

## The 2010 Nobel Prize in physics—ground-breaking experiments on graphene

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2011 J. Phys. D: Appl. Phys. 44 473001

(<http://iopscience.iop.org/0022-3727/44/47/473001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 82.132.249.50

The article was downloaded on 28/11/2011 at 16:00

Please note that [terms and conditions apply](#).

## TOPICAL REVIEW

# The 2010 Nobel Prize in physics—ground-breaking experiments on graphene

**Y Hancock**

Department of Physics, The University of York, YO10 5DD, UK

E-mail: [y.hancock@york.ac.uk](mailto:y.hancock@york.ac.uk)

Received 23 August 2011, in final form 4 October 2011

Published 4 November 2011

Online at [stacks.iop.org/JPhysD/44/473001](http://stacks.iop.org/JPhysD/44/473001)**Abstract**

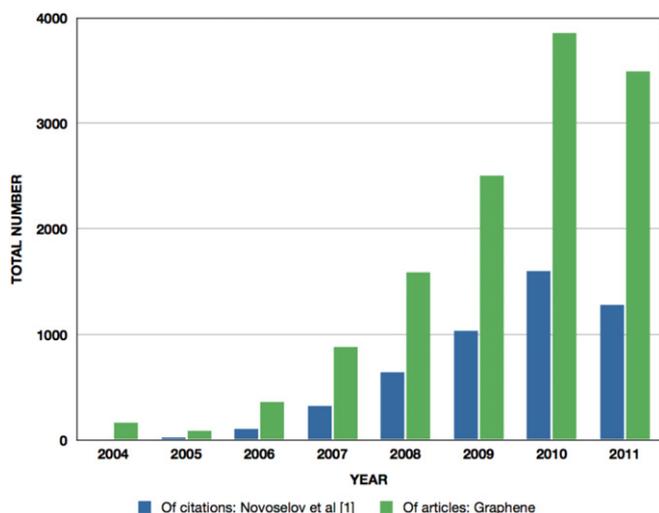
The 2010 Nobel Prize in physics was awarded to Professors Andre Geim and Konstantin Novoselov for their ground-breaking experiments on graphene, a single atomic layer of carbon, and more generally, for their pioneering work in uncovering a new class of materials, namely two-dimensional atomic crystals. This paper gives an accessible account and review of the story of graphene; from its first description in the literature, to the realization and confirmation of its remarkable properties, through to its impressive potential for broad-reaching applications. The story of graphene is written within the context of the enormous impact that Geim and Novoselovs' work has had on this field of research, and recounts their personal pathways of discovery, which ultimately led to their award of the 2010 Nobel Prize.

(Some figures may appear in colour only in the online journal)

**1. Introduction**

In October 2004, Science magazine published a paper entitled 'Electric field effect in atomically thin carbon films' by Novoselov *et al* [1], which contained optical and atomic force microscopy observations of a few-layer and single-layer, one atom-layer-thick, two-dimensional carbon material, called graphene. Also reported in this paper were transport measurements of few-layer graphene, which were soon followed by the publication of transport results on graphene itself [2, 3]. Only six years after the publication of their first paper on this topic, Andre Geim and Konstantin Novoselov, were jointly awarded the Nobel prize in physics, 'for ... producing, isolating, identifying and characterizing graphene' and for their 'ground-breaking experiments' on this material system [4]. What Geim and Novoselov had succeeded to do was to demonstrate a very simple method of extracting and identifying large, high-quality samples of few- and single-layer graphene from bulk graphite, and to then show how these samples could be used to make devices, thus demonstrating their unique transport properties.

The remarkable speed at which the Nobel prize was awarded to Geim and Novoselov gives us some indication of the high-level of scientific impact of their work. The rapid increase in graphene research, which has occurred since the publication of their 2004 paper, has been remarked upon in many reviews on the subject (see for example [5–8]). Novoselov, Geim *et al*'s 2004 paper has provided enormous stimulus for the field of graphene research, and has thus far been cited a total of 5,073 times according to the Web of Knowledge database (accessed 29 August 2011). The impressive impact of their 2004 paper can be clearly evidenced by comparing the number of citations of this paper with the total number of papers published on graphene (figure 1). The 'graphene explosion', which is apparent from figure 1, is very strongly related, in both trend and amount of citations, to this pivotal and key contribution, and can be specifically attributed to (i) the simple low-tech method that the Manchester group used to isolate and identify graphene, which could then be easily adopted by other researchers, (ii) their decision not to patent graphene, which opened up this field of research, and (iii) to their demonstration of the intrinsic high-quality



**Figure 1.** The development of the field of graphene research as indicated by the total number of papers published as a function of year. A comparison with the number of citations of Novoselov *et al*'s 2004 paper very clearly demonstrates the enormous impact of this work, and its overall influence on the trend in graphene research. (Web of Knowledge data accessed on 29 August 2011).

and impressive transport properties of graphene and few-layer graphene, making these systems particularly amenable to broad-reaching applications.

In this review, the story of graphene is recounted—from the first evidence of this system, high-lighting the theoretical prediction of its properties, through to Geim and Novoselov's pivotal Nobel prize-winning research. An overview of graphene's unique properties is given, together with a window to its future possible applications. In doing so, the very exciting tale of graphene's meteoric rise is told, justifying its place as the brightest star in condensed matter physics.

## 2. Humble beginnings, yet remarkable predictions

Graphene, a single atomic layer of  $sp^2$ -hybridized carbon arranged in a honeycomb structure, is the two-dimensional allotrope of carbon, which forms the basic building block of buckyballs (quasi-zero-dimensional), carbon nanotubes (quasi-one-dimensional) and graphite (three-dimensional) (figure 2). Long before graphene was experimentally identified, its structure was used in theoretical models as a means of approximating the electronic properties of graphite. The earliest theoretical reference of this system is Wallace's paper in 1947, which demonstrates the use of a nearest-neighbour, tight-binding model to determine an analytical expression for the electronic band structure pertaining to the pi-bonds of a monolayer of graphite [10].<sup>1</sup>

It is worth a moment to appreciate the electronic properties of graphene as derived from Wallace's analytical expression. The real-space honeycomb structure gives rise to the same symmetry in reciprocal space, and the two-atom basis per unit cell (i.e. two sublattices) (figure 3(a)) leads to two inequivalent

