

Heterointerface Effects on Lithium-Induced Phase Transitions in Intercalated MoS₂

Sajad Yazdani, Joshua V. Pondick, Aakash Kumar, Milad Yarali, John M. Woods, David J. Hynek, Diana Y. Qiu, and Judy J. Cha*



Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 10603–10611



Read Online

ACCESS |



Metrics & More



Article Recommendations



Supporting Information

ABSTRACT: The intercalation-induced phase transition of MoS₂ from the semiconducting 2H to the semimetallic 1T' phase has been studied in detail for nearly a decade; however, the effects of a heterointerface between MoS₂ and other two-dimensional (2D) crystals on the phase transition have largely been overlooked. Here, *ab initio* calculations show that intercalating Li at a MoS₂–hexagonal boron nitride (*h*BN) interface stabilizes the 1T phase over the 2H phase of MoS₂ by ~ 100 mJ m^{−2}, suggesting that encapsulating MoS₂ with *h*BN may lower the electrochemical energy needed for the intercalation-induced phase transition. However, *in situ* Raman spectroscopy of *h*BN–MoS₂–*h*BN heterostructures during the electrochemical intercalation of Li⁺ shows that the phase transition occurs at the same applied voltage for the heterostructure as for bare MoS₂. We hypothesize that the predicted thermodynamic stabilization of the 1T'–MoS₂–*h*BN interface is counteracted by an energy barrier to the phase transition imposed by the steric hindrance of the heterointerface. The phase transition occurs at lower applied voltages upon heating the heterostructure, which supports our hypothesis. Our study highlights that interfacial effects of 2D heterostructures can go beyond modulating electrical properties and can modify electrochemical and phase transition behaviors.

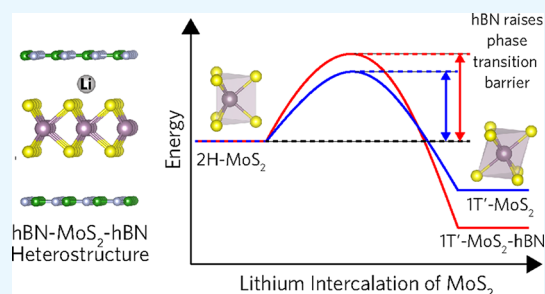
KEYWORDS: intercalation-induced phase transition, *in situ* Raman spectroscopy, MoS₂–hexagonal boron nitride (*h*BN) interface, heterointerface

INTRODUCTION

Van der Waals heterostructures composed of different two-dimensional (2D) materials^{1,2} can exhibit novel electronic and optical properties^{3–5}, in which the effect of heterointerfaces is important. Heterointerfaces may also play a central role in determining electrochemical properties and phase transitions of 2D materials. For MoS₂, intercalation of alkali metal ions such as Li⁺ into the van der Waals gaps between the layers can induce a phase transition from the semiconducting trigonal prismatic 2H phase to the semimetallic octahedral 1T phase,^{6–8} followed by an additional phase transition to the distorted 1T' phase, through electron doping by the intercalants.^{9–12} The intercalation-induced phase transition has been proven important for energy applications,^{13–17} and the thermodynamics of the electrochemical intercalation of Li⁺ in MoS₂ has been well characterized.^{18–21} Despite the extensive investigation and many applications of the intercalation-induced phase transition, the effect of a heterointerface on this process has largely been overlooked.

Herein, we investigate heterointerface effects on the intercalation-induced phase transition of MoS₂ by interfacing MoS₂ with hexagonal boron nitride (*h*BN). First, *ab initio* calculations indicate that the 1T–MoS₂–*h*BN interface is thermodynamically more stable than the 2H–MoS₂–*h*BN

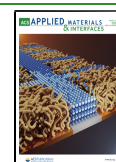
interface when Li is inserted at the interface, suggesting that interfacing MoS₂ with *h*BN could lower the thermodynamic energy barrier for the phase transition. Second, we performed electrochemical lithium intercalation on *h*BN–MoS₂–*h*BN heterostructures using electrochemical microreactors^{20–26} and studied the intercalation-induced phase change *via* Raman spectroscopy, *in situ*. In contrast to the *ab initio* results, we observe that the phase transition for *h*BN–MoS₂–*h*BN heterostructures occurs at the same applied electrochemical voltage as bare MoS₂, irrespective of the Li⁺ intercalation pathways. Thus, we hypothesize that the phase transition in Li-intercalated *h*BN–MoS₂–*h*BN heterostructures is influenced by steric hindrance imposed by the heterointerface, which would counteract the predicted stabilization of the 1T–MoS₂–*h*BN interface over the 2H–MoS₂–*h*BN interface. *In situ* heating during the electrochemical intercalation showed that the heterostructure requires a higher thermal energy than bare



Received: December 3, 2020

Accepted: February 9, 2021

Published: February 17, 2021



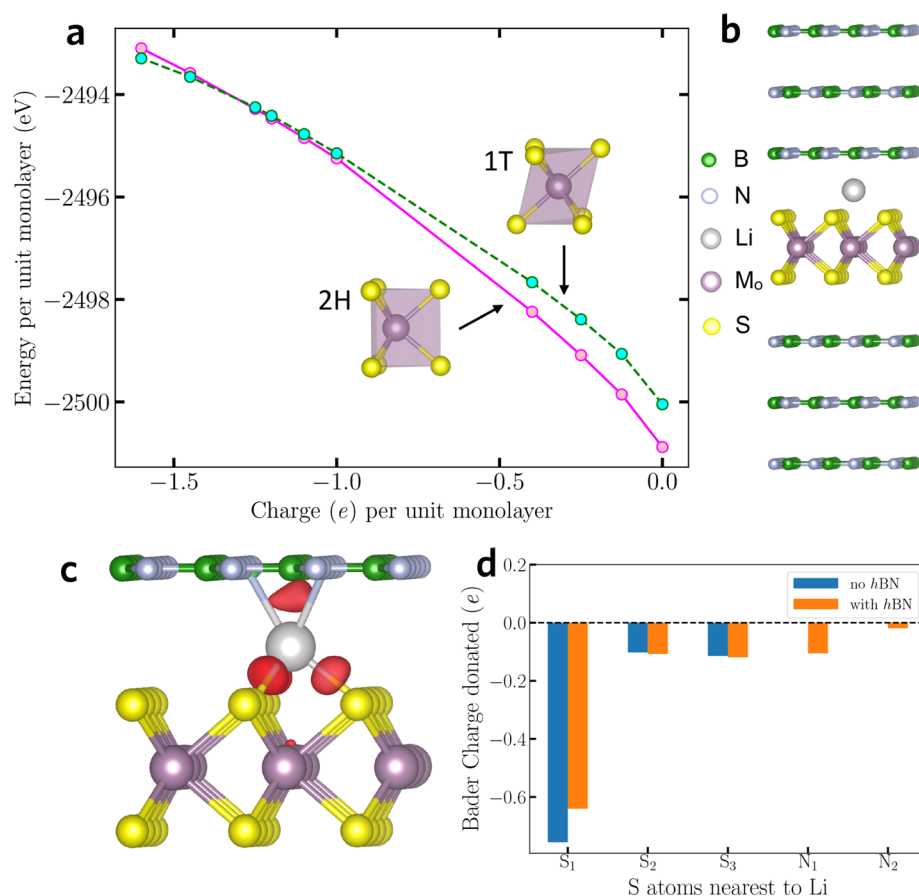


Figure 1. DFT Calculations of the 2H to 1T phase transition. (a) Total energy per monolayer of 1 unit cell of bulk MoS₂ as a function of the added implicit charge for the 2H phase (pink) and the 1T phase (cyan). Insets, the trigonal prismatic coordination of sulfur atoms (yellow) around molybdenum (purple) in 2H-MoS₂ and their octahedral coordination in 1T-MoS₂. (b) Supercell of the heterointerface with 6 layers of strained hBN, 1 layer of relaxed MoS₂, and 1 Li atom. (c) Change in the charge density when Li is added to the heterointerface. Purple atoms are Mo, yellow are S, green are B, blue are N, and the white atom is Li. Red represents the isosurface corresponding to 80% of the maximum charge density. (d) Bader charge analysis of the charge donated by the Li atom to all its nearest neighbor S atoms (first nearest-S₁, 2nd nearest-S₂, and 3rd nearest-S₃) and its nearest N atoms (N₁ and N₂) with (orange) and without (blue) hBN encapsulation. The locations of S₁, S₂, S₃, N₁, and N₂ can be found in Supporting Information Figure S2.

