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Originally published:

November 2018

Nature 564(2018), 234-239

DOI: <https://doi.org/10.1038/s41586-018-0754-2>

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1 **Reversible superdense ordering of lithium between two graphene**
2 **sheets**

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13 **Many carbon allotropes can act as host materials for reversible lithium uptake,^{1,2} laying**
14 **the grounds for existing and future electrochemical energy storage. Insights into exactly**
15 **how lithium is arranged within those are, however, challenging to obtain *in operando*.**
16 **Using *in situ* transmission electron microscopy (TEM)³⁻⁵ to probe light elements (especially**
17 **Li)^{6,7} is severely hampered by their low scattering cross section for impinging electrons**
18 **and their susceptibility to knock-on damage⁸. Here, we study the reversible Li intercalation**
19 **of bilayer graphene by *in situ* spherical and chromatic aberration-corrected low-voltage**
20 **TEM⁹, supported by electron energy loss spectroscopy (EELS) and density functional**
21 **theory (DFT) calculations. Upon their remote insertion from an electrochemical gate, we**
22 **observe Li atoms to assume multi-layered close-packed order between the two carbon**

23 sheets. The associated Li storage capacity by far exceeds the one of LiC_6 —the densest
24 configuration known under normal conditions for bulk graphitic carbon¹⁰. Our findings
25 thus point to the possible existence of distinct storage arrangements of ions in 2D layered
26 materials as compared to their bulk parent compounds.

27 Figure 1a shows a schematic of our devices, all of which are supported by Si_3N_4 -covered Si
28 substrates. The Si_3N_4 forms a $40 \times 40 \mu\text{m}^2$ membrane at the centre of the Si-chip. The bilayer
29 graphene flake is exfoliated from natural graphite and etched into a Hall bar shape. One end of
30 the flake is connected to a counter electrode *via* a Li-ion conducting solid polymer electrolyte.
31 This setup allows for the controlled electrochemical reduction/oxidation of bilayer graphene
32 according to¹



33 Similar to Refs. [11, 12], we trigger lithiation (delithiation) by applying a positive voltage $U_G =$
34 5 V ($U_G = 0$ V) to the counter electrode with respect to bilayer graphene. A grounded current
35 lead to the latter serves as a source/sink for electrons required to facilitate the reversible
36 intercalation of Li-ions at the electrolyte-covered end of bilayer graphene. Intercalated Li
37 exhibits rapid lateral diffusion that tends to establish and maintain an even distribution of Li
38 throughout the bilayer.¹³ Hence, one may study its ordering in a region well separated from the
39 electrolyte by *in situ* TEM (Figs. 1a–b), thereby also preventing exposure of the electrolyte to
40 the electron beam. In the region probed by TEM, bilayer graphene is suspended over a hole in
41 the Si_3N_4 membrane. Metallic contacts to the bilayer allow monitoring its resistivity $\rho_{xx} =$
42 U_{xx}/I in the electrolyte-uncovered region (Fig. 1a). During subsequent lithiation/delithiation
43 cycles, we typically observe reversible changes in ρ_{xx} (Fig. 1c). These relate to changes in the
44 local Li concentration *via* finite electronic charge transfer.^{12,13} The drop in ρ_{xx} during lithiation
45 reflects an increase in electron density, characteristic for ambipolar diffusion of electron-ion

47 pairs into the probed area.¹³ During delithiation, Li-ions and electrons leave the bilayer, thereby
48 restoring its initial resistivity value. The exact time evolution of ρ_{xx} depends on the kinetics of
49 several (uncontrolled) processes, related to e.g. ionic transport within the electrolyte and across
50 the solid electrolyte interphase. Yet, Fig. 1c is a qualitative characteristic of reversible Li
51 intercalation in bilayer graphene.¹³ In the following, we present *in situ* TEM data obtained in the
52 *SALVE* (Sub-Ångström Low-Voltage Electron microscopy) microscope⁹. We work at an
53 electron acceleration voltage of 80 kV, just below the threshold for knock-on damage of C atoms
54 in graphene.¹⁴ Despite these conditions, the instrument still delivers sub-Ångström resolution in
55 the images. Further details can be found in Methods (also Extended Data Figs. 1–2).

56

57 Figure 2a shows a TEM image of pristine bilayer graphene. The inset depicts its Fourier
58 transform (FT) and confirms the known value of the in-plane lattice constant $a_C = 2.46 \text{ \AA}$. The
59 image marks the beginning of a series acquired during lithiation of a bilayer graphene device
60 (Figs. 2a–c and Supplementary Video 1), but it is representative of the sample state prior to
61 application of the bias voltage $U_G = 5 \text{ V}$. In Fig. 2b, acquired after 170 s, a second crystal lattice
62 has appeared in the lower half of the probed area. White dashed lines demarcate its boundary on
63 the left and right of the image. The image in Fig. 2c is recorded at $t = 288 \text{ s}$. The additional
64 crystal structure now extends throughout almost the whole field of view. Fig. 2d is the Fourier
65 transform of Fig. 2b. Compared with the Fourier transform of pristine bilayer graphene (inset to
66 Fig. 2a), we identify three sets of additional signals, highlighted in red, green, and blue. These
67 attest to hexagonal crystalline order (as for graphene), but with an in-plane lattice constant of
68 3.1 \AA . In Fig. 2e, their spatial distribution is mapped. This allows discerning three grains none
69 of which are aligned to the encapsulating graphene lattice. In Fig. 2f the same Fourier transform
70 is shown but with a von Hann filter applied to minimize the streaks. The highlighted signals
71 stem from both bilayer graphene (cyan) and the additional crystalline phase (green) as well as

