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

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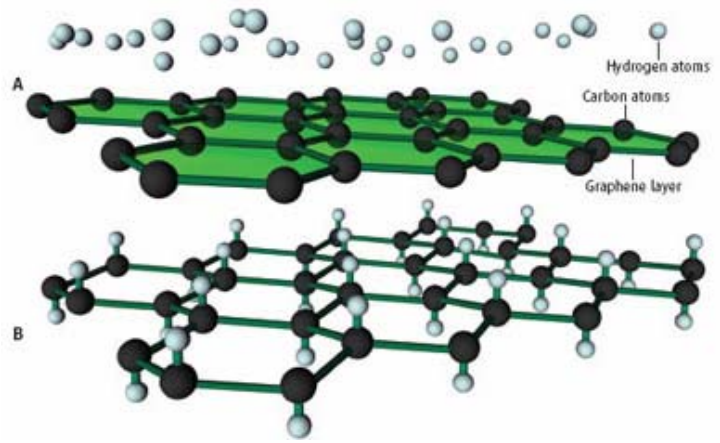
Experimental:

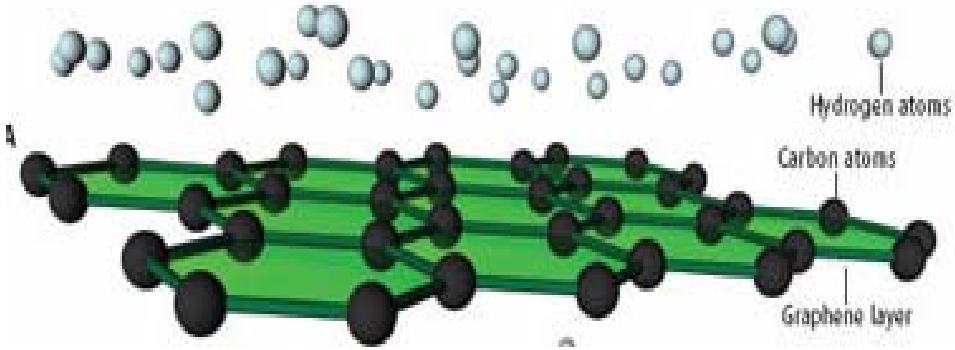


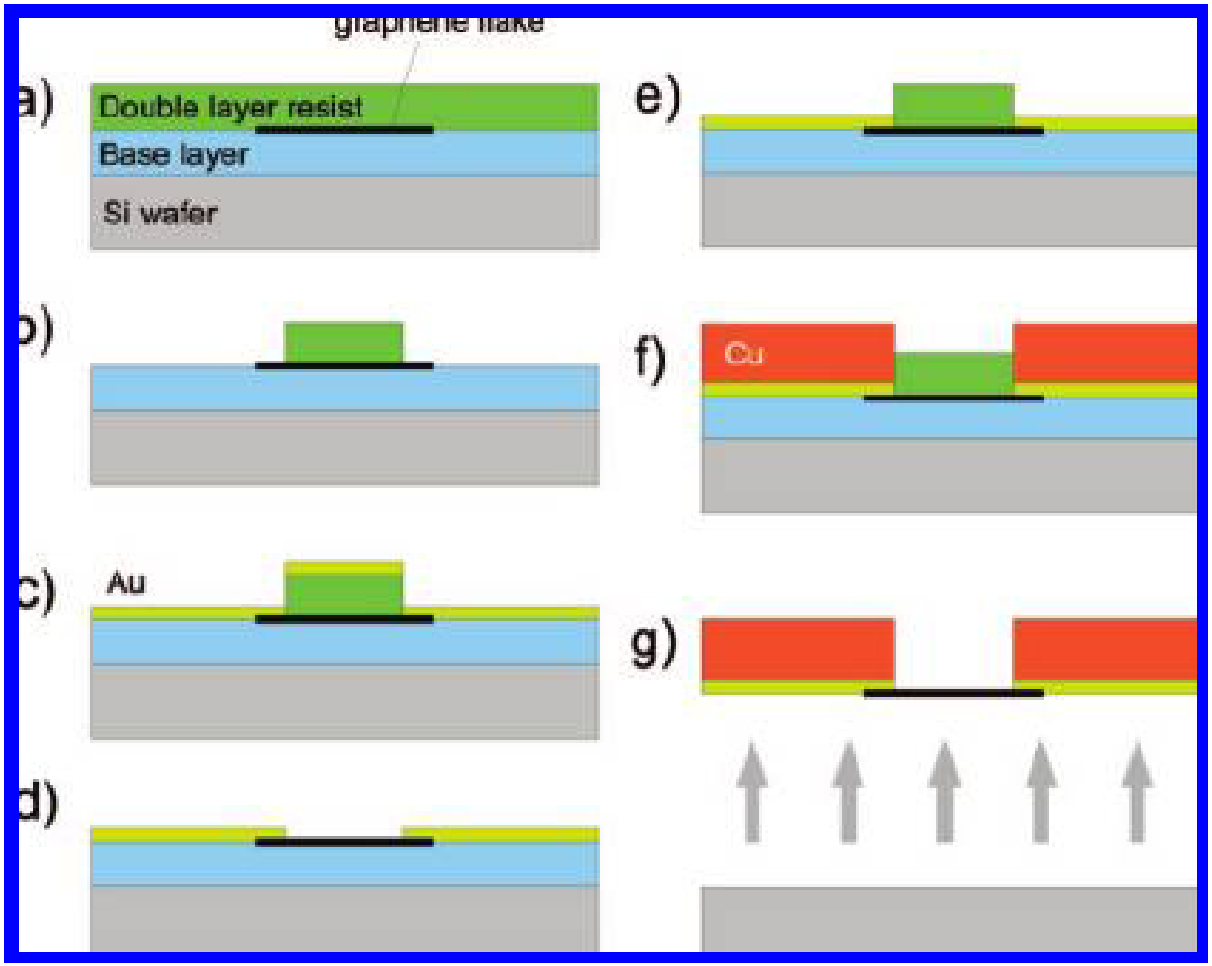
Graphene

Annealing (300°C, Ar, 4 hrs) → **Exposure to cold hydrogen plasma**

(0.1 mbar pressure, 10%H_2:90%Ar mixture, dc plasma ignited between two aluminium electrodes)

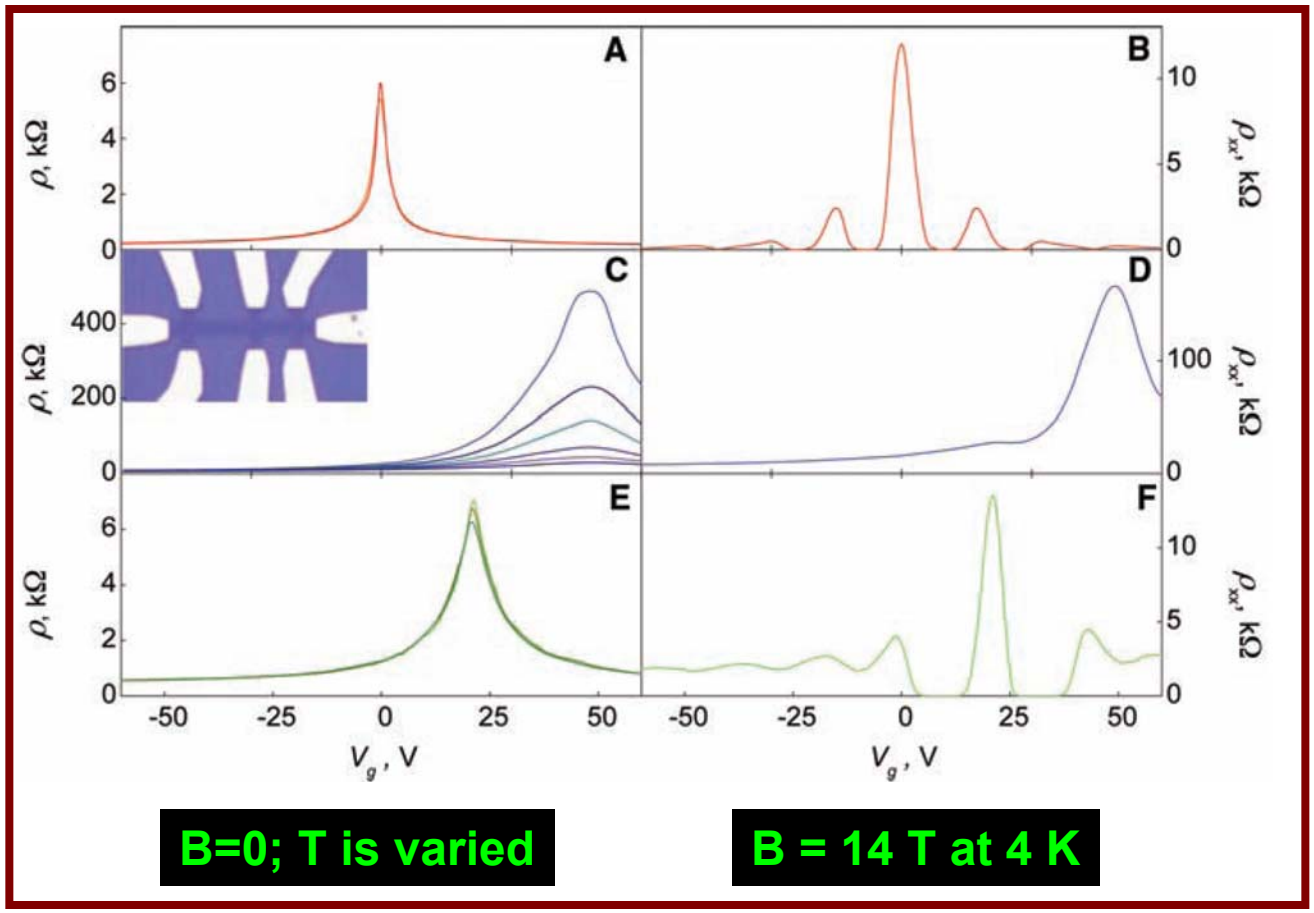
Annealing (450°C, Ar, 24 hrs)





