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Heterointerface effects in the electro-intercalation of van der Waals heterostructures

D. Kwabena Bediako,^{1,†} Mehdi Rezaee,^{2,5†} Hyobin Yoo,¹ Daniel T. Larson,¹ Shu Yang Frank Zhao,¹ Takashi Taniguchi,³ Kenji Watanabe,³ Tina L. Brower-Thomas,⁴ Efthimios Kaxiras^{1,5} and Philip Kim^{1*}

¹ Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

² Department of Electrical Engineering, Howard University, Washington, DC 20059, USA

³ National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

⁴ Department of Chemical Engineering, Howard University, Washington, DC 20059, USA

⁵ School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

† These authors contributed equally to this work

Molecular-scale manipulation of electronic and ionic charge accumulation in materials is the backbone of electrochemical energy storage. ¹⁻⁴ Layered van der Waals (vdW) crystals are a diverse family of materials that can electrochemically intercalate mobile ions into the interlamellar gaps of the host atomic lattice. ^{5,6} The structural diversity of such materials means that interfacial properties can be optimized in composites to improve ion intercalation for energy storage and electronic devices. ⁷⁻¹² However the role and ability of heterolayers to modify intercalation reactions remains elusive at an atomic level. Here, we demonstrate the electro-intercalation of lithium at the level of individual atomic interfaces of dissimilar vdW layers. Electrochemical devices based on vdW heterostructures ¹³ of stacked hexagonal boron nitride (hBN), graphene and molybdenum dichalcogenide (MoX₂; X = S, Se) layers are fabricated. We use transmission electron microscopy, in situ magnetoresistance and μ SEPP optical spectroscopy techniques, as well as low-temperature quantum magneto-oscillation measurements and ab initio calculations to resolve the intermediate stages of lithium intercalation at heterointerfaces. The creation of vdW heterointerfaces between graphene and MoX₂ results in over 10-fold accumulation of charge in MoX₂ compared to MoX₂/MoX₂ homointerfaces, while enforcing a more negative intercalation potential than that of bulk MoX₂ by at least 0.5 V. Beyond energy storage, our combined experimental and computational methodology for manipulating and characterizing the electrochemical behavior of layered systems opens new pathways to control the charge density in 2D electronic/optoelectronic devices.

To examine the role of the vdW heterointerface in intercalation, we have assembled layers of graphene (G), molybdenum dichalcogenides (MoX₂, X = S, Se), and hBN into various precise arrangements. Fig. 1a shows a series of five different heterostructures (Structures **I** through **V**) created using vdW assembly.¹⁴ Structure **I** is a simple vdW structure of graphene encapsulated by hBN, the subject of our previous studies,¹⁵ which serves as a reference point in the present study. The remaining structures (**II-V**) are combinations of atomically thin single crystals of graphene and MoX₂ encapsulated by hBN with several vdW heterointerfaces between atomic layers. The etched boundaries of the vdW stacks are exposed to the electrolyte. These electrochemical device architectures are investigated as the working electrodes (WEs) of on-chip micro-electrochemical cells as shown in Fig. 1b and c. Using the recently developed Hall potentiometry method (see methods for details), we can extract both the longitudinal resistance, R_{xx} , of the heterostructure WE as well as the Hall carrier density, n_H , while the reaction driving force (potential, E) is

altered.¹⁵ Thus, the progress of the electrochemical reaction can be precisely monitored in this mesoscopic system.

Fig. 2 presents an exemplary set of results for electro-intercalation of a heterostructure stack of Structure **II** (hBN/MoS₂/G/hBN). From the behaviors of R_{xx} and n_H as a function of E , four distinct phases (Phase 1–4) in the electrochemical reaction can be distinguished. This in-situ monitoring of R_{xx} and n_H provides more direct information of intercalation staging than that of the traditional electrochemical approaches since it is insensitive to extraneous interfacial reactions (see Extended Data Fig. 1 for such a comparison). The transport features in Phase 1 (for $E > -2.3$ V) replicate the purely electrostatic doping behavior observed in electric double layer gating of graphene.¹⁶ With increasingly negative E , several intercalation processes occur, revealed by pronounced jumps in R_{xx} and n_H . The latter features in Phases 3 and 4, specifically the peak in R_{xx} that occurs in concert with the surge in n_H , are key signatures of ion intercalation involving a high mobility graphene layer.¹⁵ The intercalation process engenders a decline in electron mobility as Li⁺ ions become closely associated with the graphene lattice and act as scattering sites for mobile electrons.¹⁷ Ultimately the resistance is driven back down as mounting carrier densities supersede this sudden decrease in mobility.¹⁵ Deintercalation by sweeping E toward 0 V potential reverses doping and recovers R_{xx} and n_H values similar to those of the pristine heterostructure (Extended Data Fig. 1a). The total carrier densities for intercalated Structure **II** stacks attain values approaching $n_H = 2 \times 10^{14}$ cm⁻² (Extended Data Fig. 3), between three and ten-times the maximal densities observed for intercalated Structure **I** ($2 - 7 \times 10^{13}$ cm⁻²).¹⁵

Insight into the participation of MoX₂ in this electrochemical reaction is provided by *operando* photoluminescence (PL) and Raman spectroelectrochemistry. In Fig. 2b, PL data reveal distinct changes to the optical profile of the semiconducting 1H-MoS₂ layer. Specifically, we find the PL peak consistent with the formation of negatively charged trions (A⁻)¹⁸ appears at the later stage of intercalation process ($E < -3$ V), signifying that a strongly electron-doped 1H-MoS₂ phase persists immediately prior to the main intercalation stage. Beyond this point the PL is fully quenched and Raman (see Extended Data Fig. 2a) spectral features of the MoS₂ (and graphene) layer are lost due to Pauli blocking.^{15,19,20} Deintercalation recovers the original Raman signatures of graphene, while revealing diminished spectral intensity of the E_{12g} and A_{1g} modes of MoS₂ as well as the emergence of a series of weak peaks between ~150 and 230 cm⁻¹ (Figure 2c). These results are consistent with an intercalation-induced phase transition from the semiconducting H-MoS₂ phase to a metallic T-phase with an additional lattice distortion (usually denoted as T').^{21–23} The low wavenumber Raman features are characteristic of the so-called “J” modes of T and T'-MoS₂.^{21,24–26} Figs. 2d–g (and Extended Data Figure 2c–g) exhibit the corresponding PL and Raman spectrum homogeneously distributed across the interfacial areas, signifying homogeneity of the intercalation/deintercalation processes.