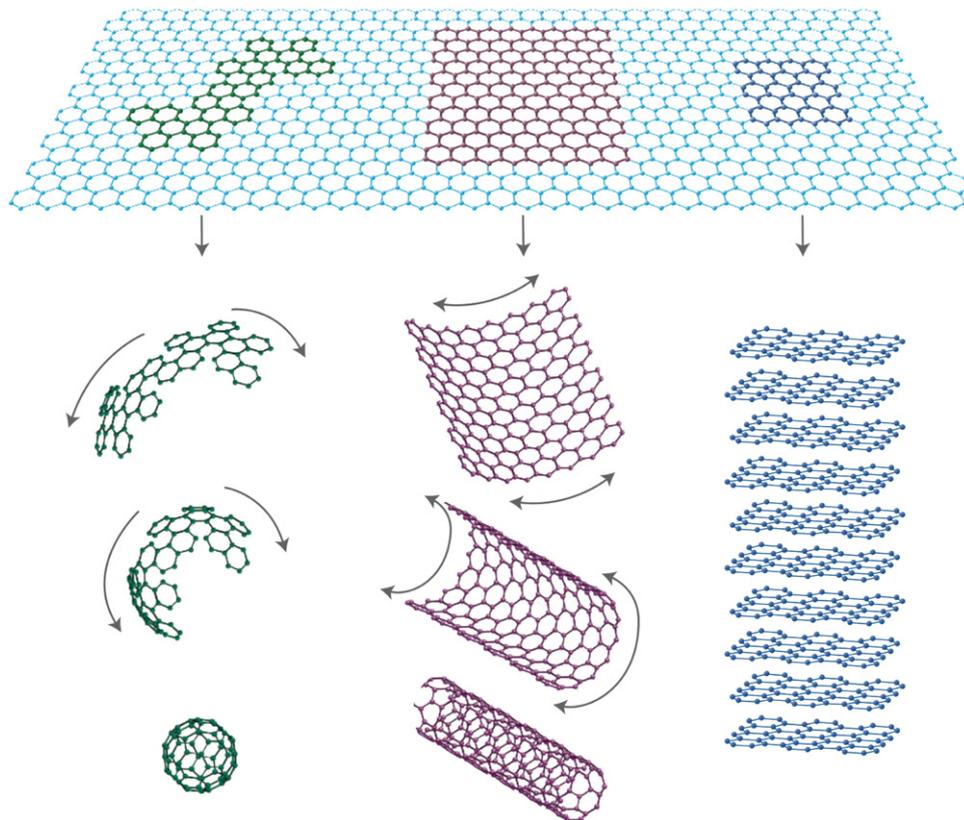
points in the two-dimensional Brillouin zone (K and K') (figure 3(b)). Graphene is a zero-overlap semi-metal—also referred to as a zero-gap semi-conductor; the valence and the conduction pi-bands touch at the Fermi level at the K and K' points and demonstrate a linear energy dispersion close to the Fermi energy (within  $\sim 1$  eV) as indicated by the conical band structure in figure 3(b). The significance of the linear dispersion was later made apparent by Semenoff [12] (see also, DiVincenzo and Mele [13]) who showed that close to the Fermi energy, the electronic properties of graphene could be described by a (2+1)-dimensional Dirac equation, and that the fundamental charge-carrier particles in this system were massless Dirac-Fermions. In this sense, K and K' are often referred to as 'Dirac points'. Semenoff's contribution was an enormous breakthrough in the understanding and explanation of graphene's exotic properties. In analogy with quantum electrodynamics (QED), this further led to the prediction of exotic, pseudo-relativistic phenomena, such as, Klein tunnelling [14] (i.e. the transmission of the graphene's charge-carrier particles through high and wide potential barriers), quasi-particle pseudospin (a property used to differentiate between the two graphene sublattices), and chirality [15], which interconnects, by inversion symmetry, the sublattice k electron and -k hole states (see also figure 4 and [16]).

In his 1984 paper, Semenoff remarks that '...there may be various types of intercalated or exfoliated graphite where the interplanar coupling is negligible. Furthermore, it may be possible to fabricate a graphite monolayer where the effects which we describe would be observable' [12]. There were in fact several attempts to isolate graphene. The first attempts were based on chemical processes that can be traced back to Brodie in 1859 [18]. Brodie used oxidizing agents, such as potassium chlorate and nitric acid to create graphite oxide from graphite. Graphite oxide is hydrophilic breaking up into single-layer flakes when placed in water. It was later determined that further chemical reduction of these flakes could then lead to graphene.

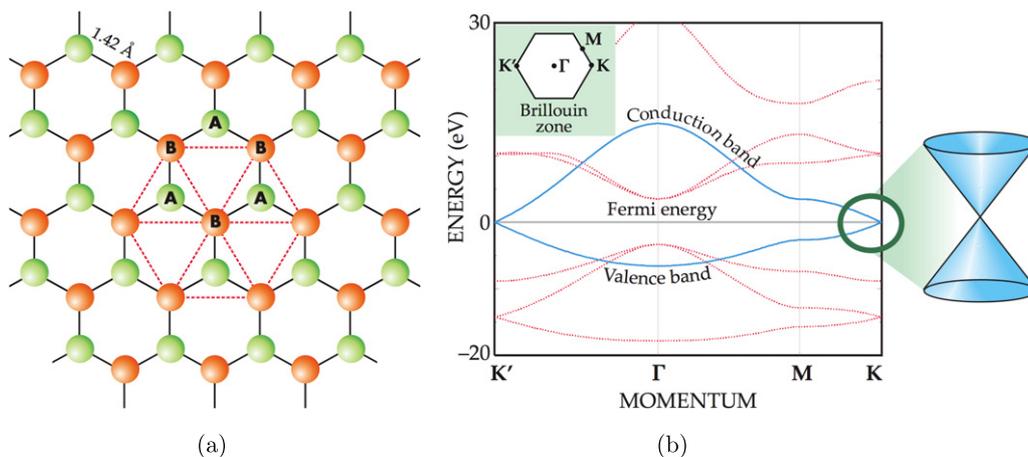
The first mention of the possibility of graphite monolayers was by Ruess and Vogt [19] who proposed a method of achieving this through the thermal decomposition of graphite oxide. This was then followed by Boehm *et al* [22, 23] who used chemical reduction of anhydrous graphite oxide ( $C_8O_2(OH)_2$ ) in a dilute alkali suspension. In forming graphite oxide, the amount of carbon, and the carbon layers, are preserved [20, 21], and this is also the case during the process of chemical reduction. Ruess and Vogt published the first transmission electron microscopy (TEM) images of few-layer graphene, which was later followed by Boehm *et al*'s TEM investigation and attempt to determine the thickness of various samples using contrast comparison [5, 22, 23]—though it is now accepted not to be possible to distinguish the number of layers of few-layer graphene using TEM contrast analysis alone [24]. A later analysis of the electron diffraction spots of graphene obtained through the chemical treatment of a graphite oxide colloidal suspension [25] was able to determine the existence of a monolayer sample [26].

Samples that were obtained using the chemical route that had started with graphite oxide, showed folding, and later

<sup>1</sup> It was not until 1994 that the term 'graphene' was coined by Boehm *et al* [11].