72 Moiré artefacts (magenta) and their origin (bold arrows). Fig. 2g is a Fourier-filtered (Methods
73 and Extended Data Fig. 3) version of panel b, where the graphene lattice, as well as the Moiré
74 effects, have been removed (see panels h and i for a magnification before and after filtering).
75 These images offer a direct view on the encapsulated crystal. The observed contrast in the images
76 also suggests regions of different thickness even within a single grain. This is worked out in
77 detail in Methods and Extended Data Fig. 4.

78

79 To narrow down the chemical composition of the additional crystal structure, EELS data has
80 been acquired on bilayer graphene before and during lithiation (Fig. 2j). Before lithiation, we
81 exclusively observe the C K-edge at 284 eV. During lithiation the Li K-edge at 55 eV on regions
82 characterized by a Fourier transform as in Fig. 2d is additionally detected. Based on the absence
83 of other signals in the explored energy range of 0–800 eV, Si (L_{2,3}-edge starting at 99 eV), S
84 (L_{2,3}-edge starting at 165 eV), N (K-edge starting at 400 eV), O (K-edge starting at 532 eV and
85 F (K-edge starting at 685 eV) are discarded as significant constituents of the new crystalline
86 phase. Likewise, Ti and Pt (electrode material) can be ruled out based on the observed light
87 atomic contrast in Fig. 2 for the case of Pt and on the absence of the distinct Ti L_{2,3}-edge at 456
88 eV in the EELS data. Although it is inherently impossible to exclude H or C, the crystalline
89 phase formed during lithiation likely consists of pure Li. The low onset in energy of the Li K-
90 edge supports this assertion.^{15,16} Also, a Li plasmon mode appears near 9 eV^{17,18} (Extended Data
91 Fig. 5a). Though the shape of the Li-K edge resembles the one of Li₂O/LiOH,^{15,16} stoichiometric
92 Li₂O/LiOH can be disqualified, since we would then expect both a more pronounced O-K edge
93 as well as an imaging contrast comparable in strength to the encapsulating graphene.¹⁹ Good
94 agreement with experiment is attained when calculating the Li-K edge shape of graphene-
95 encapsulated Li multilayers (Methods and Extended Data Fig. 5b). We do not rule out the
96 presence of trace oxygen, also suggested by the occasional observation of a weak shoulder near

97 30 eV (Extended Data Fig. 5a), previously attributed to oxidized lithium.^{17,18} Yet, the extracted
98 in-plane lattice constant of 3.1 Å matches close-packed Li.²⁰ This coincidence is surprising,
99 since normally very low temperatures and/or extreme pressures are required for Li to assume
100 this ordering.²¹

101

102 To test whether indeed the formation of a dense, multi-layered Li crystal in bilayer graphene is
103 conceivable, first-principles calculations were carried out (Methods). The chemical potential of
104 Li atoms in bulk close-packed phases was evaluated. All energies below are given with respect
105 to the hexagonal close-packed (hcp) phase, which had the lowest energy in the calculations.
106 Several layers of Li atoms inside bilayer graphene are considered (Fig. 3 and Extended Data
107 Figs. 6–8). Since the *in situ* TEM studies do not reveal evidence for a change in registry of the
108 graphene sheets (Extended Data Fig. 9), AB stacking is assumed as in the pristine device. Our
109 main conclusions, however, hold irrespective of the stacking order. The relaxation of atomic
110 coordinates of a single layer of Li atoms yields an energetically favoured C₆LiC₆ configuration,
111 with Li arranged in a commensurate ($\sqrt{3} \times \sqrt{3}$)R30° superstructure with a lattice constant of a_{LiC_6}
112 = 4.26 Å (Figs. 3a–b). Except for the graphene registry, this finding is similar to the bulk LiC₆
113 phase¹⁰ and the AA-stacked C₆LiC₆ phase²². The situation changes for a larger number of Li
114 layers. Finite clusters and infinite (periodic) hcp structures with different orientation with respect
115 to the graphene lattice were considered (Figs. 3c–f, Extended Data Figs. 7–8). The energies of
116 these systems are very close to that of the C₆LiC₆ configuration (higher by only 0.01–0.05 eV/
117 Li atom). The in-plane lattice constant a_{Li} of the Li hcp bilayer and trilayer (average distances,
118 as the positions of Li atoms are affected by nearby C atoms) is in the range of 3.05–3.15 Å,
119 matching the experimental value of 3.1 Å as well as the identical literature value.²⁰ These results
120 suggest that the formation of a multilayer close-packed Li phase between graphene sheets is
121 conceivable. Its precise stacking order may however differ from hcp as other configurations are

122 energetically similar (Extended Data Fig. 8d–e). These are hard to distinguish in these TEM
123 experiments, because we may only observe the projection along one crystal direction. Moreover,
124 some bulk diffraction selection rules do not hold in the given case of an atomically thin
125 specimen. TEM image simulations reveal comparable contrast and diffraction patterns for the
126 two extreme cases: cubic close-packed (ccp) and hexagonal close packed (Extended Data Fig.
127 2f–g).