Low temperature magnetotransport studies in the intercalated vdW heterostructure devices offer a new route to probe the distribution of charge on each 2D layer after intercalation. For an intercalated Structure **II** device, Fig. 3a shows that the Hall resistance, R_{xy} , is linear in magnetic field B from which we estimate n_H equal to 1.0×10^{14} cm⁻². The magnetoresistance, R_{xx} , exhibits a pronounced peak near $B = 0$, presumably related to the weak localization behavior due to intervalley scattering of intercalated Li⁺ ions.¹⁷ We observe well-defined Shubnikov-de Haas (SdH) oscillations^{27,28} for $B > 3$ T, signifying homogeneity of the lithium-

intercalated heterostructure and indicating high quality 2D electron gas (2DEG) with an associated carrier density of $2 \times 10^{13} \text{ cm}^{-2}$ (see Methods). The discrepancy between n_{sdH} and n_{H} lies in stark contrast with those observed for Structure **I** (Extended Data Fig. 4), and is consistent with a two-channel electronic system, where a higher mobility 2DEG produces SdH oscillations corresponding to a lower density $n_{\text{sdH}} < n_{\text{H}}$, while another channel contains the vast majority of electron density ($n_{\text{H}} - n_{\text{sdH}}$) with a lower mobility.

The decreasing SdH oscillation amplitude with increasing temperature (Figure 3b) unveils an effective mass (m^*) of electrons equal to $0.11m_0$ (m_0 is the electron rest mass), close to the value of $0.099m_0$ that we obtain for intercalated Structure **I** (hBN/graphene/hBN) doped to a density of $\sim 2 \times 10^{13} \text{ cm}^{-2}$ in graphene (additional transport quantities are summarized in Extended Data Table 1). From the Landau fan diagram of Structure **II** (Figure 3c) we observe that the SdH quantum oscillations are strongly dependent on the voltage applied to the silicon backgate, V_{g} , pointing to the graphene as the origin of the magneto-oscillations (see Methods). Correspondingly, we find that n_{sdH} and n_{H} exhibit the same dependence on V_{g} (Fig. 3d), consistent with the bottom-graphene layer (*ca.* 10^{13} electrons cm^{-2}) serving to shield the overlying MoS₂ sheet (*ca.* 10^{14} electrons cm^{-2}) from the electrostatic influence of V_{g} . In this picture, the dependence of the total density, given by n_{H} , simply follows the dependence of one of its components n_{sdH} .

Having established the carrier density distribution on these heterostructures lies strongly on the metal dichalcogenide layer, it is interesting that intercalation of Structure **III** stacks (n_{H} $1.4\text{--}1.9 \times 10^{14} \text{ cm}^{-2}$, see Extended Data Fig. 5) does not lead to carrier densities in excess of typical Structure **II** samples. This observation suggests that it is the G/MoX₂ heterointerface that harbors the vast majority of intercalated ions as opposed to hBN/MoX₂ or MoX₂/MoX₂ interfaces. To probe this further, we create heteroarchitectures wherein we design in-plane variations to the structure type along a single graphene monolayer, as depicted in Fig. 4a. Simultaneous measurement of the transport characteristics at different lateral sections of the heterostructure devices during electrochemical polarization (Fig. 4b and see also Extended Data Figs. 6 and 7) reveals that the onset of G/MoX₂ intercalation takes place at about $\Delta E^{\circ} = +0.5$ to $+0.75$ V vs. that of G/hBN. Notwithstanding the significantly negative potential, it is noteworthy that the dichalcogenides in these G/MoX₂ heterostructures are not decomposed to lithium polychalcogenides as occurs in the bulk (Extended Data Fig. 8),²⁰ indicating a widened window of electrochemical stability. This enhanced stability may be a result of dimensional confinement that restricts polysulfide/Mo₀ nucleation and product diffusion.¹² Hall resistance measurements at specific regions of the device (Fig. 4b, bottom left) unequivocally demonstrate the critical role of direct graphene–MoX₂ heterointerfaces in markedly enhancing the carrier/charge capacities in vdW heterostructure electrodes. We find that encapsulating a graphene monolayer between layers of MoX₂ (as in Structures **V** and **V***), thereby creating two graphene–dichalcogenide heterointerfaces produces intercalation capacities more than double those of the “isomeric” Structure **III** region within the same device (Fig. 4b, bottom right). The intercalation onset potentials of the different structures (Fig. 4c and Extended Data Fig. 9a) emphasize that G/MoX₂ interfaces dominate the intercalation properties; the onset of intercalation is effectively identical across Structures **II** to **V**, and distinctly lying between those of Structure **I** and bulk MoX₂. Capacities (Fig. 4c inset and Extended Data Figs. 9b,c) as high as $6.2 \times 10^{14} \text{ cm}^{-2}$ are attainable in Structure **V** devices. However, in all these structures, the graphene density (n_{sdH}) exhibits a maximum value of $\sim 2 \times 10^{13} \text{ cm}^{-2}$, indicative of a strong preference for charge transfer to the dichalcogenide layers ($n \sim 3 \times 10^{14} \text{ cm}^{-2}$ each). Assuming additive Li⁺ capacities,

we can estimate the electrochemically accessible capacity of each vdW interface as plotted in Fig. 4d, showing the ≥ 10 -fold superiority of the G/MoS₂ interface compared to other interfaces. These results highlight the criticality of the graphene heterolayer in enhancing electrochemical charge accumulation in MoX₂ while also directing intercalation at a more negative voltage than that of bulk MoX₂.