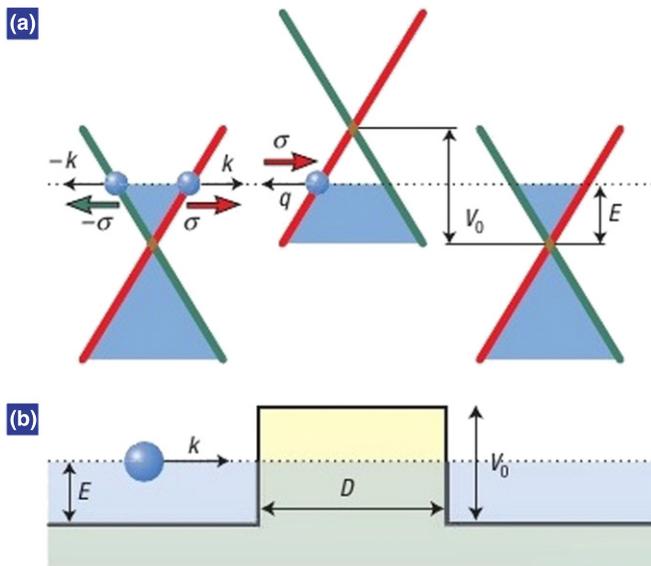
**Figure 2.** Planar (two-dimensional) graphene is the basic building block of other forms of carbon; quasi-zero-dimensional buckyballs (left), quasi-one-dimensional nanotubes (centre) and three-dimensional graphite (right). Reprinted by permission from Macmillan Publishers Ltd: Nature Materials [9], copyright 2007.



**Figure 3.** (a) The honeycomb lattice structure of graphene showing the two-atom basis. (b) The band structure of bulk graphene showing the sigma- (red) and pi- (blue) bands, where zero energy refers to the Fermi energy. States below the Fermi energy are filled, whereas those that are above it are empty. The valence and the conduction pi-bands are shown in the expanded section to touch at the Fermi energy and to have a linear dispersion about this point. The Brillouin zone of graphene is represented in the insert. Reprinted with permission from [17] Copyright 2007, American Institute of Physics.

detailed analysis of this technique demonstrated that carboxy groups remained at the layer edges with hydroxy groups bound to the carbon atoms in the layers [5]. Consequently, as a result of the impurity and structural defects, the samples obtained from the chemical processing of graphite oxide are referred to as ‘chemically modified graphene’ [27, 28], which is considered to be structurally and chemically distinct from graphene.

Chemically modified graphene exhibits a reduced electronic conductivity due to its extensive defects, even when compared with graphite [27, 29]. Other chemical methods to exfoliate graphite monolayers, for example, using intercalation of highly oriented pyrolytic graphite (HOPG), also resulted in folding as demonstrated by Shioyama [30] and then Kaner’s group [31], with the production of monolayer carbon nanoscrolls.



**Figure 4.** (b) A graphene charge-carrier particle approaches a potential barrier. (a) Shows the corresponding electronic structure, where green denotes negative pseudospin ( $-\sigma$ ) and red denotes positive pseudospin ( $\sigma$ ) states arising from graphene's two sublattices. Electron and hole states are interconnected via the pseudospin, such that  $k$  ( $-k$ ) electron states that have  $\sigma$  ( $-\sigma$ ) pseudospin are coupled to  $-k$  ( $k$ ) hole states. The coupling via the pseudospin facilitates the transmission of the charge carriers through the potential barrier as illustrated in (b). Figures (a) and (b) reprinted by permission from Macmillan Publishers Ltd: Nature physics [16], copyright 2006.

Graphene formation through thermal decomposition of SiC was first demonstrated and characterized by Van Bommel *et al* [32]. This method was later developed and further interpreted by Forbeaux *et al* [33], and then employed by de Heer's group [34] who were interested in developing epitaxially grown, graphene- and few-layer graphene-based electronic devices [35]. Graphene had also been demonstrated to grow epitaxially onto various metal substrates using electron and Argon-ion bombardment [36], and then by chemical vapour deposition through exposing metal surfaces to hydrocarbon gas at high temperatures [37–40]. It was also suggested that epitaxially grown graphene could be folded to achieve various nanogeometry designs using an atomic force microscope (AFM) or a scanning tunnelling microscope (STM) tip in a way, which was similar to folding origami [41]. Such systems were thought to have useful applications [41]. Nanographenes were also grown by heat-treatment of nanodiamond precursors onto HOPG substrates [42].

Prior to the 2004 paper by Novoselov and Geim *et al*, there had also been other reports on the preparation of thin-samples of graphite using mechanical methods, beginning with Roscoe and Thomas [43] who prepared optical microscopy samples of natural graphite using adhesive tape. Subsequent attempts to produce thin graphite samples by mechanical methods had focussed on using these specimens in transport studies, as it was much easier to contact the larger exfoliated samples than the chemically produced systems. For example, Seibert *et al* [44] used adhesive tape exfoliation of HOPG to obtain samples with thicknesses of  $\sim 350$  Å. This was followed by

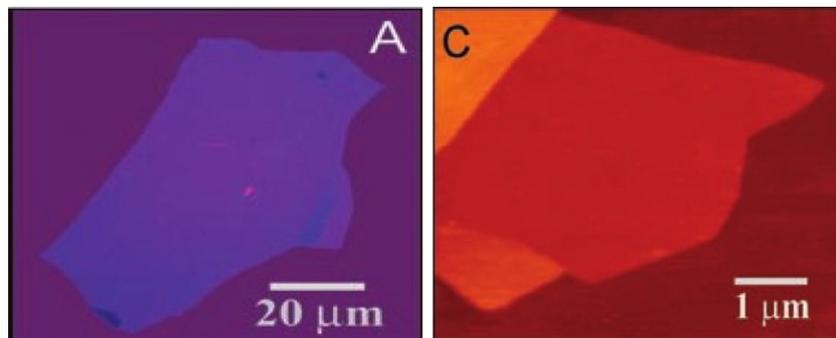
later research by Ohashi *et al* [45], and then Lu *et al* [46, 47] who used the 'drawing' method of rubbing graphite islands patterned from HOPG directly onto other material surfaces, as well as AFM tip manipulation to transfer thin graphite flakes onto other substrates, which achieved thicknesses of about 100 nm. Ebbesen's group [48, 49] also prepared thin graphite microdiscs of between 60 and 100 layer thicknesses.

Gan *et al* [50] used mechanical cleavage of HOPG and then STM tip manipulation demonstrating thicknesses down to two graphite layers. Kim's group was already very active at this time, later publishing work, which revealed their own micromechanical cleavage technique of producing thin graphite samples (obtaining thicknesses between 10 and 100 nm) [51], and later performing transport measurements [52]. McEuen's group had also started to fabricate thin graphite films as quasi-two-dimensional graphite quantum dots between a few nm to 100 nm thick, upon which they also performed transport measurements [53]. The stage was therefore set for what would be Geim and Novoselov's pivotal contribution of a simple method to identify and isolate graphene, leading to sufficient quality and quantity of the material to enable ground-breaking experimental measurements.

### 3. Andre Geim and Konstantin Novoselovs' Nobel Prize winning research

Andre Geim is no stranger to exploring new research directions, having changed his research field several times during his career. It was perhaps during his postdoc at Nottingham University in the early 1990s while he was researching ultrathin metal films grown by molecular beam epitaxy (MBE) onto GaAlAs, when Geim started to think about two pivotal concepts; (1) how could one obtain ultrathin and structurally stable, two-dimensional metallic monocrystals, and (2) could these systems be used to produce a two-dimensional metallic transistor? Geim had been impressed by the remarkable advances in the 1990s in carbon nanotube research, and namely in the demonstration of carbon nanotube transistors and transport properties [54–56]. 'Would it be possible to do the same thing for an unrolled carbon nanotube? How can I do something similar, but something different?', he wondered. It was the synthesis of these ideas that led Geim to consider thin-film graphite as one possible candidate for realizing two-dimensional, carbon-based transistors.

