

Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane

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Although graphite is known as one of the most chemically inert materials, we have found that graphene, a single atomic plane of graphite, can react with atomic hydrogen, which transforms this highly conductive zero-overlap semimetal into an insulator. Transmission electron microscopy reveals that the obtained graphene derivative (graphane) is crystalline and retains the hexagonal lattice, but its period becomes markedly shorter than that of graphene. The reaction with hydrogen is reversible, so that the original metallic state, the lattice spacing, and even the quantum Hall effect can be restored by annealing. Our work illustrates the concept of graphene as a robust atomic-scale scaffold on the basis of which new two-dimensional crystals with designed electronic and other properties can be created by attaching other atoms and molecules.

Graphene, a flat monolayer of carbon atoms tightly packed into a honeycomb lattice, continues to attract immense interest, mostly because of its unusual electronic properties and effects that arise from its truly atomic thickness (*1*). Chemical modification of graphene has been less explored, even though research on carbon nanotubes suggests that graphene can be altered chemically without breaking its resilient C-C bonds. For example, graphene oxide is graphene densely covered with hydroxyl and other groups (*2–6*). Unfortunately, graphene oxide is strongly disordered, poorly conductive, and difficult to

reduce to the original state (*6*). However, one can imagine atoms or molecules being attached to the atomic scaffold in a strictly periodic manner, which should result in a different electronic structure and, essentially, a different crystalline material. Particularly elegant is the idea of attaching atomic hydrogen to each site of the graphene lattice to create graphane (*7*), which changes the hybridization of carbon atoms from sp^2 into sp^3 , thus removing the conducting π -bands and opening an energy gap (*7, 8*).

Previously, absorption of hydrogen on graphitic surfaces was investigated mostly in con-

junction with hydrogen storage, with the research focused on physisorbed molecular hydrogen (*9–11*). More recently, atomic hydrogen chemisorbed on carbon nanotubes has been studied theoretically (*12*) as well as by a variety of experimental techniques including infrared (*13*), ultraviolet (*14, 15*), and x-ray (*16*) spectroscopy and scanning tunneling microscopy (*17*). We report the reversible hydrogenation of single-layer graphene and observed dramatic changes in its transport properties and in its electronic and atomic structure, as evidenced by Raman spectroscopy and transmission electron microscopy (TEM).

Graphene crystals were prepared by use of micromechanical cleavage (*18*) of graphite on top of an oxidized Si substrate (300 nm SiO_2) and then identified by their optical contrast (*1, 18*) and distinctive Raman signatures (*19*). Three types of samples were used: large ($>20 \mu m$) crystals for Raman studies, the standard Hall bar devices $1 \mu m$ in width (*18*), and free-standing membranes (*20, 21*) for TEM. For details of sample fabrication, we refer to earlier work (*18, 20, 21*).

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We first annealed all samples at 300°C in an argon atmosphere for 4 hours in order to remove any possible contamination (for example, resist residues). After their initial characterization, the samples were exposed to a cold hydrogen plasma. We used a low-pressure (0.1 mbar) hydrogen-argon mixture (10% H₂) with dc plasma ignited between two aluminum electrodes. The samples were kept 30 cm away from the discharge zone in order to minimize any possible damage by energetic ions. We found that it typically required 2 hours of plasma treatment to reach the saturation in measured characteristics. As a reference, we used graphene samples exposed to a pure Ar plasma under the same conditions, which showed little changes in their transport and Raman properties (22).

Typical changes induced by the hydrogenation in electronic properties of graphene are illustrated in Fig. 1. Before plasma exposure, our devices exhibited the standard ambipolar field effect with the neutrality point (NP) near zero gate voltage (*J*8). For the device shown in Fig. 1, mobility μ of charge carriers was $\approx 14,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This device exhibits a weak temperature dependence of its resistivity at all gate voltages (not visible on the scale of Fig. 1A). We observed metallic dependence close to the NP below 50 K (23) and the half-integer quantum Hall effect (QHE) at cryogenic temperatures (Fig. 1B), both of which are hallmarks of single-layer graphene [(1) and references therein].

This behavior completely changed after the devices were treated with atomic hydrogen (Fig. 1, C and D). The devices exhibited an insulating behavior such that the resistivity ρ grew by two orders of magnitude with decreasing temperature *T* from 300 to 4 K (Fig. 1C). Carrier mobility decreased at liquid-helium temperatures down to values of $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for typical carrier concentrations *n* of the order of 10^{12} cm^{-2} . The quantum Hall plateaus, so marked in the original devices, completely disappeared, with only weak signatures of Shubnikov–de-Haas oscillations remaining in magnetic field *B* of 14 T (Fig. 1D). In addition, we observed a shift of NP to gate voltages $V_g \approx +50 \text{ V}$, which showed that graphene became doped with holes in concentration of $\approx 3 \times 10^{12} \text{ cm}^{-2}$ (probably due to adsorbed water). At carrier concentrations of less than $3 \times 10^{12} \text{ cm}^{-2}$, the observed temperature dependences $\rho(T)$ can be well fitted by the function $\exp[(T_0/T)^{1/3}]$ (T_0 is the parameter that depends on V_g) (Fig. 2), which is a signature of variable-range hopping in two dimensions (24). T_0 exhibits a maximum at NP of $\sim 250 \text{ K}$ and strongly decreases away from NP (Fig. 2B). At $n > 4 \times 10^{12} \text{ cm}^{-2}$ (for both electrons and holes), changes in ρ with *T* became small (similar to those in pristine graphene), which indicates a transition from the insulating to the metallic regime.

The hydrogenated devices were stable at room *T* for many days and showed the same characteristics during repeated measurements. However, we could restore the original metallic

state by annealing (we used 450°C in Ar atmosphere for 24 hours; higher annealing *T* damaged graphene). After the annealing, the devices returned practically to the same state as before hydrogenation: ρ as a function of V_g reached again a maximum value of $\approx h/4e^2$, where *h* is Planck's constant and *e* is the electron charge, and became only weakly *T*-dependent (Figs. 1E and 2). Also, μ recovered to $\sim 3500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the QHE reappeared (Fig. 1F). Still, the

recovery was not complete: Graphene remained p-doped, the QHE did not restore at filling factors ν larger than ± 2 (compare Figure 1, B and F), and zero-*B* field conductivity σ ($=1/\rho$) became a sublinear function of *n*, which indicates an increased number of short-range scatterers (23). We attribute the remnant features to vacancies induced by plasma damage or residual oxygen during annealing. To this end, after annealing, the distance (as a function of V_g) between