Finally, we explore the atomic scale structural evolution of these layers using ex situ scanning transmission electron microscopy (STEM). As expected, data from the pristine heterostructure are fully consistent with that of *H*-MoS₂ (Fig. 5b). The onset of intercalation results in an increasingly disordered MoS₂ lattice evinced by the progressive splitting of the MoS₂ Bragg spots in selected area electron diffraction (SAED) patterns. Importantly, even before the peak in R_{xx} we observe this signature of disorder at the edges of the heterostructure, whilst the interior remains pristine (Extended Data Figs. 10). Full intercalation results in the observation of a ring in SAED data (Fig. 5c, inset). Insightfully, aberration-corrected STEM imaging (Fig. 5c and Extended Data Fig. 11) uncovers crystalline order within domains that are approximately 5–10 nm in size (Fig. 5c, right and Extended Data Fig. 11). We also distinctly observe ~ 1 nm-sized voids in the metal dichalcogenide layer that are reminiscent of what has been reported in previous TEM studies of chemically (*n*BuLi)-lithiated and exfoliated MoS₂.²² This structural disruption is likely caused by the strain introduced into the MoX₂ layer during lithiation and the attendant progression of the *H*- to *T'* phase transformation along the lattice. Despite these structural defects, the resulting basal plane charge transport in MoS₂ layers is reasonably high (as shown in Extended Data Table 1), indicating that the intercalation/deintercalation process leaves the MoS₂ structure largely intact and as an electrically contiguous layer.

The tuning of intercalation potentials using vdW heterostructures is well explained by the modification of theoretical Li binding energetics as observed in density functional theory (DFT) calculations (Fig. 5d). First, these calculations reveal that the *T'*-MoS₂ phase has a considerably stronger binding affinity for Li atoms than *H*-MoS₂. Thus, a local phase transformation upon doping should lead to a cooperative effect wherein it becomes increasingly favorable to intercalate Li into that local vdW region as the dichalcogenide undergoes the semiconductor (*H*) to metallic (*T'*) transformation, thereby lowering the activation barrier for Li⁺ insertion. This phase transition is manifested by the closing of the band gap and the Fermi level crosses a band with large density of states as shown in Fig. 5e and Extended Data Fig. 12. Furthermore, since hBN is an inert, wide-gap insulator and non redox-active, the energetics of initial Li intercalation are only slightly perturbed in the case of hBN/*T'*-MoS₂ compared to *T'*-MoS₂/*T'*-MoS₂. In contrast, G heterolayers have a substantially stronger attenuating effect on the binding energy of Li, yet still the reaction is more exergonic than that of Li with hBN/G or G/G₂₉ (Fig. 5d). As a result, we observe a positive shift in intercalation potential for the G/MoS₂ heterolayer compared to hBN/G in Figs. 4b and c.

Taken together, our experimental results are consistent with the electrochemical reaction scheme that is presented in Figure 5f. This mechanism involves charge transfer to both graphene and MoX₂ in initial stages of the electrochemical gating process. Dilute concentrations of Li⁺ ions are intercalated at modest potentials into MoX₂/hBN (and MoX₂/MoX₂) heterointerfaces. However, on the basis of SAED data of our heterostructures and prior observations of sluggish chemical lithiation of bulk MoS₂,²⁰ Li⁺ ion intercalants of these interfaces appear most concentrated proximate to the heterostructure–electrolyte interface (where the electric field is certainly strongest and some *T'*-MoS₂ can be formed locally from electrostatic double-

layer gating). The G/MoX₂ interface possesses a unique intercalation potential that is more positive than that of G/hBN and as such this is the next interface to undergo intercalation. The exceptional electronic mobility of graphene (sufficient to display quantum oscillations even after interfacial ion intercalation) furnishes a lower-resistance electronic pathway, notwithstanding a lower partial carrier density, which allows its immediate interface with the MoX₂ layer to undergo ionic doping more efficiently than adjacent MoX₂/MoX₂ homointerfaces. Eventually a highly doped, 2D nanocrystalline T'-MoX₂ is formed upon complete intercalation of the graphene–dichalcogenide heterostructure.

We note that typically, in battery electrodes consisting of layered material composites, carbonaceous additives like graphene serve primarily to improve cyclability, particularly over the course of additional conversion reactions that can form insulating and structurally expanded conversion phases.^{7,8,10,11} These approaches do not seek to create or exploit a direct vdW contact between individual atomic layers as a means of tuning the intercalation reaction itself. Our observations for Li-ion intercalation at individual atomic interfaces motivate the use of vdW heteroepitaxy as a promising strategy to realize new engineered functional interfaces for energy conversion and storage by manipulating the ion storage modes and “job-sharing”⁴ characteristics of hybrid electrodes. Furthermore, our demonstrated control over intercalation energetics, the resultant spatial carrier density profile, and realization of ultra-high charge densities using vdW heterointerfaces opens new possibilities for 2D plasmonic device schemes³⁰ that would require large variations in charge density.

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Online Content. Methods, Extended Data display items are available in the online version of the paper; references unique to these sections appear only in the online paper (<http://www.nature.com>).

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Author Contributions DKB, MR, and HY performed the experiments and analyzed the data. DKB, SYFZ and PK conceived the experiment. DTL and EK performed the theoretical computations. KW and TT provided bulk hBN crystals. DKB, MR, and PK wrote the manuscript. All authors contributed to the overall scientific interpretation and edited the manuscript.

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Figure Legends

Figure 1. Van der Waals heterostructures for lithium intercalation. **a**, Atomic models of the heterostructure series employed for investigation of heterolayers on intercalation capacities and thermodynamics. **b** Schematic model of mesoscopic electrochemical cell. **c**, Optical micrographs of an on-chip electrochemical cell for charge transport and optical measurements during electro-intercalation. Scale bars: left, 500 μm ; right, 10 μm .

Figure 2. Intercalation of Structure II devices. **a**, “Hall potentiogram” recorded at 325 K for a G/MoSe₂ device ($B = 0.5$ T). **b**, *Operando* photoluminescence (left) and resistance (middle) measurements for G/MoS₂ at 325 K, along with schematic representations of the exciton quasiparticles (right). **c**, *Ex situ* Raman spectra of a pristine (bottom), cycled (middle), and subsequently annealed (top) heterostructure. Inset: Raman spectra after annealing of (from bottom to top) MoS₂, G/MoS₂, 2L-MoS₂, and G/2L-MoS₂. **d**, Optical micrograph of device used in spectroscopic mapping. Scale bar: 5 μm . **e–g**, *Ex situ* photoluminescence (**e,f**) and 200–250 cm^{-1} Raman (**g**) spatial maps of the device in **d** before intercalation (**e**) after one cycle (**f**) and after subsequent annealing (**g**).