Geim's interest in the possibility of two-dimensional carbon-based electronics was further driven by a review paper by Dresselhaus and Dresselhaus [57] which indicated a large deficit in understanding of the properties of ultrathin, graphite films. At that time, two decades after the publication of the Dresselhaus and Dresselhaus paper, it was still apparent that a robust technique for producing high-quality, free-standing, thin-film graphite specimens had not yet been achieved. It was also thought to be impossible to obtain large enough samples of thin-film graphite at the very high temperatures required to grow carbon ( $\sim 2000$  K)—for example, graphene was calculated to be thermodynamically unstable for sizes  $< 24000$  atoms (or  $< 20$  nm) [58]. Above this size, and



**Figure 5.** (left) an optical image of few-layer graphene with a thickness of approximately 3 nm on a SiO<sub>2</sub>/Si substrate. (right) an AFM image of single- and multi-layer graphene on a SiO<sub>2</sub>/Si substrate. Figure from [1]. Reprinted with permission from AAAS.

graphene will scroll, or form islands, thus taking the form of a three-dimensional object [48, 59]. To highlight the difficulties in the synthesis of graphene, the largest graphene macromolecule that had been produced at that time was only 222 carbon atoms in size, or 37 benzene-rings [60].

Geim had become Professor in 2001 at The University of Manchester. Having just started his appointment, he was ‘looking for something new, which would still be possible’ using his current lab facilities. ‘Friday night experiments’, which were devised at Nijmegen and later continued at Manchester after Geim established his microfabrication facility through EPSRC and university funding, were to encapsulate the idea of research play. Research play was, and still is, Geim’s trademark approach, which has led to notable contributions such as the levitating frog [61], winning Geim the Ig Nobel prize in 2000 (shared with Professor Sir Michael Berry), and gecko-tape [62]. Graphene, according to Geim, began as another ‘Friday night experiment’, which was to merge at a later stage into the PhD project of his student Da Jiang in 2002. The initial idea that Geim had was to ‘polish’ a 2.5 cm diameter sample of high-density pyrolytic graphite (HDPG) down to a few hundred nanometres in thickness using his newly purchased polishing machine. Although polishing HDPG did not achieve this aim (only 5–10 μm thick samples were made), what did emerge was an alternative and very simple method of using adhesive tape to exfoliate thin-layers of graphite material from the bulk specimen. The suggestion to use this method has been attributed to Geim’s senior postdoc, Oleg Shklyarevskii, who also proposed using HOPG instead of HDPG due of its superior cleavage properties.

By holding the adhesive tape up to the light, the residue was seen to be very thin flakes of graphite, some so thin that they were transparent. Geim recalls the shock of this finding within the context of his experience with MBE and the known difficulties in growing monolayer samples [63], namely, that a surprisingly simple method could be easily used to achieve what had been perceived to be impossible using conventional growth techniques, that is, a one-atom-thick sample of graphene. Graphene, it seemed, could only be obtained from the three-dimensional state—by being grown epitaxially, and then later being removed from the substrate, by chemically separating the graphite layers (chemical exfoliation), or by this very simple method of ‘sticky-tape’ exfoliation under ambient conditions. By placing the exfoliated graphite onto a suitable

substrate, such as SiO<sub>2</sub>/Si, the graphene became visible through a change in optical contrast relative to the substrate, which was then confirmed by AFM studies (figures 5(a) and (b)). After several months of perfecting the exfoliation technique, the Manchester group had been able to demonstrate the production of high-quality, micrometre-sized, few-layer graphene and graphene samples [1], which later approached almost 1 mm in size. Such samples were of sufficient quality and large enough to be used in ground-breaking transport measurements.

The ‘sticky-tape’ exfoliation of graphite and the production of few-layer and single-layer graphene samples were the start of a series of experiments that led to the Nobel prize-winning research. Konstantin Novoselov, who had been Geim’s PhD student at Nijmegen in the Netherlands, had followed Geim to the University of Manchester and was instrumental in the making of the first few-layer graphene devices. These devices were first made on glass slides and then onto oxidized silicon wafers. Requiring enormous skill to work on such a small scale, Novoselov hand-made the first devices by placing silver contacts onto the 50 × 100 μm<sup>2</sup> few-layer graphene sample using a toothpick. In August 2003, the group had produced the first working few-layer graphene devices, which demonstrated metallic transistor properties, with the resistance changing as much as 3% as a function of the gate voltage  $V_g$  (figure 6). Although this was a modest on-off response, it did, however, demonstrate the potential of these systems, particularly as these first devices were not made under ideal, nor high-tech conditions.

The next step was to go from the rudimentary sample to using sophisticated fabrication techniques (i.e. lithography, etc) to produce high-quality, single and few-layer graphene devices (see also [1]). The 2D transport characteristics of the few-layer graphene were confirmed through studies of the Shubnikov–de Haas oscillations (SdHOs), which were found to depend upon only the perpendicular component of the applied magnetic field [1]. The SdHO frequencies were also seen to be proportional to  $V_g$  (figure 7(a)), which implied that the Fermi energies were linearly proportional to the concentration of charge carriers (electrons or holes). Linear conductivity characteristics as a function of  $V_g$  were also measured on few-layer graphene (figure 7(b)). An ambipolar field effect, reminiscent of semi-conductor systems, was also reported. By changing the gate voltage via an external electric

