

From graphite to graphene and now to graphane!

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Graphite is an important allotrope of carbon with a crystal structure shown in Figure 1. This structure is composed of layers of hexagonally arranged carbon atoms, with each carbon atom being bonded to three coplanar neighbouring atoms by strong covalent bonds of length 1.42 Å and the distance between planes is 3.35 Å. The interlayer bonds are rather weak, as they are held together by van der Waals type of forces¹.

Graphene, by definition is a single layer of graphite and was prepared first in 2004 by a team of physicists led by Andre Geim² of Manchester University, UK by a simple peeling of the top layer of a highly oriented pyrolytic graphite with a scotch tape (Figure 2). As graphene is a 2D nanomaterial possessing several distinct properties³, it has been recognized as a viable alternative to silicon. Intensive research has been undertaken to evolve simpler and reliable methods to prepare⁴ and process⁵ graphene on a large scale and to exploit it in several technological applications⁶ including gas sensors, energy storage and nanoelectronics. Incidentally, an end-to-end rolled graphene sheet forms the carbon nanotube,

the discovery of which by Iijima⁷ in 1991 has already created an explosion of research in nanotechnology. The chemical functionalization of carbon nanotubes has opened up additional possibilities to exploit them fully in various applications⁸. This gives hope that the chemical modification of graphene can herald another avenue for making new materials with novel properties. Sofo *et al.*⁹ predicted through first-principles total energy calculations that graphene could be fully hydrogenated to form a stable two-dimensional hydrocarbon. They called the new hydrocarbon as graphane and proposed it to have potential applications in hydrogen storage and nanoelectronics. This theoretical prediction has been very quickly translated into reality through the co-operative research efforts of Geim's group¹⁰ at Manchester University with scientists at Cambridge University, UK and Radboud University, The Netherlands. Interestingly, there have been some attempts by various groups to hydrogenate various forms of carbon including graphite and diamond. Also, physisorption and chemisorption of hydrogen on carbon nanotubes have been

studied in the context of hydrogen storage^{11,12}. Now, Geim's group¹⁰ has experimentally demonstrated for the first time that a single layer of graphene can be hydrogenated to graphane which has been until now only a theoretical material. The hydrogenation of graphene was effected by using a cold hydrogen plasma for 2 h. Based on electrical and structural characterization, the formation of graphane was confirmed. In contrast to graphene, graphane exhibited an insulating behaviour such that the resistivity grew by two orders of magnitude when the temperature was decreased from 300 to 4 K. The observed temperature dependencies of resistivity of graphane could be fitted to a variable-range hopping model. The carrier mobility changed from $14,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ down to values of nearly $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at liquid-helium temperatures. The quantum Hall plateaus completely disappeared with only weak signatures of Shubnikov-de Haas oscillation remaining in a magnetic field of 14 T. Graphene's ambipolar field effect with the neutrality point near zero-gate-voltage has not been observed after its hydrogenation. Graphane was found to

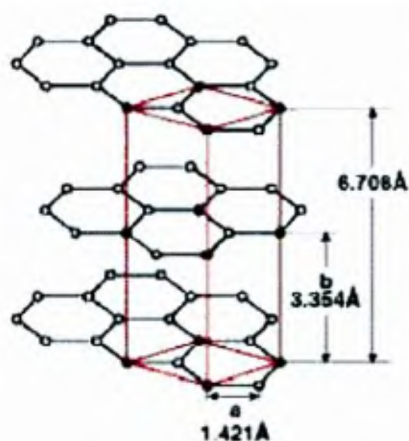


Figure 1. Crystal structure of graphite.



Figure 2. Extracting graphene from graphite.