MoS₂ to induce the phase transition at the same applied electrochemical voltage, supporting the hypothesis that the heterointerface imposes a barrier to intercalation. Lastly, we demonstrate that the basal planes of commercial hBN are ionically conductive for Li⁺.

RESULTS

Ab Initio Calculations of the MoS₂-hBN Interface with Li⁺ Intercalation. We performed density functional theory (DFT) calculations to investigate the energetics of the 2H to 1T phase transition of MoS₂ in the presence and absence of an hBN interface (see Methods). We note that the high symmetry 1T structure was used instead of the distorted 1T' structure to reduce computational cost and because 1T is an intermediate state in the 2H to 1T' phase transition. In the absence of hBN, the 2H to 1T phase transition in MoS₂ is thermodynamically driven, with the 1T phase becoming more favorable (lower in energy) than the 2H phase when bulk MoS₂ is doped above -1.3 electrons per monolayer formula unit (f.u.) (Figure 1a), consistent with previous calculations.^{27,28} In the presence of an hBN interface, in which monolayer MoS₂ is encapsulated by 6 layers of hBN (Figure 1b), the binding energy of the hBN-MoS₂ interface is

increased for 1T-MoS₂ over 2H-MoS₂ by ~100 mJ m⁻² when a Li atom is intercalated in the van der Waals gap between MoS₂ and hBN (Table 1 and see Methods for the heterostructure supercell and details of relaxation). We also considered the effect of MoS₂ thickness on the binding energy. Upon the introduction of a Li atom in the van der Waals gap, the binding energies of the monolayer MoS₂ and the bilayer MoS₂ interfaced with hBN in the heterostructures are still

Table 1. Binding Energy of the 2H-MoS₂-hBN and 1T-MoS₂-hBN Heterointerfaces With and Without Li^a

heterointerface	$\bar{E}_{\text{bind}}$ (mJ/m ²)	$\bar{E}_{\text{bind,Li}}$ (mJ/m ²)
2H-MoS ₂ -hBN	-139 (-139)	-378 (-397)
1T-MoS ₂ -hBN	-142 (-142)	-496 (-499)

^aThe values in parentheses are the binding energies for a bilayer MoS₂-hBN for comparison with the monolayer MoS₂-hBN heterostructure. The addition of Li increases the binding energy of the 1T-MoS₂-hBN heterointerface by 354 (357) mJ/m² and the binding energy of the 2H-MoS₂-hBN interface by 239 (258) mJ/m². Overall, the introduction of Li increases the binding energy of the 1T-MoS₂-hBN heterointerface relative to the 2H-MoS₂-hBN heterointerface by 118 (102) mJ/m², whereas the binding energies are almost the same without Li.

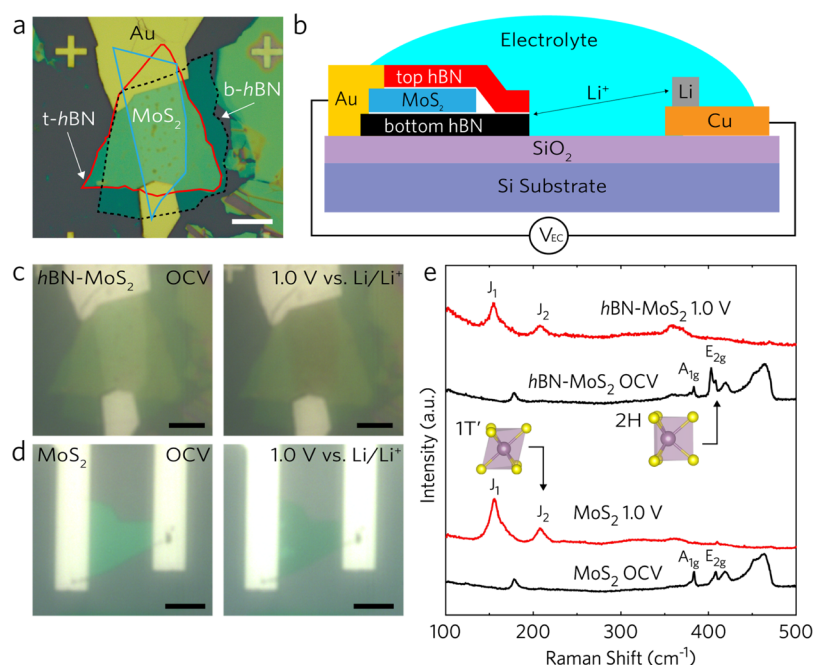


Figure 2. Li⁺ intercalation of *hBN*–*MoS*₂–*hBN* heterostructures. (a) Optical micrograph of an *hBN*–*MoS*₂–*hBN* heterostructure with Cr/Au contacts to *MoS*₂, scale bar 10 μm. The *MoS*₂ flake (blue outline) is sandwiched between the top and bottom *hBN* flakes, denoted *t-hBN* (red outline) and *b-hBN* (dashed-black outline), respectively. (b) Schematic of an electrochemical microreactor for intercalating *hBN*–*MoS*₂–*hBN*. (c) *In situ* optical micrographs of the heterostructure in (a) at open circuit (OCV) and 1.0 V vs. Li/Li⁺, scale bars 10 μm. (d) *In situ* optical micrographs of bare *MoS*₂ at OCV and 1.0 V vs. Li/Li⁺, scale bars 10 μm. (e) *In situ* Raman spectra of the devices shown in (c–d), with black and red indicating the 2H and 1T' phases, respectively. *Insets*, the trigonal prismatic coordination of sulfur atoms (yellow) around molybdenum (purple) in 2H–*MoS*₂ and their octahedral coordination in 1T'–*MoS*₂.

within 19 and 3 mJ/m² for the 2H and 1T phases, respectively (Table 1 and Supporting Information Figure S1). Therefore, we conclude that at the DFT level, *MoS*₂ thickness has a negligible effect on the binding energy of the interface whether Li is intercalated or not. The significant decrease in the interfacial energy for 1T–*MoS*₂–*hBN* over 2H–*MoS*₂–*hBN* with Li intercalated at the interface suggests that the nucleation barrier for the intercalation-induced phase transition would be lower for *hBN*–*MoS*₂–*hBN* heterostructures than for bare *MoS*₂.