Microfabrication steps used in the production of graphene membranes.

Fig. 1. Control of the electronic properties of graphene by hydrogenation



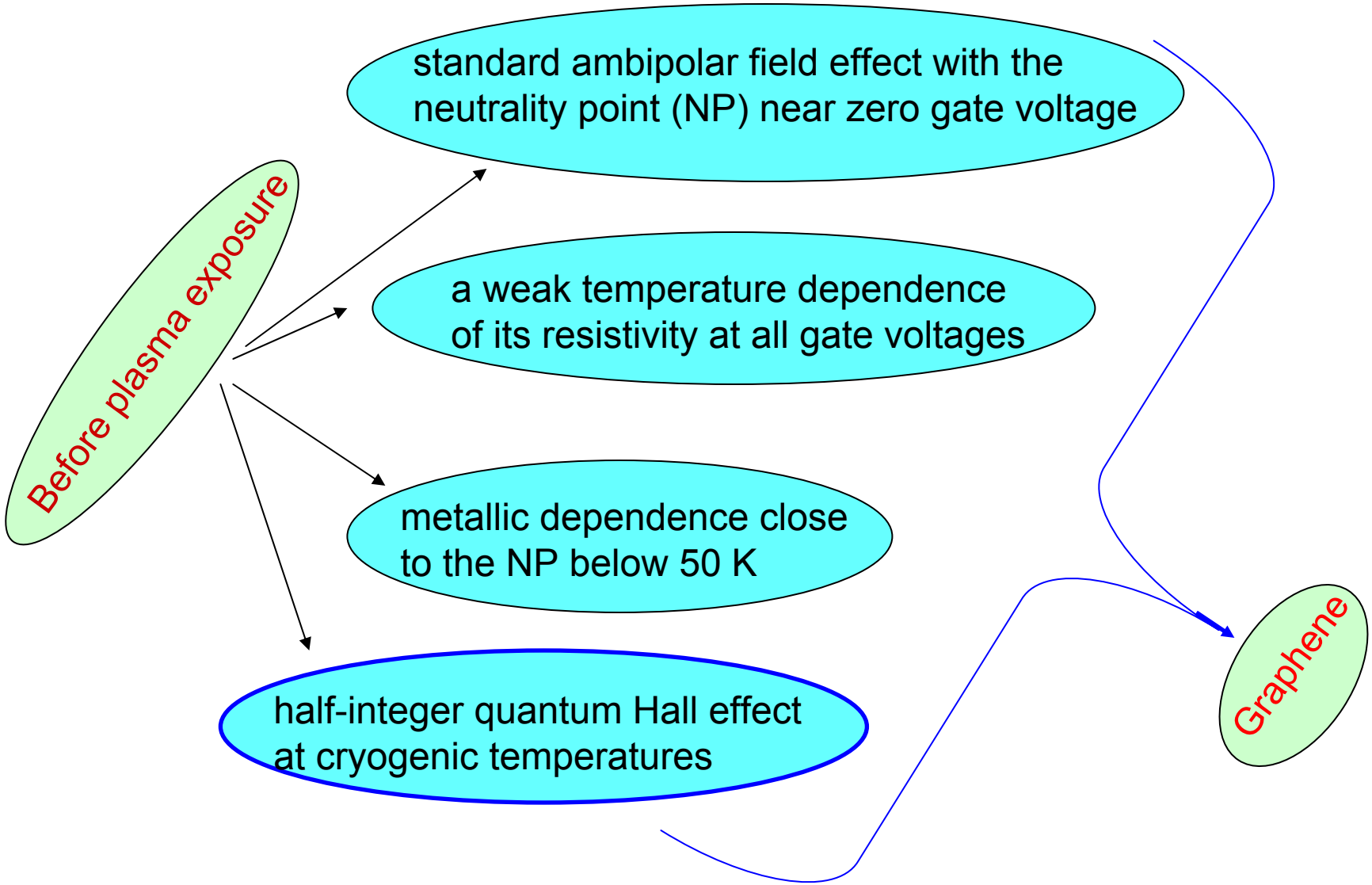
*** **(A and B)** : ***The sample before its exposure to atomic hydrogen; curves in* (A) *for three temperatures (40, 80,and 160 K) practically coincide*.**

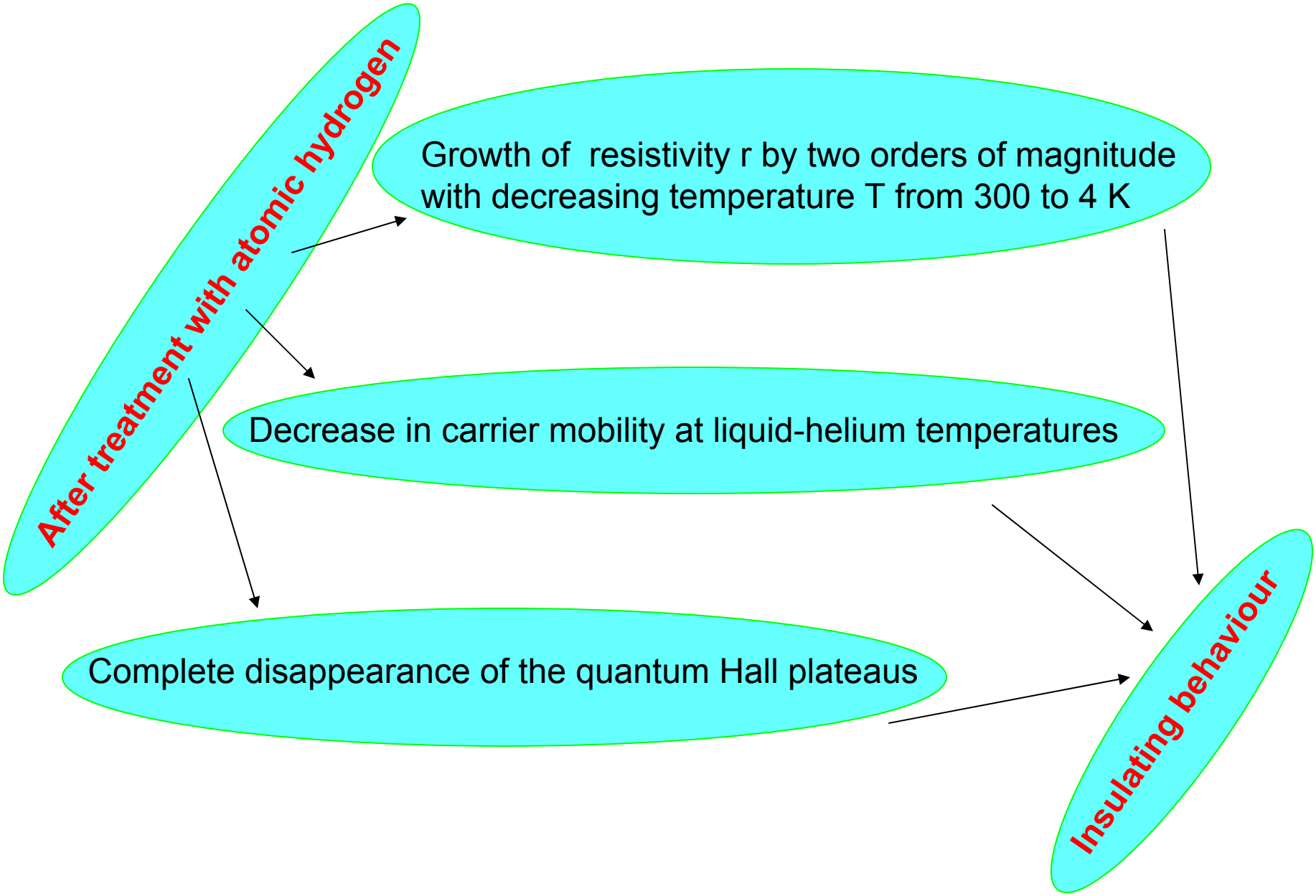
*** **(C and D)** : ***After atomic hydrogen treatment. In* (C), *temperature increases from the top; T = 4, 10, 20, 40, 80, and 160 K*.**