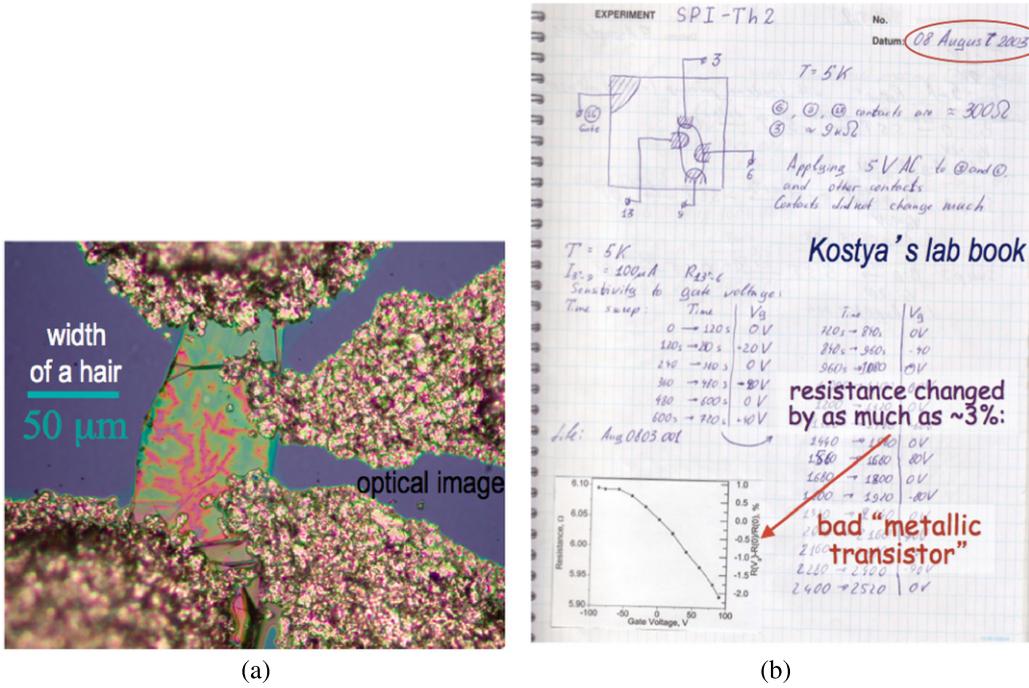


Figure 6. (a) An optical image of a few-layer graphene device made by Konstantin Novoselov (b) Extract from Konstantin Novoselov's lab book. Reprinted with permission from Geim [64].

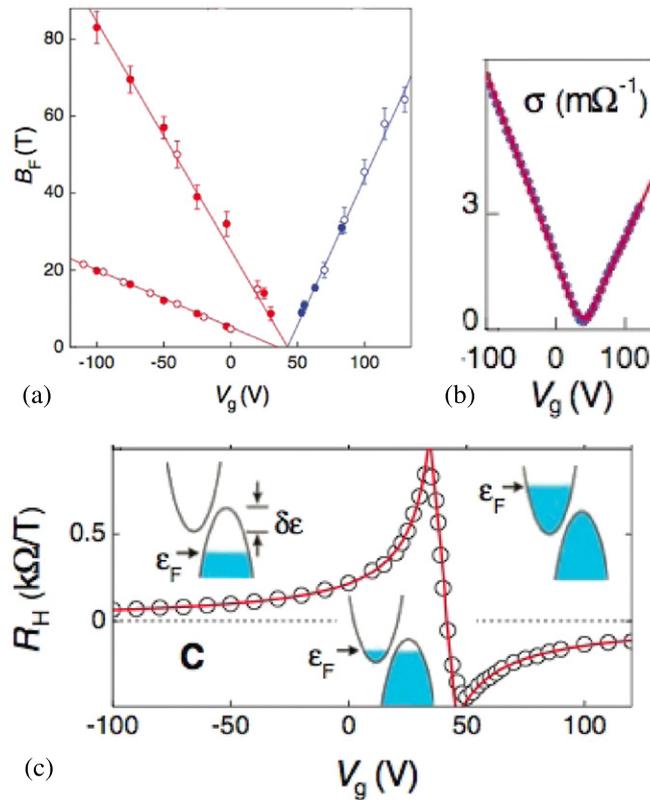
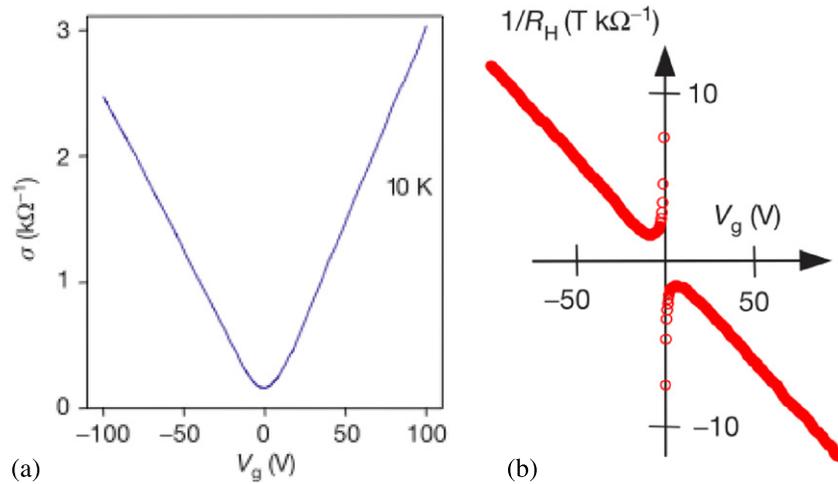


Figure 7. (a) SdHO frequencies  $B_F(T)$  as a function of the gate voltage  $V_g$  for a few-layer graphene device. Solid and open symbols correspond to systems with band overlaps of 6 meV and 20 meV, respectively. (b) Linear conductivity  $\sigma$  as a function of  $V_g$  for a few-layer graphene device measured at 70 K. (c) Corresponding Hall coefficient  $R_H$  as a function of  $V_g$ , demonstrating the ambipolar field effect of the few-layer graphene device. The change in sign of  $R_H$  from positive to negative as a function of  $V_g$  represents a change in charge-carrier types from holes (positive  $R_H$ ) to electrons (negative  $R_H$ ). The positive value of  $V_g$ , which corresponds to the minimum conductivity and change in sign of  $R_H$ , was found to be due to impurity doping effects. Figures (a), (b) and (c) from [1]. Reprinted with permission from AAAS.



**Figure 8.** (a) Conductivity  $\sigma$  as a function of the gate voltage  $V_g$  for graphene measured at 10 K. The sample has been carefully annealed to remove impurities, hence the minimum conductivity occurs at  $V_g = 0$ . (b) Corresponding Hall coefficient measurements. Figures (a) and (b) reprinted by permission from Macmillan Publishers Ltd: Nature [3], copyright 2005.

field, the properties of the few-layer graphene system could be changed from a metal that has hole or electron charge carriers at high concentrations, through a mixed state containing both electrons and holes, that has a minimum conductivity (figures 7(b) and (c)) [1]. The carefully made, few-layer graphene devices demonstrated an improved on-off resistance ratio of up to 30% at room temperature compared with the systems, which were originally prepared [1]. These systems exhibited astonishing electronic quality, with mobilities up to  $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and charge-carrier concentrations of  $n \approx 5 \times 10^{12} \text{ cm}^{-2}$  [1]—the result being ballistic transport (conductivity without scattering) on a submicrometre scale under ambient conditions!<sup>2</sup>

#### 4. Lifting the Veil on graphene

Subsequent work on graphene continued to reveal its remarkable properties. In 2005, the Manchester group published conductivity results for graphene as a function of the gate voltage  $V_g$  showing the linear conductivity relationship and minimum conductivity [2]. This was then followed by more detailed transport results, which showed not only the conductivity (figure 8(a)) but also the change in sign of the Hall coefficient as a function of  $V_g$  (figure 8(b)) [3]. Similar to the few-layer graphene system, the conductivity of graphene was found to be directly proportional to  $V_g$ , and therefore also to the number of charge carriers, with charge densities of  $7.2 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1}$  being measured [2]. The minimum conductivity was found to be approximately  $(4e^2)/h$  in the limit of no charge carriers<sup>3</sup>, which is the case at  $V_g = 0$ , and corresponds to the Fermi level at the

Dirac point [3]. Analysis of the Hall coefficient  $R_H$  as a function of  $V_g$  revealed ambipolar properties that were in keeping with the previously reported properties of few-layer graphene. Ballistic transport at submicrometre scales under ambient conditions was also achieved, with mobilities up to  $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the temperature range 10–100 K. Both the minimum conductivity and the mobility were found to be independent of the temperature for measurements between 10 and 100 K [3].