We also considered in-plane strain because of the lattice mismatch between *MoS*₂ and *hBN*, which may influence the calculated thermodynamic stability of the 2H– and 1T–*MoS*₂–*hBN* interface. To create a commensurate 3 × 3 *MoS*₂–4 × 4 *hBN* supercell, we applied an in-plane strain of roughly 4% to *hBN*, but this strain can be reduced to about 2% by utilizing a larger 4 × 4 *MoS*₂–5 × 5 *hBN* supercell. However, the calculated binding energies of the two interfaces did not change in these two strain states (Supporting Information Table S1), so we conclude that the in-plane strain on *hBN* did not have an effect on the increased thermodynamic stability of the intercalated 1T–*MoS*₂–*hBN* interface.

Intercalated Li may donate charge to *hBN* at the *MoS*₂–*hBN* interface, which may reduce the effective doping of *MoS*₂. To quantify this doping, we calculated the amount of charge transfer from an intercalated Li atom to the adjacent *MoS*₂ and *hBN* layers. Figure 1c shows the isosurface of the charge density with a Li atom in the van der Waals gap of 2H–*MoS*₂–*hBN*, which shows that the majority of the charge is donated to the three S atoms that are the nearest neighbor of the Li. Some charge is also donated to the N atoms of *hBN* closest to Li

(Supporting Information Figure S2). Bader charge analysis²⁹ shows that the total charge donated to the three S atoms is –0.97 electrons for a freestanding monolayer of 2H–*MoS*₂ and is reduced to –0.87 electrons in the presence of *hBN* with about –0.1 electrons donated to N atoms of *hBN* (Figure 1d). Notably, the amount of charge transfer falls off rapidly with increasing distance from the Li, with >90% of the charge transfer confined within the ring of the nearest neighbor atoms (Supporting Information Figure S2). Thus, the intercalated Li at the *MoS*₂–*hBN* interface still dopes *MoS*₂ strongly and contributes to the overall electron doping required for the phase transition of *MoS*₂. We therefore predict that the critical electron density and, by extension, lithium concentration required to induce the phase transition would either be similar or even lowered by interfacing *MoS*₂ with *hBN*, given the lower binding energy of the 1T–*MoS*₂–*hBN* interface.

Electrochemical Intercalation of *hBN*–*MoS*₂–*hBN* Heterostructures. Motivated by the theoretical prediction, we performed electrochemical lithium intercalation on *hBN*–*MoS*₂–*hBN* heterostructures in which several layer thick *MoS*₂ flakes were sandwiched between exfoliated flakes of *hBN* (see Methods section and Figure 2a). The *hBN*–*MoS*₂–*hBN* heterostructure devices were integrated into electrochemical microreactors^{20–24} and intercalation was controlled potentiostatically by sweeping the electrochemical potential (*V*_{EC}) between the *hBN*–*MoS*₂–*hBN* working electrode and a lithium reference/counter electrode. Cr/Au metal contacts directly deposited onto the top surface of *MoS*₂ in the heterostructures served as the working electrode, while lithium metal pressed onto copper foil served as the reference/counter electrode (Figure 2b). As *V*_{EC} is lowered from the open circuit voltage (OCV), Li⁺ ions diffuse through the electrolyte and

intercalate into the interlayer gaps of the heterostructure. We note that while multilayer MoS_2 flakes are used in experiments unlike the monolayer MoS_2 used in calculations, the computational predictions remain valid as they examine the binding energy of the MoS_2 – $h\text{BN}$ interface for 1T– and 2H– MoS_2 , which we determined to be independent of increasing the thickness of MoS_2 up to two layers.

Intercalation dynamics of $h\text{BN}$ – MoS_2 – $h\text{BN}$ heterostructures were compared to those of bare MoS_2 by sequentially lowering V_{EC} from OCV (~ 2.5 V vs Li/Li^+) to 0.2 V versus Li/Li^+ at a decrement of 0.2 V. At each potential, V_{EC} was held constant for several minutes to acquire Raman spectra *in situ*, after which the samples were allowed to recover to OCV before lowering V_{EC} to the next potential. *In situ* optical microscopy of a heterostructure during intercalation revealed that MoS_2 turned dark at 1.0 V versus Li/Li^+ (Figure 2c), and bare MoS_2 also darkened at 1.0 V versus Li/Li^+ (Figure 2d). The color change may indicate a phase transition to the 1T' phase,²¹ and *in situ* Raman spectroscopy confirmed the 2H–1T' phase transition of MoS_2 in the heterostructure at 1.0 V versus Li/Li^+ and also in bare MoS_2 at 1.0 V versus Li/Li^+ (Figure 2e). The phase transition from 2H– to 1T'– MoS_2 is clearly observed *via* the suppression of the characteristic E_{2g} and A_{1g} Raman modes of 2H– MoS_2 and the concurrent growth of the J_1 and J_2 modes of 1T'– MoS_2 .^{30,31} We note that, due to the low intensity of $h\text{BN}$ Raman modes (Supporting Information Figure S3), we were unable to determine what effect lithium has on the structure of $h\text{BN}$. Supporting Information Figure S4 shows the full intercalation range of the heterostructure, including the transition to an amorphous state in which the MoS_2 layered structure is destroyed because of the conversion reaction from MoS_2 to Mo and Li_2S induced by high concentrations of intercalated lithium.^{20,32} This occurs at 0.4 V versus Li/Li^+ , the same as in the bare MoS_2 case (Supporting Information Figure S5). We also characterized MoS_2 with cyclic voltammetry to confirm the phase transition and amorphization (Supporting Information Figure S6). Therefore, our key finding is that while encapsulating MoS_2 with $h\text{BN}$ should theoretically significantly increase the thermodynamic stability of 1T'– MoS_2 , it has no observable effect on the electrochemical voltage required to induce the 2H–1T' phase transition of lithium-intercalated $h\text{BN}$ – MoS_2 – $h\text{BN}$.

Lithium Diffusion Pathways in $h\text{BN}$ – MoS_2 – $h\text{BN}$ Heterostructures. One possible explanation for the lack of an observable difference between bare MoS_2 and $h\text{BN}$ – MoS_2 – $h\text{BN}$ heterostructures is an increased Li^+ diffusion pathway in the heterostructure. Li^+ ions must diffuse over longer distances to access the MoS_2 flake in the heterostructure because the $h\text{BN}$ flakes completely encase MoS_2 (Figure 2a), such that Li^+ ions in the electrolyte do not have direct access to the edges of the MoS_2 flake. To investigate this, we fabricated a $h\text{BN}$ – MoS_2 – $h\text{BN}$ heterostructure and reactively ion-etched its perimeter, directly exposing the edges of MoS_2 to the liquid electrolyte while still covering the top and bottom surfaces of MoS_2 with $h\text{BN}$ (Figure 3a). Consistent with the results in Figure 2, the 2H–1T' phase transition occurs at an applied V_{EC} of 1.0 V versus Li/Li^+ for the edge-exposed heterostructure, as shown by *in situ* Raman spectroscopy and optical microscopy (Figure 3b and Supporting Information Figure S7). Further intercalation yielded amorphous MoS_2 at 0.4 V versus Li/Li^+ just as in the heterostructure without exposed edges. Therefore, despite Li^+ ions having direct access to the