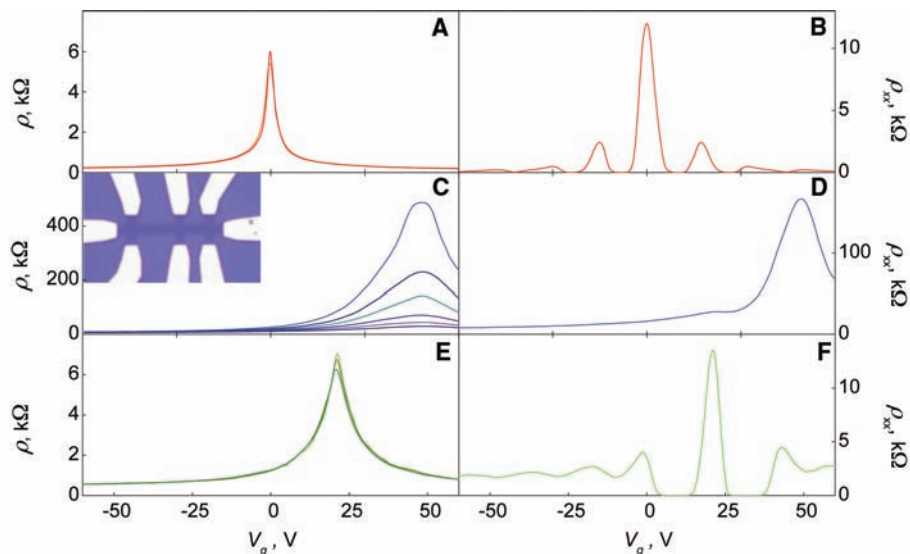
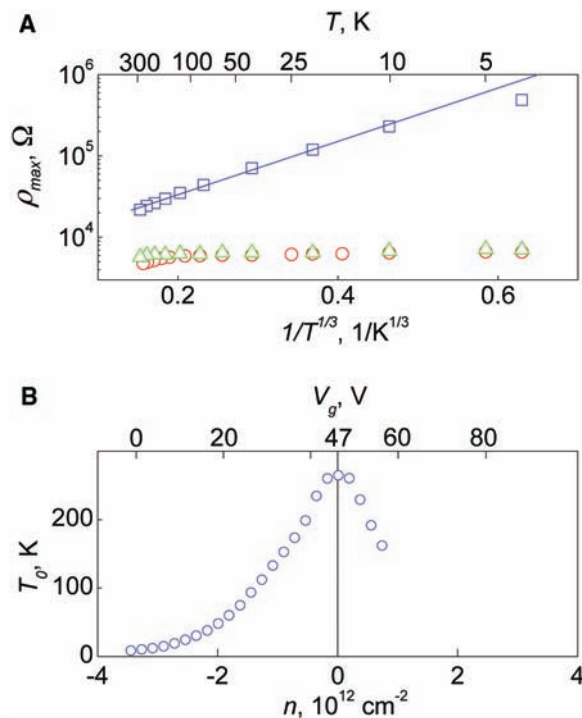


Fig. 1. Control of the electronic properties of graphene by hydrogenation. The electric field effect for one of our devices at zero *B* at various temperatures *T* (left column) and in *B* = 14 T at 4 K (right). (A and B) The sample before its exposure to atomic hydrogen; curves in (A) for three temperatures (40, 80, and 160 K) practically coincide. (C and D) After atomic hydrogen treatment. In (C), temperature increases from the top; *T* = 4, 10, 20, 40, 80, and 160 K. (E and F) The same sample after annealing. (E) *T* = 40, 80, and 160 K, from top to bottom. (Inset) Optical micrograph of a typical Hall bar device. The scale is given by its width of 1 μm .

Fig. 2. Metal-insulator transition in hydrogenated graphene. (A) Temperature dependence of graphene's resistivity at NP for the sample shown in Fig. 1. Red circles, blue squares, and green triangles are for pristine, hydrogenated, and annealed graphene, respectively. The solid line is a fit by the variable-range hopping dependence $\exp[(T_0/T)^{1/3}]$. (B) Characteristic exponents T_0 found from this fitting at different carrier concentrations.



the peaks in ρ_{xx} at $v = 0$ and $v = \pm 4$ became notably greater ($\sim 40\%$) than that between all the other peaks for both annealed and original devices. The greater distance indicates the presence of mid-gap states (25) [such as vacancies (26)] that were induced during the processing, which was in agreement with the observed sub-linear behavior of the conductivity. The extra charge required to fill these states (25) yields their density as of about $1 \times 10^{12} \text{ cm}^{-2}$ (with an average spacing of $\approx 10 \text{ nm}$).

The changes induced by hydrogenation have been corroborated by Raman spectroscopy. The main features in the Raman spectra of carbon-based materials are the G and D peaks that lie at around 1580 and 1350 cm^{-1} , respectively. The G peak corresponds to optical E_{2g} phonons at the Brillouin zone center, whereas the D peak is caused by breathing-like modes (corresponding to transverse optical phonons near the K point) and requires a defect for its activation via an intervalley double-resonance Raman process (19, 27–29).

Both the G and D peaks arise from vibrations of sp^2 -hybridized carbon atoms. The D peak intensity provides a convenient measure for the amount of disorder in graphene (27–29). Its overtone, the 2D peak, appears around 2680 cm^{-1} and its shape identifies monolayer graphene (19). The 2D peak is present even in the absence of any defects because it is the sum of two phonons with opposite momentum. In Fig. 3, there is also a peak at $\sim 1620 \text{ cm}^{-1}$, called D', which occurs via an intervalley double-resonance process in the presence of defects.

