

Chemical Stabilization of 1T' Phase Transition Metal Dichalcogenides with Giant Optical Kerr Nonlinearity

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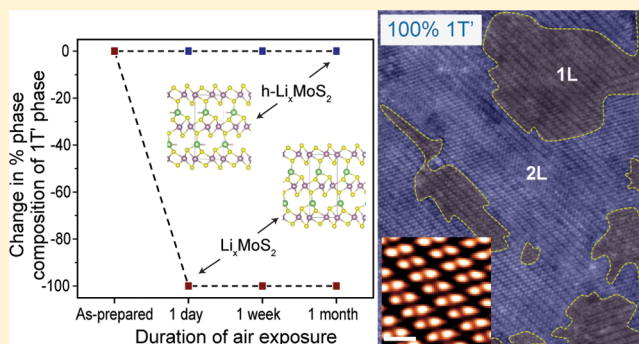
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Supporting Information

ABSTRACT: The 2H-to-1T' phase transition in transition metal dichalcogenides (TMDs) has been exploited to phase-engineer TMDs for applications in which the metallicity of the 1T' phase is beneficial. However, phase-engineered 1T'-TMDs are metastable; thus, stabilization of the 1T' phase remains an important challenge to overcome before its properties can be exploited. Herein, we performed a systematic study of the 2H-to-1T' phase evolution by lithiation in ultrahigh vacuum. We discovered that by hydrogenating the intercalated Li to form lithium hydride (LiH), unprecedented long-term (>3 months) air stability of the 1T' phase can be achieved. Most importantly, this passivation method has wide applicability for other alkali metals and TMDs. Density functional theory calculations reveal that LiH is a good electron donor and stabilizes the 1T' phase against 2H conversion, aided by the formation of a greatly enhanced interlayer dipole–dipole interaction. Nonlinear optical studies reveal that air-stable 1T'-TMDs exhibit much stronger optical Kerr nonlinearity and higher optical transparency than the 2H phase, which is promising for nonlinear photonic applications.



INTRODUCTION

Transition metal dichalcogenides (TMDs) represent a large family of layered materials with MX_2 stoichiometry, where M is a transition metal and X is a chalcogen. The lack of an inversion symmetry in monolayer or odd-layered TMDs enables the exploitation of second order effects such as second and third harmonic generation. Giant optical nonlinearity in 2D TMDs is ascribed to its 2D confinement, strong enhancement of light-matter interactions by excitonic effects and band edge resonances. Depending on the electron filling in the valence d -orbitals of the transition metal, TMDs can manifest in different polymorphs which exhibit a diverse range of electronic and optical properties. For example, group VI TMDs such as MoS_2 and WSe_2 exist in the stable semiconducting 2H phase,

while the distorted, metallic 1T (1T') phase is unstable at ambient conditions. The 1T' phase has been recently predicted to exhibit interesting phenomena, such as quantum spin Hall effect,¹ Weyl semimetal,^{2,3} dipolar ferroelectricity,⁴ and charge density wave formation,⁵ and plays a pivotal role in the fabrication of low-resistance contacts for 2D TMD transistor devices.^{6–8} While much attention has been focused on studying the nonlinear optical properties of the 2H-semiconducting phase of MoS_2 , little work has been carried out on the 1T' phase, which are expected to possess interesting optical

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properties due to the low symmetry of the distorted phase and its anisotropic optical properties.

Several methods have been employed to induce 2H-to-1T' phase transition in TMDs, including intercalation with alkali metals,^{9–11} electron beam irradiation,^{12,13} mechanical strain,¹⁴ and plasmonic excitation.¹⁵ The weak van der Waals bonding between the TMD layers allows alkali metal ions to intercalate, forming ternary compounds which are highly anisotropic and possessing pseudo two-dimensional properties.^{16,17} The 1T' domains are usually found in low concentrations with respect to the 2H phase, especially after air-exposure,¹⁸ mild annealing, or aging.^{19,20} Lacking a method to stabilize the 1T' phases against 2H conversion means that many 1T'-associated properties are short-lived in air, which prevents detailed investigation into the intriguing properties of this phase. It is therefore essential to develop a phase engineering strategy which not only achieves complete phase conversion, but also stabilizes the 1T' phase against degradation in air.

Herein, we report an effective phase engineering method which can achieve complete 2H-to-1T' phase conversion in TMDs. Most importantly, the 1T' phase can be stabilized against conversion to the 2H phase for extended periods of time in air. Our method involves intercalating MoS₂, a prototypical TMD, by lithium atoms generated from a standard getter source, followed by thermally activated hydrogenation of the intercalated Li to form LiH. The ability to achieve stable and homogeneous 1T' phase in TMDs allows us to study its nonlinear optical properties as a function of laser power in air, where giant optical Kerr nonlinearities in 1T'-MoS₂ and 1T'-WS₂ are discovered.