128

129 By analysing the electronic structure and charge distribution, the charge transfer between Li and
130 graphene can be estimated. Fig. 3b,d and f display colour renditions of the charge probability
131 distribution as compared to isolated graphene and Li crystals consisting of a single, double or
132 triple layer. As can be seen from Fig. 3f in the triple layer case, charge transfer is significant
133 only for the outer Li layers directly neighbouring a graphene sheet. Inner Li layers retain their
134 metallic character as electronic charge is distributed between the Li^+ lattice sites. Extended Data
135 Fig. 8c depicts the average charge transfer per Li atom, which drops as the close-packed Li phase
136 gets thicker. Renormalizing by the number of atoms in the outermost Li layers only, we find a
137 constant charge transfer of approximately $0.33 \text{ e}^-/\text{outer Li atom}$, irrespective of how many
138 (metallic) Li layers (with nearly zero charge transfer) are packed in between. This is consistent
139 with the observation that the resistivity ρ_{xx} measured during lithiation tends to saturate rather
140 than to decrease progressively as more Li enters bilayer graphene (Fig. 1c). Note that although
141 for C_6LiC_6 (Figs. 3a–b) a higher value of $0.85 \text{ e}^-/\text{Li atom}$ for the charge transfer applies resulting
142 in an estimated density of transferred electrons of $2.7 \cdot 10^{14} \text{ cm}^{-2}$ per graphene sheet, the much
143 denser arrangement of Li atoms in the close-packed structure yields a higher electron density
144 per graphene sheet of $4 \cdot 10^{14} \text{ cm}^{-2}$ despite the smaller charge transfer value.

145

146 During lithiation, the close-packed Li phase grows laterally between the graphene sheets (Fig.
147 4a and Supplementary Video 1). In Fig. 4a, The graphene signals have been Fourier filtered in
148 order to reveal the Li crystal structure. Three grains of varying in-plane orientation have been
149 coloured for the sake of illustration. While the grain boundary between the central grain (green)
150 and the lower right grain (blue) is rather sharp and stable, the one with the left grain (red) appears
151 more fuzzy and mobile as their orientation nearly matches. Regions of different thickness can
152 be identified even within a single grain (Extended Data Fig. 4). The specimen is too thin to
153 reliably extract its exact thickness t from EELS (we typically obtain $t/\lambda < 0.1$, where λ is the
154 inelastic mean free path of our 80 keV electrons). One may nonetheless determine relative
155 variations (see Methods). When imaging an extremely thin slab of weakly scattering elements
156 in a microscope with sufficient resolving power, the imaging contrast does increase with
157 increasing specimen thickness. This is quantified in the Extended Data Figs. 4e–f, revealing that
158 thinner parts of the close-packed Li phase tend to be located closer to its perimeter. At the leading
159 edge, single atoms can be identified (Methods, Extended Data Fig. 1). From the image time
160 series, a lateral growth rate of the order of 1 Å/s can be extracted. During delithiation the close-
161 packed Li phase disassembles and gradually disappears (Fig. 4b). Eventually, the pure bilayer
162 graphene lattice remains behind. The degree of reversibility of this process is limited by the
163 number of defects in the graphene lattice and their irreversible formation during prolonged
164 imaging (electron irradiation). Given the combined slow image acquisition (on the order of 1 s)
165 and low sensitivity to light atoms, Li diffusing at speed in less ordered configuration remains
166 concealed to the TEM observer. Such processes are nonetheless present in parallel with the close
167 packing as well as beyond the boundaries of this phase and are likely responsible for the initial
168 abrupt change in resistivity ρ_{xx} during lithiation (Fig. 1c).

169

170 We note that the observed crystalline phase of Li proves stable between intact graphene planes
171 only. With the incident electron energy exceeding the threshold for displacement damage of Li
172 (\sim 20 keV), conditions are such that Li readily “boils” under the electron beam^{16,18}. The close-
173 packed phase is volatile when imaged near bilayer edges or in the presence of a high density of
174 defects in the graphene lattice. Constituents may escape from between graphene sheets *via* such
175 edges or defects upon electron-beam induced melting of the crystalline phase. Likewise, we find
176 material having escaped from within and agglomerated on the outer bilayer surfaces near such
177 defects to quickly evaporate under electron beam irradiation. The protective encapsulation by
178 two impermeable atomic sheets may thus be regarded a prerequisite to safe probing by TEM of
179 the crystal formation therein, akin to the situation in graphene liquid cells²³.

