



GRAPHENE: MATERIALS IN THE FLATLAND

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by

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GRAPHENE AND ITS UNUSUAL PROPERTIES

Graphene is a two-dimensional (2D) atomic crystal which consists of carbon atoms arranged in a hexagonal lattice (Fig. 1).

researchers from a myriad of different backgrounds. It is the first example of 2D atomic crystals, whose properties from the thermodynamics point of view are significantly different from those of 3D objects. It is also a novel electronic system with unprecedented characteristics [4]. It can be thought of as a giant molecule which is available for chemical modification [5-6] and is promising for applications [7-8] ranging from electronics [7-9] to composite materials [8, 10-11]. These factors allow for true multi- and cross-disciplinary research.

As it is not possible to give a comprehensive overview of all of graphene's properties in one lecture, I will limit myself to just three, which, in my opinion, give the best possible impression of graphene: (i) it is the first example of 2D atomic crystals, (ii) it demonstrates unique electronic properties, thanks to charge carriers which mimic massless relativistic particles, and (iii) it has promise for a number of applications.

Graphene creation

The simplest implementation of this method for graphitic materials is to use bulk graphite and exfoliate it into individual planes. Graphite is a layered material and can be considered as a stack of individual graphene layers. High-quality graphite typically requires growth temperatures of above 3000K, but exfoliation can be done at room temperatures – an order of magnitude lower than the growth temperatures.

There are also well-known graphene-growing recipes from surface science. Catalytic cracking of hydrocarbons, or precipitation of dissolved carbon on a metal surface with subsequent graphitisation, has long been known to produce high-quality graphene layers [50-57]. A similar process is the graphitisation of excess carbon atoms after sublimation of silicon from the surface of silicon carbide [58-59]. One should note that it is also true in these cases that graphene must be a part of the 3D structure, as the underlying substrate aids in quenching the diverging fluctuations at high temperatures.

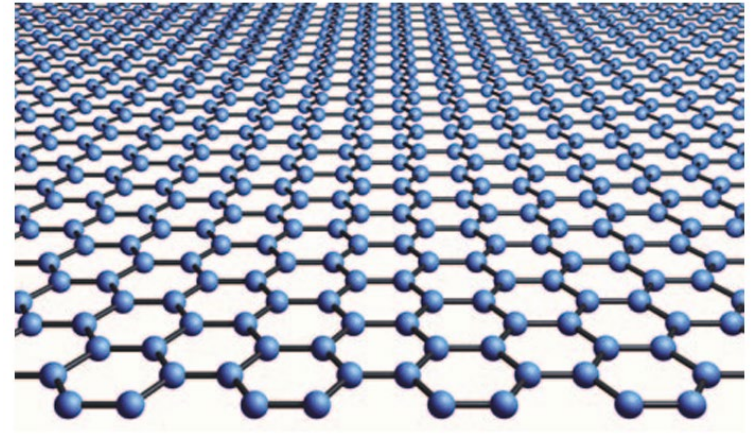


Figure 1. The crystal structure of graphene – carbon atoms arranged in a honeycomb lattice.

Carbon atoms in graphene are sp^2 -hybridised, meaning that only three electrons form the strong σ -bonds and the fourth has a communal use forming the so-called π -bonds. So, graphene is a zero-overlap semimetal and conducts electricity very well (in contrast to diamond, where each carbon atom is in versatility of carbon atoms, then, gives us an idea of how to create novel 2D crystals: one can attach something to carbon atoms, creating a new material with a different chemical composition and exciting properties.

A wide variety of chemicals can be attached to graphene. So far only two crystallographically-ordered chemical modifications of graphene have been predicted and achieved: graphane (when one hydrogen atom is attached to each of the carbon atoms) [64–65] and fluorographene (Fig. 5) [66–69]. Both derivatives are insulators (exhibiting large band-gaps) of very high crystallographic quality and very stable at ambient temperatures (though it should be mentioned that fluorographene generally exhibits more robust properties, probably due to stronger C-F bonding in comparison to C-H). Graphane and fluorographene open the floodgates for the chemical modification of graphene and for the appearance of novel two-dimensional atomic crystals with predetermined properties. It would be interesting to see other

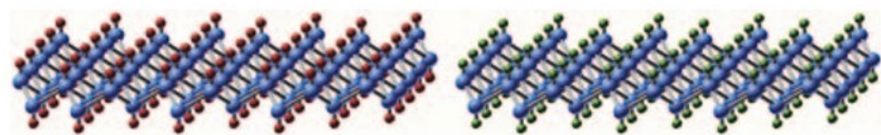


Figure 5. Chemically modified graphene. One can add different species (like hydrogen or fluorine) to graphene scaffolding. Carbon atoms are represented by blue spheres.