RESULTS

Lithium is evaporated on few-layered MoS₂ using a SAES Li getter source (Supporting Information (SI), Figure S1). Evaporated lithium atoms are highly diffusive and can intercalate 2D MoS₂ as well as 3D MoS₂ crystals up to a depth of ~50 nm, as is confirmed by secondary ion mass spectrometry (SI, Figure S2). As shown in Figure 1a, upon Li intercalation, the Mo 3d core level peaks chemically shift such that its binding energies are 1.0 eV lower than that of pristine 2H samples, which is assigned to the 1T' phase of MoS₂ (confirmed by Raman and TEM discussed later). The decrease in binding energy is due to the chemical reduction of Mo from the +4 to the +3 oxidation state.^{7,9} The Li evaporation flux can be controlled readily, thus allowing the staged phase transformation of Li_xMoS₂ to be captured using *in situ* X-ray photoemission spectroscopy (XPS), as shown in the inset of Figure 1a. The first order 2H-to-1T' phase transformation occurs at $x > 0.2$. A full 1T' phase conversion can be obtained at higher stoichiometric ratio of Li ($x > 1.2$), as evidenced by the complete reduction of Mo⁴⁺ to Mo³⁺ in the XPS spectra. There is no significant change in the full width at half-maximum (fwhm) of Mo 3d core level peaks, suggesting that the crystallinity of the sample is preserved. This is consistent with our *ex situ* X-ray diffraction (XRD) results which also indicate no broadening in the fwhm of the diffraction peaks (SI, Figure S3), confirming that the dry intercalation method here yields high-quality Li_xMoS₂ crystals. The obtained Li_xMoS₂ is stabilized by annealing in a hydrogen atmosphere at 473 K (Figure 1b). Upon hydrogenation, the binding energies and peak areas of the Mo 3d and S 2p core level peaks do not change, indicating that hydrogenation does not affect the phase composition of Li_xMoS₂. However, the binding energy of the Li

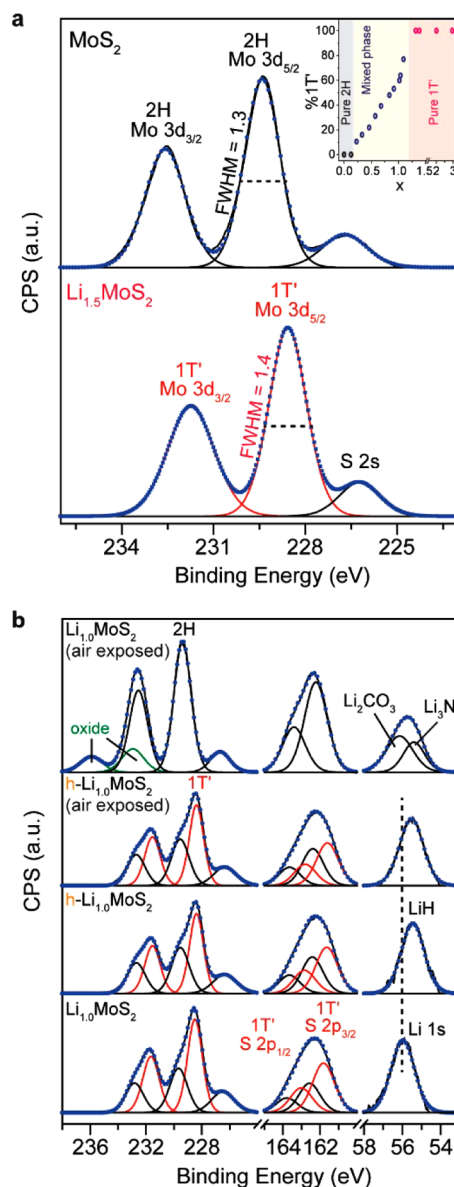


Figure 1. *In situ* XPS of h-Li_xMoS₂. (a) XPS spectra showing Mo 3d core levels of pristine 2H-MoS₂ (top) and fully converted 1T'-Li_{1.5}MoS₂ (bottom). The FWHM values of the Mo 3d_{5/2} core levels are indicated next to the peaks. Inset shows the plot of 1T' phase composition against amount of Li (x) in Li_xMoS₂. (b) XPS spectra showing the Mo 3d, S 2p, and Li 1s core levels of hydrogenated (h-Li_{1.0}MoS₂) and non-hydrogenated (Li_{1.0}MoS₂) samples before and after air exposure, taken with a spot size of 5 mm. Mo 3d and S 2p core level peaks associated with 1T' (2H) phase are labeled and colored in red (black).

1s core level decreases by 0.5 eV to 55.5 eV, which is consistent with the formation of LiH.²¹ Additionally, we observe the Li-H stretching mode in the high-resolution electron energy loss (HREELS) spectra (SI, Figure S4). In order to test the stability of h-Li_xMoS₂, we exposed the sample to air. Remarkably, ambient exposure did not produce any change in the Mo 3d and S 2p core level peaks associated with the 1T' phase.

Lithium is known to be highly susceptible to hydrolysis and nitrogeneration in air;^{22–24} however, the Li 1s core level peak of the h-Li_xMoS₂ peak did not change upon ambient exposure. Control experiment shows that without the hydrogenation-stabilization step, air-exposed Li reacts to form Li₂CO₃ and