180

181 Close-packing of Li intercalated between graphene sheets, as demonstrated here, results in a
182 structure with Li-content in great excess of LiC₆. Although enhanced Li storage has been
183 proposed to occur on the outside of graphene planes^{24,25} previously, suggested atomistic
184 configurations were contradictory among the different works and could neither be addressed nor
185 verified by microscopic means. The same holds for the scarce reports claiming the formation of
186 nanocrystallites of close-packed Li during the lithiation of different carbon allotropes.^{26,27} At
187 elevated temperatures, a similar configuration of Li, as we report here, may, as a matter of fact,
188 have been left unidentified in bulk graphite.²⁸ Since the energy cost for close-packing of Li in
189 the van der Waals gap of bilayer graphene as compared to forming C₆LiC₆ is very similar (Fig.
190 3), close-packing may be the answer of the system for having to accommodate a larger amount
191 of Li supplied within a short time. The activation energy for Li diffusion in bilayer graphene has
192 been calculated (Methods). It points toward facile diffusion of Li between graphene sheets, even
193 in the presence of a close-packed Li phase. Even though, a bilayer can be regarded as the
194 fundamental unit of bulk graphite, it may still feature considerably distinct properties and in

195 particular its layers may spread more easily to accommodate for dense intercalate ordering. It
196 should also be noted that Li-graphite intercalation compounds only occupy a small region in the
197 C-Li binary alloy phase diagram.²⁹ In the miscibility gap beyond LiC₆, alternative configurations
198 may be available for storing larger amounts of lithium in layered carbons.³⁰

199

- 200 1. Winter, M. & Besenhard, J. O. Lithiated carbons. In *Handbook of Battery Materials* Edn.
201 2 (Daniel, C. & Besenhard, J. O., eds.) 433–478 (Wiley-VCH, Weinheim, Germany,
202 2011).
- 203 2. Kaskhedikar, N. A. & Maier, J. Lithium storage in carbon nanostructures. *Adv. Mater.* **21**,
204 2664–2680 (2009).
- 205 3. Zheng, H., Meng, Y. S. & Zhu, Y. Frontiers of in situ electron microscopy. *MRS Bull.* **40**,
206 12–18 (2015).
- 207 4. Qian, D., Ma, C., More, K. L., Meng, Y. S. & Chi, M. Advanced analytical electron
208 microscopy for lithium-ion batteries. *NPG Asia Mater.* **7**, e193 (2015).
- 209 5. Liu, X. H. *et al.* In situ TEM experiments of electrochemical lithiation and delithiation of
210 individual nanostructures. *Adv. Energy Mater.* **2**, 722–741 (2012).
- 211 6. Shao-Horn, Y., Croguennec, L., Delmas, C., Nelson, E. C. & O’Keefe, M. A. Atomic
212 resolution of lithium ions in LiCoO₂. *Nat. Mater.* **2**, 464–467 (2003).
- 213 7. Oshima, Y. & Murakami, Y. (eds.) *Microscopy 66, Number 1, Special Issue: Challenges
214 for Lithium Detection* (Oxford University Press Tokyo, Japan, 2017).
- 215 8. Reimer, L. & Kohl, H. *Transmission Electron Microscopy* (Springer Series in Optical
216 Sciences, Springer, New York, 2008).

- 217 9. Linck, M. *et al.* Chromatic aberration correction for atomic resolution TEM imaging from
218 20 to 80 kV. *Phys. Rev. Lett.* **117**, 076101 (2016).
- 219 10. Enoki, T., Suzuki, M. & Endo, M. *Graphite intercalation compounds and applications*
220 (Oxford University Press, New York, 2003).
- 221 11. Yu, Y. *et al.* Gate-tunable phase transitions in thin flakes of 1T-TaS₂. *Nat. Nanotech.* **10**,
222 270–276 (2015).
- 223 12. Bediako, D. K. *et al.* Heterointerface effects in the electrointercalation of van der Waals
224 heterostructures. *Nature* **558**, 425–429 (2018).
- 225 13. Kühne, M. *et al.* Ultrafast lithium diffusion in bilayer graphene. *Nat. Nanotech.* **12**, 895–
226 900 (2017).
- 227 14. Meyer, J. C. *et al.* Accurate measurement of electron beam induced displacement cross
228 sections for single-layer graphene. *Phys. Rev. Lett.* **108**, 196102 (2012).
- 229 15. Mauchamp, V., Boucher, F., Ouvrard, G. & Moreau, P. Ab initio simulation of the
230 electron energy-loss near-edge structures at the Li K edge in Li, Li₂O, and LiMn₂O₄. *Phys.*
231 *Rev. B* **74**, 115106 (2006).
- 232 16. Wang, F. *et al.* Chemical distribution and bonding of lithium in intercalated graphite:
233 Identification with optimized electron energy loss spectroscopy. *ACS Nano* **5**, 1190–1197
234 (2011).
- 235 17. Liu, D.-R. & Williams, D. B. The electron-energy-loss spectrum of lithium metal. *Phil.
236 Mag. B* **53**, L123–L128 (1986).
- 237 18. Hightower, A., Ahn, C. C., Fultz, B. & Rez, P. Electron energy-loss spectrometry on
238 lithiated graphite. *Appl. Phys. Lett.* **77**, 238–240 (2000).