Effect of mechanical deformation

wells in GaAs/AlGaAs heterostructures. Graphene is a truly 2D atomic crystal as well as having electronic properties as in 2D. Essentially the thinnest possible fabric, it can be easily deformed mechanically and can be stretched [12, 17, 112–116], compressed [117], folded [80, 118], rippled [119] – even torn into pieces [120]. Needless to say, each of these mechanical manipulations would result in strong changes to the electronic structure [121–123].

Graphene optics

Can one expect anything interesting from the optical properties of graphene? Rather counterintuitively, despite being only one atom thick, graphene absorbs quite a large fraction of light. In the infrared limit the absorption coefficient is exactly $\pi a \approx 2.3\%$ (where $a = e^2/\hbar c$ is the fine structure constant), and the corrections to this number in the visible range of the spectrum are less than 3% [131–134]. Such a significant absorption coefficient makes it possible to see graphene without the use of a microscope; thus, one can

Bilayer graphene

Although the addition of one layer on top of graphene is all that is needed to arrive at bilayer graphene, the properties of the latter are not simply twice those of the monolayer crystal; this is one of those cases where ‘one plus one is greater than two’. Bilayer graphene is remarkably different – sometimes even richer in its properties than its monolayer cousin – and fully deserves to be called a different material in its own right.

Two graphene layers, when placed together, do not like to lie exactly one on top of each other with each atom having a counterpart in the adjacent layer (unlike boron-nitride, which does exactly that). Instead, bilayer graphene is mostly found [78] in so-called A–B or Bernal stacking [138] (named after the crystallography, who determined the structure of graphite in 1924). In such an arrangement, only half of the carbon atoms have a neighbour in another layer and the other half do not (and so are projected right into the middle of

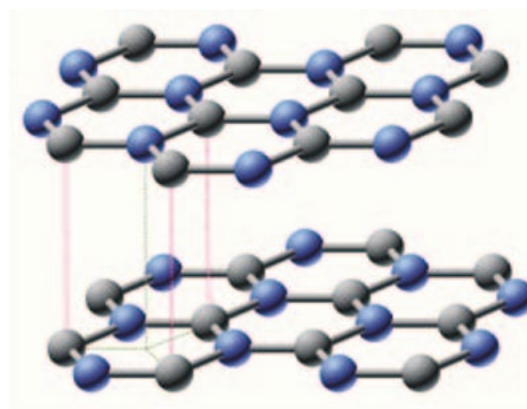


Figure 9. Crystal structure of bilayer graphene.

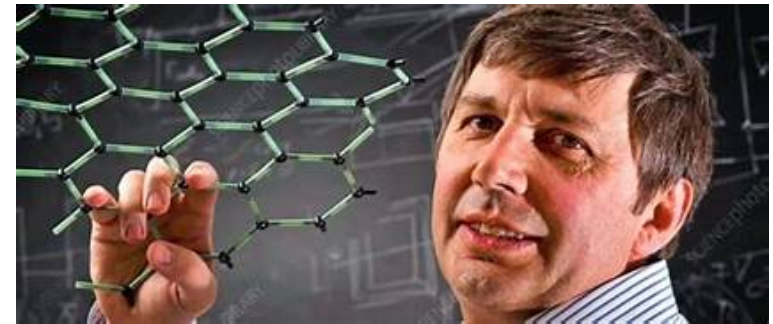
GRAPHENE APPLICATIONS

The fact that one of the first practical uses of this material was not in a high-expectation, predictable field like transistors or photonics, but instead in the entertainment industry indicates its great potential and versatility. Indeed, in graphene we have a unique combination of properties, which are not seen together anywhere else: conductivity and transparency, mechanical strength and elasticity.

Graphene is an ultimately thin, ultimately conductive, ultimately mechanically strong and crystallographically ordered material, and it would be strongly beneficial to use it as a support for nano-objects when observing them in TEM. Its mechanical strength provides rigidity and ease in sample preparation, and it has a very high radiation damage threshold (in the order of 80 keV). High conductivity eliminates the problem of charging of the support. As it is only one atom thick (and also made of a very light element), graphene ensures the highest possible contrast (one can only go higher in contrast if suspending the object).

Graphene composites

The unique combination of graphene's electronic, chemical, mechanical and optical properties can be utilised in full in composite materials. It is also relatively easy to prepare graphene for such an application: one can either use the direct chemical exfoliation of graphene [48–49], which allows a rather high yield of graphene flakes in a number of organic solvents or go through an oxidation process to prepare graphite oxide – which can be easily exfoliated in water – with subsequent reduction in a number of reducing media [10].



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Konstantin Novoselov in his lab

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