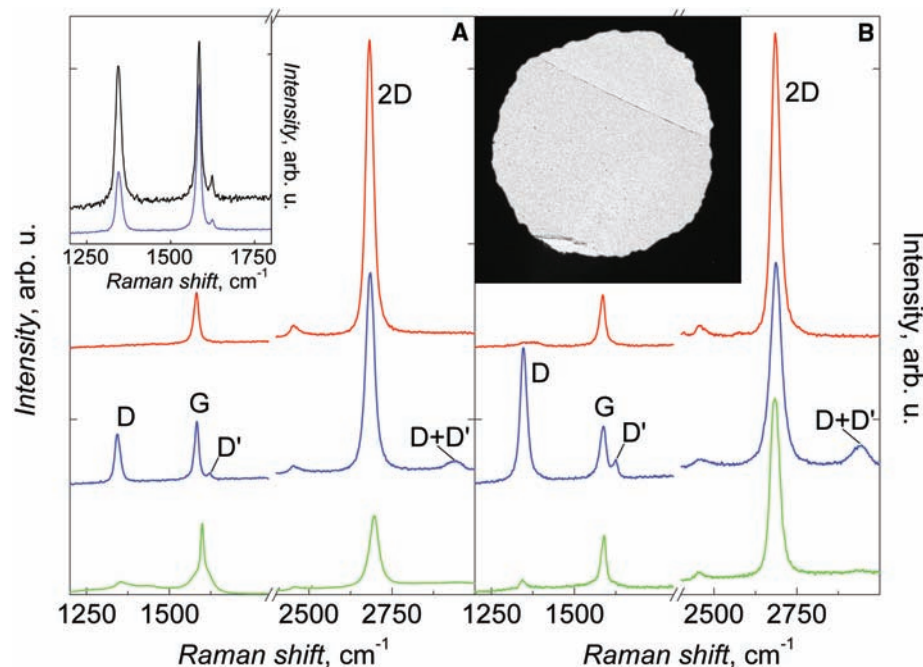


Fig. 3. Changes in Raman spectra of graphene caused by hydrogenation. The spectra are normalized to have a similar intensity of the G peak. (A) Graphene on SiO_2 . (B) Free-standing graphene. Red, blue, and green curves (top to bottom) correspond to pristine, hydrogenated, and annealed samples, respectively. Graphene was hydrogenated for ~ 2 hours, and the spectra were measured with a Renishaw spectrometer at wavelength 514 nm and low power to avoid damage to the graphene during measurements. (Left inset) Comparison between the evolution of D and D' peaks for single- and double-sided exposure to atomic hydrogen. Shown is a partially hydrogenated state achieved after 1 hour of simultaneous exposure of graphene on SiO_2 (blue curve) and of a membrane (black curve). (Right inset) TEM image of one of our membranes that partially covers the aperture $50 \mu\text{m}$ in diameter.

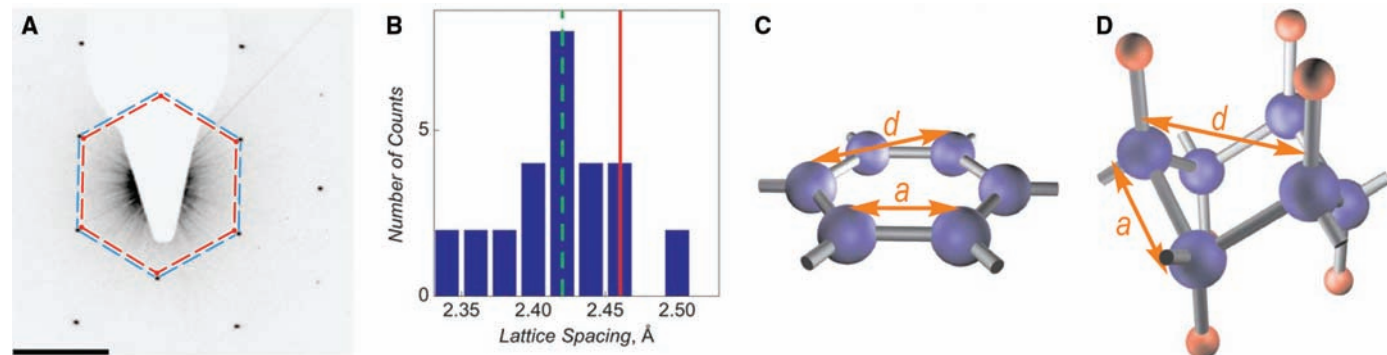


Fig. 4. Structural studies of graphene via TEM [we used a Tecnai F30 (FEI, Eindhoven, the Netherlands)]. (A) Changes in the electron diffraction after ~ 4 hours exposure of graphene membranes to atomic hydrogen. Scale bar, 5 nm^{-1} . The blue hexagon is a guide to the eye and marks positions of the diffraction spots in graphene. The equivalent diffraction spots in graphene under the same conditions are shown by the red hexagon. (B) Distribution of

the lattice spacing d found in hydrogenated membranes. The green dashed line marks the average value, whereas the red solid line shows d always observed for graphene (both before hydrogenation and after annealing). (C and D) Schematic representation of the crystal structure of graphene and theoretically predicted graphene. Carbon atoms are shown as blue spheres, and hydrogen atoms are shown as red spheres.

defect-related peaks (D, D', and D+D') were strongly suppressed. However, two broad low-intensity bands appeared, overlapping a sharper G and residual D peaks. These bands are indicative of some residual structural disorder (29). The 2D peak remained relatively small with respect to the G peak when compared with the same ratio in the pristine sample, and both became shifted to higher energies, indicating that the annealed graphene is p-doped (30). The observed changes in Raman spectra are in broad agreement with our transport measurements.

For graphene on a substrate, only one side is accessible to atomic hydrogen, and the plasma exposure is not expected to result in graphane (which assumes hydrogen atoms attached on both sides). For more effective hydrogenation, we employed free-standing graphene membranes (Fig. 3B, inset) (20, 21). The experiments described below refer to membranes that had some free edges to facilitate the relaxation of strain induced by hydrogenation [membranes with all the sides fixed to a metal scaffold are discussed in (22)]. Raman spectra for hydrogenated and subsequently annealed membranes (Fig. 3B) were rather similar to those described above for graphene on SiO₂, but with some notable differences. If hydrogenated simultaneously and before reaching the saturation, the D peak for a membrane was by a factor of two greater than that for graphene on a substrate (Fig. 3A, inset), which indicates the formation of twice as many C-H bonds in the membrane. This result agrees with the general expectation that atomic hydrogen attaches to both sides of membranes. Moreover, the D peak could become up to three times greater than the G peak after prolonged exposures of membranes to atomic hydrogen (Fig. 3B).

Further information about hydrogenated membranes was obtained with TEM. For graphene, the electron-diffraction (ED) patterns observed on dozens of the studied membranes were always the same, exhibiting the hexagonal symmetry with the lattice constant $d = 2.46 \pm 0.02$ Å. Prolonged exposure to atomic hydrogen preserved the hexagonal symmetry and hence crystallinity, but led to drastic changes in the lattice constant d , which could decrease by as much as 5% (Fig. 4A). Generally, the compression was not uniform, and different parts of membranes exhibited locally different in-plane periodicities (Fig. 4B; diameters of the selected area for the ED and studied membranes were 0.3 μm and 30 to 50 μm, respectively). Such nonuniformity is generally not unexpected because the crystals were fixed to the scaffold (Fig. 3) that restricted their isotropic shrinkage. We found that the more extended free edges a membrane had, the more uniformly it became hydrogenated (22). In the extreme case of all the edges being fixed to the scaffold, even domains with a stretched lattice could be observed (22). Annealing led to complete recovery of the original periodicity observed in TEM.