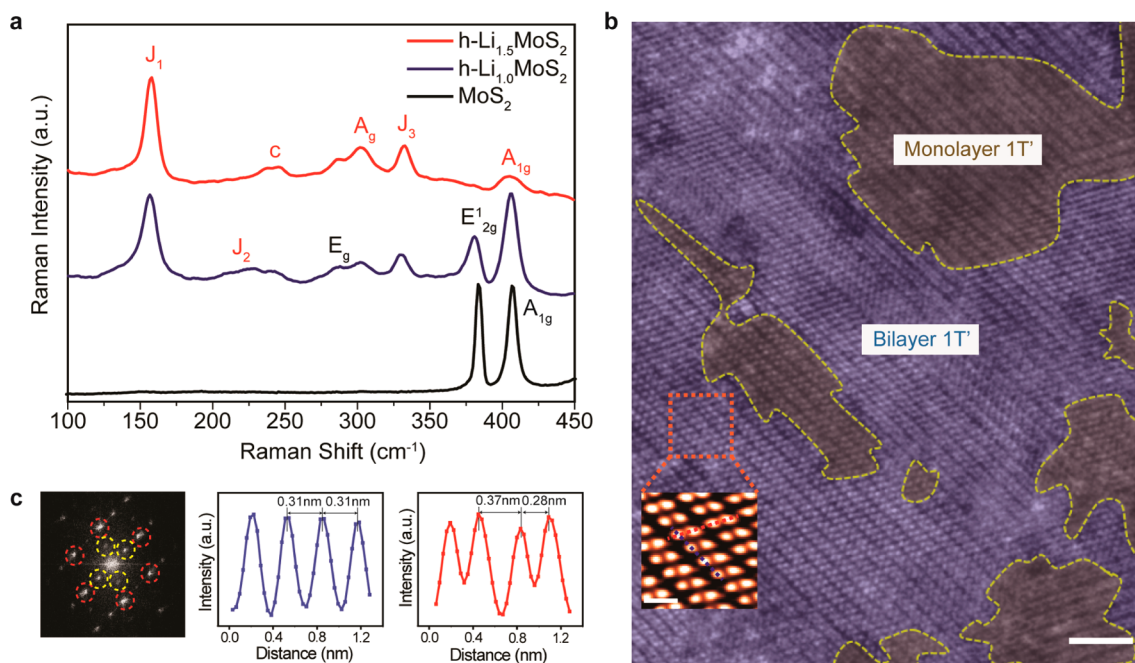


Figure 2. *Ex situ* characterizations of $h\text{-Li}_x\text{MoS}_2$. (a) Raman spectra of pristine 2H-MoS_2 , mixed $2\text{H}/1\text{T}'$ phase $h\text{-Li}_{1.0}\text{MoS}_2$, and pure $1\text{T}'$ phase $h\text{-Li}_{1.5}\text{MoS}_2$ taken with 532 nm laser. Raman modes unique to the $1\text{T}'$ phase are labeled in red. (b) Annular dark-field scanning transmission electron microscopy image of monolayer and bilayer $h\text{-Li}_x\text{MoS}_2$ regions with false color to differentiate the different layers. Inset shows the magnified filtered image of $1\text{T}'$ phase region indicated by the dotted orange box. Scale bars for image and inset are 2.5 and 0.5 nm, respectively. (c) Fast Fourier transform pattern of (b) (left panel) and intensity profiles (middle and right panels) of blue and red lines indicated by inset of (b) showing alternating atomic spacing along one direction with spacing corresponding to zigzag Mo chains from $1\text{T}'\text{-MoS}_2$.

Li_3N^{25} immediately, and Li_xMoS_2 reverts to the 2H phase (Figure 1b). Consistent with our XPS results, *ex situ* Raman spectroscopy confirms a full 2H -to- $1\text{T}'$ phase conversion at higher stoichiometric ratios of Li. 2H-MoS_2 can be unambiguously identified by the zone-center Raman modes at 383 cm^{-1} (E_{2g}^1 mode) and 409 cm^{-1} (A_{1g} mode).^{26,27} In particular, the E_{2g}^1 mode is unique to the 2H phase and absent in the $1\text{T}'\text{-MoS}_2$; the absence of the E_{2g}^1 mode is observed in the $h\text{-Li}_{1.50}\text{MoS}_2$ sample, indicating a full 2H -to- $1\text{T}'$ phase conversion (Figure 2a). In addition to the signature Raman peaks of $1\text{T}'\text{-MoS}_2$ at 158 , 218 , 301 , and 334 cm^{-1} , which correspond to the J_1 , J_2 , A_g , and J_3 peaks, respectively,²⁸ a peak labeled “c”, corresponding to the out-of-plane Li–S Raman mode of Li-intercalated MoS_2 ,²⁹ is also observed. Interestingly, the intensity of the J_2 peak is very weak in the mixed phase sample ($h\text{-Li}_{1.0}\text{MoS}_2$) and disappears in the pure $h\text{-Li}_{1.5}\text{MoS}_2$. J_2 is assigned to the longitudinal acoustic mode at the M -point and is only allowed by disorder; thus, it was previously observed in solution-phase chemical exfoliated samples and MoS_2 nanoparticles with fullerene-like geometry.^{26,30} At the intermediate stage before full $1\text{T}'$ coverage is attained ($\text{Li}_{0.2 < x < 1.2}\text{MoS}_2$), a mixture of 2H and $1\text{T}'$ polytypes, joined by disordered grain boundaries, coexists in the MoS_2 film. The defect-related J_2 peak may emanate from the grain boundary regions, since this peak vanishes when a full $1\text{T}'$ phase is developed at full lithiation ($x \approx 1.2$).

Scanning transmission electron microscopy (STEM) images of the $h\text{-Li}_x\text{MoS}_2$ sample reveal the presence of alternating one-dimensional zigzag stripes on the basal plane, with measured Mo–Mo distances of 0.37 and 0.28 nm , corresponding to the $1\text{T}'$ phase unit cells with 2×1 superstructure³¹ (Figure 2b), which is confirmed also by the presence of the half-order superstructure spots in the FFT diffraction image shown in

Figure 2c (0.17 \AA^{-1} d -spacing, highlighted as yellow circles). The increased stability of our $h\text{-Li}_x\text{MoS}_2$ ($1\text{T}'$) sample is also reflected in the much higher $1\text{T}'$ -to- 2H phase conversion temperature, determined using *in situ* XPS. It was observed that the $1\text{T}'$ -to- 2H phase transition proceeds only above 673 K , which is markedly increased compared to $1\text{T}'\text{-MoS}_2$ samples (373 K) prepared by solution-phase method.⁹ The increased thermal stability of our $h\text{-Li}_x\text{MoS}_2$ samples is useful because it will facilitate the subsequent device fabrication process, which often requires post-annealing treatment.