Figure 3. Quantum transport. **a**, Four-terminal R_{xx} and R_{xy} as a function of perpendicular B for intercalated Structure II. **b**, Temperature, T , dependence of SdH oscillations. Top inset: SdH amplitude as a function of T at five values of B . Solid lines depict fits according to the Lifshitz–Kosevich formalism. Bottom inset: effective masses, m^* , extracted from fits (where m_0 is the free electron mass). **c**, Landau fan diagram $R_{xx}(V_g, B)$ after intercalation. Inset: schematic of the intercalated heterostructure used with the graphene layer beneath MoS₂. **d**, V_g dependence of n_{SdH} (open circles) and n_{Hall} (filled circles). Lines represent fits assuming a Si backgate capacitance of 1.2×10^{-8} F cm^{-2} .

Figure 4. Tuning intercalation with vdW heterolayers. **a**, Optical micrograph (false color) of a device consisting of multiple heterostructure types (depicted in the associated illustration) arrayed along a G monolayer. Scale bar: 5 μm . **b**, Top: R_{xx} during electrochemical gating of two regions of the device in **a**. Bottom left: Hall data following polarization of the device in **a** to -5.0 V. Bottom right: n_{H} from each region of the device. **c**, Intercalation onset potentials of vdW heterostructures and bulk MoX₂ (see also Extended Data Fig. 9a). Error bars, where present, represent the standard deviation (from left to right, $n = 3, 6, 4, 2, 1, 3$) of measurements from multiple devices and/or distinct contact pairs. Inset: Mean charge densities after intercalation. n_{H} , indicative of the total density, is depicted by the overall bar height, and graphene partial densities from SdH data (where available) are indicated by the lighter sub-bars. **d**, Estimated doping level of vdW interfaces.

Figure 5. Structural evolution of vdW heterostructures with intercalation. **a**, Schematic of vdW heterostructure device for (S)TEM analysis. Inset shows optical micrograph of a representative device. Scale bar: 10 μm . **b,c**, High angle annular dark field (HAADF) STEM images of Structure **II** devices before intercalation (**b**) and after one cycle (**c**). Scale bars: 5 nm. Insets show selective area electron diffraction (SAED) patterns. Diffraction features originating from $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes of MoS_2 are marked with red and green circles/arrows, respectively. In **c**, fast Fourier transforms (FFT) obtained from the regions indicated with the dashed boxes are shown on the right. **d**, Computed Li atom binding energy as a function of number of lithium atoms in the supercell (see Methods). 2L-G and hBN/G data are adapted from ref. 29. **e**, Computed relaxed structures (top) and density of states plots (bottom) for pristine (left), and Li-intercalated (middle: 1 Li; right: 4 Li) heterostructures. **g**, Proposed mechanism of vdW heterostructure intercalation.

Methods

Sample fabrication. Samples were fabricated a similar way described in previous work.^{31,32} Briefly, mechanical exfoliation of Kish graphite (Covalent Materials Corp.) and molybdenum dichalcogenides, MoX₂ (X = S, Se) (HQ graphene) onto *p*-doped silicon with 285 nm SiO₂ furnishes crystals of the desired thickness, which are identified by optical contrast. Hexagonal boron nitride (hBN) flakes of thickness 15–30 nm are similarly exfoliated and used to pick up graphene and/or MoX₂ layers in the designed order. Finally, release of these stacks onto a second flake of hBN results in hBN encapsulated heterostructures that are subjected to annealing in ultra-high vacuum for 30 minutes at 350 °C. For the devices fabricated on silicon nitride membranes, thinner hBN flakes (≤ 5 nm) were used. Standard electron-beam lithography followed by evaporation of Cr/Pt (1 nm / 9 nm) electrodes is used to define on-chip counter and pseudo-reference electrodes. Reactive ion etching (RIE) using a mixture of CHF₃, Ar, and O₂ is subsequently used to shape the heterostructure into a hall bar. Another round of lithography is used to delineate an etch mask that overlaps with the protruding legs of the Hall bar. Immediately following another RIE step, the same etch mask is used as the metal deposition mask with Cr/Pd/Au (5 nm / 15 nm / 70 nm) contacts. This results in a one-dimensional edge-contact to the active layers and low contact resistances.

Electrochemical doping & intercalation. In an Ar-filled glovebox, 3.7 mL of anhydrous (dried with 3 Å molecular sieves) acetonitrile (Sigma-Aldrich) is added to 0.3 g of polyethylene oxide, PEO (Sigma-Aldrich), and 50 mg of lithium bis(trifluoromethane)sulfonamide, LiTFSI. After stirring overnight, a 10–15 μ L droplet of this electrolyte solution is cast onto the Si chip possessing the electrically contacted heterostructure stack such that the droplet encompasses both the stack and the counter/reference electrodes. Rapid evaporation of the acetonitrile solvent yields a solid polymer electrolyte for electrochemical studies. Additional extraneous solvent was removed by vacuum drying the electrolyte overnight. Immediately before measurements the measurement device was isolated from ambient moisture and oxygen using a glass cover slip affixed to the chip carrier with vacuum grease. The device is then removed from the glovebox and transferred promptly to the cryostat and vacuum-sealed.

At a temperature of 325 K, the potential between the heterostructure working electrode and Pt counter electrode is swept at a rate of ~ 1 mV/s in the presence of a small magnetic field, B , of 0.5 T. Simultaneously, the resistance of the device is monitored by applying a small AC (17.777 Hz) current (I_{ds}) of 0.1–1 μ A between the source and drain terminals and measuring the four-terminal longitudinal voltage drop, V_{xx} , and Hall voltage, V_{xy} , using a lock-in amplifier (Stanford Research SR830). The resistances R_{xx} and R_{xy} are then obtained by $R_{xx} = V_{xx}/I_{ds}$ and $R_{xy} = V_{xy}/I_{ds}$. The Hall carrier density, n_H , is then computed from: $n_H = B/(e \cdot R_{xy})$, where e is the elementary charge 1.602×10^{-19} C. The Hall mobility, μ_H , during the sweep is also determined from $\mu_H = (e \cdot n_H \cdot \rho_{xx})^{-1}$, where the resistivity, ρ_{xx} is given by $\rho_{xx} = R_{xx} \cdot W/L$,

where W represents the width of the conducting channel and L denotes the length of the channel between contacts. A voltmeter (Agilent 34401A Digital Multimeter) with a high internal impedance of $>10\text{ G}\Omega$ is used to measure the voltage between the heterostructure working electrode and the Pt pseudo-reference electrode.