- 239 19. Liu, X. H. *et al.* In situ transmission electron microscopy of electrochemical lithiation,
240 delithiation and deformation of individual graphene nanoribbons. *Carbon* **50**, 3836–3844
241 (2012).
- 242 20. Wyckoff, R. W. G. *Crystal structures Vol. 1* Edn. 2 (John Wiley & Sons, 1963).
- 243 21. Ackland, G. J. *et al.* Quantum and isotope effects in lithium metal. *Science* **356**, 1254–
244 1259 (2017).
- 245 22. Sugawara, K., Kanetani, K., Sato, R. & Takahashi, T. Fabrication of Li-intercalated
246 bilayer graphene. *AIP Adv.* **1**, 022103 (2011).
- 247 23. Yuk, J. M. *et al.* High-resolution EM of colloidal nanocrystal growth using graphene
248 liquid cells. *Science* **336**, 61–64 (2012).
- 249 24. Sato, K., Noguchi, M., Demachi, A., Oki, N. & Endo M. A mechanism of lithium storage
250 in disordered carbons. *Science* **264**, 556–558 (1994).
- 251 25. Deschamps, M. & Yazami, R. Great reversible capacity of carbon lithium electrode in
252 solid polymer electrolyte. *J. Power Sources* **68**, 236–238 (1997).
- 253 26. Wang, Q. *et al.* Investigation of lithium storage in bamboo-like CNTs by HRTEM. *J.*
254 *Electrochem. Soc.* **150**, A1281–A1286 (2003).
- 255 27. Lee, B.-S. *et al.* Face-centered-cubic lithium crystals formed in mesopores of carbon
256 nanofiber electrodes. *ACS Nano* **7**, 5801–5807 (2013).
- 257 28. Kambe, N. *et al.* Intercalate ordering in first stage graphite-lithium. *Mater. Sci. Eng.* **40**,
258 1–4 (1979).
- 259 29. Okamoto, H. C-Li (Carbon-Lithium). In *Binary alloy phase diagrams Vol. 1* Edn. 2
260 (Massalski, T. B., Okamoto, H., Subramanian, P. R. & Kacprzak, L., eds.) 857 (ASM
261 International, 1990).

262 30. Lin, D. *et al.* Layered reduced graphene oxide with nanoscale interlayer gaps as a stable
263 host for lithium metal anodes. *Nat. Nanotech.* **11**, 626–632 (2016).

264

265 **Acknowledgments** We acknowledge financial support from the Baden-Württemberg Stiftung
266 gGmbH (project CT 5) as well as the European Union graphene flagship. We are grateful to
267 FEI/ThermoFisher Scientific for providing drawings and specifications of the NanoEx-i/v
268 holder. F. B., J. B. and U. K. acknowledge funding from the German Research Foundation
269 (DFG) and the Ministry of Science, Research and the Arts (MWK) of the federal state of Baden-
270 Württemberg, Germany, in the frame of the SALVE project. A. V. K. thanks the Academy of
271 Finland for the support under Project No. 286279 and the DFG under project KR 4866. The
272 theoretical study of Li diffusion (A. V. K) was supported by the Russian Science Foundation
273 (Project identifier: 17-72-20223). We thank K. v. Klitzing for discussions and support as well
274 as J. Popovic for useful comments on the manuscript. We acknowledge CSC Finland and
275 PRACE (HLRS, Stuttgart, Germany) for generous grants of CPU time.

276 **Author Contributions** J. H. S and U. K. composed the project. M. K. and S. F. fabricated the
277 samples and performed the electrochemical measurements. F. B. performed the TEM and EELS
278 experiments. M. G. and A. V. K. did the DFT calculations. J. B. helped with TEM and EELS
279 experiments and did TEM imaging simulations. U. K. supervised the TEM work. D. S.
280 contributed to the electrochemical design of the experiment. M. K. and J. H. S. wrote the
281 manuscript and all authors contributed to it.

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283 www.nature.com/reprints. The authors declare no competing financial interests. Readers are
284 welcome to comment on the online version of the paper. Correspondence and requests for
285 materials should be addressed to J. H. S. (j.smet@fkf.mpg.de) or U. K. (ute.kaiser@uni-ulm.de).