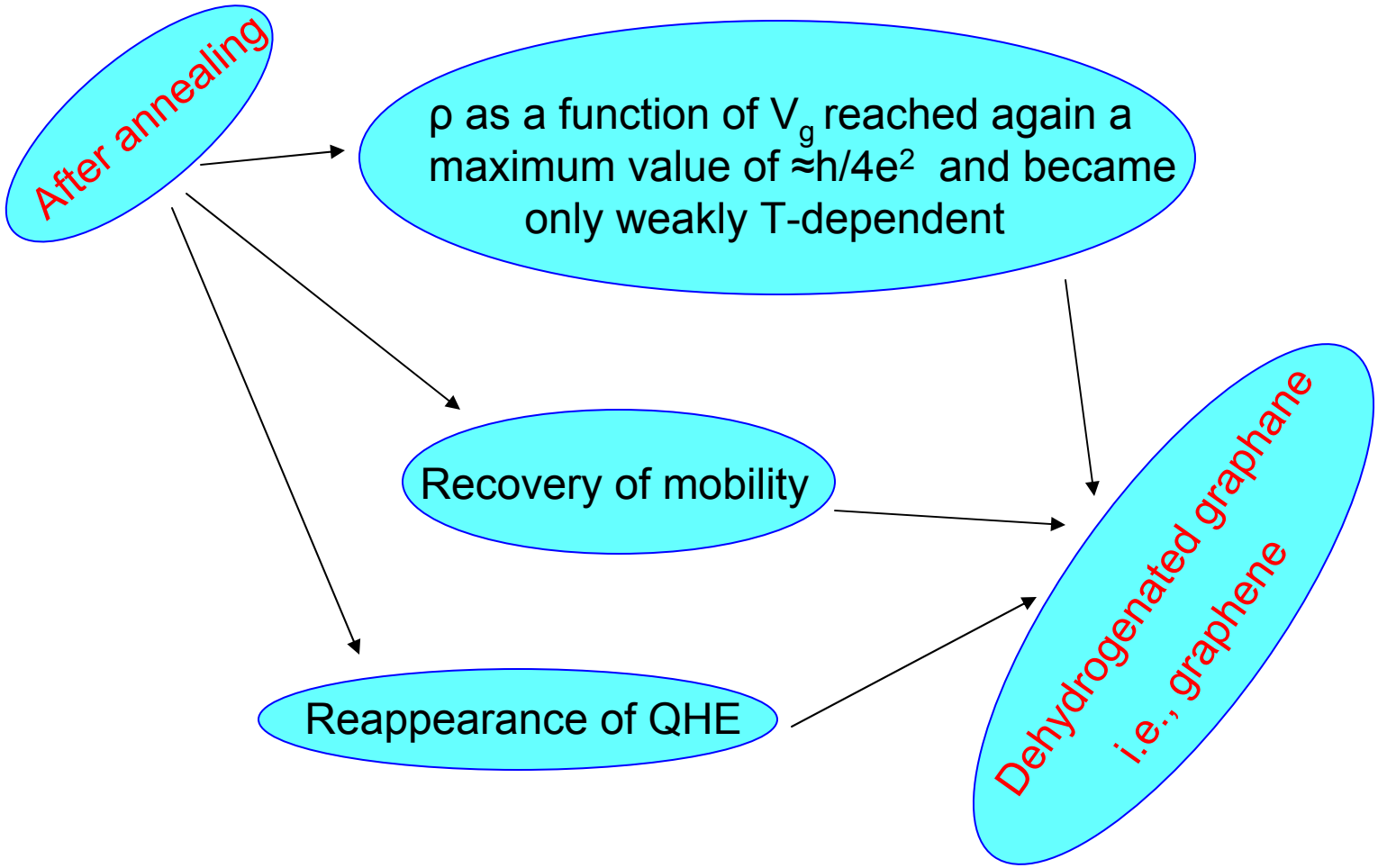
*** **(E and F)** : ***The same sample after annealing.* (E) *T = 40, 80, and 160 K, from top to bottom*.**

*** **(Inset)** ***Optical micrograph of a typical Hall bar device*.**

*** ***The scale is given by its width of 1 mm*.**


Before plasma exposure
standard ambipolar field effect with the neutrality point (NP) near zero gate voltage
a weak temperature dependence of its resistivity at all gate voltages
metallic dependence close to the NP below 50 K
half-integer quantum Hall effect at cryogenic temperatures
Graphene


After treatment with atomic hydrogen
Growth of resistivity r by two orders of magnitude with decreasing temperature T from 300 to 4 K
Decrease in carrier mobility at liquid-helium temperatures
Complete disappearance of the quantum Hall plateaus
Insulating behaviour


After annealing
ρ as a function of V_g reached again a maximum value of ≈h/4e² and became only weakly T-dependent
Recovery of mobility
Reappearance of QHE
Dehydrogenated graphane i.e., graphene