Upon reaching the desired potential, the temperature of the system is rapidly cooled to 200 K (10 K/min), thereby freezing the polymer electrolyte and effectively suspending any electrochemical reactions, after which additional magnetic field or temperature dependent sweeps are conducted as desired. Further cooling to base temperature (1.8 K) is carried out at a slower rate of 2 K/min.

Provided potential excursions did not exceed -6 V we found transport behavior to be stable to multiple cycles of these heterostructures.

Raman & Photoluminescence spectroscopy studies. Raman and photoluminescence (PL) spectroscopy (Horiba Multiline) is conducted using a 532 nm laser excitation at a power of 5–10 mW with 20 s acquisition times and 4 accumulations. For *operando* studies, the electrochemical cell/device is loaded in a glovebox environment into a cryostat (Cryo Industries of America, Inc.) possessing an optical window. The cryostat is then sealed, transferred out of the glovebox and the measurement chamber evacuated to ultra-high vacuum for spectroelectrochemical measurements. The potential bias is swept at a rate of 2 mV/s to the desired potentials (0, -1 , -2 , -3 , -4 , and -5 V) and held at these potentials for acquisition of Raman and Photoluminescence spectra (~ 10 minutes) before resuming the sweep. After intercalation, the heterostructure is deintercalated by sweeping the potential to $+3\text{ V}$ and then back to 0 V. Removal of the electrolyte is accomplished by briefly washing in deionized water followed by isopropanol. Additional spectra are subsequently acquired in this state. The deintercalated heterostructure is then annealed at 300 °C for 1 h in ultra-high vacuum.

In the pristine heterostructure, the trigonal prismatic coordination in $H\text{-MoS}_2$ results in only in-plane E_{12g} and out-of-plane A_{1g} modes at about 383 cm^{-1} and 408 cm^{-1} . After a full cycle of intercalation and deintercalation, the E_{12g} and A_{1g} peaks are diminished and new peaks are observed at 154, 184, and 226 cm^{-1} . These low-wavenumber peaks grow in intensity with increasing number of MoS_2 layers—confirming their association with the dichalcogenide—and are still present, albeit slightly diminished, after annealing for 1 h at 300 °C. In contrast the Raman peaks for the E_{12g} and A_{1g} modes recover spectral intensity after annealing. The 154 and 226 cm^{-1} peaks are attributed to the J_1 and J_2 modes of $T'\text{-MoS}_2$ ^{24,25} and the 184 cm^{-1} feature is assigned to the J_1 mode of $T\text{-MoS}_2$.²⁶ The corresponding Raman spectrum peak of the J_2 mode for $T\text{-MoS}_2$ is expected²⁶ at $\sim 203\text{ cm}^{-1}$ and therefore explains the low wavenumber tail of the T' J_2 peak observed in Figure 2c. We do not observe the emergence of any Raman signatures for lithium polysulfides (746 cm^{-1})¹¹ during the entire intercalation–deintercalation processes, suggesting the overall

chemical integrity of MoS₂ remained intact upon lithiation, with a mixed phase of metastable *T*- and *T'*-MoS₂ persisting upon deintercalation, and partial recovery of *H*-MoS₂ after annealing.

Raman and PL spatial mapping is carried out *ex situ* (after removal of electrolyte) using 1.0 μm step sizes, 2-second acquisition times and 2 accumulations at each pixel/step point.

Low-temperature charge transport and magnetoresistance analysis

Shubnikov-de Haas carrier densities. Shubnikov-de Haas (SdH) oscillations in $R_{xx}(B)$ arise due to the formation of Landau levels at high magnetic fields.²⁷ Plotting $R_{xx}(B)$ as a function of B^{-1} confirms that these oscillations are periodic in B^{-1} with a frequency B_F . The associated carrier density of the 2DEG, n_{sdH} , can then be determined from the relation $n_{sdH} = \left(\frac{g \cdot e \cdot B_F}{h}\right)$ where g is the Landau level degeneracy, e is the elementary charge and h is Planck's constant. For these electron-doped graphene or MoX₂ layers, it is reasonable to assume $g = 4$. Spin-valley locking in the valence band of *H*-MoX₂ layers gives rise to degeneracies $g = 2$, whereas the conduction band-edges are almost spin degenerate leading to degeneracies closer to 4 for electron-doped *H*-MoS₂.¹⁸ Theoretical studies to-date do not reveal spin split conduction bands in *T*- or *T'*-phases of MoS₂.^{33,34} Regardless, the backgate voltage (V_g) dependence of Hall and SdH carrier densities provides additional validation for our assignment of the origin of SdH oscillations in the intercalated heterostructures. We find that in the case of a Structure **I** stack consisting of a single graphene monolayer encapsulated by hBN and biased up to $E = -5.5$ V for intercalation, n_{sdH} and n_H equal $\sim 2.6 \times 10^{13}$ cm⁻² at $V_g = 0$ V, change in concert, and are effectively indistinguishable from each other for V_g between -100 V and $+100$ V (Extended Data Fig. 7). This reveals SdH and Hall measurements dominated by a single band as expected. In the case of an hBN-encapsulated MoS₂-graphene heterostructure (Structure **II**) studied here, the graphene monolayer channel is positioned in closer proximity to the back gate, underneath the MoS₂ channel. The Landau fan diagram (Fig. 3c), where R_{xx} is plotted as a function of both V_g and B reveals that the SdH quantum oscillations are strongly dependent on V_g , pointing to the graphene as the origin of the magneto-oscillations. Were it the case that the MoS₂ layer served as the origin of the SdH oscillations, the SdH channel would be electrostatically screened by graphene and the associated density would therefore be independent of V_g . We find that n_{sdH} changes with V_g in a manner consistent with the capacitance of the SiO₂/Si backgate (Fig. 3d). Indeed, we estimate the backgate capacitance, $C = 1.2 \times 10^{-8}$ F cm⁻² using $\Delta n_H = C \cdot V_g / e$, whose value is in a good agreement with the thickness of SiO₂ and hBN layers serving as the gate dielectric. Considering that n_H is the total density of the heterostructure that incorporates n_{sdH} , we deduce that the density in only one layer (corresponding to n_{sdH}) is dependent on V_g . This result reveals that the layer in closest proximity to the backgate (graphene) is responsible for SdH oscillations (lower density), and therefore allows us to determine the degree of charge transfer to the individual MoX₂ and graphene layers.