The in-plane compression of graphene's lattice can only be the result of chemical modi-

fication as opposed to physical forces, because any compression that is not stabilized on an atomic scale should cause the membranes to buckle. Furthermore, strains of the order of a few percent would result in massive variations of the Raman peaks, which was not the case. The most obvious candidate for the modified crystal lattice is graphane (7, 8). In this until-now-theoretical material, hydrogen attaches to graphene's sublattices A and B from the two opposite sides, and carbon atoms in A and B move out of the plane ("buckle"), as shown in Fig. 4D. The in-plane periodicity probed by TEM would then substantially shrink if the length a of the C-C bond were to remain the same as in graphene (1.42 Å). However, the change in hybridization from sp² to sp³ generally results in longer C-C bonds, which is the effect opposing to the lattice shrinkage by atomic-scale buckling. Recent calculations (8) predicted a in graphane to be ≈ 1.53 Å (near that of diamond) and the in-plane periodicity d to be $\approx 1\%$ smaller than in graphene. Although the maximum in the observed distribution of d occurs at ≈ 2.42 Å (that is, near the theoretical value for graphane) (Fig. 4B), the observation of more compressed areas (such as in Fig. 4A) suggests that the equilibrium d (without strain imposed by the scaffold) should be smaller. The latter implies either shorter or stronger buckled C-C bonds, or both, are present. Alternatively, the experimentally produced graphane may have a more complex hydrogen bonding than the one suggested by theory.

Finally, let us return to the graphene hydrogenated on a substrate (Figs. 1 and 3). Single-sided hydrogenation of ideal graphene would create a material that is thermodynamically unstable (7, 8), and therefore our experiments seem to be in conflict with the theory [for the case of graphene on a substrate, we can exclude the possibility of double-sided hydrogenation because the diffusion of hydrogen along the graphene-SiO₂ interface is negligible (31)]. However, realistic graphene samples are not microscopically flat but always rippled (20, 21), which should facilitate their single-sided hydrogenation. Indeed, attached hydrogen is expected to change the hybridization of carbon from sp² to (practically) sp³ with angles of $\sim 110^\circ$ acquired between all of the bonds (7). These constraints necessitate the movement of carbon atoms out of the plane in the direction of the attached hydrogen, at the cost of an increase in elastic energy. However, for a convex surface, the lattice is already deformed in the direction that favors sp³ bonding, which lowers the total energy. As shown in (22), single-sided hydrogenation becomes energetically favorable for a typical size of ripples observed experimentally (20). Because of the random nature of ripples, single-sided graphane is expected to be a disordered material, similar to graphene oxide, rather than a new graphene-based crystal. The formation of a disordered material also explains the observation of variable-range hopping in our transport experiments. The importance of

ripples for hydrogenation of graphene on a substrate is further evidenced in experiments involving bilayer samples, which show a substantially lower level of hydrogenation than monolayers under the same conditions (22). We attribute this observation to the fact that bilayer graphene is less rippled (20).

The distinct crystal structure of hydrogenated graphene and pronounced changes in its electronic and phonon properties reveal two new graphene derivatives, one crystalline and the other disordered. The results show that conversion of graphene into other giant molecules with a regular structure is possible.

References and Notes

1. A. K. Geim, K. S. Novoselov, *Nat. Mater.* **6**, 183 (2007).
2. S. Stankovich et al., *J. Mater. Chem.* **16**, 155 (2006).
3. S. Stankovich et al., *Nature* **442**, 282 (2006).
4. X. Wang, L. Zhi, K. Mullen, *Nano Lett.* **8**, 323 (2008).
5. S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.* **7**, 3394 (2007).
6. C. Gomez-Navarro et al., *Nano Lett.* **7**, 3499 (2007).
7. J. O. Sofo, A. S. Chaudhari, G. D. Barber, *Phys. Rev. B* **75**, 153401 (2007).
8. D. W. Boukhvalov, M. I. Katsnelson, A. I. Lichtenstein, *Phys. Rev. B* **77**, 035427 (2008).
9. A. C. Dillon et al., *Nature* **386**, 377 (1997).
10. F. L. Dackrim, P. Malbrunot, G. P. Tartaglia, *Int. J. Hydrogen Energy* **27**, 193 (2002).
11. A. Züttel et al., *Int. J. Hydrogen Energy* **27**, 203 (2002).
12. T. Yildirim, O. Gulseren, S. Ciraci, *Phys. Rev. B* **64**, 075404 (2001).
13. B. N. Khare, M. Meyyappan, A. M. Cassell, C. V. Nguyen, J. Han, *Nano Lett.* **2**, 73 (2002).
14. P. Ruffieux et al., *Phys. Rev. B* **66**, 245416 (2002).
15. D. Neumann et al., *Appl. Phys. A* **55**, 489 (1992).
16. A. Nikitin et al., *Phys. Rev. Lett.* **95**, 225507 (2005).
17. L. Hornekær et al., *Phys. Rev. Lett.* **96**, 156104 (2006).
18. K. S. Novoselov et al., *Science* **306**, 666 (2004).
19. A. C. Ferrari et al., *Phys. Rev. Lett.* **97**, 187401 (2006).
20. J. C. Meyer et al., *Nature* **446**, 60 (2007).
21. T. J. Booth et al., *Nano Lett.* **8**, 2442 (2008).
22. Supporting online material is available on Science Online.
23. S. V. Morozov et al., *Phys. Rev. Lett.* **100**, 016602 (2008).
24. N. F. Mott, *Philos. Mag.* **19**, 835 (1969).
25. T. O. Wehling et al., *Nano Lett.* **8**, 173 (2008).
26. V. M. Pereira, F. Guinea, J. M. B. Lopes dos Santos, N. M. R. Peres, A. H. Castro Neto, *Phys. Rev. Lett.* **96**, 036801 (2006).
27. A. C. Ferrari, *Solid State Commun.* **143**, 47 (2007).
28. F. Tuinstra, J. L. Koenig, *J. Chem. Phys.* **53**, 1126 (1970).
29. A. C. Ferrari, J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).
30. A. Das et al., *Nat. Nanotechnol.* **3**, 210 (2008).
31. J. S. Bunch et al., *Nano Lett.* **8**, 2458 (2008).
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Supporting Online Material

www.sciencemag.org/cgi/content/full/323/5914/610/DC1
SOM Text
Figs. S1 to S7
References

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Supplementary Online Material

”Control of graphene’s properties by reversible hydrogenation” by D. C. Elias *et al*

SUPPLEMENTARY TEXT

1. Non-uniform Hydrogenation of Graphene Membranes

In the main text, we described graphene crystals exhibiting lattice periodicity d notably shorter than that in graphene. We have observed a range of d values rather than a single period expected for homogenous graphene. This was attributed to the inevitable mechanical strain induced when parts of the crystal rigidly attached to a metal scaffold had to shrink during conversion of graphene into graphane (its adhesion to an evaporated metal is expected to be very strong as graphene deposited on plastic can already sustain strains of $> 1\%$ (*S1*)). To minimize the effect of strain, we chose to work with partially broken membranes that allowed at least a part of the strain to relax due to the presence of free boundaries.