Despite subjecting the $h\text{-Li}_x\text{MoS}_2$ samples to multiple characterizations over an extended period in air, we find that the $1\text{T}'$ phase remains relatively stable, as judged by its steady spectroscopic signatures in Raman, XRD, and XPS when sampled periodically over time (Figure 3a). Raman spectra of $h\text{-Li}_x\text{MoS}_2$ aged for three months in air show no discernible degradation of the $1\text{T}'$ -related peaks (Figure 3b). This is in stark contrast to the samples which are not hydrogenated, for which the signal decays rapidly within a day. One possible reason is the rapid oxidation and nitrogenation of lithium in air²² (Figure 1b), which reduced its electron donating ability. The 2H -to- $1\text{T}'$ phase change has an electronic origin. The formation of the d^3 configuration after electron transfer to the Mo $4d$ orbitals destabilizes the trigonal prismatic structure in the 2H phase in favor of the octahedral structure adopted by the $1\text{T}'$ phase.³² Intercalated Li atoms act as electron donors, therefore, the reduction in their electron donating ability after exposure to air will destabilize the $1\text{T}'$ phase against the 2H phase.

One question is whether the stabilization achieved by the formation of alkali metal hydride is generic for other combinations of layered 2D materials and alkali metal intercalants. As a further proof of principle, we demonstrate

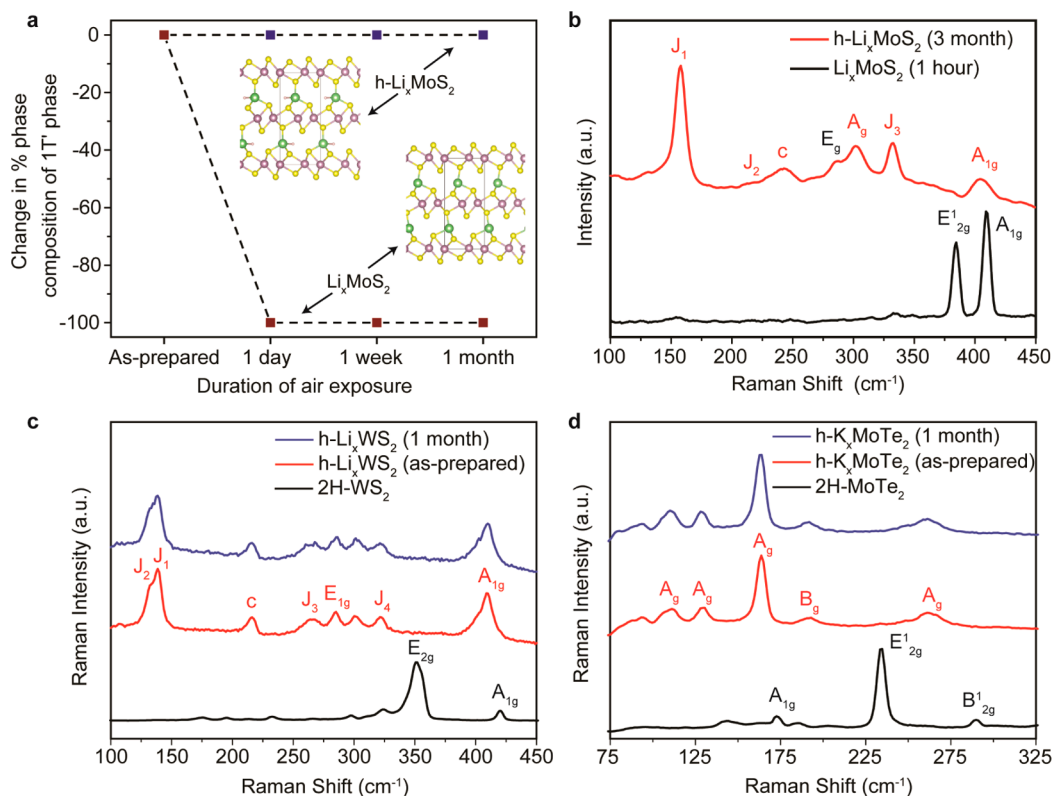


Figure 3. Degradation rate and long-term stability investigation of stabilized alkali metal intercalated TMDs. (a) Degradation of $\text{h-Li}_x\text{MoS}_2$ in ambient conditions, investigated by the change in % $1\text{T}'$ phase composition as determined by XPS. (b) Raman spectra of $\text{h-Li}_x\text{MoS}_2$ and Li_xMoS_2 . Duration of air exposures are indicated in brackets next to their label. Raman modes unique to the $1\text{T}'$ phase are labeled in red. (c) Raman spectra of pristine 2H-WS_2 (black) and hydrogenated lithium-intercalated WS_2 ($\text{h-Li}_x\text{WS}_2$) as-prepared (red) and after ambient exposure for 1 month (blue) showing the persistence of signature $1\text{T}'$ peaks. (d) Raman spectra of pristine 2H-MoTe_2 (black) and potassium hydride-intercalated MoTe_2 ($\text{h-K}_x\text{MoTe}_2$) as-prepared (red) and after ambient exposure for 1 month (blue) showing the persistence of signature $1\text{T}'$ peaks. All peaks originating from $1\text{T}'$ (2H) phase are labeled in red (black) for clarity.