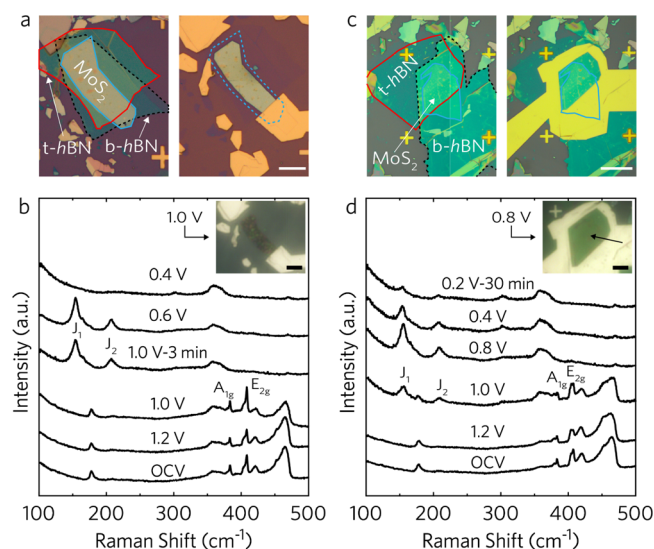


Figure 3. Different Li^+ diffusion pathways during the intercalation of $h\text{BN}$ – MoS_2 – $h\text{BN}$ heterostructures. (a) Optical micrographs of $h\text{BN}$ – MoS_2 – $h\text{BN}$ before (left) and after (right) etching to expose the edges directly to liquid electrolyte, scale bar 10 μm . The blue-dashed line (right) indicates the original extent of MoS_2 . (b) *In situ* Raman spectra of the device in (a) while V_{EC} vs Li/Li^+ is lowered. Inset, optical micrograph of the device at 1.0 V vs Li/Li^+ , scale bar 10 μm . (c) Optical micrographs of $h\text{BN}$ – MoS_2 – $h\text{BN}$ before (left) and after (right) covering the edges with gold, scale bar 10 μm . (d) *In situ* Raman spectra of the device in (c) while V_{EC} vs Li/Li^+ is lowered. Inset, optical micrograph of the device at 0.8 V vs Li/Li^+ with a black arrow indicating the darkened region, scale bar 10 μm .

edges of MoS_2 , the edge-exposed $h\text{BN}$ – MoS_2 – $h\text{BN}$ heterostructure still required a V_{EC} of 1.0 V versus Li/Li^+ to induce the 2H–1T' phase transition. Thus, longer Li^+ diffusion pathways cannot explain the lack of observable difference in V_{EC} required for the phase transition in the heterostructure and bare MoS_2 .

To further investigate the effects of lithium diffusion pathways, we fabricated a $h\text{BN}$ – MoS_2 – $h\text{BN}$ heterostructure, in which the heterostructure edge is covered with a thick layer of gold to block edge intercalation (Figure 3c).³³ While there exists an interface between the gold and bottom $h\text{BN}$ flake, thermally evaporated gold has been shown to degrade the surface of 2D materials,³⁴ so we do not expect this interface to allow lithium diffusion. Therefore, with this architecture, Li^+ ions could only reach MoS_2 through the basal planes of the top $h\text{BN}$ flake. *In situ* Raman spectra showed the onset of the 2H–1T' phase transition at an applied V_{EC} of 1.0 V versus Li/Li^+ as shown by a mixture of both the A_{1g} and E_{2g} peaks of 2H– MoS_2 and the J_1 and J_2 peaks of 1T'– MoS_2 (Figure 3d and Supporting Information Figure S8). The complete transition to 1T'– MoS_2 occurred at 0.8 V versus Li/Li^+ , marked by the disappearance of the A_{1g} and E_{2g} peaks. In addition, *in situ* Raman spectra showed that the intensity of the J_1 and J_2 peaks drops significantly after 30 min at a V_{EC} of 0.2 V versus Li/Li^+ , indicating that the onset of the conversion reaction occurs at a lower V_{EC} than 0.4 V versus Li/Li^+ observed in the previous two heterostructures (Figure 3a,b and Supporting Information Figures S4 and S7). Thus, our results from the edge-covered heterostructure suggest that, while $h\text{BN}$ is electrically insulating, it is ionically conductive, allowing Li^+ ions to diffuse through its basal planes. We attribute the ionic conductivity of the $h\text{BN}$ basal plane to intrinsic defects

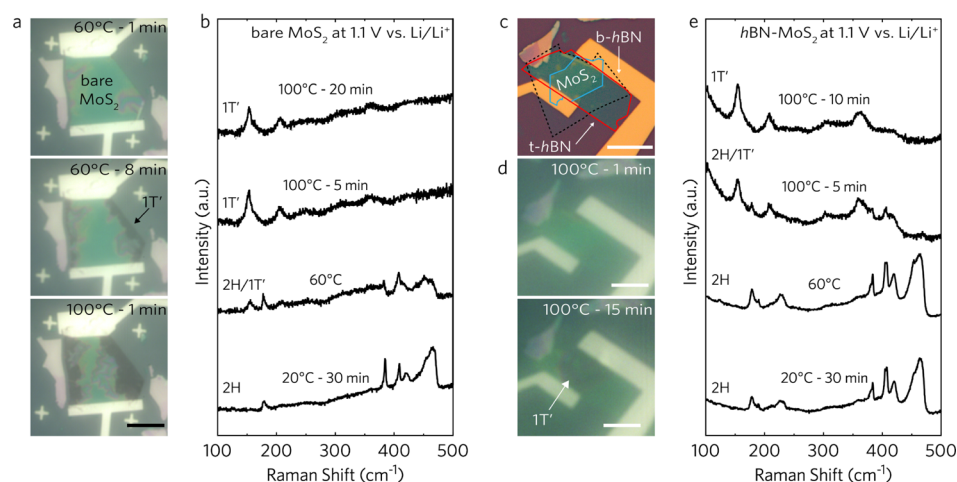


Figure 4. 2H to 1T' phase transition in bare MoS₂ and hBN–MoS₂–hBN as a function of temperature. (a) *In situ* optical micrographs of bare MoS₂ taken at 1.1 V *vs* Li/Li⁺ at 60 and 100 °C, scale bars 20 μm. The darkened region visible after 8 min at 60 °C indicates the 1T' phase. (b) Raman spectra taken from the bare MoS₂ flake in (a) at 1.1 V *vs* Li/Li⁺ at room temperature (20 °C) and during heating. The onset of the 2H–1T' phase transition is observed at 60 °C, with a full transition to 1T'–MoS₂ after 5 min at 100 °C. (c) Optical micrograph of the pristine hBN–MoS₂–hBN device, scale bar 10 μm. (d) *In situ* optical micrographs of the heterostructure in (c) taken at 1.1 V *vs* Li/Li⁺ at 100 °C, scale bars 10 μm. The darkened region visible at 15 min indicates the 1T' phase. (e) Raman spectra from the heterostructure in (c–d) taken at 1.1 V *vs* Li/Li⁺ at room temperature (20 °C) and during heating. The onset of the 2H–1T' phase transition is observed after 5 min at 100 °C, with a full transition to 1T'–MoS₂ after 10 min.

present in the commercially purchased hBN crystals (Supporting Information Figure S3d), as pristine 2D hBN crystals have been shown to be impermeable even to protons³⁵ but can become ionically conductive through intrinsic^{33,36} or engineered defects.^{37,38} The phase transitions in the edge-covered heterostructure were slightly delayed compared to the other two heterostructures, which is consistent with a previous report that suggests an increased energy barrier to lithium diffusion through the basal plane of bare MoS₂ as compared to through the interlayer gaps.³³ Irrespective of the Li⁺ diffusion pathways, all three hBN–MoS₂–hBN heterostructures undergo the 2H–1T' phase transition at 1.0 V *versus* Li/Li⁺, the same V_{EC} to induce the phase transition in bare MoS₂. We thus show clearly that the presence of a hBN–MoS₂ heterointerface does not allow for the 2H–1T' transition at a lower applied V_{EC} than bare MoS₂ in contrast to the prediction from DFT calculations.