To emphasize the importance of strain effects, here we describe in addition what happens in the extreme case when a graphene membrane has no free boundaries. Figure S1A shows a TEM micrograph of a hydrogenated crystal that completely covers a $50\ \mu\text{m}$ aperture in a $15\ \mu\text{m}$ thick copper film (*S2*). For this membrane, we observed not only the regions that contracted but also those that drastically expanded. The former exhibited d down to $2.37 \pm 0.02\ \text{\AA}$ (i.e. 4% smaller than in graphene), in agreement with the results for partial and ruptured membranes reported in the main text. In the expanded regions, d could be as large as $\approx 2.7\ \text{\AA}$ (i.e. the lattice was stretched isotropically by nearly 10% with respect to pristine graphene). Figure S1B shows an example of such an extremely stretched graphene lattice. One can see that the diffraction spots occur inside the red hexagon indicating the diffraction pattern in graphene, which is directly opposite to Fig. 4A that shows the same diffraction spots but outside the red hexagon. This amount of stretching is close to the limit of possible elastic deformations in graphene (*S3*) and, indeed, we observed some of our membranes to rupture during their hydrogenation. We believe that the stretched regions are likely to remain non-hydrogenated.

It is hardly surprising that if a part of a rigidly fixed membrane shrinks, other parts have to extend. However, we found that instead of exhibiting random stretching, graphene membranes normally split into domain-like regions. The symmetry within each domain remained hexagonal

but with either increased or decreased d . In other words, not only contraction due to hydrogenation was isotropic (as already discussed in the main text) but also the expansion was mostly isotropic. Having said that, we also observed expanded regions, for which the hexagonal diffraction pattern was stretched along some preferential direction (usually, a crystallographic one) and the diffraction spots were blurred. Analysis of many diffraction images revealed that a typical domain size was of the order of 1 μm and the uniaxial part of strain was significantly smaller than its isotropic component and never exceeded $\approx 2\%$. The annealing of membranes (without free boundaries) also led to complete recovery of the original periodicity in both stretched and compressed domains.

2. Binding of Hydrogen to Ripples

In the main text, we have presented a simple argument that atomic hydrogen should preferentially bind to apexes of corrugated graphene due to a contribution from elastic energy. However, there is also a contribution from the electronic energy which works in parallel and promotes the local bonding of atomic hydrogen. The electronic structure of a non-hydrogenated curved graphene is characterized by the appearance of so-called mid-gap states (*S4*) (see the red curve in Figure S2). Our numerical simulations show that the attachment of a pair of hydrogen atoms leads to the splitting of the mid-gap peak, leading to the formation of symmetric (donor and acceptor) quasi-localized states (blue curve). For denser hydrogen coverage, an energy gap opens in the electronic spectrum of rippled graphene (green curve). One can see that the splitting moves the mid-gap states away from zero energy, leading to a gain in total energy. This mechanism seems to be rather general: humps in graphene can stabilize themselves by catching impurity states, and also favours hydrogenation of convex regions.

3. Estimate for the Energy Gap Induced by Hydrogenation of Graphene on Substrate

The notion of preferential hydrogenation of humps on a graphene surface can be combined with the concept of graphene sheets being generally rippled (*S5,S6,S7*). The combination leads to the following scenario for the disordered chemical derivative obtained by single-sided hydrogenation. This derivative is likely to consist of two phases: convex regions decorated with hydrogen and concave areas that remain non-hydrogenated (see Fig. 3A). In the hydrogenated regions, carbon atoms acquire sp^3 hybridisation and an energy gap opens, whereas non-

hydrogenated regions retain their sp^2 metallic character (see the calculations in Fig. S2). The corresponding electronic spectra are schematically shown in Fig. S3B.

The two-phase picture allows a rough estimate for the energy gap in the hydrogenated convex regions. To this end, we assume that at the neutrality point the metallic concave regions are well separated by the gapped regions so that the system as a whole is insulating. By applying gate voltage, we add charge carriers that fill in the localized states in the gapped regions and the Dirac cones in the metallic ones (see Fig. S3B,C). Eventually, the Fermi level reaches the bottom (top) of the conduction (valence) in the hydrogenated regions, thus bringing the whole system into the metallic regime. Experimentally, this occurs at $n \approx 4 \times 10^{12} \text{ cm}^{-2}$ (see the main text), which corresponds to a shift of the Fermi energy by $\sim 0.25 \text{ eV}$. This yields an energy gap of $\sim 0.5 \text{ eV}$ for the single-sided hydrogenation. This estimate provides a lower bound for the energy gap as it neglects a contribution from the localised states, quantum confinement effects and a smaller capacitance to the gate for the case of microscopic regions.

To explore the nature of the insulating state of single-sided graphene we measured its I - V characteristics (Fig. S4). They have exhibited strongly non-linear behaviour, in contrast to the case of graphene. The level of non-linearity varies with carrier concentration, and the curves become practically linear for carrier concentrations above $\sim 5 \times 10^{12} \text{ cm}^{-2}$, which further supports our conclusions above and in the main text. The nonlinearity disappears with increasing T (Fig. S4; inset), with conductivity at zero bias following the $\exp[-(T_0/T)^{1/3}]$ dependence.

4. Mass Spectrometry of Gas Desorption from Hydrogenated Graphene

To confirm the presence of hydrogen on the surface of graphene after its hydrogenation, we performed mass-spectrometry of gases desorbed from its surface during thermal annealing. To this end, we started with a graphene suspension in DMF (dimethylformamide), which was prepared by ultrasonic exfoliation (S8,S9) of natural graphite flakes (S10). SiO_2/Si wafers were then spin-coated using this suspension, which resulted in uniform thin films consisting of overlapping submicron flakes of graphene. They were then exposed to the hydrogen-argon plasma for 2 hours. After hydrogenation the samples were heated up to 350°C in vacuum while the atmosphere in the chamber was monitored by a mass-spectrometer. The observed intermittent flow of hydrogen (Fig. S5) clearly proves that it gets adsorbed at the surface of graphene even during single-sided hydrogenation and can then be desorbed by modest heating. In a control

experiment, we used samples prepared in parallel with those measured in Fig. S5 but exposed only to pure argon plasma under the same conditions. The control samples exhibited a significantly lower hydrogen signal attributed to desorption of water from heated surfaces (Fig. S5).

5. Corrugation of Hydrogenated Graphene

We have also performed electron diffraction studies of hydrogenated graphene membranes in a tilted geometry (S5,S6). The blurring of diffraction spots provides information about the flatness of the membranes (S5,S6). The hydrogenated membranes that exhibited only a slightly shorter lattice periodicity showed the same level of corrugation as pristine graphene (Fig. S6A,B,E). On the other hand, those membranes that had a strongly compressed lattice showed significantly lower corrugations (Fig. S6C,D,E).