that lithium hydride-intercalated WS_2 ($\text{h-Li}_x\text{WS}_2$) and potassium hydride-intercalated MoTe_2 ($\text{h-K}_x\text{MoTe}_2$) undergo complete 2H -to- $1\text{T}'$ phase transformation and are stabilized against 2H phase conversion, similar to $\text{h-Li}_x\text{MoS}_2$ demonstrated above (other combinations can be found in SI, Figures S5–S7). As shown in Figure 3c, as-exfoliated WS_2 displayed two characteristic 2H phase Raman peaks at 352 and 420 cm^{-1} , corresponding to the in-plane E_{2g} and out-of-plane A_{1g} modes, respectively. The other weaker peaks belong to the second order Raman modes.³³ Upon Li intercalation and formation of the hydride, we observed the disappearance of the 2H phase Raman peaks and the emergence of peaks at 132 , 139 , 265 , 285 , 321 , and 409 cm^{-1} , corresponding to the theoretically predicted J_2 , J_1 , J_3 , E_{1g} , J_4 , and A_{1g} modes of $1\text{T}'\text{-WS}_2$, respectively.³⁴ To the best of our knowledge this is the first complete experimental Raman assignment of $1\text{T}'\text{-WS}_2$, which is made possible by the enhanced stabilization of the $1\text{T}'$ phases by the passivation method reported here. Remarkably, the $1\text{T}'$ phase of WS_2 displays high ambient stability (at least 1 month) using our hydrogenation–stabilization method, which attests to the usefulness of the alkali metal hydride method in stabilizing metastable $1\text{T}'\text{-TMDs}$.

The stability of the alkali metal hydrides is known to decrease with an increase in the ionic radius of the metal.³⁵ The strongest lattice is formed by Li cations and hydrides, which have the most compatible ion sizes. This trend explains the increasing reactivity of the hydrides from NaH to CsH , whereas LiH is more inert. Due to the much higher reactivity of K,

neither the stability, nor the existence of the $1\text{T}'$ phase in K-intercalated TMDs has been reported previously. Zheng et al. attempted the chemical intercalation of MoS_2 using potassium naphthalenide, and discovered that the much higher reactivity of potassium causes the intercalant to be hydrated rapidly in air.³⁶ As shown in Figure 3d, the $1\text{T}'$ phase is stabilized in potassium hydride-intercalated MoTe_2 ($\text{h-K}_x\text{MoTe}_2$). Our as-exfoliated 2H-MoTe_2 samples displayed three characteristic Raman modes of the 2H phase at 173 , 234 , and 290 cm^{-1} , corresponding to the A_{1g} , E_{2g}^1 , and B_{2g}^1 modes, respectively.³⁷ The weaker peaks belong to the second order Raman modes of 2H-MoTe_2 .³⁸ After K intercalation and hydride formation, we observed the disappearance of the 2H peaks and emergence of $1\text{T}'$ -associated MoTe_2 Raman modes³⁹ at 111 , 129 , 164 , 193 , and 262 cm^{-1} , which remained unchanged in intensities even after 1 month of ambient exposure.

Compared to the laser-induced generation of Te defects in MoTe_2 for engineering 2H -to- $1\text{T}'$ phase conversion,⁴⁰ the in situ alkali metal intercalation method is advantageous because it does not rely on defect generation and can be scaled up over the entire surface of the TMDs to obtain full $1\text{T}'$ phase conversion. The generic applicability of this stabilization method is highly significant because it paves the way for fabricating stable 2D to 3D alkali metal hydride-intercalated TMDs, thus opening opportunities to examine air-stable devices.

The increased stability of the $1\text{T}'$ phase in LiH -intercalated MoS_2 has various origins. First, the formation of lithium