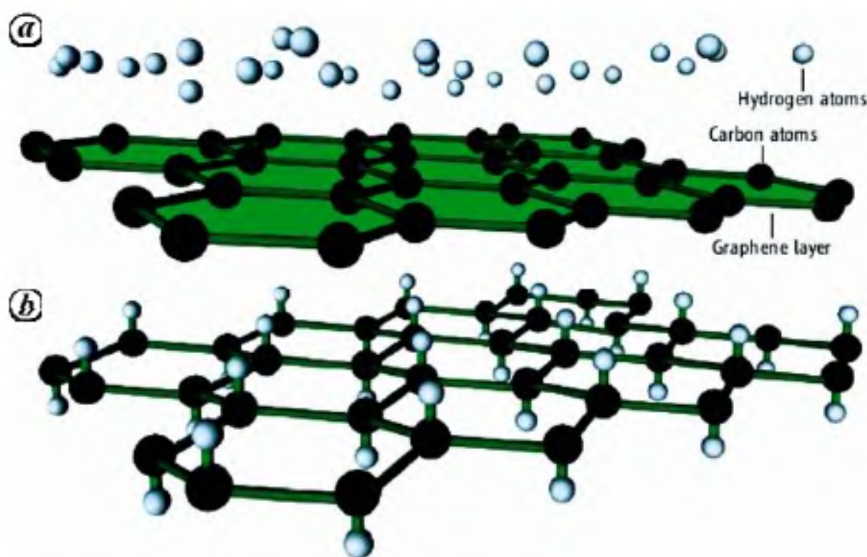


Figure 3. Graphene hydrogenation. **a**, A graphene layer, where delocalized electrons are free to move between carbon atoms, is exposed to a beam of hydrogen atoms. **b**, In non-conductive graphane, the hydrogen atoms bond their electrons with electrons of carbon atoms and pull the atoms out of the plane (from Savchenko¹⁴). Reprinted with permission from AAAS.

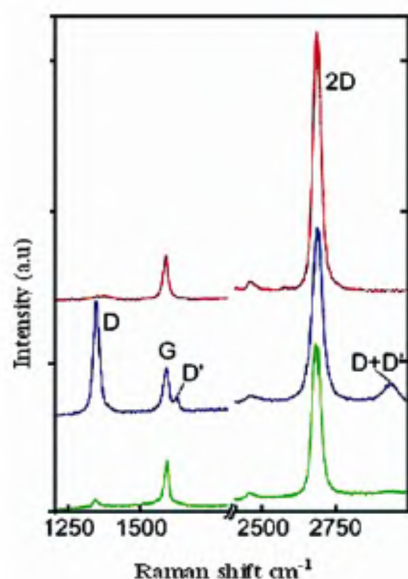


Figure 4. Raman spectra of pristine (red line), hydrogenated (blue line) and annealed samples (green line). From Elias *et al.*¹⁰. Reprinted with permission from AAAS.

be stable at room temperature for many days and could be reconverted to graphene by annealing at 450°C in Ar atmosphere for 24 h, albeit the carrier mobility could be recovered to only about 3500 cm² V⁻¹ s⁻¹. The electrical measurements revealed the presence of short-range scatterers which were attributed to vacancies induced by plasma damage or residual oxygen during annealing.

The electron-diffraction pattern of graphane indicated that hydrogenation of graphene did not change the hexagonal symmetry and hence crystallinity, but resulted in a drastic decrease of lattice constant by about 5%. The C–C bond length in graphane could be expected to be higher than the value of 1.42 Å in graphene due to a change in the carbon hybridization from *sp*² to *sp*³. A recent theoretical prediction indicated a value of 1.53 Å for C–C bond length in graphane¹³. But the observed lower lattice constant implied the presence of either shorter or stronger buckled C–C bonds. Geim's paper¹⁰ suggested that the grap-

hane might exhibit a more complex hydrogen bonding. The TEM results indicated that unlike the planar graphene, graphane can have a puckered structure¹⁴ (Figure 3). After all, graphane is composed of fused cyclohexanes which do exist in a puckered chair conformation.

Clear identification of the structural differences among the pristine graphene, its hydrogenated product and the annealed samples was successfully accomplished by Raman spectroscopy. The Raman spectra of the three samples shown in Figure 4 clearly indicate distinct features. The G peak corresponds to optical E_{2g} phonons and D peak is caused by breathing-like modes¹⁰. The intensity of D peak is a measure for the amount of disorder in graphene. The Raman spectrum of graphene (red line) was typical of a defect-free monolayer. Hydrogenation of graphene (blue line) led to the appearance of additional peaks viz. D, D' and D + D', along with simultaneous broadening and reduction in intensity of the 2D and G peaks. The activation of the sharp D peak was attributed to breaking of the translational symmetry of C–C *sp*² bonds. After annealing, the defect-related D peaks were strongly suppressed (green line).

Another interesting result of the study is that, unlike the free-standing graphene, hydrogenation of graphene supported on a SiO₂ substrate led to only a disordered material. Due to lack of diffusion of hydrogen along the grapheme–SiO₂ interface, only one side of graphene which was directly exposed to hydrogen plasma became hydrogenated.

The successful production of high-quality crystals of graphane from graphene indeed opens a new way of making many other ultra-thin crystalline materials based on graphene. The most striking feature is that the semi-metal graphene is transformed into an insulator, graphane. This astounding change in the electronic property of graphene on the addition of hydrogen has fuelled the idea of fine tuning its electronic properties by attaching various atoms and groups to its scaffolding. Therefore, the dream of fabricating nano-scale transistors from graphene

wafer with all interconnects made from highly conductive, pristine graphene while other parts are modified chemically to produce semiconductors can be realized. In short, the transistor will contain only graphitic materials, providing thus a new light after the anticipated end of silicon era. Another great anticipation of the hydrogenation experiment of graphene is that graphane due to its low mass and large surface area can be an ideal material for hydrogen storage.

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