Effective mass determination, quantum scattering and mobilities. The effective mass, m^* , of the band giving rise to SdH oscillations is determined from the temperature dependence of the SdH amplitude, ΔR_{xx} (Manuscript Fig. 4b), by fitting these data to the Lifshitz–Kosevich theory,²⁸

$$\Delta R_{xx}(B, T) \propto \frac{\frac{\alpha T}{\Delta E_N(B)}}{\sinh\left(\frac{\alpha T}{\Delta E_N(B)}\right)} e^{\left(\frac{-\alpha T_D}{\Delta E_N(B)}\right)}$$

where B is the magnetic field position of the N th minimum in R_{xx} , $\Delta E_N(B) = \hbar e B / 2\pi m^*$ is the energy gap between the N th and $(N+1)$ th Landau levels (m^* is the effective mass, e is the elementary charge, and \hbar is the Planck constant), $T_D = \frac{\hbar}{4\pi^2 \tau k_B}$ is the Dingle temperature (k_B is Boltzmann's constant, τ_q is the quantum lifetime of carriers), and $\alpha = 2\pi^2 k_B$ is the momentum space area including spin degeneracy. In our experiment, ΔE_N and T_D are the only two fitting parameters. The pre-exponential in this expression is the only temperature dependent portion and permits the straightforward determination of m^* and τ_q . In the case of intercalated Structure **II** (hBN/MoS₂/G/hBN), we determine $m^* = 0.11 m_0$, and a Dingle temperature T_D of 36.2 K, which indicates $\tau_q = 33.6$ fs and a mean free path, $l = v_f \cdot \tau_q$ (where v_f is the Fermi velocity that is taken as 10^6 m s⁻¹ for graphene) of ~ 34 nm. We also determine the quantum mobility, $\mu_q = \frac{e \tau_q}{m^*} = 558$ cm² V⁻¹ s⁻¹ as compared to a Hall mobility μ_{Hall} of 270 cm² V⁻¹ s⁻¹. These values are compared to the parameters obtained for intercalated Structure **I** (hBN/graphene/hBN) in Extended Data Table 1.

(Scanning) transmission electron microscopy, (S)TEM. VdW heterostructures were fabricated as described above and finally transferred onto a holey amorphous silicon nitride membrane. Upon sweeping the potential, E , to the desired phase in the R_{xx} vs. E plot, the potential was immediately returned to 0 V after which the electrolyte was removed by washing in distilled water followed by isopropanol. The delithiated heterostructure was then analyzed by TEM. Aberration-corrected high-angle annular dark field (HAADF) and bright field (BF) scanning transmission electron microscopy (STEM) imaging and selected area electron diffraction (SAED) were conducted by Jeol ARM 200F equipped with cold field emission gun. STEM was operated at 80 kV with the probe convergence angle of 23 mrad. The inner collection semi angle for HAADF STEM imaging was 68 mrad. BF and dark field TEM imaging and SAED were performed on a Tecnai F20 operated at 120 kV. SAED data were acquired using a 300 nm aperture. Although STEM imaging is based on projected atomic structures, we still obtain atomic resolution images of monolayer MoS₂ from the heterostructures by exploiting Z (atomic number)-contrast in HAADF-STEM imaging and by using few-layer hBN crystals. All STEM images shown in Figures 5b and 5c represent the raw, unfiltered data. For the BF STEM image in Extended Data Fig. 11d, a Wiener filter³⁵ was applied to

remove noise. Fast Fourier transforms (FFT) of atomic resolution images in specified regions (Figure 5c), as well as the inverse FFT analysis (Extended Data Fig. 11) uncovers local crystallinity with domain sizes on the order of 5–10 nm.

Density Functional Theory (DFT) computations. DFT computations were performed using the projector augmented wave (PAW) method³⁶ as implemented in the VASP code.^{37–40} Van der Waals interactions are included using the zero damping DFT-D3 method of Grimme.⁴¹ The heterobilayer graphene/MoS₂ system is modeled with a super-cell consisting of a layer of 5×5 unit cells of fully relaxed graphene, a layer of 4×4 unit cells of MoS₂ uniformly compressed by 2.5% (in order to match the graphene lattice spacing), and over 17 Å of vacuum space between successive layers in the direction perpendicular to the layer plane. There are 98 total atoms in the bilayer supercell. All calculations were performed with an energy cutoff of 400 eV. A Γ -centered k-point mesh of 5×5×1 was used for structural relaxations until all forces were smaller in magnitude than 0.01 eV (for 0 and 1 intercalated Li ions) or 0.05 eV (for 2 or more Li ions). The k-point mesh was increased to 11×11×1 for electronic DOS and band structure computations. When relaxing the ions within the supercell, one Mo atom was held fixed as a reference point, and the C atom directly above it was held fixed in the plane of the graphene layer to preserve the registration of the two layers, but was free to relax in the vertical direction. All other atoms were unconstrained. We determine the energetic stability of different intercalation states in various vdW heterostructures by calculating the binding (intercalation) energy per Li atom, E_l (Figure 5d):²⁹

$$E_l = \frac{1}{n} [E(M, nLi) - E(M) - nE(Li)]$$

where:

n is the number of Li atoms intercalated

$E(M)$ is the energy of the empty structure M (i.e. 0 Li added),

$E(M, nLi)$ is the energy of the structure M with n number of Li atoms intercalated,

$E(Li)$ is the energy of a Li atom in bulk Li.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Extended Data Figure 1. Additional electrochemical and Hall data of structure II graphene–MoSe₂ stack. **a**, Forward (solid lines) and reverse (dashed lines) sweeps of four-probe resistance (red), Hall carrier density (blue), and Hall mobility (purple) as a function of potential at the heterostructure (vs. the counter

electrode/electrolyte gate—i.e. in a two-electrode electrochemical configuration) in a LiTFSI/PEO electrolyte at 325 K in the presence of a magnetic field, $B = 0.5$ T. Inset: optical micrograph of heterostructure stack working electrode. **b**, Identical experiment as in **a** with the Resistance (red) and Hall carrier density (blue) plotted as a function of the potential measured relative to a Pt pseudoreference electrode. **c**, Conventional cyclic voltammetric electrochemical current response (gray) overlaid with the resistance (red) over the course of the sweep showing peaks that are difficult to directly assign to any specific reaction, likely incorporating side reactions at the Pt– and Au–electrolyte interfaces. **d**, Hall resistance, R_{xy} , as a function of field at 325 K after intercalation ($E = -4.5$ V).