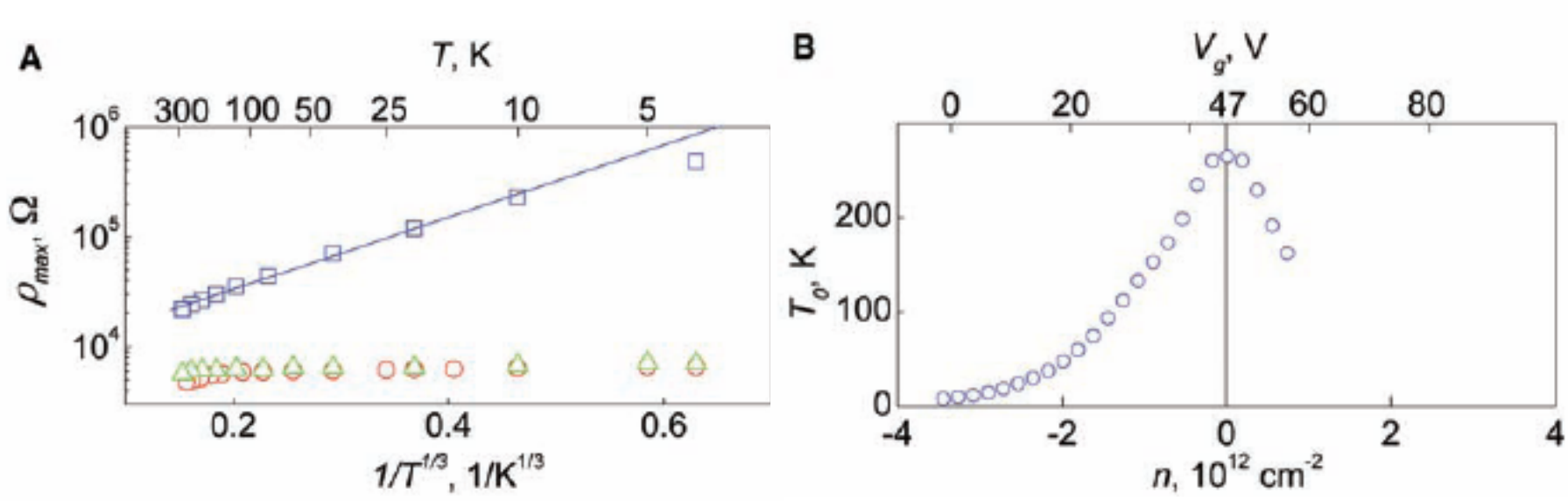
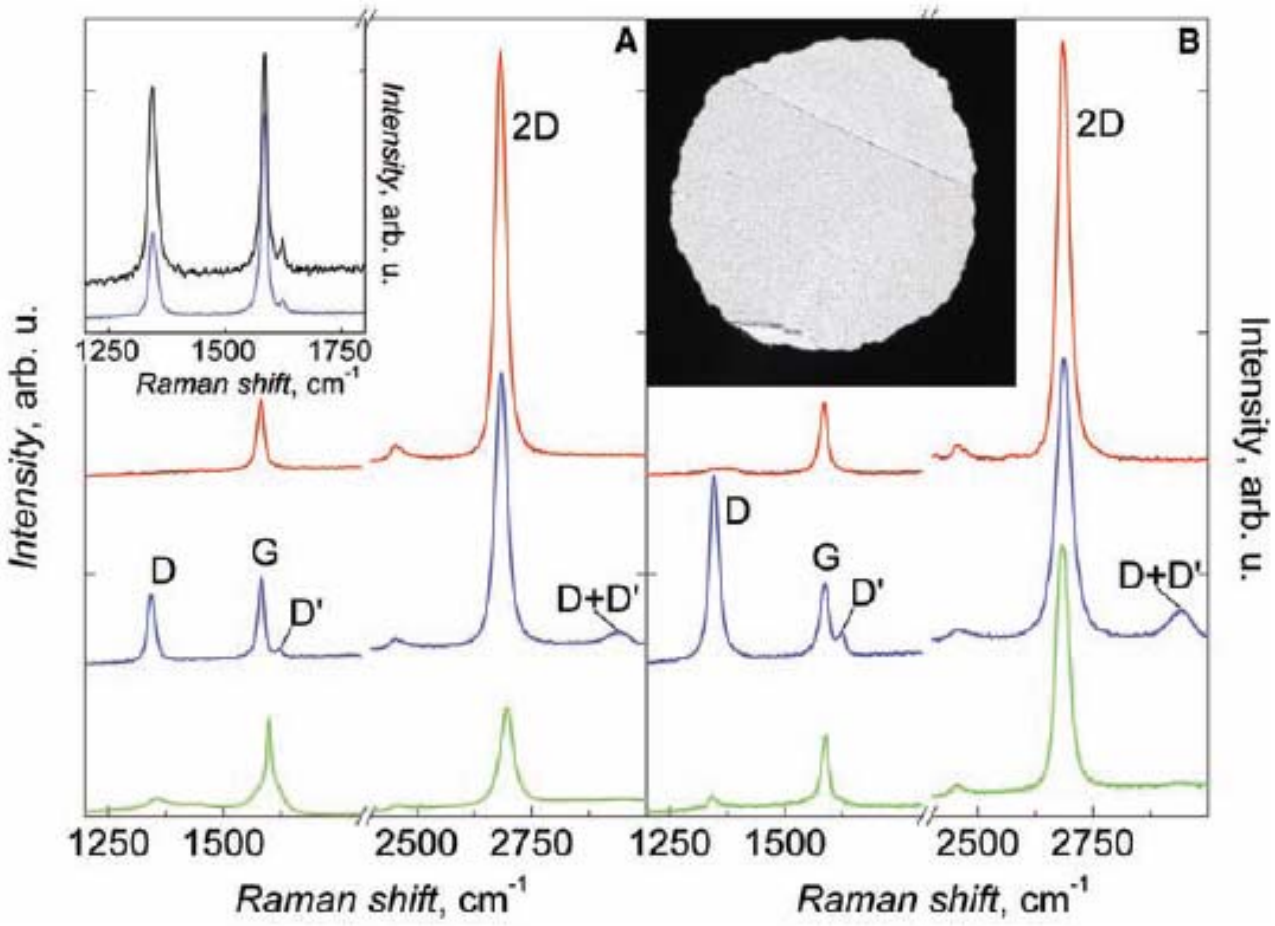


Fig. 2. Metal-insulator transition in hydrogenated graphene. **(A)** ***Temperature dependence of graphene's resistivity at NP for the sample shown in*** **Fig. 1.** ***Red circles, blue squares, and green triangles are for pristine, hydrogenated, and annealed graphene, respectively. The solid line is 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.***

*** *Carrier concentrations are estimated from the device capacitance and applied gate voltage*

Fig. 3: Changes in Raman spectra of graphene caused by hydrogenation

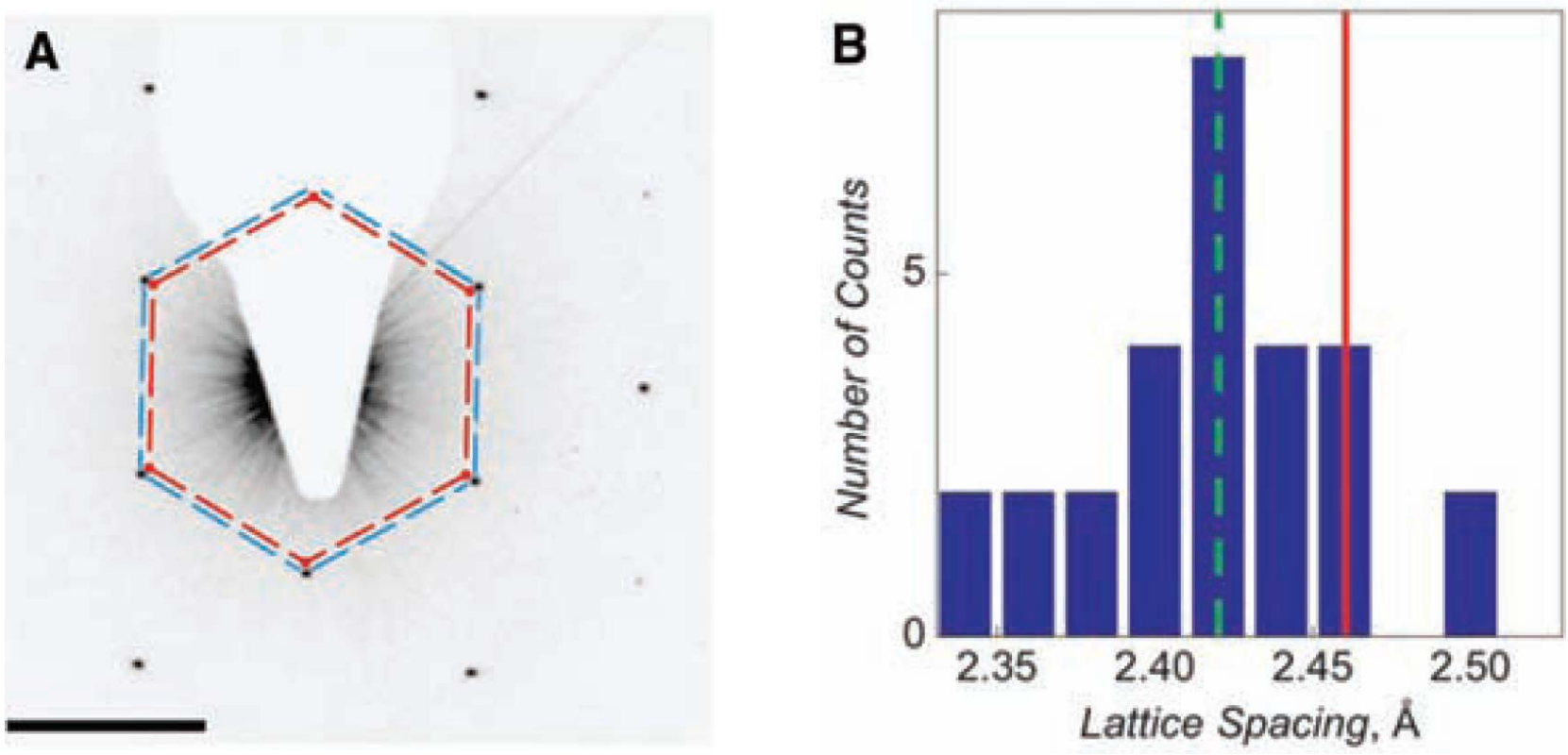


(A) Graphene on SiO_2.
(B) Free standing graphene
Red: Pristine
Blue: Hydrogenated (2 hrs)
Green: Annealed

*Left inset: *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 mm in diameter.*

*The spectra are normalized to have a similar intensity of the G peak. Comparison between the evolution of D and D′ peaks for single- and double sided exposure to atomic hydrogen.