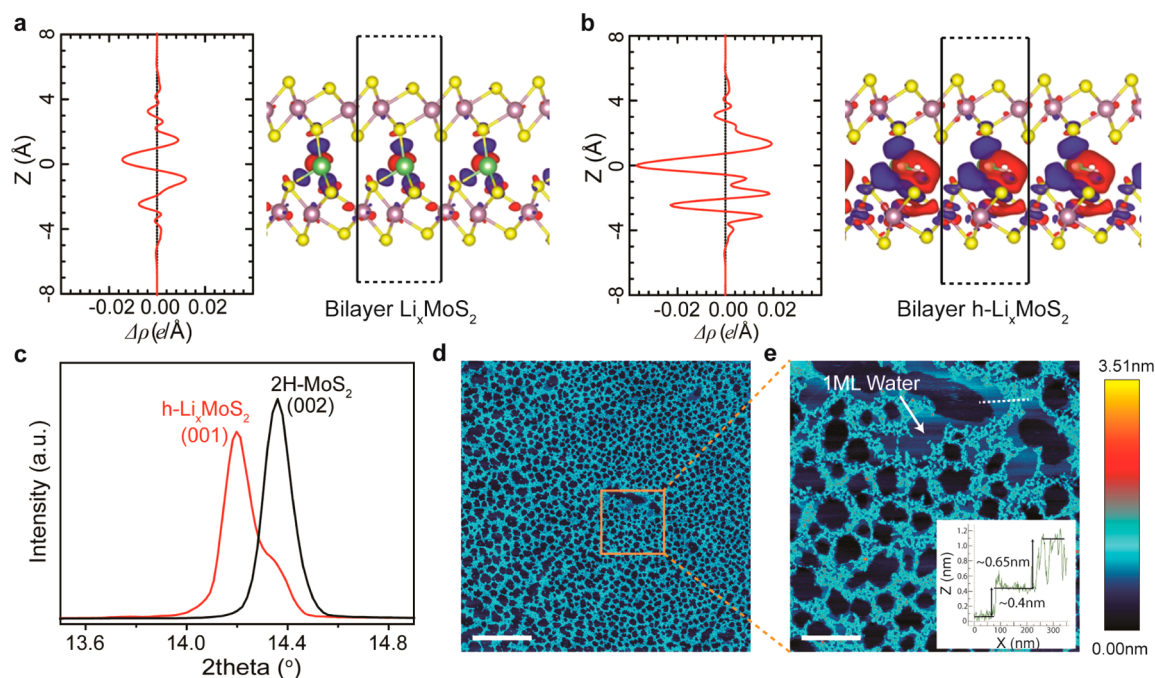


Figure 4. Electronic and steric stabilization of $h\text{-Li}_x\text{MoS}_2$. (a,b) DFT-calculated differential charge density after intercalation of Li (a) and LiH (b) into bilayer $1T'\text{-MoS}_2$. Plane-averaged differential charge density ($\Delta\rho(z)$) plots are shown in the left panels of the region marked by a black box of the isosurface side-view profile at 0.02 \AA^{-3} in the right panels. The black dashed lines refer to an interface with vacuum. The red (blue) color of the isosurface plots denotes loss (accumulation) of electrons in the system. (c) Powder XRD spectra of pristine 2H-MoS_2 (black) and $h\text{-Li}_x\text{MoS}_2$ (red) of the (002) plane region. (d,e) NC-AFM images of surface exfoliated $h\text{-Li}_x\text{MoS}_2$. Large-scale topography image is shown in (d), and the zoomed-in region marked by the orange box is shown in (e), together with the height profile of water (1 monolayer) and aggregated Li clusters along the white dotted line. Scale bars for the images are $1.9 \mu\text{m}$ and 400 nm , respectively.

hydride passivates the Li from reacting with air (78% nitrogen) to form Li_3N . The heat of reaction for LiH(s) and $\text{N}_2(\text{g})$ to form Li_3N is endothermic ($+41 \text{ kJ/mol}$), whereas that of Li(s) and $\text{N}_2(\text{g})$ to give the same is exothermic (-55 kJ/mol); LiH also is less reactive with water compared to Li (see reaction enthalpies in SI, Table S1). Second, LiH can act as a good Lewis base. To understand the role of the LiH intercalant in stabilizing the $1T'\text{-MoS}_2$, we calculate the differential charge density (DCD), $\Delta\rho(r)$, of Li_xMoS_2 and $h\text{-Li}_x\text{MoS}_2$ (Figure 4a,b). The model is based on a $1 \times 2 \times 2$ supercell of $\text{Li}_{0.5}\text{MoS}_2$ constrained by AB-stacked 2H-MoS_2 with the lattice parameters $a = 3.18 \text{ \AA}$ and $c = 6.24 \text{ \AA}$, as determined from experimental XRD and STEM data of our samples. The energetically optimized configuration of intercalated LiH (structure can be found in the insets of Figure 3a) has a binding energy of 0.24 eV on the MoS_2 layers. The magnitude of this binding energy is similar to a hydrogen bond, implying facile intercalation and de-intercalation. To quantify the amount of charge transfer from LiH to MoS_2 , we calculate the plane-averaged DCD along the direction normal to the surface by integrating $\Delta\rho(r)$ within the $x\text{-}y$ plane. The excess electrons transferred from lithium atoms to MoS_2 is about $0.818e$ per lithium atom ($0.41e$ per MoS_2 unit cell); however, it increases to $0.879e$ per lithium hydride molecule upon the formation of LiH ($0.44e$ per MoS_2 unit cell). These results imply that LiH can act as an effective electron donor, and is capable of inducing $2\text{H-to-}1T'$ phase transition in MoS_2 . The DFT calculations also reveal a significant charge redistribution induced by the relatively large dipole moment of LiH, especially in between the MoS_2 layers, as shown by the isosurface plots. The bond angle of Li-H-Li is about 83° , and the dipole is tilted with respect to the MoS_2 plane. Due to the large

polarized electron cloud of LiH, the charge transfer to the top and bottom MoS_2 layers is nonequivalent, leading to charge polarization between the top and bottom MoS_2 plane (Figure 4a,b). The increased free carrier density in MoS_2 layers upon charge transfer allows creation of image dipoles for screening the huge dipole of LiH. Consequently, the perpendicular dipole moment generated is 0.123 D per unit cell for $h\text{-Li}_x\text{MoS}_2$, which is of 2 orders of magnitude larger than that of Li_xMoS_2 (0.00616 D per unit cell). The giant increase in dipole-dipole interactions creates a strong intermolecular force which decreases the chemical energy of the system. The enhanced interlayer coupling in $h\text{-Li}_x\text{MoS}_2$ resulting from the increased dipole-dipole interactions contracts the interlayer distance. This is consistent with XRD results, where we observe only a 0.14 \AA increase in the c -spacing of $h\text{-Li}_x\text{MoS}_2$ compared to 2H-MoS_2 , following intercalation by LiH, as evidenced by the shift of the (002) peak of 2H-MoS_2 from 14.4° to 14.2° (Figure 4c).

In order to verify whether the sandwich layered structure of MoS_2 layers protects the LiH intercalant from reacting with the ambient environment, we exfoliated the top layers of $h\text{-Li}_x\text{MoS}_2$ flakes to expose the inner surface. AFM images of the air-exposed surface showed a reticular network of nanoparticles and liquid films (Figure 4d). In the absence of a protecting MoS_2 layer, the intercalated LiH undergoes rapid oxidation and hydration (SI, Figure S8). With the encapsulation of the alkali metal hydrides by MoS_2 layers, LiH intercalated- MoS_2 is highly robust, as judged from the stable $1T'$ signature in Raman even after 1 day of immersion in water (SI, Figure S9).