Steric Hindrance to the Phase Transition by hBN.

Because our calculations indicate that the 1T–MoS₂–hBN interface is thermodynamically more stable than the 2H–MoS₂–hBN interface with Li intercalation, the lack of an observable difference in the 2H–1T' phase transition between bare MoS₂ and hBN–MoS₂–hBN suggests that there may be an additional energy barrier that influences the phase transition for the heterostructure. We conclude that steric hindrance from hBN at the heterointerface introduces an additional energy barrier to the nucleation of 1T'–MoS₂ at the interface, counteracting the thermodynamic stabilization of the 1T'–MoS₂–hBN interface. This is supported by the results from the edge-covered heterostructure (Figure 3c), where the nucleation of the 1T' phase must be initiated at the top hBN–MoS₂ interface because the Li⁺ concentration is the highest at the top hBN–MoS₂ interface as Li⁺ entered through the basal planes of the top hBN flake. The phase transition still occurred at 1.0 V *versus* Li/Li⁺, suggesting an interface-induced barrier to the nucleation of the 1T' phase. We hypothesize that this energy barrier in hBN–MoS₂–hBN heterostructures is driven by sluggish kinetics because of the heterointerface. The phase transition requires atomic rearrangements of the sulfur atoms

from a trigonal prismatic to an octahedral coordination surrounding the molybdenum atoms. This rearrangement is likely impeded by steric hindrance induced by the presence of the hBN layer in close proximity to the sulfur atoms, thus creating an activation energy barrier for the nucleation of the 1T' phase.

To test our hypothesis that there is an activation energy barrier for the 2H–1T' phase transition introduced by the hBN–MoS₂ interface, we investigated the phase transition of bare MoS₂ and hBN–MoS₂–hBN heterostructures as a function of both V_{EC} and temperature (Figure 4). Increasing the temperature provides an additional thermal energy to overcome the activation energy barrier and should allow for the intercalation-induced phase transition to occur at a higher V_{EC} than the observed 1.0 V *versus* Li/Li⁺ at room temperature. Initially at room temperature, *in situ* Raman spectroscopy showed that lowering V_{EC} to 1.1 V *versus* Li/Li⁺ did not induce the phase change in bare MoS₂ (Figure 4b), which is consistent with our previous data. After relaxing the device back to OCV, the microreactor was heated to 60 °C, and then V_{EC} was lowered to 1.1 V *versus* Li/Li⁺. At 60 °C, the flake began to undergo the phase transition as indicated by the presence of both 2H and 1T' Raman peaks and optical discoloration of the flake (Figure 4a,b). Further heating to 100 °C induced the complete transition to the 1T' phase (Figure 4b). We confirmed that the phase transition was not induced purely by the increased thermal energy by showing that an unbiased flake remained in the 2H phase after heating at 100 °C for 25 min in the presence of the electrolyte and lithium metal (Supporting Information Figure S9).

A hBN–MoS₂–hBN heterostructure (Figure 4c) was then heated during electrochemical intercalation. At 1.1 V *versus* Li/Li⁺, *in situ* optical micrographs and Raman spectra indicated that MoS₂ remained in the 2H phase at room temperature and upon heating to 60 °C (Figure 4d,e). Further heating to 100 °C was required to induce a mixed 2H/1T' phase after 5 min and a full phase transition after 10 min as shown by optical images and Raman spectroscopy (Figure 4d,e). Because the

heterostructure required an additional 40 °C of applied thermal energy than bare MoS₂ to induce the phase transition, these results support our hypothesis that *h*BN imposes an energy barrier to the phase transition. We also show that thermal energy reduces the applied electrochemical voltage required to induce the phase transition by 0.1 V. Because the ionic conductivity of the liquid electrolyte at room temperature is already very high (10^{−3} S cm^{−1}) and does not show a significant increase upon heating,³⁹ we do not expect the application of thermal energy to significantly increase the intercalation of lithium. Thus, the heating experiments support the hypothesis that the MoS₂–*h*BN heterointerface introduces an activation energy barrier to the 2H–1T' phase transition because of steric hindrance.

CONCLUSIONS

In summary, we studied the role of the heterointerface in the phase stability and transition of a *h*BN–MoS₂–*h*BN heterostructure. We show that intercalation-induced phase changes can be manipulated *via* multimodal control over applied electrochemical voltage, temperature, and heterointerfaces. While we show that the *h*BN–MoS₂ interface did not show any observable differences in the electrochemical energy required to induce the MoS₂ 2H–1T' phase transition, interfacing MoS₂ with other 2D materials may change the kinetics of the phase transition or modify the relative thermodynamic stabilities of 2H– and 1T'–MoS₂. This has broad implications for van der Waals heterostructured devices, in which heterointerfaces could modulate the kinetics of phase changes of 2D materials. Given the wide range of phases achievable in 2D materials,⁴⁰ our approach suggests opportunities to build devices with targeted electrochemical switching of material properties for a wide variety of applications.

METHODS

Ab Initio Calculations. The DFT calculations were carried out using the Quantum Espresso⁴¹ package using a plane-wave basis set. Norm-converging pseudopotentials⁴² were used to describe the valence electrons which included the semi-core 4s and 4p electrons of Mo, and the exchange–correlation was treated at the local density approximation⁴³ (LDA) level, which is in excellent agreement with the experimental structure of bulk 2H and 1T–MoS₂. The kinetic energy cutoff for the expansion of plane waves was 2040 eV for all calculations.

We accounted for the effect of doping on the structure of the 2H and 1T–MoS₂ by relaxing bulk 2H and 1T–MoS₂ at various levels of implicit doping. The unit cell was allowed to relax until the energy was converged to within 0.02 meV/atom and the forces on atoms were smaller than 2.5 × 10^{−3} eV/Å. A Monkhorst and Pack⁴⁴ shifted *k*-mesh of 42 × 42 × 8 was used for the calculations. The lattice parameters found in this relaxation were carried over to the calculations on the larger supercell with the heterointerface.

To model the heterointerface, we constructed supercells with one monolayer of 3 × 3 (2H– or 1T–) MoS₂ encapsulated in 6 layers of 4 × 4 *h*BN (Figure 1b). We note that while the experiment is performed on few-layer MoS₂, the calculations are performed on monolayer MoS₂ to reduce computational cost. Increasing the number of MoS₂ layers to two does not change our reported results (Table 1 and Supporting Information Figure S1). In the supercell, the lattice parameters of 2H and 1T were constrained to the relaxed parameters of bulk MoS₂ (as described above). The stand-alone *h*BN was relaxed in the out-of-plane *c* direction while strained in the *a*–*b* plane (−4.78% for 1H and −4.32% for 1T) to create a commensurate heterostructure. Then, the equilibrium distance between MoS₂ and

*h*BN was determined by minimizing the total energy as the distance between the MoS₂ and *h*BN was rigidly adjusted. To determine the binding energy of the MoS₂–*h*BN heterointerface, we then calculated the total energy of the supercell with the heterointerface (*E*_{hetero}), as well as supercells with freestanding monolayer MoS₂ (*E*_{MoS₂}) and a 6-layer slab of *h*BN (*E*_{BN}^{*}, where * shows that the *h*BN was strained as described above) with 25 Å of vacuum. The binding energy is defined as

$$\bar{E}_{\text{bind}} = \frac{E_{\text{hetero}} - (E_{\text{MoS}_2} + E_{\text{BN}}^*)}{2 \cdot A} \quad (1)$$

where *A* is the cross-sectional area of the heterointerface. We also tested a larger (less strained) supercell with a 4 × 4 (2H– or 1T–) MoS₂ and 5 × 5 *h*BN heterostructure consisting of 348 atoms. Because the reduced in-plane strain had little effect on the binding energies of the MoS₂–*h*BN interface (Supporting Information Table S1), we used the 3 × 3 MoS₂–4 × 4 *h*BN supercell for the remaining calculations because it is computationally less expensive.