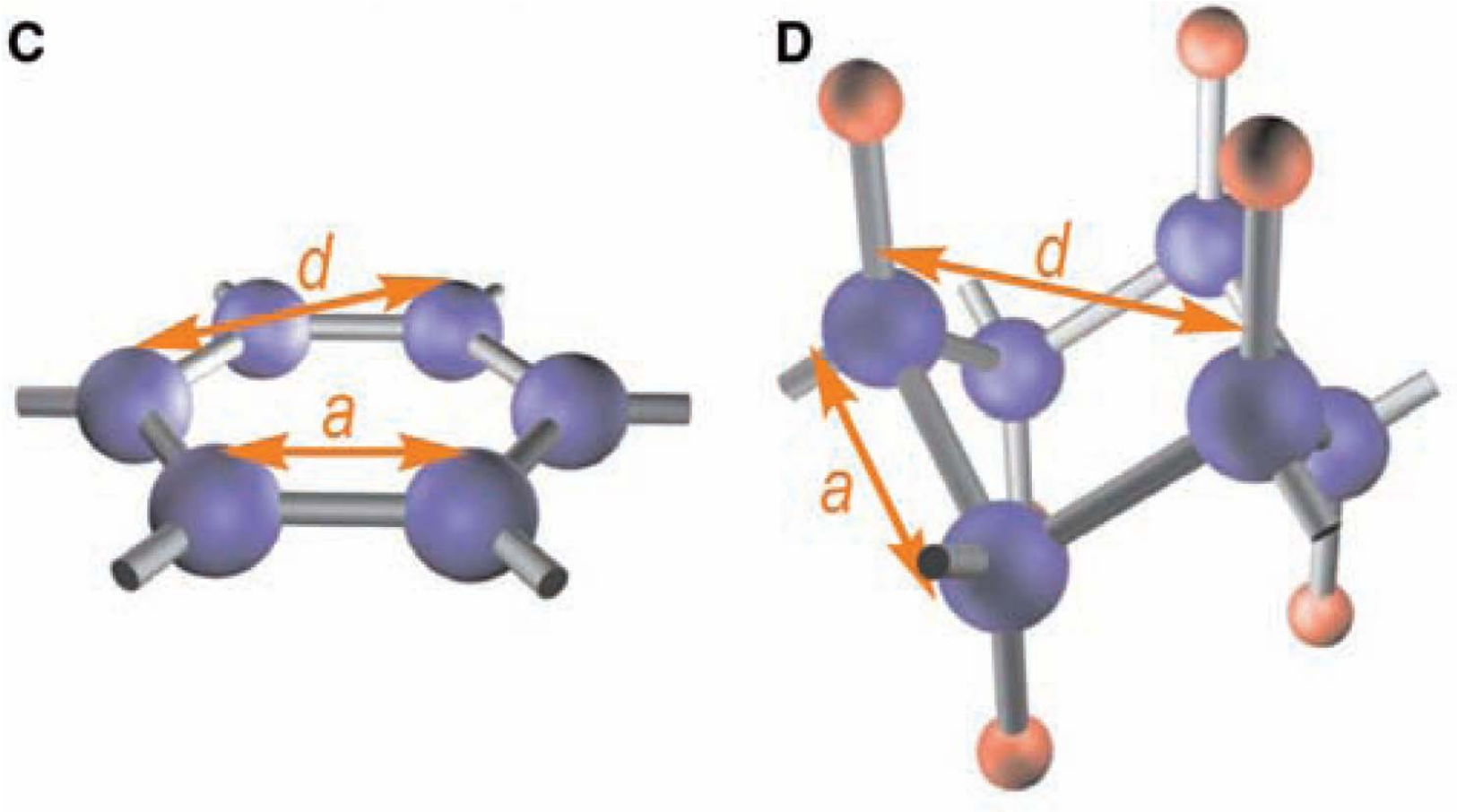
Fig 4: Structural studies of graphane via TEM



(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 graphane. 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).***

Fig 4: Structural studies of graphane via TEM



(C and D):
Schematic representation of the crystal structure of graphene and theoretically predicted graphane.
******Carbon atoms are shown as blue spheres, and hydrogen atoms are shown as red spheres.***

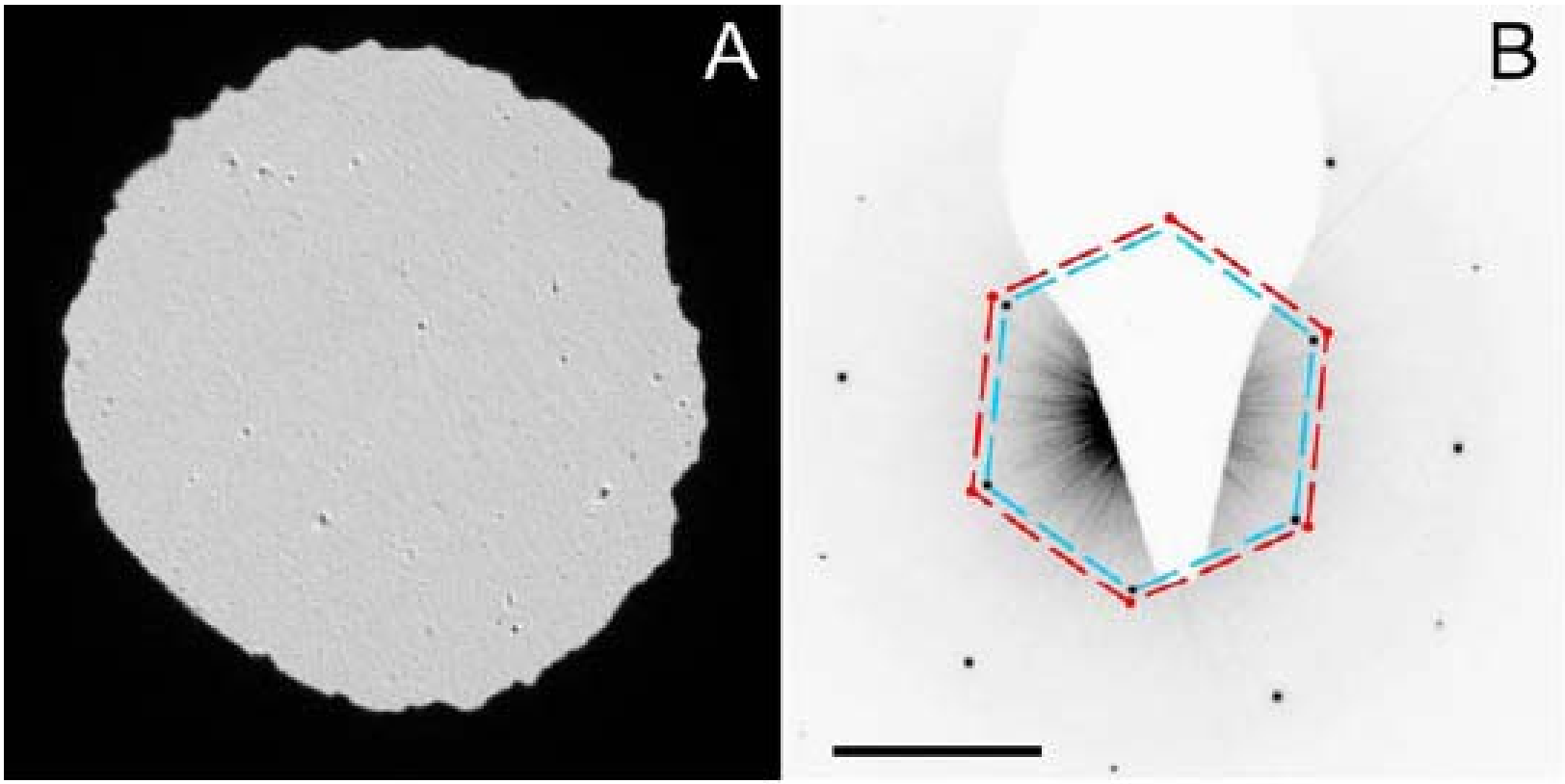


Figure S1. (A) - TEM micrograph of one of our graphene membranes without free boundaries. The presence of a graphene crystal covering the whole aperture is evidenced only by some particulate in the image. (B) - Changes in the lattice constant after extended exposure of this membrane to atomic hydrogen. The scale bar is 5 nm^{-1}. The diffraction pattern is for an unusual case of a region with a strongly stretched lattice (d ≈2.69 Å). The beam diameter used for selected area electron diffraction is 0.3 μm. 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.