In order to investigate the optical properties of $h\text{-Li}_x\text{MoS}_2$, we performed spectral measurements using dual microscope set up where the sample was illuminated by a broadband beam via an inverted microscope to characterize the optical transmission

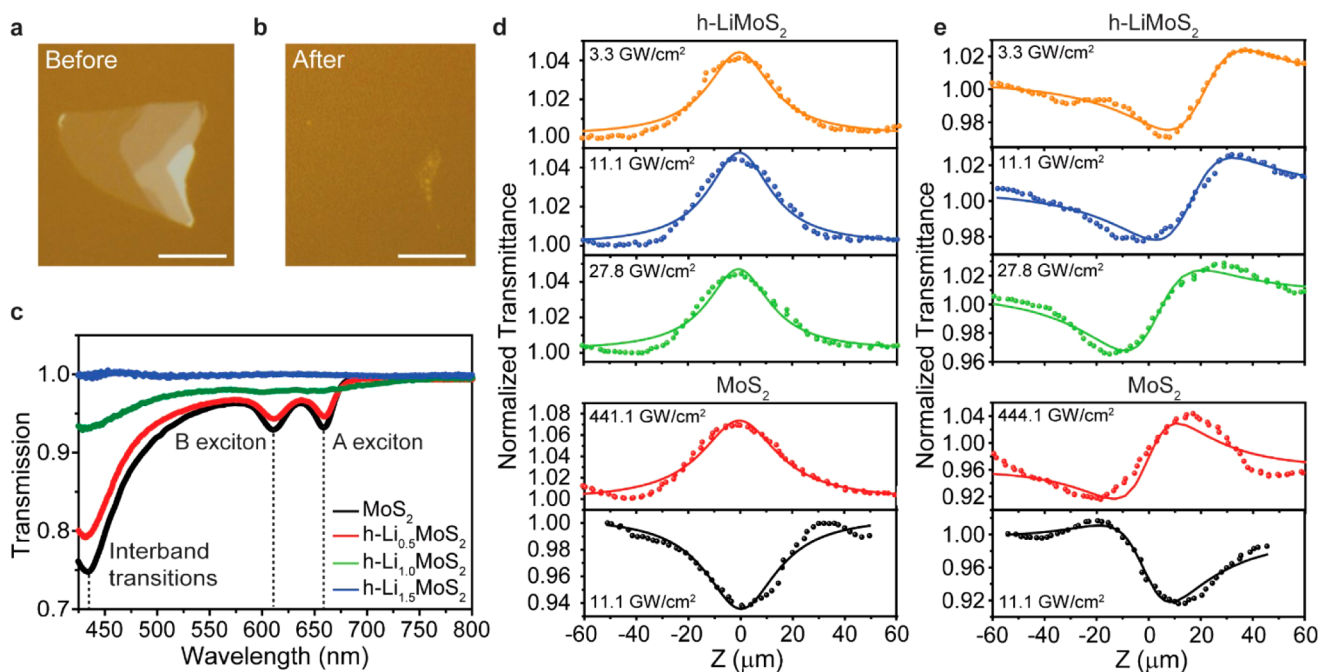


Figure 5. Optical characterizations of $h\text{-Li}_x\text{MoS}_2$. (a,b) Optical images of MoS_2 nanosheets on quartz before (a) and after (b) Li intercalation and chemical stabilization showing transparency of $h\text{-Li}_x\text{MoS}_2$. Scale bar is $10\ \mu\text{m}$. (c) Optical transmission spectra of bilayer $h\text{-Li}_x\text{MoS}_2$ flakes with various amounts of Li intercalated. Transmission spectrum of bilayer 2H-MoS_2 is added as a comparison. (d,e) Open (d) and closed (e) aperture Z-scan measurements of $h\text{-LiMoS}_2$ and MoS_2 at different input laser power, indicated at the top left of each curve, showing saturable absorption and self-focusing behavior of $h\text{-LiMoS}_2$ at a lower pumping power.

before and after lithiation. We exfoliated MoS_2 flakes onto quartz substrates and subjected the flakes to UHV Li evaporation and chemical stabilization processes (Figure Sa,b). Figure 5c shows the transmission spectra of $h\text{-Li}_x\text{MoS}_2$ at various Li dosages. As shown, the absorption of pristine 2H-MoS_2 is dominated by three resonance features. The two absorption bands in the region of $575\text{--}675\ \text{nm}$ are the characteristic direct exciton transitions between the split valence band maxima and conduction band minimum located at the high-symmetry K-point of the Brillouin zone⁴¹ while the strong absorption below $450\ \text{nm}$ feature can be attributed to optical transitions in the band nested regions around the Γ point.⁴² We observed significant enhancement in transmission with increasing dosage of Li at wavelengths between 425 and $675\ \text{nm}$, as well as a slight decrease in transmission at wavelengths greater than $675\ \text{nm}$ when the ratio of Li is $x = 1$. Free carrier in the semimetallic $1\text{T}'$ phase screens the electron–hole attraction and weakens excitonic effects; thus, the transmission spectrum becomes relatively flat. Interestingly, we were able to observe an extremely high optical transparency ($>99\%$) in the $h\text{-Li}_{1.5}\text{MoS}_2$ nanoflakes. As observed in Figure 5b, the thinner nanoflakes, which are 100% $1\text{T}'$ phase, are barely visible in the optical images.