For the Li-doped heterostructures, a Li atom was placed over the Mo site, which is one of the most favored intercalation sites,⁴⁵ and its separation from the Mo atom was systematically varied to locate the equilibrium position. With a Li atom included, the heterointerface binding energy is accordingly defined as

$$(\bar{E}_{\text{bind,Li}}) = \frac{E_{\text{hetero}} - (E_{\text{MoS}_2} + E_{\text{BN}}^* + E_{\text{Li}})}{2 \cdot A} \quad (2)$$

where *E*_{Li} is the energy of an isolated Li atom in vacuum.

Heterostructure Assembly and Device Fabrication. MoS₂ (SPI Supplies) and *h*BN (HQ Graphene) flakes were mechanically exfoliated from bulk crystals onto SiO₂/Si substrates using the scotch-tape method. The substrates were sonicated in acetone and isopropyl alcohol and treated with O₂ plasma prior to exfoliation. Flakes of the desired size and thickness were transferred to dry thermal oxide SiO₂/Si substrates using a KOH-assisted technique, and MoS₂ and *h*BN flakes were stacked on each other to form *h*BN–MoS₂–*h*BN heterostructures as follows. A hemispherical droplet of epoxy (Scotch-Weld, Series DP100Plus) about 0.5 mm in diameter was cured on a glass slide. Then, a 13 wt % solution of polypropylene carbonate (PPC, Sigma-Aldrich) in anisole was spun-coated onto the epoxy at 3000 rpm for 2 min and cured at 90 °C for 2 min. Using an optical microscope and a micromanipulator that holds the glass slide, the epoxy/PPC droplet was positioned above a flake of interest and carefully lowered to contact the flake. About 30 μL of a 2 M aqueous solution of potassium hydroxide (KOH, Sigma-Aldrich) was added to the substrate to etch the top few Å of SiO₂, releasing the flake from the substrate onto the epoxy/PPC droplet (the portion of the glass slide in contact with the KOH was covered with a thin layer of epoxy to prevent etching of the glass). The glass slide with the epoxy/PPC/flake was then rinsed with deionized water to remove any KOH residue. Each flake was released from the glass slide by melting the PPC at 95–100 °C for 5 min, while contacting a target substrate. The PPC was subsequently dissolved in chloroform overnight.

For electrochemical lithium intercalation, electrodes were patterned with electron beam lithography (Vistec Raith EBPG 5000+) and then 10 nm Cr/100 nm Au was deposited using thermal evaporation (Mbraun EcoVap). For the heterostructure device with exposed edges, polymethyl methacrylate (PMMA) and hydrogen silsesquioxane (HSQ) were used as a mask for dry etching. First, a layer of PMMA A3 was spun-coated on the heterostructure at 4000 rpm for 2 min and cured at 180 °C for 2 min. HSQ was subsequently spun-coated at 3000 rpm with no baking. Electron beam lithography was used to pattern the PMMA/HSQ mask, which was developed in a MF-312 developer (Rohm and Haas Electronic Materials) for 4 min. After developing, the device was rinsed in multiple DI-water baths in order to remove the developer. The finished mask protected the heterostructure, leaving only the edges exposed for reactive ion etching (Oxford Plasmalab 100). PMMA not covered by HSQ was first removed with O₂ plasma (20 sccm) under 50 W RF power for 15

s, exposing the edges. A mixture of O₂ (4 sccm) and CHF₃ (40 sccm) gases under 60 W RF power⁴⁶ for 2 min was used to etch the edges of the heterostructure. After etching, the PMMA/HSQ mask was removed with acetone.

Electrochemical Cell Fabrication. The electrochemical intercalation was performed directly on the heterostructure and bare MoS₂ devices. All devices fabricated on SiO₂/Si were attached to a glass slide, and the gold contacts of the devices were wire bonded to copper tape for connection to electrical instrumentation. All subsequent steps were conducted in an argon glovebox.

For all *in situ* Raman experiments, intercalation was conducted with a liquid electrolyte using an enclosed cell that holds the device and electrolyte and is sealed with an optical-grade glass top cover.^{20,21,33} Three sides of the glass top cover were first sealed by epoxy, leaving one side open. After the epoxy was cured, a small piece (~3 × 3 mm) of lithium metal (0.38 mm-thick ribbon, Sigma-Aldrich) was pressed onto copper foil using a mechanical plier to ensure good contact. The lithium/copper foil was then inserted into the open side of the glass top cover. The liquid electrolyte, a battery-grade solution of 1 M lithium hexafluorophosphate in 50/50 v/v ethylene carbonate/diethyl carbonate (LiPF₆ in EC/DEC, Sigma-Aldrich), was added to the cell to submerge the device and lithium metal. The open side was then covered with epoxy and allowed to cure, forming an air-tight seal.

***In Situ* Raman Characterization During Intercalation.** Intercalation cells were connected to a Biological SP300 potentiostat/galvanostat for the electrochemical intercalation of Li⁺. The Cr/Au contacts to the device served as the working electrode, while the lithium/copper served as the reference/counter electrode. Before intercalation, a Raman spectrum was taken at OCV (typical OCV values were 2.4–2.7 V vs Li/Li⁺). Lithium was intercalated into the heterostructures potentiostatically by dropping V_{EC} versus Li/Li⁺ at a scan rate of 10 mV s⁻¹. Upon reaching the desired V_{EC} , the cell was held at that potential while Raman spectra were collected. For multiple intercalation cycles, cells were allowed to recover to OCV before the next intercalation. Cyclic voltammetry scans were conducted using a Biological SP300 potentiostat/galvanostat at a scan rate of 0.8 mVs⁻¹. *In situ* heating experiments were conducted by placing the glass slide supporting the intercalation devices onto a hot-plate during intercalation.

All Raman spectra were taken with a HORIBA LabRAM HR Evolution Spectrometer using a 633 nm HeNe laser with an 1800 lines/mm diffraction grating. Before intercalation, all samples were characterized at a laser power of ~3 mW to avoid damage, but after cell fabrication, a laser power of ~7.5 mW was used to increase the signal-to-noise ratio because of scattering by the electrolyte. *In situ* Raman spectra were collected with fifteen 5 s exposures.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c21495>.