Extended Data Figure 2. Additional Raman & photoluminescence spectroscopy data. **a**, Raman spectra of an hBN/graphene/MoS₂ Structure II device (identical device of Figure 2b in main text) over the course of electrochemical intercalation, showing the disappearance of graphene and MoS₂ spectral features after full intercalation at -5.0 V, consistent with Pauli blocking in addition to the $2H \rightarrow 1T'$ phase transition of MoS₂. Deintercalation returns graphene peaks, and annealing at 300 °C for 1 h restores the $2H$ –MoS₂ peaks. Each spectrum is offset for clarity. **b–g**, Schematic diagram (**b**), photoluminescence spectra (**c–e**), photoluminescence map (**f**), and Raman map over 350–450 cm⁻¹ range (**g**) of an hBN-encapsulated multi-structure device (identical device in Figures 2d–g in main text) consisting of a graphene monolayer straddling a monolayer MoS₂ crystal at one end and a bilayer MoS₂ crystal at the other. Data were acquired on the pristine stack before intercalation (**c**), after deintercalation followed by removal of electrolyte (**d**), and after subsequent annealing at 300 °C for 1 h (**e–g**). The sharp peak at almost 2 eV is the graphene 2D peak. Photoluminescence spatial maps in the pristine state and after deintercalation are presented in Figure 2e and 2f of the main text and the map of the spatial intensity of the J₂ Raman peak of the T' phase (~ 226 cm⁻¹) after annealing is shown in Fig. 2g of the main text.

Extended Data Figure 3. Additional electrochemical and Hall data of structure II graphene–MoS₂ stack. **a,b**, Resistance (red) and Hall carrier density (blue) as a function of potential in a two—potential versus counter—(**a**) and three—potential versus Pt pseudo reference (**b**)—electrode electrochemical configuration in a LiTFSI/PEO electrolyte at 325 K in the presence of a magnetic field, B , of 0.5 T. Inset: optical micrograph of heterostructure stack “working electrode”. **c**, Conventional cyclic voltammetric electrochemical current response (gray) overlaid with the resistance (red) over the course of the sweep. **d**, Temperature dependence of resistance (red) and Hall mobility (purple) between 200 K and 1.8 K. **e**, Hall resistance, R_{xy} , as a function of magnetic field after cooling to 200 K immediately following the termination of a sweep to -4.8 V. **f**, Hall resistance, R_{xy} , as a function of magnetic field at 1.8 K.

Extended Data Figure 4. Electrochemical and Hall data of structure III graphene–MoS₂ stack. **a**, Resistance (red) and Hall carrier density (blue) as a function of potential in a two—potential versus counter—**(a)** and three—potential versus Pt pseudo reference **(b)**—electrode electrochemical configuration in a LiTFSI/PEO electrolyte at 325 K in the presence of a magnetic field, B , of 0.5 T. Inset: optical micrograph of heterostructure stack “working electrode”. **c**, Conventional cyclic voltammetric electrochemical current response (gray) overlaid with the resistance (red) over the course of the sweep. **d**, Temperature dependence of resistance (red) and Hall mobility (purple) between 200 K and 1.8 K **e**, Hall resistance, R_{xy} , as a function of magnetic field at 1.8 K. This device shows a carrier density of 1.4×10^{14} cm⁻². Maximum carrier density observed for Structure III devices is 1.9×10^{14} cm⁻².

Extended Data Figure 5. Dependence of carrier densities of intercalated heterostructures on backgate voltage. **a**, Hall resistance, R_{xy} , and **b**, magnetoresistance, R_{xx} (individually offset for clarity), as a function of magnetic field strength, B , in the case of a Structure I device with varying backgate voltage, V_g . **c**, Dependence of change in Hall (filled circles) and SdH (open circles) carrier densities on V_g . Solid lines represent fits that assume a Si backgate capacitance of 1.2×10^{-8} F cm⁻².

Extended Data Figure 6. Additional data on multi-structure-device #1. **a**, Optical micrograph (false color) of a device consisting of multiple hBN-encapsulated graphene/MoS₂ heterostructure types (depicted in the associated illustration) arrayed along a single graphene monolayer (identical device as in Fig. 4b of main text). **b,c**, Zonal resistances as a function of potential in a two-electrode (potential versus counter) **(b)** and three-electrode (potential versus Pt pseudo reference **(c)**) electrochemical configuration. Intercalation (indicated by the arrows) initiates at ~ 0.6 V more positive potentials at zones B and D (structures **III** and **II**) than at A (structure **I**). **d**, Conventional cyclic voltammetric electrochemical current response (gray) of the entire device overlaid with the resistances of the various device regions over the course of the sweep. CV cannot distinguish between the intercalation of G/MoS₂ and G/hBN regions in this device. **e**, Hall resistance, R_{xy} , as a function of magnetic field at 1.8 K for the different regions of the device after electrochemical polarization up to -5.0 V, displaying the resulting Hall carrier densities obtained. **f–h**, magnetoresistance data at 1.8 K for zones A **(f)**, C **(g)**, and D **(h)**, showing associated SdH carrier densities, n_{SdH} extracted from the periodicities of oscillations in B^{-1} . **i**, Temperature dependence of resistance for the various device regions between 200 and 1.8 K during warming.

Extended Data Figure 7. Additional data on multi-structure-device #2. **a**, Optical micrograph (false color) of a device consisting of multiple hBN-encapsulated graphene–MoS₂ heterostructure types (depicted in the associated illustration) arrayed along a single graphene monolayer. **b,c**, Zonal resistances as a

function of potential in a two-electrode (potential versus counter (**b**)) and three-electrode (potential versus Pt pseudo reference (**c**)) electrochemical configuration. Intercalation (indicated by the arrows) initiates at ~ 0.7 V more positive potentials at zones B (Structure **II**) and C (Structure **V**) than at zone A (Structure **I**). **d**, Conventional cyclic voltammetric electrochemical current response (gray) of the entire device overlaid with the resistances of the various device regions over the course of the sweep. CV cannot distinguish between the intercalation of G/MoS₂ and G/hBN regions in this device. **e**, Hall resistance, R_{xy} , as a function of magnetic field at 1.8 K for the different regions of the device after electrochemical polarization up to -5.5 V, displaying the resulting Hall carrier densities obtained. **f–h**, Magnetoresistance data at 1.8 K for regions A (**f**), B (**g**), and C (**h**) that reveal associated SdH carrier densities, n_{SdH} from the periodicities of oscillations.