The broadening of the diffraction peaks at zero tilt provides the information about the uniformity of our samples. This broadening for hydrogenated graphene was found to be very similar to that in pristine graphene, which indicates that our membranes were uniformly hydrogenated (at least over the areas used for the electron diffraction – $0.3\mu\text{m}$). The probable reason for the uniform hydrogenation is high mobility of hydrogen atoms along the surface (S11), which allows them to achieve the lowest energy configuration characteristic of graphane.

6. Hydrogenation of Bilayer Graphene

We have applied our hydrogenation procedures also to bilayer graphene. Bilayer samples on a substrate exhibited significantly lower affinity to hydrogen as revealed in measurements of their Raman spectra and transport characteristics. Bilayer samples showed little change in their charge carrier mobility and only a small D peak, as compared to single-layer graphene exposed to the same hydrogenation procedures (Fig. S7).

This observation is in agreement with the theory that hydrogen cannot be adsorbed on one side of a flat graphene surface and our conclusions that hydrogen adsorption for graphene on a substrate is facilitated by ripples (see above). We believe that higher rigidity of bilayers suppresses their rippling (S5,S6), thus reducing the probability of hydrogen adsorption.

SUPPLEMENTARY FIGURES

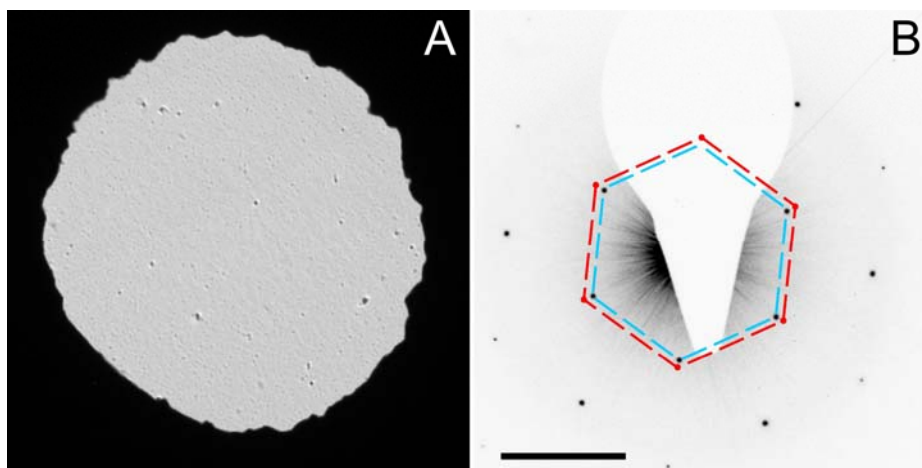


Figure S1. (A) - TEM micrograph of one of our graphene membranes without free boundaries. The presence of a graphene crystal covering the whole aperture is evidenced only by some particulate in the image. (B) - Changes in the lattice constant after extended exposure of this membrane to atomic hydrogen. The scale bar is 5 nm^{-1} . The diffraction pattern is for an unusual case of a region with a strongly stretched lattice ($d \approx 2.69 \text{ \AA}$). The beam diameter used for selected area electron diffraction is $0.3 \text{ }\mu\text{m}$. The blue hexagon is a guide to the eye and marks the positions of the diffraction spots. The equivalent spots in unstrained graphene under the same conditions are shown by the red hexagon and dots.

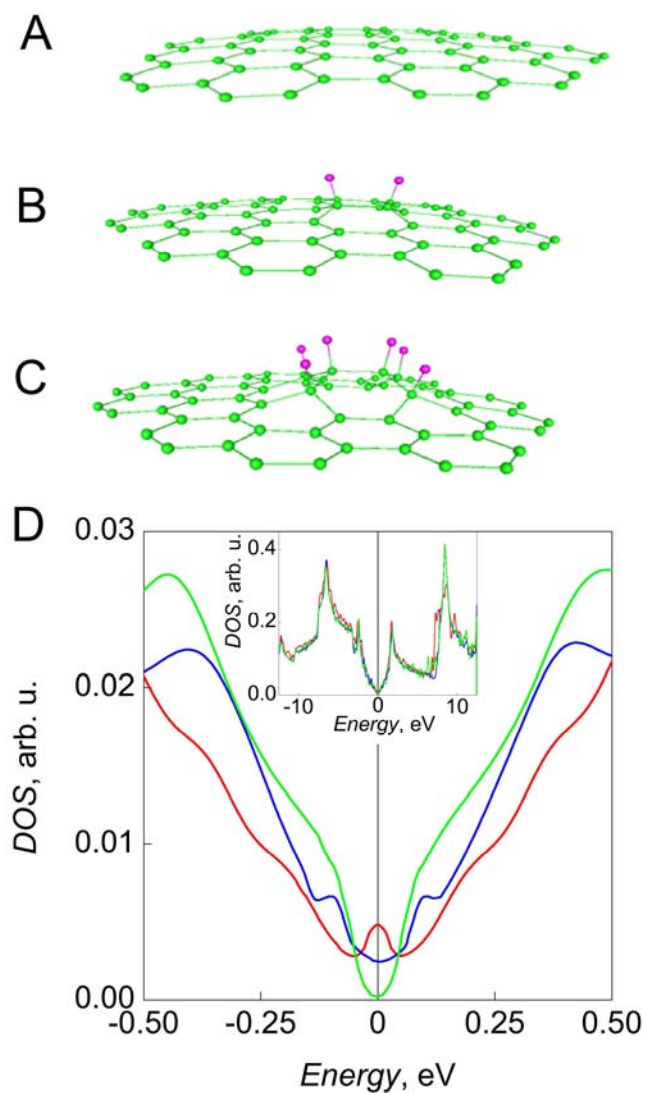


Figure S2. Convex graphene sheet with none (A), two (B) and six (C) hydrogen atoms adsorbed. Atomic coordinates for (B) and (C) were optimized using density functional calculations with the SIESTA code. Configuration (A) was deduced from (B) by removing hydrogen atoms and eliminating the excess displacement for the two carbon atoms that bound hydrogen. (A) corresponds to a ripple of diameter 1.07 nm and height 0.094 nm. (D) – Electronic density of states for configurations A, B and C (red, blue and green curves, respectively). The mid-gap state at zero energy (A; red) becomes split due to adsorption of two hydrogen atoms (B; blue) and a gap opens if more atoms are attached (C; green). Inset: Same calculations for a wider energy range.