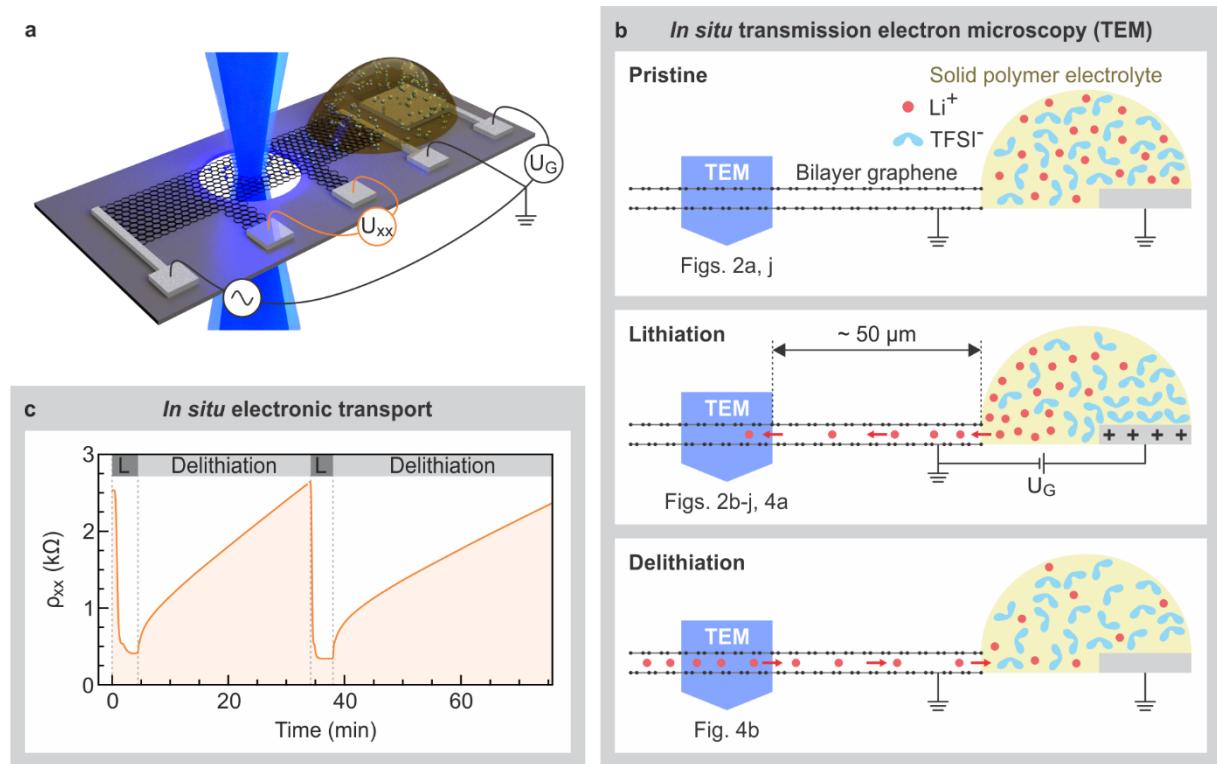
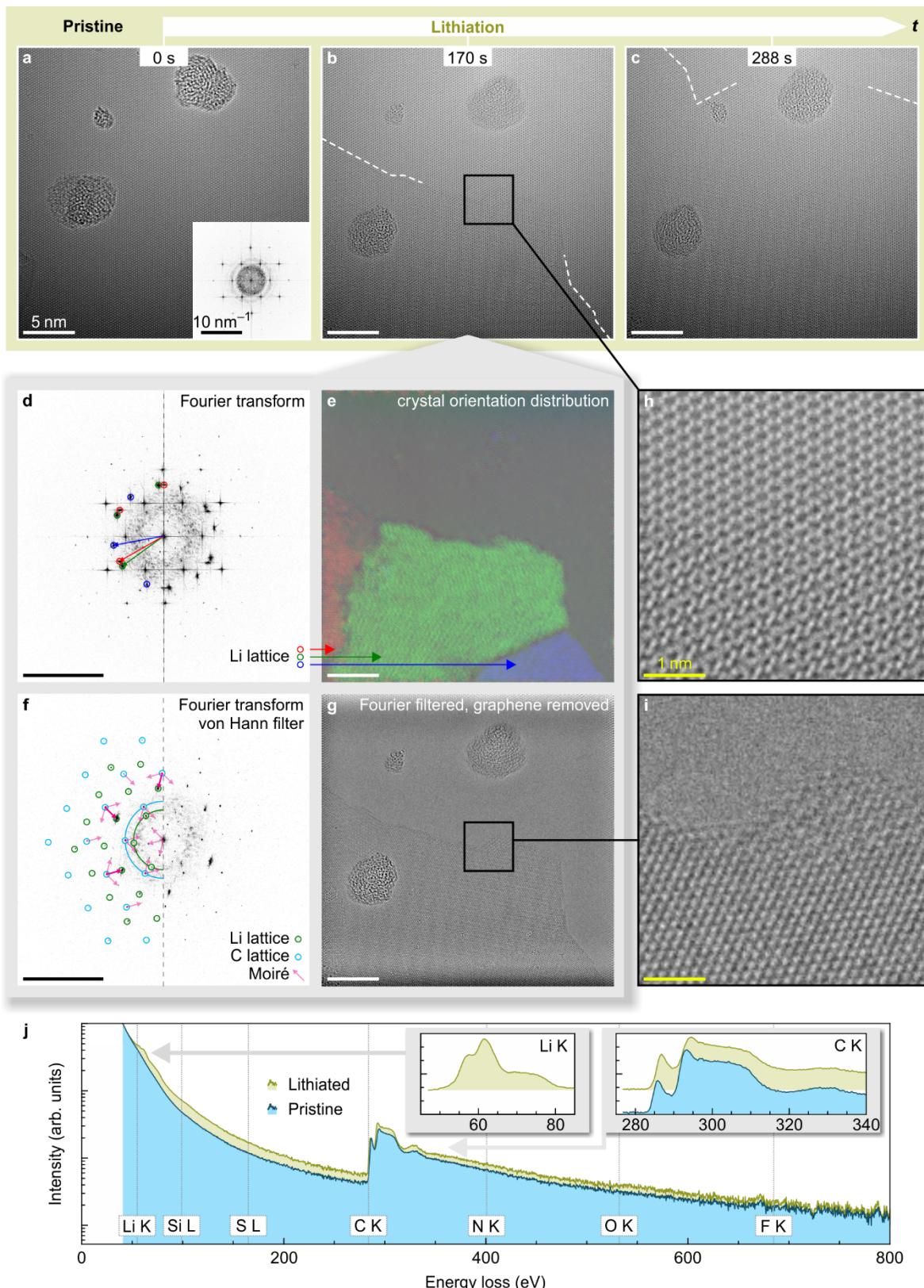