Extended Data Figure 8. Electrochemical gating of non-encapsulated few-layer (4–5 layers) MoX₂.

a,b, Four terminal resistance, R_{xx} , of a few layer MoSe₂ crystal on a linear (**a**) and logarithmic (**b**) scale, during electrochemical gating in an electrolyte comprised of LiTFSI/DEME-TFSI. Intercalation takes place between -2.5 and -3 V (red arrow) and the device loses electrical contact (demonstrated by the disruption in the phase of the lock-in amplifier (inset)). **c**, Four-terminal resistance, R_{xx} , of a few-layer MoS₂ device during electrochemical gating in a LiTFSI/PEO electrolyte. As in **a**, the resistance of this device begins to increase at ~ -3.5 V and is completely insulating beyond -4.25 V, indicative of conversion to lithium polysulfide.

Extended Data Figure 9. Onset potentials and charge capacities of various heterostructures. a,

Intercalation onset potentials (vs. Pt pseudoreference electrode) for different vdW heterostructure types as well as few-layer MoX₂. Error bars represent standard deviations (from left to right, $n = 3, 5, 4, 2, 1, 3$) of measurements from multiple devices or distinct contact pairs. **b**, Carrier densities attained after intercalation of various hBN/graphene/MoCh₂ heterostructures. Circles, squares and triangles represent densities reached after intercalation up to -5 , -5.5 , and -6 V, respectively. Filled symbols designate densities determined from Hall data (revealing approximate MoX₂ carrier densities, except in the case of Structure **I**), whereas hollow symbols represent densities extracted from SdH oscillations (revealing graphene carrier densities). **c**, Average capacity values from devices in **b**, expressed in units of C/g (gravimetric capacity) and (C/cm³) volumetric capacity

Extended Data Figure 10. Transmission electron microscopy data of incompletely intercalated Structure II devices. a,

Resistance, R_{xx} , as a function of applied potential, E , of an hBN/MoS₂/G vdW heterostructure fabricated onto a 50 nm holey amorphous silicon nitride membrane. The electrochemical

reaction is suspended as the upturn in R_{xx} is commencing by immediately sweeping the potential back to 0 V. **b**, $g_{\text{MoS}_2} = 11\bar{2}0$ dark-field (DF) TEM image of the device after removal of the electrolyte. **c**, Selected area electron diffraction (SAED) patterns acquired from the regions designated 1, 2, and 3 in **b**. SAED data reveal a pristine MoS₂ structure in region 1, but splitting of the Bragg spots (insets) at the edges of the heterostructure (regions 2 and 3) indicative of the formation of two or more domains. **d**, Resistance, R_{xx} , as a function of applied potential, E , of an hBN/MoS₂/G/hBN vdW heterostructure. The electrochemical reaction is suspended as R_{xx} is approaching a maximum by immediately sweeping the potential back to 0 V. **e**, $g_{\text{MoS}_2} = 11\bar{2}0$ DF TEM image of the device after removal of the electrolyte. **f**, SAED patterns of the regions designated 1, 2, 3, and 4 in **e**. SAED data reveal a pristine MoS₂ structure in region 1, but strong splitting of the Bragg spots (insets) towards the edge of the heterostructure (region 3) indicative of the formation of multiple domains. In region 4, the diffuse scattering from the underlying amorphous silicon nitride membrane obscures any diffraction features from the MoS₂, which in that region must be significantly disordered with any domain sizes \ll 300 nm (aperture size).

Extended Data Figure 11. (Scanning) transmission electron microscopy, (S)TEM, data of fully intercalated Structure II device. **a**, Resistance, R_{xx} , as a function of applied potential, E , of an hBN/MoS₂/G/hBN vdW heterostructure fabricated onto a 50 nm holey silicon nitride membrane. The potential is reversed to 0 V after R_{xx} returns to a minimum (full intercalation) at ~ -5 V. **b**, Bright-field (BF) TEM image of the device after removal of the electrolyte. **c**, Selected area electron diffraction (SAED) patterns of the regions designated 1 and 2 in **b** in both the on-axis (beam perpendicular to the plane of the heterostructure) and off-axis (sample tilted) conditions. The off-axis condition permits the minimization of double diffraction phenomena associated primarily with the top and bottom hBN flakes. SAED data at the suspended (no amorphous silicon nitride) window reveal two rings associated with the MoS₂ layer, indicating significant disorder in the x–y plane with a domain size \ll 300 nm (aperture size). SAED data acquired over the membrane (region 2) cannot resolve these MoS₂ diffraction features owing to the diffuse scattering from the amorphous silicon nitride membrane in that region. **d**, Aberration-corrected BF STEM image of the heterostructure (left: raw data; right: filtered data), which is dominated by the hBN in the structure. The bright periodic patches arise due to the moiré pattern of the two hBN crystals. **e**, Aberration-corrected high angle annular dark field (HAADF) STEM image of the device showing the nanostructure of the MoS₂ layer after one cycle. Filtered inverse Fourier transform data resolve x–y rotational disorder in the MoS₂ atomic chains (top row white dashed lines), revealing the approximate domain sizes as 5–10 nm (bottom row).

Extended Data Figure 12. Density functional theory (DFT)-computed electronic structures of G/MoS₂ heterobilayers over the course of Li intercalation. Relaxed geometries (left), band structures (middle), and density of states plots (right) for G/MoS₂ structures as Li atoms are incrementally added (top to bottom), and the phase of MoS₂ is changed from *H* to *T'*. The reason for the large carrier density in MoS₂ versus that in graphene upon intercalation is evident from the relative DOS associated with MoS₂ compared to that of G.

Extended Data Table 1. Charge transport parameters. Comparison of transport parameters for two classes of intercalated heterostructures. The relative similarity in quantum scattering time and mean free compound support the contention that SdH oscillations observed for intercalated Structure II arise from the graphene sublayer.

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