Effect of in-plane strain on the stability of the hBN–MoS₂ heterointerface; supercells of bilayer MoS₂–hBN heterostructures with Li in the van der Waals gap; distribution of charge density and atoms near Li in a hBN–MoS₂–hBN heterostructure; Raman characterization of hBN–MoS₂–hBN heterostructures; additional data for the hBN–MoS₂–hBN device; additional data for the bare MoS₂ device; characterization of bare MoS₂ using cyclic voltammetry and *in situ* Raman; additional data for the edge-exposed hBN–MoS₂–hBN device; additional data for the edge-covered hBN–MoS₂–hBN device; and *in situ* Raman spectrum of bare, unbiased MoS₂ at 100 °C in 1 M LiPF₆ in EC/DEC (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Judy J. Cha – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States; orcid.org/0000-0002-6346-2814; Email: judy.cha@yale.edu

Authors

Sajad Yazdani – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States

Joshua V. Pondick – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States; orcid.org/0000-0003-3380-2686

Aakash Kumar – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States

Milad Yarali – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States

John M. Woods – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States

David J. Hynek – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States

Diana Y. Qiu – Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States; Energy Sciences Institute, West Haven, Connecticut 06516, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsami.0c21495>

Author Contributions

S.Y. and J.V.P. authors contributed equally. S.Y. and J.J.C. conceived the project. S.Y. carried out the experiments and analyzed data with assistance from J.V.P. *Ab initio* calculations were performed by A.K. and D.Y.Q. J.V.P., M.Y., J.M.W., and D.J.H. contributed to the development of experimental methods and characterization techniques. S.Y., J.V.P., and J.J.C. wrote the manuscript with input from all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.Y. acknowledges support from the Army Research Office (W911NF-18-1-0367) for device fabrication and intercalation experiments. J.V.P. was supported by the National Defense Science and Engineering Graduate (NDSEG) Fellowship Program, sponsored by the Air Force Research Laboratory (AFRL), the Office of Naval Research (ONR), and the Army Research Office (ARO). J.J.C. acknowledges support from the National Science Foundation (CAREER #1749742). Device fabrication and characterization was carried out at the Yale

Institute for Nanoscience and Quantum Engineering, the Yale West Campus Materials Characterization Core, the Yale West Campus Cleanroom, and the Yale School of Engineering & Applied Science Cleanroom. The calculations of the heterointerface used resources of the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC02-05CH11231; the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1548562; and the Oak Ridge Leadership Computing Facility at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC05-00OR22725. We thank the Yale Center for Research Computing for use of the research computing infrastructure, specifically the Grace cluster, which was used for calculations on bulk MoS₂.

REFERENCES

- (1) Geim, A. K.; Grigorieva, I. V. Van Der Waals Heterostructures. *Nature* **2013**, *499*, 419–425.
- (2) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. 2D Materials and van Der Waals Heterostructures. *Science* **2016**, *353*, aac9439.
- (3) Cao, Y.; Fatemi, V.; Fang, S.; Watanabe, K.; Taniguchi, T.; Kaxiras, E.; Jarillo-Herrero, P. Unconventional Superconductivity in Magic-Angle Graphene Superlattices. *Nature* **2018**, *556*, 43–50.
- (4) Yankowitz, M.; Chen, S.; Polshyn, H.; Zhang, Y.; Watanabe, K.; Taniguchi, T.; Graf, D.; Young, A. F.; Dean, C. R. Tuning Superconductivity in Twisted Bilayer Graphene. *Science* **2019**, *363*, 1059–1064.
- (5) Finney, N. R.; Yankowitz, M.; Muraleetharan, L.; Watanabe, K.; Taniguchi, T.; Dean, C. R.; Hone, J. Tunable Crystal Symmetry in Graphene–Boron Nitride Heterostructures with Coexisting Moiré Superlattices. *Nat. Nanotechnol.* **2019**, *14*, 1029–1034.
- (6) Kertesz, M.; Hoffmann, R. Octahedral vs. Trigonal-Prismatic Coordination and Clustering in Transition-Metal Dichalcogenides. *J. Am. Chem. Soc.* **1984**, *106*, 3453–3460.
- (7) Dungey, K. E.; Curtis, M. D.; Penner-Hahn, J. E. Structural Characterization and Thermal Stability of MoS₂ Intercalation Compounds. *Chem. Mater.* **1998**, *10*, 2152–2161.
- (8) Wang, L.; Xu, Z.; Wang, W.; Bai, X. Atomic Mechanism of Dynamic Electrochemical Lithiation Processes of MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2014**, *136*, 6693–6697.
- (9) Dresselhaus, M. S., Ed. *Intercalation in Layered Materials*; Springer Science+Business Media LLC: New York, 1986.
- (10) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS₂. *Nano Lett.* **2011**, *11*, 5111–5116.
- (11) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.
- (12) Wan, J.; Lacey, S. D.; Dai, J.; Bao, W.; Fuhrer, M. S.; Hu, L. Tuning Two-Dimensional Nanomaterials by Intercalation: Materials, Properties and Applications. *Chem. Soc. Rev.* **2016**, *45*, 6742–6765.
- (13) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S. Enhanced Hydrogen Evolution Catalysis from Chemically Exfoliated Metallic MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2013**, *135*, 10274–10277.
- (14) Wang, H.; Lu, Z.; Xu, S.; Kong, D.; Cha, J. J.; Zheng, G.; Hsu, P.-C.; Yan, K.; Bradshaw, D.; Prinz, F. B.; Cui, Y. Electrochemical Tuning of Vertically Aligned MoS₂ Nanofilms and Its Application in Improving Hydrogen Evolution Reaction. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 19701–19706.
- (15) Voiry, D.; Fullon, R.; Yang, J.; de Carvalho Castro e Silva, C.; Kappera, R.; Bozkurt, I.; Kaplan, D.; Lagos, M. J.; Batson, P. E.; Gupta, G.; Mohite, A. D.; Dong, L.; Er, D.; Shenoy, V. B.; Asefa, T.; Chhowalla, M. The Role of Electronic Coupling between Substrate and 2D MoS₂ Nanosheets in Electrocatalytic Production of Hydrogen. *Nat. Mater.* **2016**, *15*, 1003–1009.
- (16) Sood, A.; Xiong, F.; Chen, S.; Wang, H.; Selli, D.; Zhang, J.; McClellan, C. J.; Sun, J.; Donadio, D.; Cui, Y.; Pop, E.; Goodson, K. E. An Electrochemical Thermal Transistor. *Nat. Commun.* **2018**, *9*, 4510.
- (17) Yazdani, S.; Yarali, M.; Cha, J. J. Recent Progress on in Situ Characterizations of Electrochemically Intercalated Transition Metal Dichalcogenides. *Nano Res.* **2019**, *12*, 2126–2139.
- (18) Zhou, X.; Wan, L.-J.; Guo, Y.-G. Facile Synthesis of MoS₂@CMK-3 Nanocomposite as an Improved Anode Material for Lithium-Ion Batteries. *Nanoscale* **2012**, *4*, 5868–5871.
- (19) Wang, H.; Lu, Z.; Kong, D.; Sun, J.; Hymel, T. M.; Cui, Y. Electrochemical Tuning of MoS₂ Nanoparticles on Three-Dimensional Substrate for Efficient Hydrogen Evolution. *ACS Nano* **2014**, *8*, 4940–4947.
- (20) Wan, J.; Bao, W.; Liu, Y.; Dai, J.; Shen, F.; Zhou, L.; Cai, X.; Urban, D.; Li, Y.; Jungjohann, K.; Fuhrer, M. S.; Hu, L. In Situ Investigations of Li-MoS₂ with Planar Batteries. *Adv. Energy Mater.* **2015**, *5*, 1401742.
- (21) Xiong, F.; Wang, H.; Liu, X.; Sun, J.; Brongersma, M.; Pop, E.; Cui, Y. Li Intercalation in MoS₂: In Situ Observation of Its Dynamics and Tuning Optical and Electrical Properties. *Nano Lett.* **2015**, *15*, 6777–6784.
- (22) Kühne, M.; Paolucci, F.; Popovic, J.; Ostrovsky, P. M.; Maier, J.; Smet, J. H. Ultrafast Lithium Diffusion in Bilayer Graphene. *Nat. Nanotechnol.* **2017**, *12*, 895–900.
- (23) Bediako, D. K.; Rezaee, M.; Yoo, H.; Larson, D. T.; Zhao, S. Y. F.; Taniguchi, T.; Watanabe, K.; Brower-Thomas, T. L.; Kaxiras, E.; Kim, P. Heterointerface Effects in the Electrointercalation of van Der Waals Heterostructures. *Nature* **2018**, *558*, 425–429.
- (24) Zhao, S. Y. F.; Elbaz, G. A.; Bediako, D. K.; Yu, C.; Efetov, D. K.; Guo, Y.; Ravichandran, J.; Min, K.-A.; Hong, S.; Taniguchi, T.; Watanabe, K.; Brus, L. E.; Roy, X.; Kim, P. Controlled Electrochemical Intercalation of Graphene/h-BN van Der Waals Heterostructures. *Nano Lett.* **2018**, *18*, 460–466.
- (25) Zhou, Y.; Silva, J. L.; Woods, J. M.; Pondick, J. V.; Feng, Q.; Liang, Z.; Liu, W.; Lin, L.; Deng, B.; Brena, B.; Xia, F.; Peng, H.; Liu, Z.; Wang, H.; Araujo, C. M.; Cha, J. J. Revealing the Contribution of Individual Factors to Hydrogen Evolution Reaction Catalytic Activity. *Adv. Mater.* **2018**, *30*, 1706076.
- (26) Zhou, Y.; Pondick, J. V.; Silva, J. L.; Woods, J. M.; Hynek, D. J.; Matthews, G.; Shen, X.; Feng, Q.; Liu, W.; Lu, Z.; Liang, Z.; Brena, B.; Cai, Z.; Wu, M.; Jiao, L.; Hu, S.; Wang, H.; Araujo, C. M.; Cha, J. J. Unveiling the Interfacial Effects for Enhanced Hydrogen Evolution Reaction on MoS₂/WTe₂ Hybrid Structures. *Small* **2019**, *15*, 1900078.
- (27) Sun, L.; Yan, X.; Zheng, J.; Yu, H.; Lu, Z.; Gao, S.-p.; Liu, L.; Pan, X.; Wang, D.; Wang, Z.; Wang, P.; Jiao, L. Layer-Dependent Chemically Induced Phase Transition of Two-Dimensional MoS₂. *Nano Lett.* **2018**, *18*, 3435–3440.
- (28) Gao, G.; Jiao, Y.; Ma, F.; Jiao, Y.; Wacławik, E.; Du, A. Charge Mediated Semiconducting-to-Metallic Phase Transition in Molybdenum Disulfide Monolayer and Hydrogen Evolution Reaction in New 1T' Phase. *J. Phys. Chem. C* **2015**, *119*, 13124–13128.
- (29) Tang, W.; Sanville, E.; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias. *J. Phys. Condens. Matter* **2009**, *21*, 082004.
- (30) Jiménez Sandoval, S.; Yang, D.; Frindt, R. F.; Irwin, J. C. Raman Study and Lattice Dynamics of Single Molecular Layers of MoS₂. *Phys. Rev. B* **1991**, *44*, 3955–3962.
- (31) Kappera, R.; Voiry, D.; Yalcin, S. E.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M. Phase-Engineered Low-Resistance Contacts for Ultrathin MoS₂ Transistors. *Nat. Mater.* **2014**, *13*, 1128–1134.