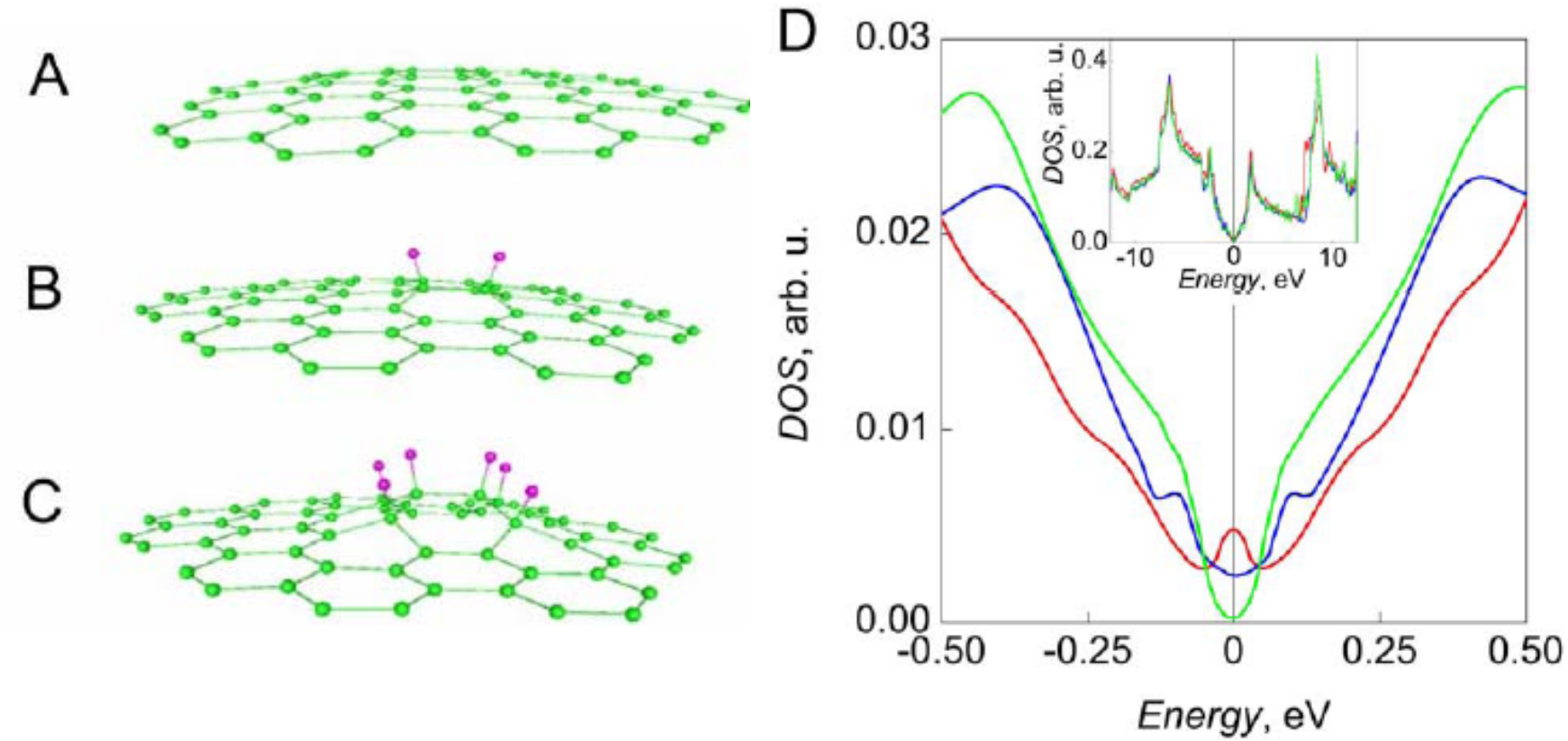


Figure S2. Convex graphene sheet with none (A), two (B) and six (C) hydrogen atoms adsorbed. Atomic coordinates for (B) and (C) were optimized using density functional calculations with the SIESTA code. Configuration (A) was deduced from (B) by removing hydrogen atoms and eliminating the excess displacement 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.

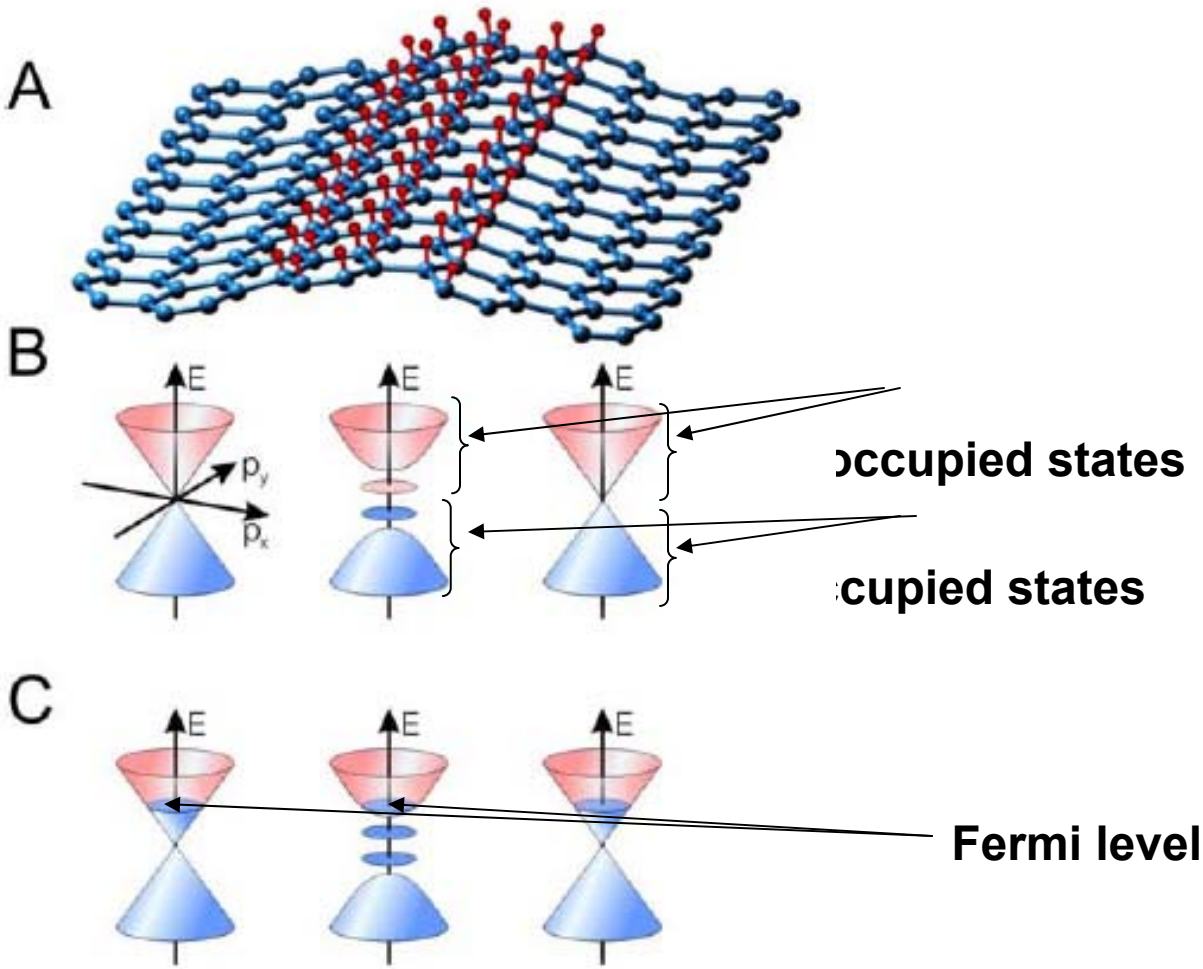


Figure S3. Metal-insulator transition in the disordered graphene derivative obtained by single sided hydrogenation. (A) – Two-phase model for this derivative: hydrogenated convex regions are adjoined by non-hydrogenated concave ones. Blue (red) spheres represent the carbon (hydrogen) atoms. (B) – Schematic 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 localise 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 conductance band in the hydrogenated region.

