¹) started to show up (at 1.1 V) and then became prominent (at 1.0 V). At the same time, the A_{1g} mode intensity dropped significantly at 1.1 V and then was further suppressed to almost noise level at 1.0 V. During the delithiation process, we could see that as Li ions move out of MoS₂, the A_{1g} mode intensity increases at 2.5 V and then return to its original level (similar E_{2g}¹ to A_{1g} ratio) when MoS₂ is fully delithiated at 3.0 V.



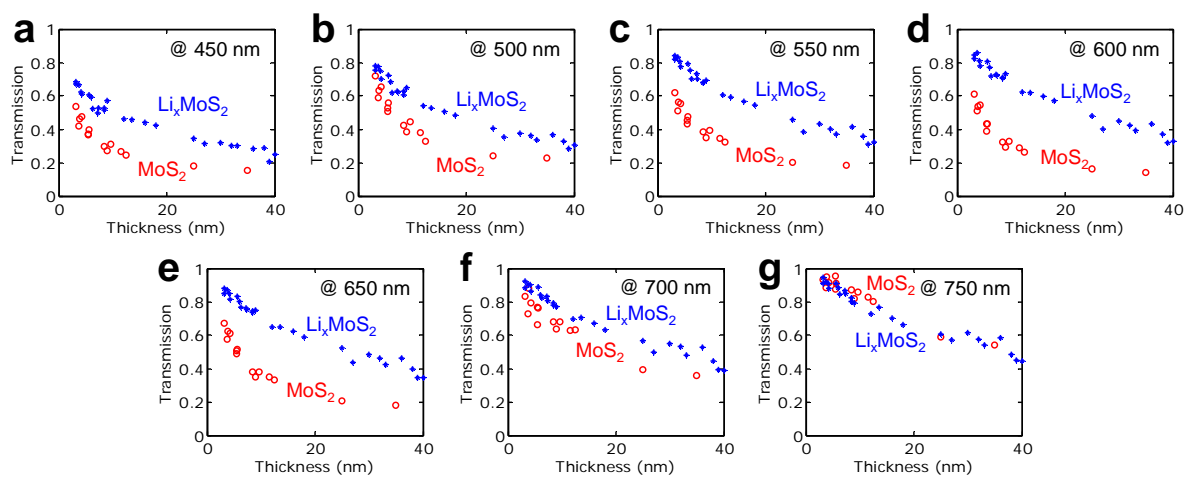
Supplementary Figure 4. Reversible lithiation. (a-d) Optical images of MoS₂ before encapsulation, before lithiation, after lithiation and after delithiation, respectively. The scale bar is 5 μm.



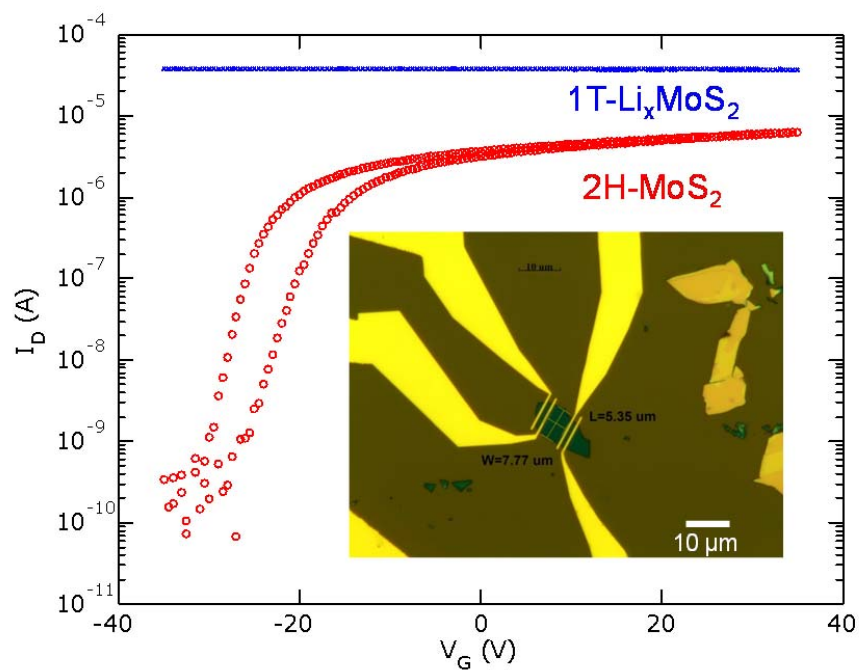
Supplementary Figure 5. Raman spectroscopy. (a) Raman spectroscopy of an electrochemically lithiated MoS₂ flake. (b) Raman spectroscopy of a chemically lithiated MoS₂ flake. The differences in peak locations in these two cases are possibly due to the oxidation of Li_xMoS₂ in air and the organic residues in the chemically lithiated flake. Electrical and XPS measurements (Supplementary Figures 8 and 9) confirm Li intercalation in chemically lithiated samples.