- (32) Xiao, J.; Choi, D.; Cosimbescu, L.; Koech, P.; Liu, J.; Lemmon, J. P. Exfoliated MoS₂ Nanocomposite as an Anode Material for Lithium Ion Batteries. *Chem. Mater.* **2010**, *22*, 4522–4524.
- (33) Zhang, J.; Yang, A.; Wu, X.; van de Groep, J.; Tang, P.; Li, S.; Liu, B.; Shi, F.; Wan, J.; Li, Q.; Sun, Y.; Lu, Z.; Zheng, X.; Zhou, G.; Wu, C.; Zhang, S.; Brongersma, M. L.; Li, J.; Cui, Y. Reversible and Selective Ion Intercalation through the Top Surface of Few-Layer MoS₂. *Nat. Commun.* **2018**, *9*, 5289.
- (34) Liu, Y.; Guo, J.; Zhu, E.; Liao, L.; Lee, S.-J.; Ding, M.; Shakir, I.; Gambin, V.; Huang, Y.; Duan, X. Approaching the Schottky–Mott Limit in van Der Waals Metal–Semiconductor Junctions. *Nature* **2018**, *557*, 696–700.
- (35) Hu, S.; Lozada-Hidalgo, M.; Wang, F. C.; Mishchenko, A.; Schedin, F.; Nair, R. R.; Hill, E. W.; Boukhvalov, D. W.; Katsnelson, M. I.; Dryfe, R. A. W.; Grigorieva, I. V.; Wu, H. A.; Geim, A. K. Proton Transport through One-Atom-Thick Crystals. *Nature* **2014**, *516*, 227–230.
- (36) Caglar, M.; Silkina, I.; Brown, B. T.; Thorneywork, A. L.; Burton, O. J.; Babenko, V.; Gilbert, S. M.; Zettl, A.; Hofmann, S.; Keyser, U. F. Tunable Anion-Selective Transport through Monolayer Graphene and Hexagonal Boron Nitride. *ACS Nano* **2020**, *14*, 2729–2738.
- (37) Surwade, S. P.; Smirnov, S. N.; Vlassiuk, I. V.; Unocic, R. R.; Veith, G. M.; Dai, S.; Mahurin, S. M. Water Desalination Using Nanoporous Single-Layer Graphene. *Nat. Nanotechnol.* **2015**, *10*, 459–464.
- (38) Rollings, R. C.; Kuan, A. T.; Golovchenko, J. A. Ion Selectivity of Graphene Nanopores. *Nat. Commun.* **2016**, *7*, 11408.
- (39) Kufian, M. Z.; Majid, S. R. Performance of Lithium-Ion Cells Using 1 M LiPF₆ in EC/DEC (v/v = 1/2) Electrolyte with Ethyl Propionate Additive. *Ionics* **2010**, *16*, 409–416.
- (40) Yang, H.; Kim, S. W.; Chhowalla, M.; Lee, Y. H. Structural and Quantum-State Phase Transition in van Der Waals Layered Materials. *Nat. Phys.* **2017**, *13*, 931–937.
- (41) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys. Condens. Matter* **2009**, *21*, 395502.
- (42) Troullier, N.; Martins, J. L. Efficient Pseudopotentials for Plane-Wave Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, *43*, 1993–2006.
- (43) Perdew, J. P.; Zunger, A. Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1981**, *23*, 5048–5079.
- (44) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B: Solid State* **1976**, *13*, 5188–5192.
- (45) Nasr Esfahani, D.; Leenaerts, O.; Sahin, H.; Partoens, B.; Peeters, F. M. Structural Transitions in Monolayer MoS₂ by Lithium Adsorption. *J. Phys. Chem. C* **2015**, *119*, 10602–10609.
- (46) Wang, L.; Meric, I.; Huang, P. Y.; Gao, Q.; Gao, Y.; Tran, H.; Taniguchi, T.; Watanabe, K.; Campos, L. M.; Muller, D. A.; Guo, J.; Kim, P.; Hone, J.; Shepard, K. L.; Dean, C. R. One-Dimensional Electrical Contact to a Two-Dimensional Material. *Science* **2013**, *342*, 614–617.