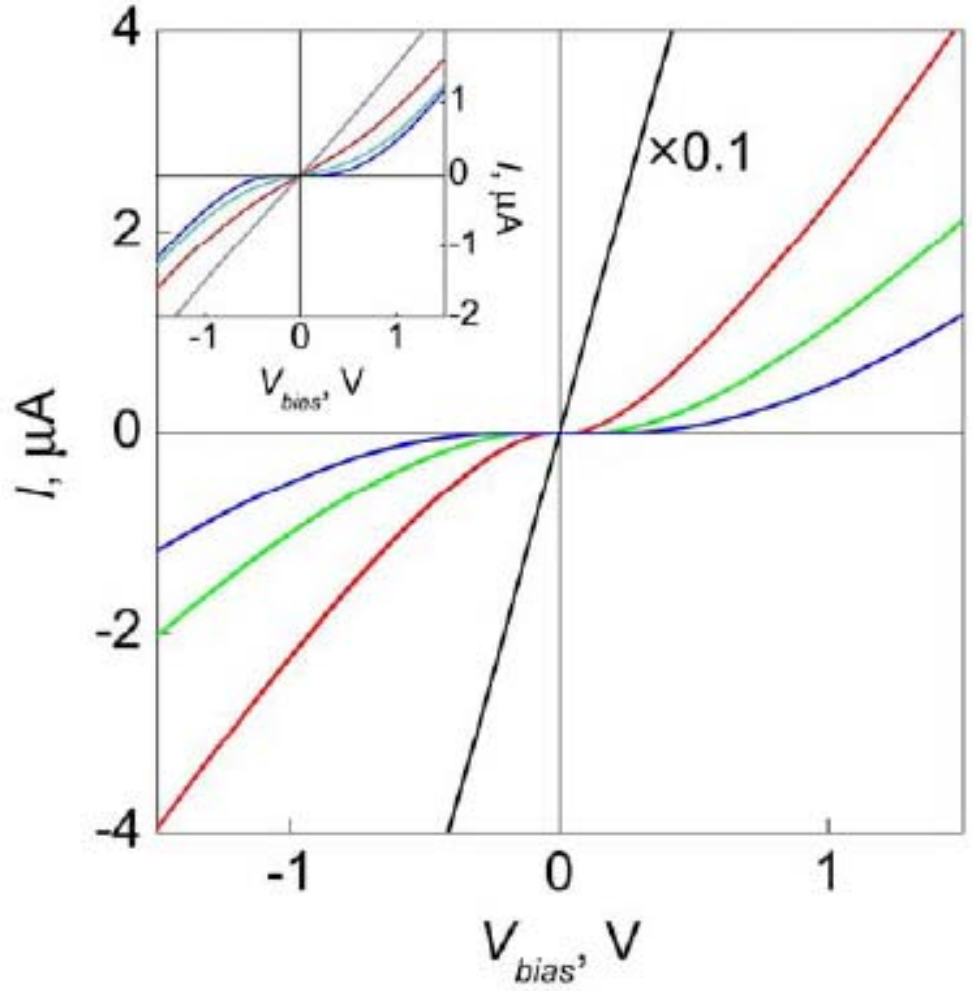


Figure S4. I-V characteristics of a hydrogenated graphene sample; T=2.5K. The blue curve is taken at the neutrality point (Vg = 47V); green – at a hole concentration of ≈1.5×1012 cm^{-2}; red – hole concentration ≈3×1012 cm^{-2} (carrier concentrations are estimated from the device capacitance and applied gate voltage). The black curve is for the hydrogenated device after its thermal annealing at the neutrality point. 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 = 2.5K; 40K; 80K; 160K.

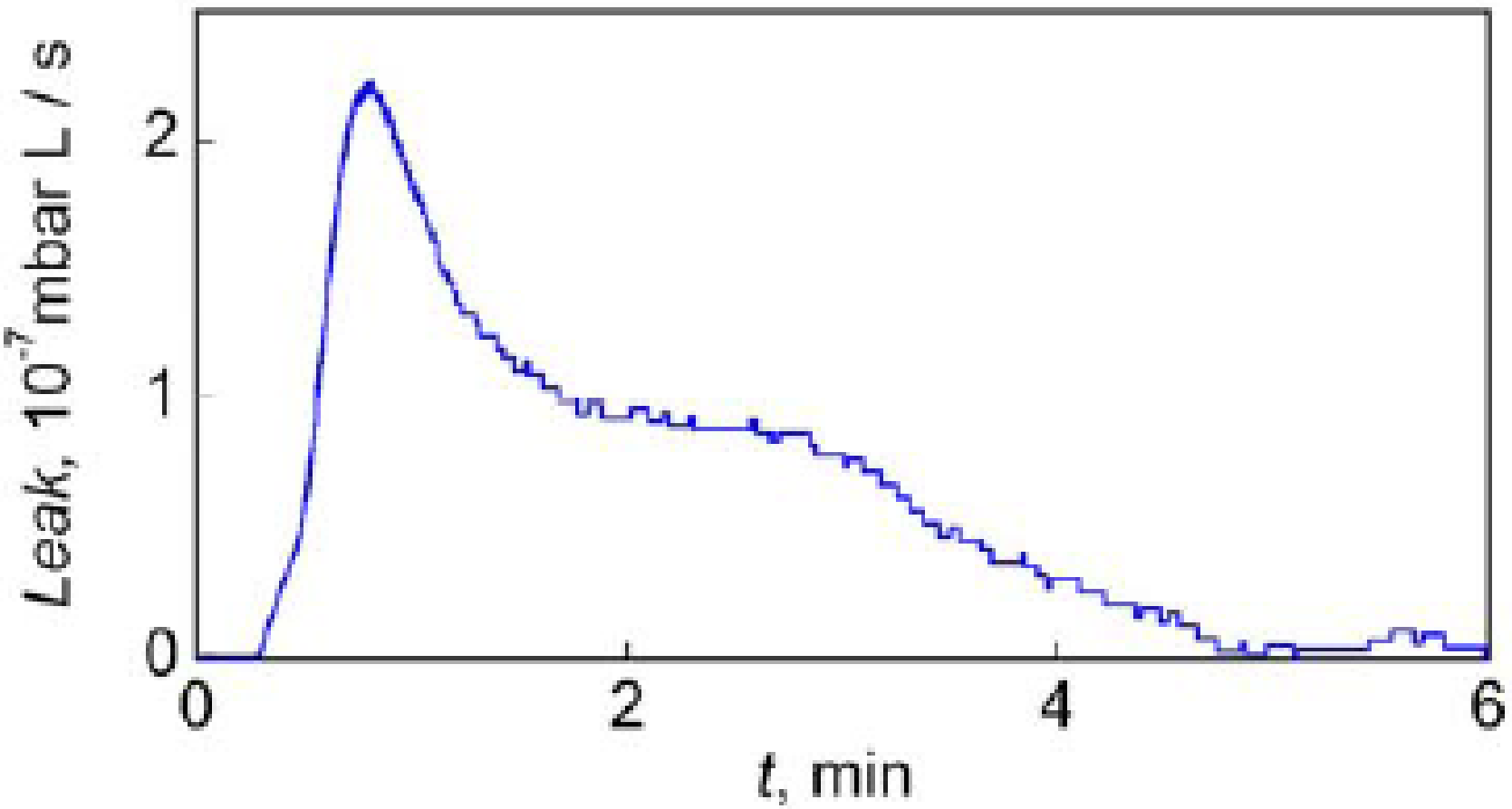


Figure S5. Desorption of hydrogen from single-sided graphane. The measurements were done by using a leak detector tuned to sense molecular hydrogen. The sample was heated to 300°C (the heater was switched on at t = 10s). Control samples (exposed to pure argon plasma) exhibited much weaker and featureless response (<5×10-8 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).