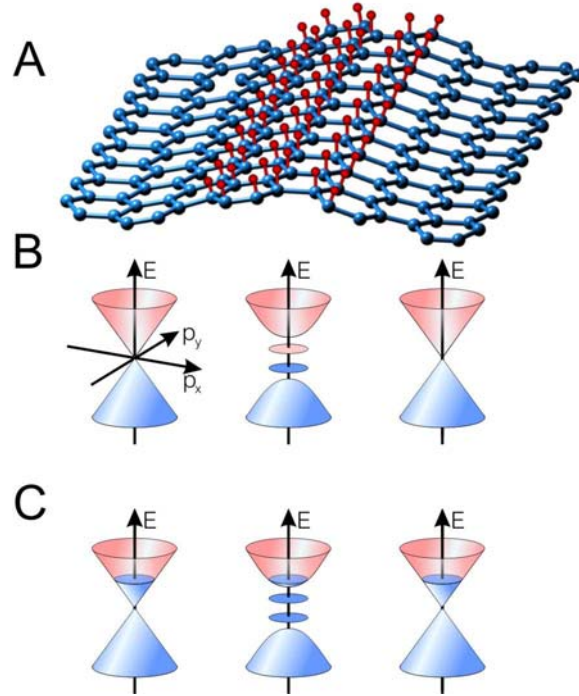


Figure S3. Metal-insulator transition in the disordered graphene derivative obtained by single-sided hydrogenation. (A) – Two-phase model for this derivative: hydrogenated convex regions are adjoined by non-hydrogenated concave ones. Blue (red) spheres represent the carbon (hydrogen) atoms. (B) – Schematic band diagrams for the two phases shown in (A). The diagrams are positioned under the corresponding graphene regions. Hydrogenated regions are represented by a gapped spectrum whereas the concave regions are assumed to be gapless (these are simplified versions of the spectra shown by the red and green curves Fig. S2D). The occupied (unoccupied) states are indicated by blue (pink). The ellipsoids inside the gap represent localised states. The Fermi level in (B) is at the neutrality point. (C) – Same as (B) but the system is doped by electrons so that the Fermi level reaches the bottom of the conduction band in the hydrogenated region.

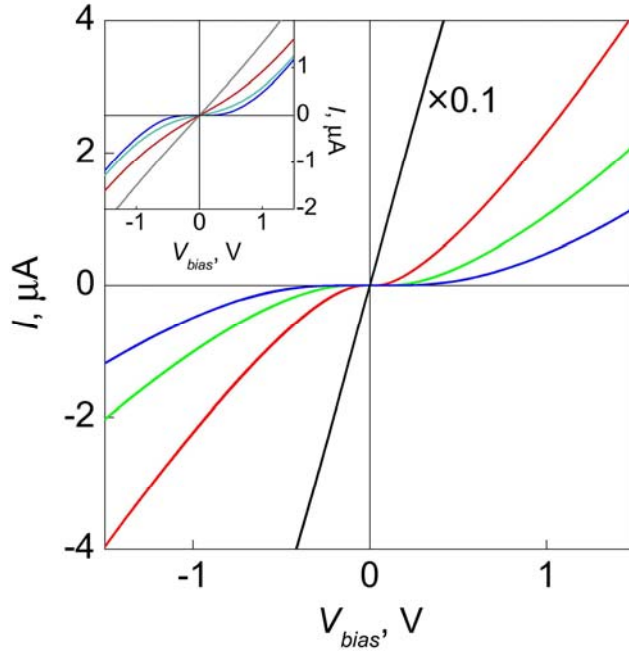


Figure S4. I - V characteristics of a hydrogenated graphene sample; $T=2.5\text{K}$. The blue curve is taken at the neutrality point ($V_g = 47\text{V}$, see Fig. 1C of the main text); green – at a hole concentration of $\approx 1.5 \times 10^{12} \text{ cm}^{-2}$; red – hole concentration $\approx 3 \times 10^{12} \text{ cm}^{-2}$ (carrier concentrations are estimated from the device capacitance and applied gate voltage). The black curve is for the hydrogenated device after its thermal annealing at the neutrality point (note the difference in scales). I - V characteristics for pristine graphene practically coincide with the black curve. Inset: Temperature dependence of the I - V characteristics at the neutrality point for hydrogenated graphene. From bottom to top: $T = 2.5\text{K}$; 40K ; 80K ; 160K .

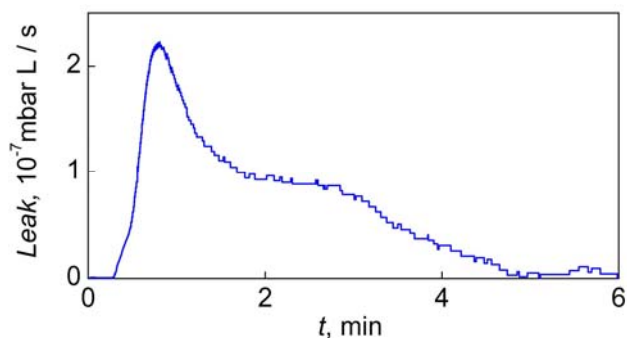


Figure S5. Desorption of hydrogen from single-sided graphane. The measurements were done by using a leak detector tuned to sense molecular hydrogen. The sample was heated to 300°C (the heater was switched on at $t = 10$ s). Control samples (exposed to pure argon plasma) exhibited much weaker and featureless response ($<5 \times 10^{-8}$ mbar L/s), which is attributed to desorption of water at heated surfaces and subtracted from the shown data (water molecules are ionized in the mass-spectrometer, which also gives rise to a small hydrogen signal).