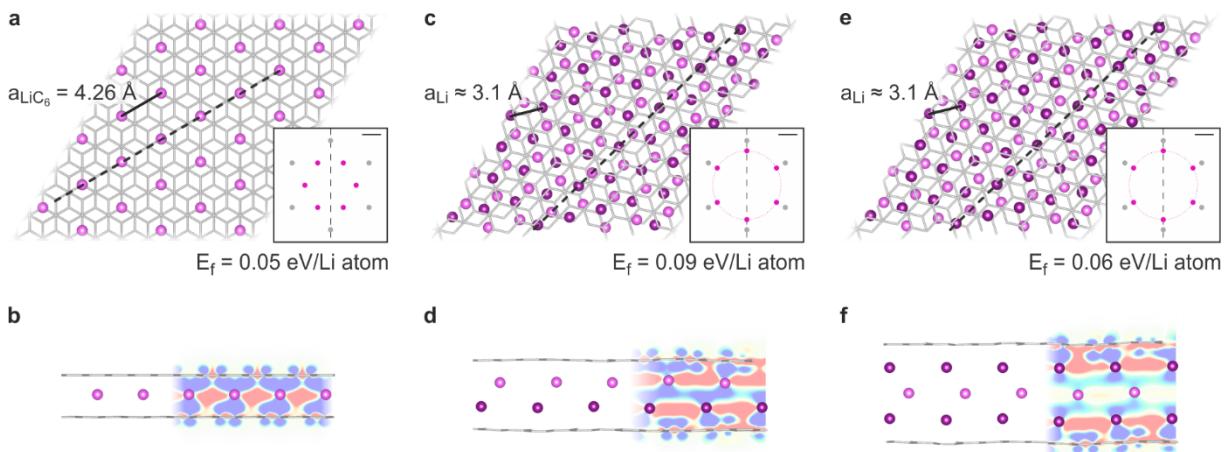
Figure 1 | Device layout and working principle. **a**, Schematic of the device (not to scale). Bilayer graphene (black) on a substrate (dark grey) is contacted by several metallic electrodes (bright grey). A Li-ion (white spheres) conducting electrolyte (yellow) connects the bilayer with a metallic counter electrode. On the order of $50 \mu\text{m}$ away from its electrolyte-covered end, bilayer graphene is partially suspended over a hole allowing for transmission electron microscopy (TEM) investigations (electron beam illustrated in blue). **b**, Schematic side view of the pristine device as well as during lithiation and delithiation. Reference to TEM data acquired at the respective state is given. **c**, Bilayer graphene's resistivity ρ_{xx} measured *in situ* during two lithiation (L)/delithiation cycles inside the SALVE microscope with the electron beam blanked. As schematically shown in **(a)**, a four point probe configuration serves to reveal reversible changes in the electrolyte-uncovered region of the device.



298

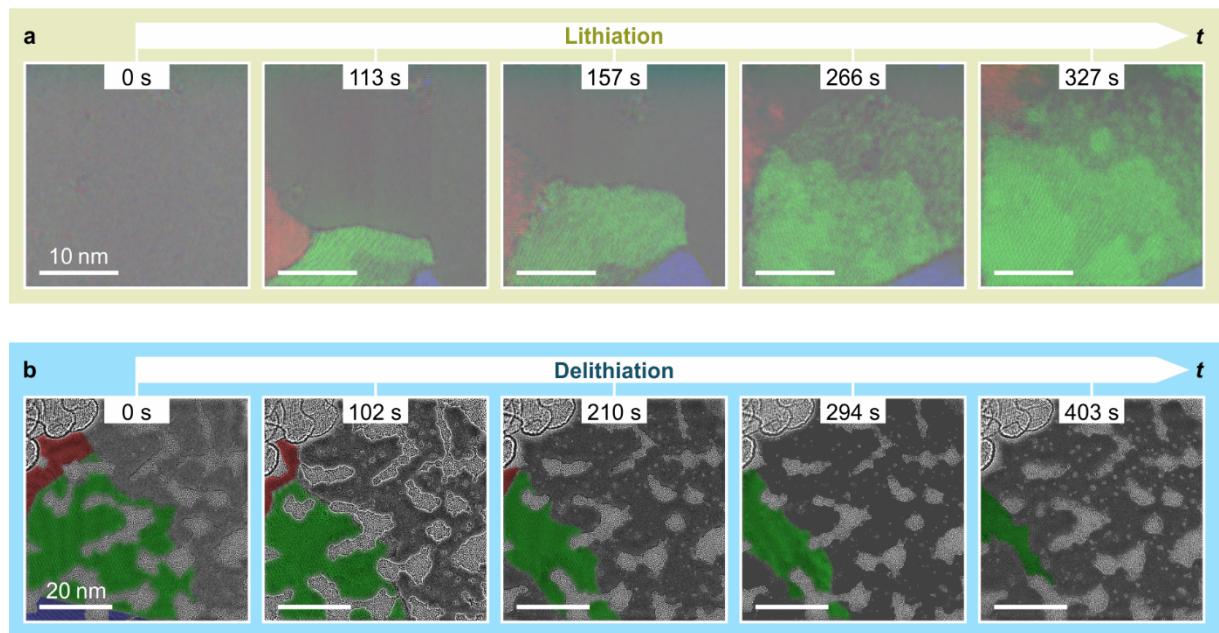
299 **Figure 2 | *In situ* TEM measurements.** a–c, TEM images showing the propagating front of a
 300 Li crystal forming inside bilayer graphene during lithiation. The images are acquired on the