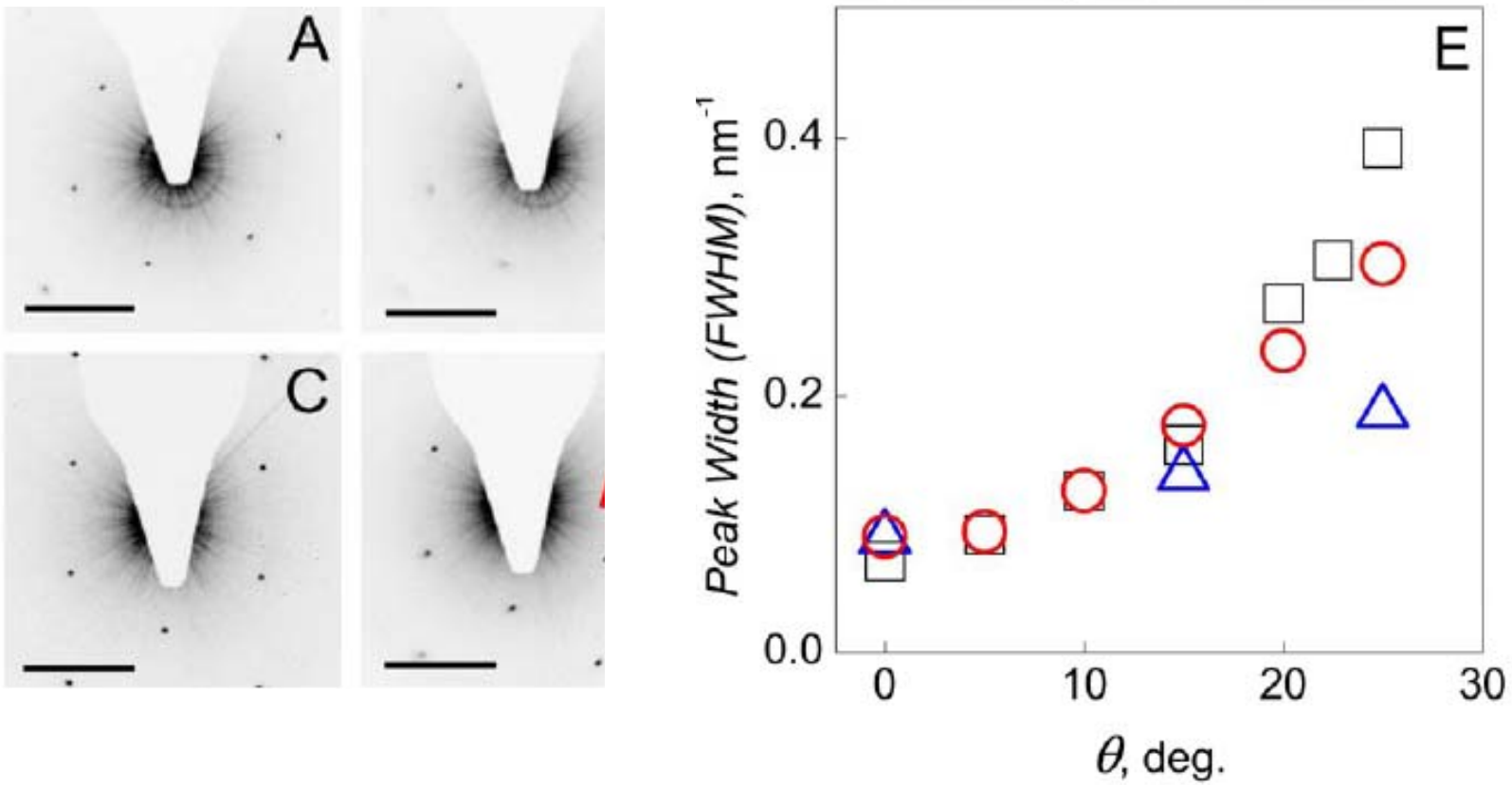


Figure S6. Broadening of (0-110) electron diffraction peaks in graphane. A (B) – Region of hydrogenated graphene with d ≈2.42 Å; tilt angle is 0º (15º). There is strong blurring of the (0- 110) diffraction spot (marked by the red arrow). C (D) – Region with d ≈2.35 Å; tilt angle is again 0º (15º). The 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 ≈2.42 Å; and blue triangles graphane (d ≈2.35 Å).

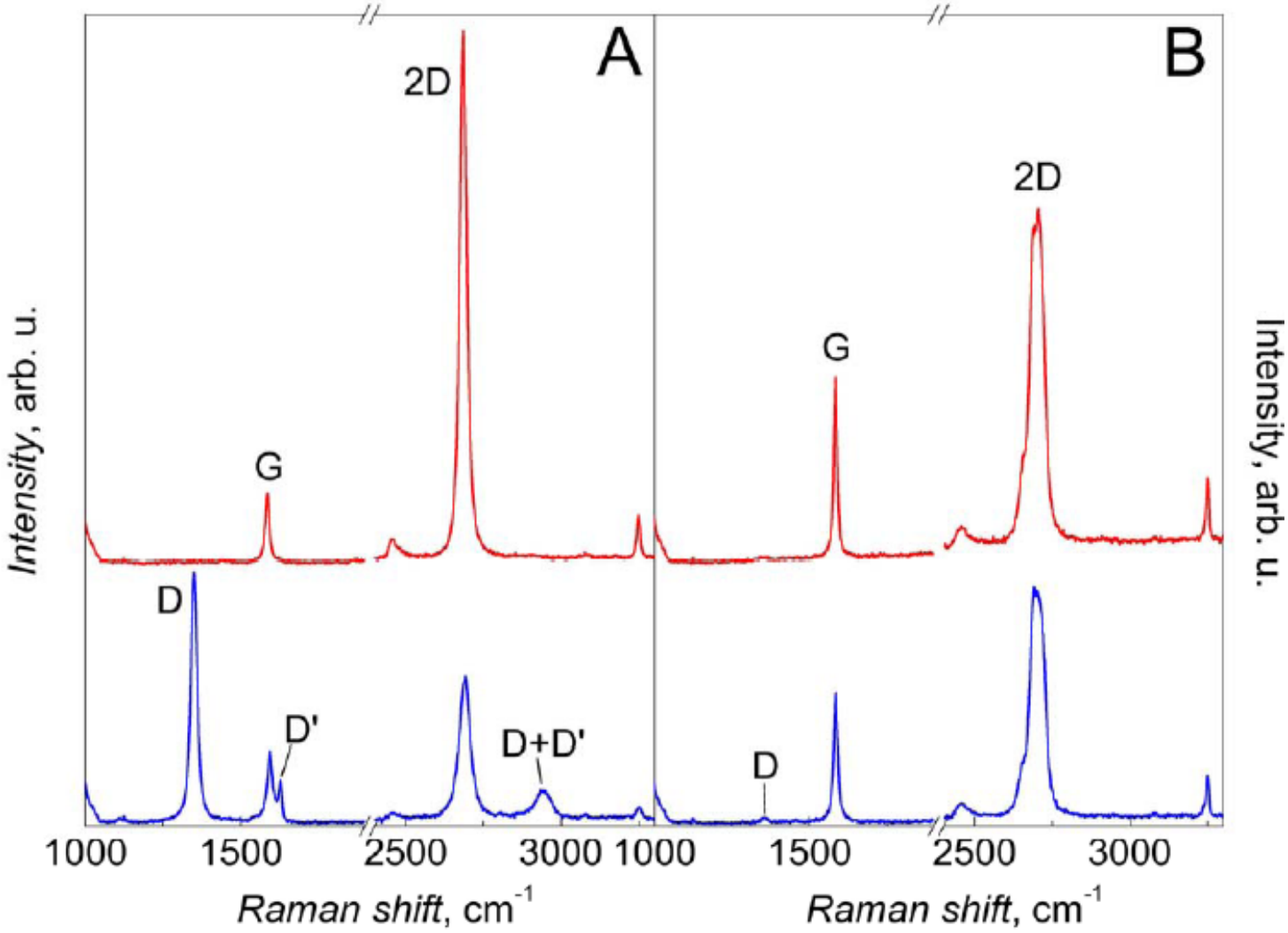


Figure S7. ***Changes in Raman spectra of single-layer*** **(A)** ***and bilayer graphene*** **(B)** ***induced by hydrogenation. Both samples were on the same*** SiO_2***/Si wafer and were hydrogenated simultaneously for 2 hours. Red and blue curves correspond to pristine and hydrogenated samples, respectively.***

Conclusion

***Conversion from conductive graphene to insulating graphane is possible without affecting the crystallinity.
***Graphene hydrogenated in only one side is disordered.

***Conversion of graphene into other giant molecules with a regular structure is possible.