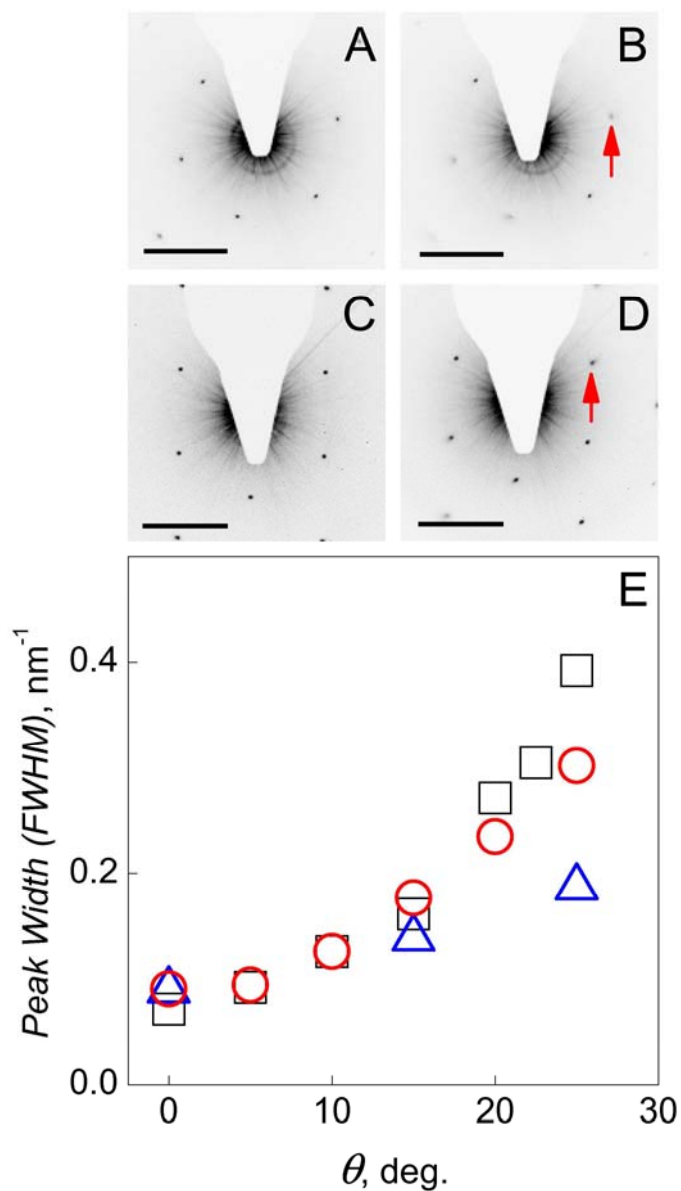


Figure S6. Broadening of (0-110) electron diffraction peaks in graphane. A (B) – Region of hydrogenated graphene with $d \approx 2.42$ Å; tilt angle is 0° (15°). Note the strong blurring of the (0-110) diffraction spot (marked by the red arrow). C (D) – Region with $d \approx 2.35$ Å; tilt angle is again 0° (15°). The broadening of the same spot is smaller than in B. E – broadening of the (0-110) diffraction peak as a function of tilt angle θ . Black squares indicate pristine graphene; red circles hydrogenated graphene with $d \approx 2.42$ Å; and blue triangles graphane ($d \approx 2.35$ Å).

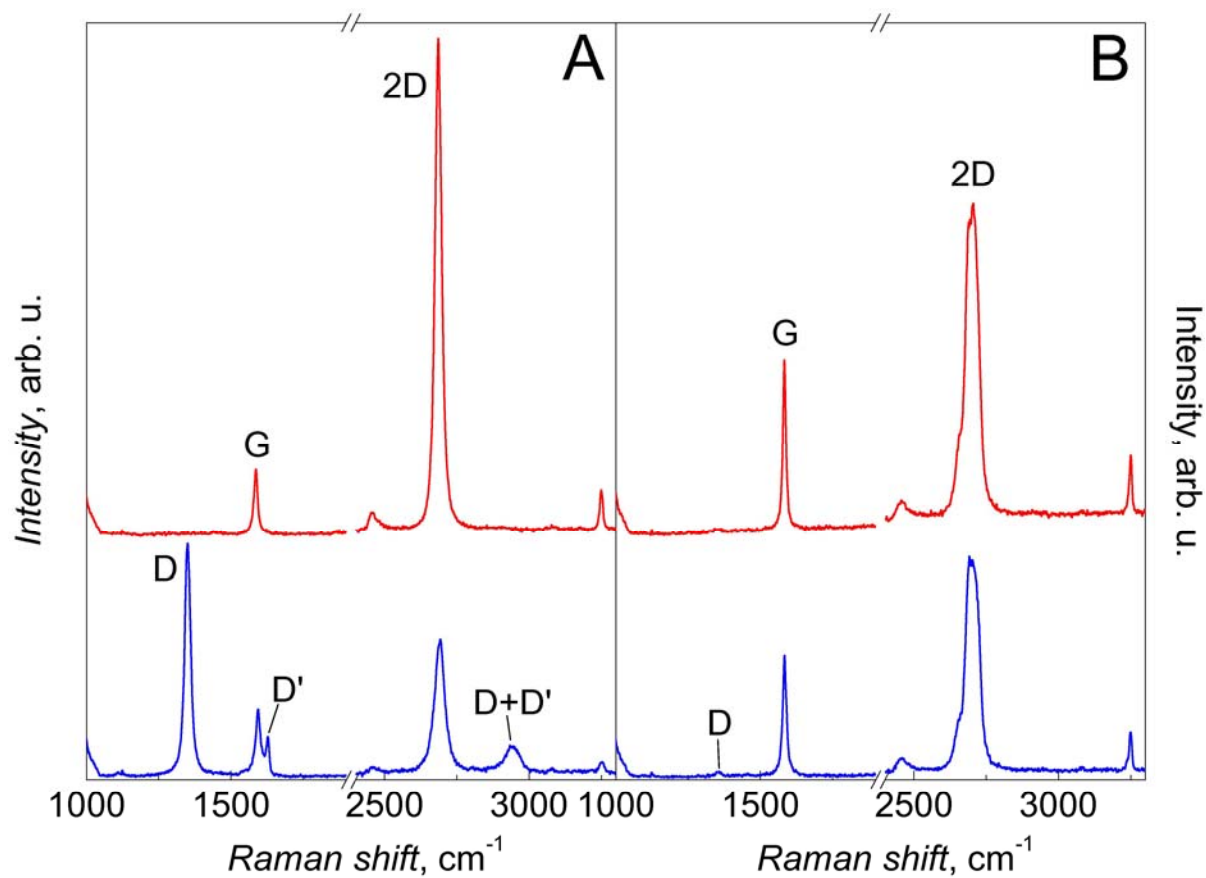


Figure S7. Changes in Raman spectra of single-layer (A) and bilayer graphene (B) induced by hydrogenation. Both samples were on the same SiO₂/Si wafer and were hydrogenated simultaneously for 2 hours. Red and blue curves correspond to pristine and hydrogenated samples, respectively. The spectra were measured with a Renishaw spectrometer at a wavelength of 514 nm and using low power to avoid graphene's damage during measurements.

SUPPLEMENTARY REFERENCES

^{s1} Zhen Hua Ni *et al.*, arXiv:0810.3476.

^{s2} T. J. Booth *et al.*, *Nano Lett.* **8**(8), 2442-2446 (2008).

^{s3} C. Lee, X.ei, J. W. Kysar, J. Hone, *Science* **321**, 385 – 388 (2008).

^{s4} F. Guinea, M. I. Katsnelson, M. A. Vozmediano, *Phys. Rev. B* **77**, 075422 (2008).

^{s5} J. C. Meyer *et al.*, *Nature* **446**, 60-63 (2007).

^{s6} J. C. Meyer *et al.*, *Solid State Commun.* **143**, 101-109 (2007).

^{s7} E. Stolyarova *et al.*, *Proc. Natl Acad. Sci. USA* **104**, 9209-9212 (2007).

^{s8} P. Blake *et al.*, *Nano Letters* **8**(6) 1704 – 1708 (2008).

^{s9} Y. Hernandez *et al.*, *Nature Nanotech.* **3**, 563 - 568 (2008).

^{s10} www.grafite.com

^{s11} J. C. Meyer *et al.*, *Nature* **454**, 319 - 322 (2008).