301 same sample area at consecutive times as indicated. Amorphous hydrocarbon adsorbates appear
302 as few nm-large blobs, located above or below the bilayer. The inset in **(a)** is its Fourier
303 transform. **d**, Fourier transform of **(b)**. Three sets of spots marked in red, green, and blue are
304 rotated relative to each other as they stem from three different Li crystal grains. The cross-shaped
305 streaks are edge artefacts from the Fourier transform. **e**, Spatial distribution of the Li grains in
306 **(b)** with the colour coding from **(d)**. **f**, von Hann-filtered Fourier transform of **(b)**. Fourier
307 transforms are point symmetric, therefore, marks on the left side do not mask information.
308 Signals from bilayer graphene (Li) are highlighted in cyan (green); (the origin of) Moiré artefacts
309 are highlighted in (bold) magenta. The anisotropic smearing of the Li signals is due to the sharp
310 propagation front. Signals originating from the grains coloured red and blue in **e** are damped
311 away by the applied von Hann filter. Half circles represent the fundamental periodicities of 0.213
312 nm for graphene (cyan) and 0.276 nm for Li (green). **g**, Fourier-filtered version of **(b)** where the
313 graphene lattice, as well as the Moiré effects, are filtered out and only the Li crystal structure is
314 left. The contrast at the edge of the figure is an artefact from the Fourier filter. **h**, **i**, Magnified
315 detail from the demarcated areas in **b** and **g** respectively, showing the Li crystal edge. Scale bars
316 of equal size are coloured identically but labelled only once in **(a–g)**. **j**, EELS data with
317 logarithmic intensity scale before (blue) and during (yellow) lithiation acquired on an area as in
318 **(a)** and **(c)**, respectively. Highlighted are the energies of the relevant major edges. Insets show
319 the near-edge structure of the Li and C K-edges on a linear intensity scale and after individual
320 subtraction of an inverse-power law background. Note that EELS data get noisy at high energies
321 because of the exponential decay of the signal.



322

323 **Figure 3 | Atomistic models of Li crystals between AB-stacked graphene sheets obtained**
 324 **from DFT calculations.** **a, b,** The ‘conventional’ C_6LiC_6 configuration with Li arranged in a
 325 commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure between graphene sheets. **c, d,** Fully optimized
 326 bilayer Li crystal. **e, f,** Fully optimized trilayer Li crystal (one of two energetically close stacking
 327 configurations, compare with Extended Data Fig. 8d). The projection of the latter two structures
 328 matches well the experimental observations. (**a, c, e**) are top views and (**b, d, f**) are side views
 329 along the dashed line given in the respective top view. C atoms and sp^2 -bonds are grey, Li atoms
 330 are magenta. The insets in (**a, c, e**) schematically show diffraction patterns associated with the
 331 respective structure (scale bar is 2 nm^{-1}), with first order diffraction spots from the Li (C) lattice
 332 indicated in magenta (grey). The close-packed Li phase in (**c, e**) may assume any relative rotation
 333 angle with respect to the bilayer graphene lattice at virtually no additional energy cost (see
 334 Extended Data Fig. 7b). A faint magenta circle indicates that the Li diffraction spots may
 335 therefore be rotated with respect to those of graphene. E_f is the energy required to take a Li atom
 336 from a bulk Li crystal and insert it between graphene sheets in the corresponding configuration.
 337 Contour plots in (**b, d, f**) represent the charge transfer between Li and graphene as compared to
 338 the isolated graphene and Li crystals. An increase in the electron density (negative charge) is
 339 blue, and a decrease in the electron density (positive charge) is red. Note the smaller average
 340 charge transfer to graphene for the multilayer Li crystals.



341

342 **Figure 4 | Li crystal growth between two graphene sheets. a, b,** Time series of TEM images
 343 after Fourier filtering of the bilayer graphene signal acquired during **(a)** lithiation and **(b)**
 344 delithiation. Crystal grains of different in-plane orientation are coloured in red, green, and blue.
 345 An increased amount of amorphous, immobilized residues (grey areas, essentially composed of
 346 carbon) are present within the field of view in **(b)**, an unavoidable consequence of extended
 347 electron beam illumination. In both **(a, b)** the interface with the electrolyte (not contained in the
 348 images) is oriented towards the bottom of the page.