Burstein–Moss type band filling effects is known to broaden optical transparency window in degenerately doped semiconductors, although it is not clear at this stage if it applies due to the semimetallic $1\text{T}'$, which is predicted to have a gap of $0.08\ \text{eV}$.¹ Another factor is due to the upshift of plasma oscillations to the UV range with increasing Li doping in MoS_2 , leading to the reflection of electromagnetic waves with frequencies below the plasma frequency.⁴³ Furthermore, the broken inversion symmetry in $1\text{T}'\text{-TMDs}$, coupled with carrier-dependent renormalization of electron–hole interactions, can give rise to rich nonlinear optical properties. Therefore, we probed the

nonlinear optical response of $1\text{T}'\text{-TMDs}$ by performing open aperture (OA) and closed aperture (CA) Z-scan measurements on few-layered $h\text{-LiMoS}_2$ and $h\text{-NaWS}_2$ flakes using a femtosecond laser ($900\ \text{nm}$, $80\ \text{MHz}$, $140\ \text{fs}$). The OA Z-scan measurements for MoS_2 and $h\text{-LiMoS}_2$ are shown in Figure 5d ($h\text{-NaWS}_2$ can be found in SI, Figure S10). We find that $h\text{-LiMoS}_2$ exhibits saturable absorption even at low power level. The extracted nonlinear absorption coefficients, β , are -1.182×10^{-4} , -3.876×10^{-4} , and $-1.507 \times 10^{-5}\ \text{cm/W}$, with the corresponding input powers of 3.3 , 11.1 , and $27.8\ \text{GW/cm}^2$, respectively. There is no two-photon absorption observed at any power in our experiment for $h\text{-LiMoS}_2$. In comparison, pristine MoS_2 exhibits obvious two-photon absorption at low power levels (for example at $11.1\ \text{GW/cm}^2$ the β value is $5.816 \times 10^{-5}\ \text{cm/W}$) as the laser excitation wavelength sits between the single-photon ($1.378\ \text{eV}$) and two-photon ($2.756\ \text{eV}$) absorption bands. The threshold power for saturable absorption in pristine MoS_2 is comparatively higher at $444.1\ \text{GW/cm}^2$, which is 2 orders of magnitude larger than that required for $h\text{-LiMoS}_2$. This has led to a nonlinear absorption coefficient $\beta = -1.562 \times 10^{-6}\ \text{cm/W}$ in pristine MoS_2 , which is 2 orders of magnitude lower than that of $h\text{-LiMoS}_2$. The ease of obtaining saturable absorption implies that upon phase conversion, $h\text{-LiMoS}_2$ has a much higher conduction band electron occupancy, which can explain the high optical transparency in $1\text{T}'\text{-TMDs}$ due to Pauli Coulomb blockade. It is known that $1\text{T}'\text{-TMDs}$ exhibit metallic character and have lower resistance than the 2H phase. Coupled with its high optical transparency, air-stable $1\text{T}'\text{-TMDs}$ have the potential to be used as transparent conductor and saturable absorber for mode-locked and Q-switched ultrafast lasers in ultrafast photonics.

Additionally, as shown in Figure 5e, our CA Z-scan results reveal that $h\text{-LiMoS}_2$ exhibit strong optical Kerr nonlinearity effect, with derived nonlinear refractive indexes, n_2 , of $2.033 \times$

10^{-9} , 5.51×10^{-10} , and 2.897×10^{-10} cm^2/W , with the corresponding input powers of 3.3, 11.1, and 27.8 GW/cm^2 , respectively. Typical semiconductor materials such as Si ($n_2 = 0.5 \times 10^{-13}$ cm^2/W) and GaAs ($n_2 = 1.5 \times 10^{-13}$ cm^2/W) used in current electronic devices fall short of the required nonlinear refractive index ($>10^{-10}$ cm^2/W) to produce attractive index change for optical devices.⁴⁴ The strong optical Kerr nonlinearity discovered in h-LiMoS₂ and h-NaWS₂, which outperforms most of the other two-dimensional materials, suggests that air-stable 1T'-TMDs can be potentially used for optical signal modulation in optoelectronic platforms. Furthermore, we observe a valley–peak type curve for h-LiMoS₂ at any input power, while pristine MoS₂ exhibit a peak–valley type curve for most of the power levels (for example at 11.1 GW/cm^2), indicating self-focusing and self-defocusing behaviors, respectively. Only at high input powers (with a threshold at 444.1 GW/cm^2), MoS₂ exhibit peak–valley shapes with a derived threshold nonlinear refractive index, n_2 , of 3.69×10^{-11} cm^2/W , which is 2 orders of magnitude lower than that of h-LiMoS₂. The strong nonlinear optical susceptibilities and switchable self-focusing behavior of air-stable phase-engineered TMDs, together with its low linear absorption loss and nonlinear two-photon absorption loss, open up tremendous possibilities for applications as waveguides and ultrafast switches in integrated photonic circuits.

CONCLUSION

In summary, we have shown that full 1T' phase can be engendered in MoS₂ by the controlled evaporation of Li in vacuum to produce Li_xMoS₂ ($x > 1.2$). By exploiting the interlayer diffusivity of hydrogen, the reactivity of intercalated alkali metals in TMDs is reduced by the formation of alkali metal hydride. A synergistic interaction is observed between the host and intercalant: intercalated alkali metal hydrides are good electron donors and stabilize the 1T' phase in air, while the TMDs layers sandwich and protect the alkali metal hydrides from reactive species in the ambient environment. The generic applicability of this method has been verified in other kinds of TMDs (e.g., WS₂ and MoTe₂) and also with different alkali metal hydrides (e.g., LiH and KH). Giant optical Kerr nonlinearity and higher optical transparency has been observed in 1T'-MoS₂, where its chemical stability permits high-power laser irradiation. The ability to prepare air-stable, large area, homogeneous 1T' phase of MoS₂ allows the material to be exploited as a nonlinear optical material which can be used as saturable absorber or optical limiters. Finally, the ability to generate in TMD material two phases (e.g., 2H and 1T') with markedly different nonlinear refractive index and extinction coefficient suggests the potential for phase and amplitude modulations, enabling applications in flat lenses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13238.

Experimental details and supporting figures (PDF)

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Notes

The authors declare no competing financial interest.

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