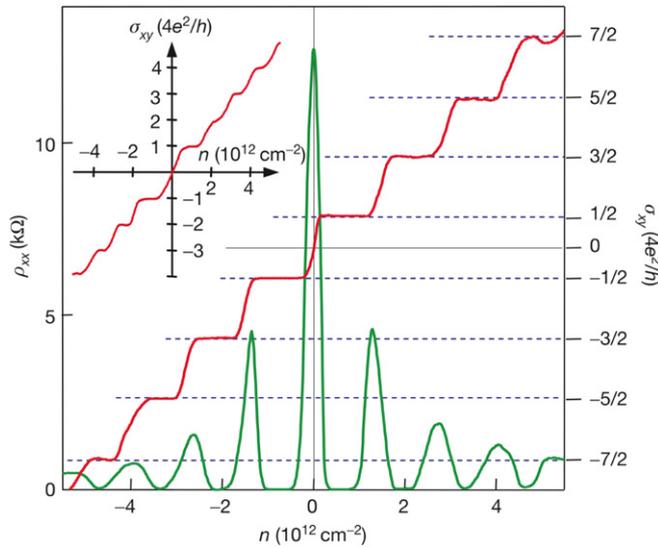
The Manchester group confirmed that the electron transport of graphene could be related to the relativistic properties of massless charge-carrier particles, also referred to as Dirac-Fermions [3]. Further characterization of graphene involved the study of SdHOs, which, unlike few-layer graphene, showed the same type of behaviour for both electrons and holes [3]. By studying the SdHO amplitude as a function of temperature, it was determined that the charge carriers have a finite cyclotron mass  $m_c$ , which varies as the square root of the charge-carrier concentration, despite having a zero rest mass as indicated by the linear, low-energy dispersion. Further studies involving the SdHO frequency revealed that graphene’s charge carriers travel at an effective speed of light corresponding to  $c^* \approx 10^6 \text{ m s}^{-1}$ , where  $m_c = E/c^{*2}$  [3].

At low temperatures, the Hall conductivity  $\sigma_{xy}$  in graphene has an anomalous effect, namely the half-integer quantum Hall effect (QHE), which is seen to be direct evidence of QED-like behaviour in this system. A quantized Landau level at zero energy is utilized by both electron and holes, which means that for Dirac-Fermions this level has half the degeneracy of the other levels, hence, this can be related to the two-fold degeneracy of the pseudospin. The anomalous half-integer property therefore results from the halved degeneracy of the zero-energy Landau level (figure 9). These observations were also independently made and documented at the same time in the work of Kim’s group (see also [52]).<sup>4</sup>

<sup>2</sup> Some details in this section were sourced from [64].

<sup>3</sup> The minimum conductivity was later shown to be a function of the amount of impurities in graphene [66]. Theory predicts that the minimum conductivity should be  $(4e^2)/(\pi h)$  in the limit of vanishing disorder [67], although experiments have shown that this value can only be achieved for graphene of certain sizes and shapes [68, 69]. For a long time, this discrepancy was known as ‘the case of the missing  $\pi$ ’.

<sup>4</sup> In 2007 Novoselov *et al* also reported measurements of the QHE in graphene at room temperature [65].



**Figure 9.** Hall conductivity  $\sigma_{xy}$  and corresponding longitudinal resistivity  $\rho_{xx}$  of graphene as a function of the charge-carrier density  $n$  measured at  $B = 14$  T and  $T = 4$  K. The anomalous half-integer property of the quantum Hall effect (QHE) is explained by the halved degeneracy of the zero-energy Landau level. The insert shows the Hall conductivity for bilayer graphene, which, in comparison, exhibits an integer QHE. Reprinted by permission from Macmillan Publishers Ltd: Nature [3], copyright 2005.

## 5. Recent developments and future directions

As these early papers demonstrate, graphene has remarkable properties, resulting from its unique Dirac-like, electronic spectrum and excellent material quality. Graphene's charge-carrier mobilities have been measured more recently to be more than  $40000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  on a  $\text{SiO}_2/\text{Si}$  substrate [70, 71] and up to  $150000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  on a substrate, containing boron nitride between the graphene and  $\text{SiO}_2$  [71]. Chen *et al* showed that the mobility of graphene could be limited by impurity scattering due to the substrate, and that its intrinsic (phonon-limited mobility) would be greater than  $200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in suspended graphene (i.e. graphene with no substrate support) at 300 K [70]<sup>5</sup>. This was later measured and verified by Bolotin *et al* showing graphene's intrinsic mobility to be more than 100 times that of silicon [72].

Graphene has a current density, which is a measure of the density of flow of charged carrier particles, that is a million times that of copper [74], and boasts a micrometre-range mean-free path, which is the longest measured for any material [72]. Graphene's impressive electronic properties can be explained by its remarkable relativistic characteristics, namely, its massless Dirac-like charge carriers, which are able to penetrate high and wide potential barriers [75, 76] and exhibit Klein tunnelling [14] (see also section 2 and figure 4). The high charge-carrier mobilities in graphene are not affected by the large carrier concentrations that are induced by an applied gate voltage, nor are they affected by chemical doping [77]. A band-gap can also be induced by

<sup>5</sup> It is currently understood that charge-carrier mobilities in suspended graphene are primarily limited by out of plane vibrations, known as flexural phonons [73].

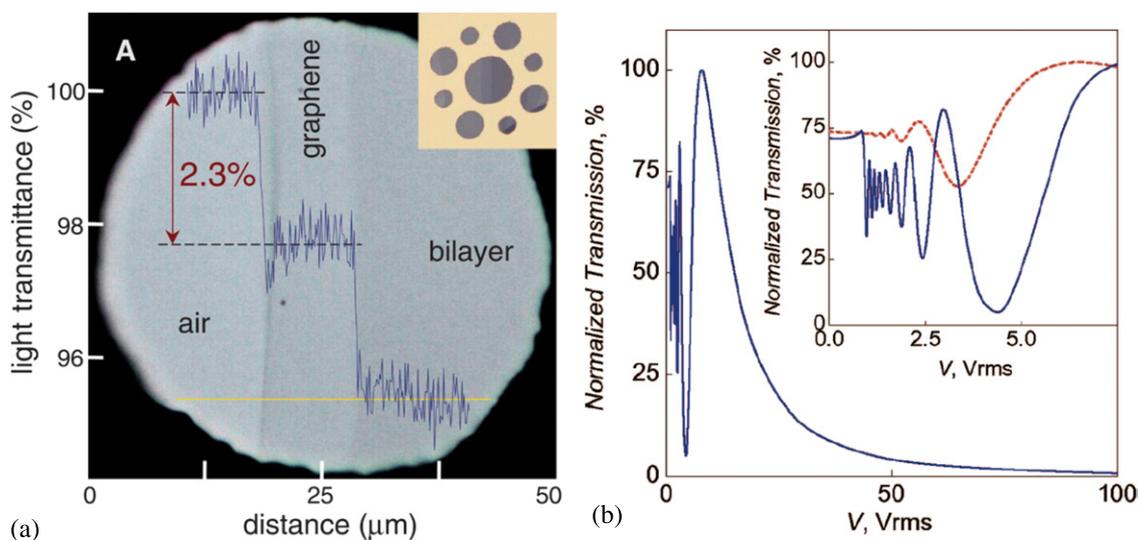
confinement effects in making nanoscale graphene, through substrate interactions [78] or by molecule adsorption [79]. All of these properties make graphene an excellent material for future electronic applications, having perhaps the highest potential for realizing ballistic devices at room temperature [9].