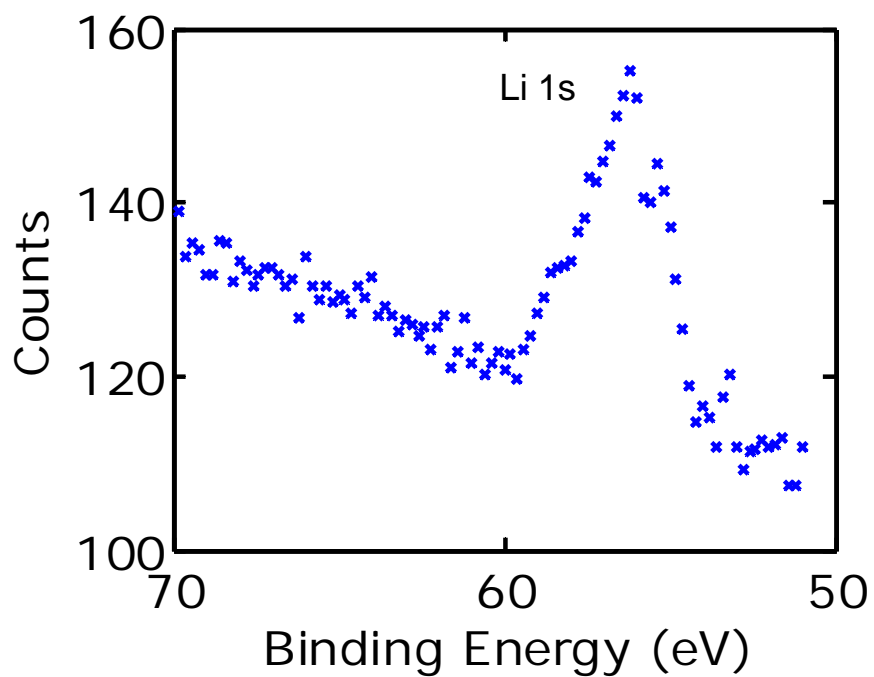
Supplementary Figure 6. TEM image of MoS₂ before and after lithiation. (a-b) TEM images of a MoS₂ flake before and after chemical Li intercalation (an hour in n-butyl lithium). The in-plane lattice constant remains the same at 3.1 Å after intercalation.



Supplementary Figure 7. Optical transmission measurement. (a-g) Optical transmission of MoS₂ flakes before (red) and after (blue) Li intercalations plotted as a function of flake thickness at different wavelengths.



Supplementary Figure 8 | MoS₂ phase transition. Drain current vs. gate voltage (I_D vs. V_G) characteristics of a typical MoS₂ flake before and after chemical intercalation. We observe a semiconducting (2H) to metallic (1T) phase transition up chemical lithiation. The inset is the optical image of the device.



Supplementary Figure 9 | X-ray Photoelectron Spectroscopy (XPS) measurement. XPS spectra of a chemically lithiated sample showing Li 1s peak, confirming Li intercalation.

Supplementary Discussions

***In-situ* optical/Raman characterizations**

In order to capture the dynamics of Li intercalation in MoS₂, we carried out *in-situ* optical and Raman characterizations of our device during the electrochemical intercalation process. We transfer the sample onto a glass slide after fabrication and encapsulation (Figure 1e). We then use wire-bond to connect each electrode (Li pellet and MoS₂) to a Cu lead so that we could connect them to the Bio-Logic tester via crocodile connectors (Figure S2). A 50× long working distance objective is employed for optical and Raman measurements since the samples are thick.

Calculation of MoS₂ refractive index

Since the spot size of the light is much smaller than our MoS₂ flakes, we can calculate the transmission of MoS₂ from the optical transmission measurements (Figure S7). We assume that the incident light enters the thin film normally and experiences multiple reflections at the top and bottom interfaces. The total transmission is the interference of every transmission component. We can use Transfer Matrix Method (TMM) to deduce the function of transmission $T(n,k,d)$, where n and k are the real and imaginary parts of the refractive index of MoS₂, and d is the thickness of the MoS₂ flake and measured by atomic force microscopy (AFM). We then perform a least square regression to find the best fitting results of the refractive indexes (n and k). We repeat the fitting at every wavelength to get the entire spectrum of MoS₂'s refractive index.