Graphene has a very high optical transmission with only 2.3% absorption of white light [80]. Optical properties, such as the optical transmission [81] (figure 10) and infrared reflectivity [82] can be tuned as a function of the applied voltage. Hence, graphene also lends itself nicely to photonic applications, such as liquid crystal displays [81] and touch-screens [83], which have recently become a possibility with the advent of CVD-grown graphene sheets that are approaching a metre in size [84–86]. Graphene's optical properties have also found application as transparent, conductive electrodes, with application in liquid crystals [87] and solar cell systems [88, 89]. Graphene has also been used in light emitting diodes [90] and can now be transferred and placed onto TEM supports (figure 11(a)) to enable the visualization of atoms, molecules [91] and biological materials [92] (figure 11(b)). For a detailed review of graphene's optical properties and potential applications, see Bonaccorso *et al* [93].

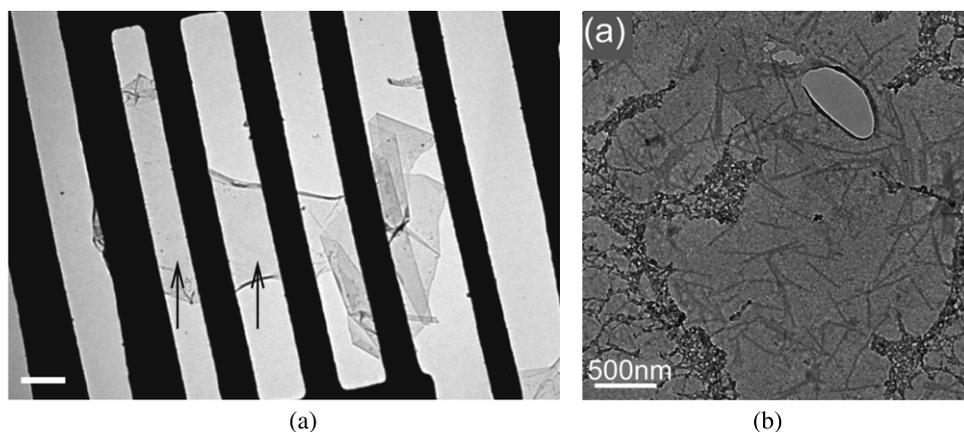
Continuing work on graphene has also revealed its impressive structural properties, namely, that it is the strongest material ever measured ( $\sim 42 \text{ N m}^{-1}$ ) [94], it is also the stiffest known material (Young's modulus  $\sim 1.0 \text{ TPa}$ ) [94] and is structurally stable, perhaps even down to a single benzene ring [9] therefore opening the door to the design of future, ultra-small devices by top-down, lithography patterned approaches. On the nanoscale, graphene is a semi-conductor, and when made into nanometre-width ribbons demonstrates a tunable band-gap, which varies inversely as a function of the ribbon-width [95–97]. The band-gap properties of graphene nanoribbons are being exploited in the fabrication of nano-sized field effect transistors [98]. Single electron transistors [99, 100] have also been demonstrated.

Speeds of between 100 and 300 GHz have been measured for graphene-based field effect transistors operating at room temperature under ambient conditions [101, 102]. This has been followed by a recent report of the first room temperature, fully integrated graphene circuit [103]. Investigations into magnetic device applications of graphene are also underway, with the demonstration of graphene spin-valves [104, 105], flash memory [106] and current-induced magnetism in graphene, which may have application in spintronics [107]. Top-down fabrication processes often result in structural disorder, which can radically alter the properties of these systems, with edge-quality in nanoscale graphene being seen as a limiting factor in the development of devices [108, 109]. Bottom-up synthesis methods such as templated epitaxial growth [110] or chemical synthesis [111] may therefore provide future solutions to producing structurally pristine, nanoscale graphene.

Despite being one atom thick, graphene has been demonstrated to be enormously flexible. Graphene can be stretched elastically on a silicone substrate up to 6% [90, 112], with a failure strain of up to 12%. When graphene is transferred to a pre-strained silicone substrate it can be stretched even



**Figure 10.** (a) A 50  $\mu\text{m}$  aperture partially covered with graphene and bilayer graphene showing the intensity of the transmitted light. (b) The transmitted light through a graphene liquid crystal device as a function of the applied voltage  $V$  across the cell. Figures (a) from [80]. Reprinted with permission from AAAS. Figure (b) reprinted (adapted) with permission from [81]. Copyright (2008) American Chemical Society.



**Figure 11.** (a) A bright-field TEM image of suspended graphene on a metal scaffold. (b) A TEM image of graphene with tobacco mosaic virus visualized on top. Figure (a) is reprinted by permission from Macmillan Publishers Ltd: Nature [24], copyright 2007. Figure (b) is reprinted with permission from [92]. Copyright 2010, American Institute of Physics.

further, up to 25%. The measured resistance in graphene was found to remain stable up to 11% stretching, with an order of magnitude change at approximately 25% stretching [112]. Many of graphene's properties arising from its band structure, namely its electronic and optical properties remain stable under stretched conditions, therefore lending graphene to application in the new field of 'flexible' electronics [86, 112–114].

As well as its structural and electronic properties, graphene's thermal properties have also been measured recently and are equally impressive. Graphene has been reported to have a record thermal conductivity, which is higher than diamond at  $\sim 5300 \text{ W m}^{-1} \text{ K}^{-1}$ , thus it has the potential to be used as a thermal control material in electronic devices [115]. Graphene's chemical properties have also been exploited, with one of graphene's first applications being as a gas sensor [77, 116]. New spin-off materials have been made using graphene's chemistry, namely hydrogenated graphene, or graphane [117] and also more recently fluorographene

(graphene + fluorine) [118], the two-dimensional version of Teflon, with both materials demonstrating insulating properties. Graphene can not only be grown on a variety of substrates, it can also be transferred to any type of substrate [119, 120], therefore opening up further possibilities of realizing new graphene-based effects.

Despite the substantial progress in the development of graphene-based transistors and other devices there are still many challenges that need to be overcome before practical implementations or commercial products can be made [108]. The rapid progress demonstrated thus far remains remarkable, and given the intensity of research, the realization of future graphene-based products, such as 'graphenium chips', may not be too far away.

As Geim remarked at the end of his Nobel lecture, 'Graphene is like the 'Philosopher's stone' ... 'Whenever you 'touch any phenomena' with graphene, then there is always something new and something unique. It is really a very rich

system, which we have not experienced before' [64]. The world now eagerly awaits the future prospects and creations that lie ahead on the graphene horizon.

## Acknowledgments

The author very gratefully acknowledges Professors Andre Geim and Konstantin Novoselov for their comments on section 3 and permission to use figures 6(a) and (b). The author would also like to thank Drs Fredrik Schedin, Romain Danneau and Professor Pertti Hakonen for their careful reading of the manuscript and for also providing very helpful comments.

## References

- [1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films *Science* **306** 666
- [2] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Two-dimensional atomic crystals *Proc. Natl. Acad. Sci. USA* **102** 10451
- [3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Two-dimensional gas of massless Dirac fermions in graphene *Nature* **438** 197
- [4] The 2010 Nobel Prize in Physics - Press Release. Nobelprize.org. [http://nobelprize.org/nobel\\_prizes/physics/laureates/2010/press.html](http://nobelprize.org/nobel_prizes/physics/laureates/2010/press.html)
- [5] Boehm H P 2010 Graphene—How a laboratory curiosity suddenly became extremely interesting *Angew. Chem. Int. Edn Engl.* **49** 9332
- [6] Allen M J, Tung V C and Kaner R B 2010 Honeycomb carbon: a review of graphene *Chem. Rev.* **110** 132–45
- [7] Katsnelson M I 2007 Graphene: carbon in two dimensions *Mater. Today* **10** 20–7
- [8] Dresselhaus M S and Araujo P T 2010 Perspectives on the 2010 Nobel prize in physics for graphene *ACS Nano* **4** 6297
- [9] Geim A K and Novoselov K S 2007 The rise of graphene *Nature* **6** 183
- [10] Wallace P R 1947 The band theory of graphite *Phys. Rev.* **71** 622
- [11] Boehm H-P, Setton R and Stumpp E 1994 Nomenclature and terminology of graphite intercalated compounds *Pure Appl. Chem.* **66** 1893
- [12] Semenoff G W 1984 Condensed-matter simulation of a three-dimensional anomaly *Phys. Rev. Lett.* **53** 2449
- [13] DiVincenzo D P and Mele E J 1984 Self-consistent effective-mass theory for intralayer screening in graphite intercalation compounds *Phys. Rev. B* **29** 1685
- [14] Klein O 1929 Die Reflexion von Elektronen an einem Potentialsprung nach der relativistischen Dynamik von Dirac *Z. Phys.* **53** 157
- [15] Haldane F D M 1988 Model for a quantum Hall effect without Landau levels: condensed-matter realization of the parity Anomaly *Phys. Rev. Lett.* **61** 2015
- [16] Katsnelson M I, Novoselov K S and Geim A K 2006 Chiral tunnelling and the Klein paradox in graphene *Nature Phys.* **2** 620
- [17] Geim A K and MacDonald A H 2007 Graphene: exploring carbon flatland *Phys. Today* **60** 35
- [18] Brodie B C 1859 On the atomic weight of graphite *Phil. Trans. R. Soc. Lond. Ser. A* **149** 249
- [19] Ruess G and Vogt F 1948 Höchstlamellarer Kohlenstoff aus graphitoxhydroxyd *Monatsh. Chem.* **78** 222
- [20] Hofmann U and Frenzel A 1930 Quellung von graphit und die Bildung von Graphitsäure *Ber. Deutsch. Chemischen. Ges. A and B Series* **63** 1248
- [21] Boehm H P, Eckel M, Scholz W 1967 Untersuchungen am Graphitoxid V. Über den Bildungsmechanismus des Graphitoxids *Z. Anorg. allg. Chem.* **353** 236
- [22] Boehm H P, Clauss A, Fischer G O and Hofmann U 1962 Dünne Kohlenstoff-Foilen *Z. Naturforschg.* **17b** 150
- [23] Boehm H P, Clauss A, Fischer G O and Hofmann U 1962 Surface properties of extremely thin graphite lamellae *Proc. 5th Biennial. Conference on Carbon* vol 2 (Oxford: Pergamon Press) p 73
- [24] Meyer J C, Geim A K, Katsnelson M I, Novoselov K S, Booth T J and Roth S 2007 The structure of suspended graphene sheets *Nature* **446** 60
- [25] Horiuchi S *et al* 2003 Carbon nanofilm with a new structure and property *Japan J. Appl. Phys.* **42** L1073–76
- [26] Horiuchi S, Gotou T, Fujiwara M, Asaka T, Yokosawa T and Matsui Y 2004 Single graphene sheet detected in a carbon nanofilm *Appl. Phys. Lett.* **84** 2403–5
- [27] Park S and Ruoff R S 2009 Chemical methods for the production of graphenes *Nature Nanotechnol.* **4** 217
- [28] Wilson N R, Pandey P A, Beanland R, Rouke J P, Lupo U, Rowlands G and Römer R A 2010 On the structure and topography of free-standing, chemically modified graphene *New J. Phys.* **12** 125010
- [29] Shin H-J *et al* 2009 Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance *Adv. Funct. Mater.* **19** 1987
- [30] Shioyama H 2001 Cleavage of graphite to graphene *J. Mater. Sci. Lett.* **20** 499
- [31] Viculis L M, Mack J J and Kaner R B 2003 A chemical route to carbon nanoscrolls *Science* **299** 1361
- [32] Van Bommel A J, Crombeen J E and Van Tooren A 1975 Leed and auger electron observations of the SiC (0001) surface *Surf. Sci.* **48** 463
- [33] Forbeaux I, Themlin J-M and Debever J-M 1998 Heteroepitaxial graphite on 6H-SiC(0001): interface formation through conduction-band electronic structure *Phys. Rev. B* **58** 16396
- [34] Berger C *et al* 2004 Ultrathin epitaxial graphite: 2d electron gas properties and a route toward graphene-based nanoelectronics *J. Phys. Chem. B* **108** 19912
- [35] For information on the de Heer group's 2003 patent on epitaxially grown, graphene-based electronics, see <http://smartech.gatech.edu/xmllui/handle/1853/31270>
- [36] Grant J T and Haas T W 1970 A Study of Ru(001) and Rh(111) surfaces using LEED and Auger electron spectroscopy *Surf. Sci.* **21** 76
- [37] McConville C F, Woodruff D P, Kevan S D, Weinert M and Davenport J W 1986 Electronic structure of the (2 × 2)C r4g carbide phase on Ni{100} *Phys. Rev. B* **34** 2199
- [38] Land T A, Michely T, Behm R J, Hemminger J C and Comsa G 1992 STM investigation of a single layer graphite structure produced by Pt(111) by hydrocarbon deposition *Surf. Sci.* **264** 261
- [39] Nagashima A, Nuka K, Satoh K, Itoh H, Ichinokawa T and Oshima C 1993 Electronic structure of monolayer graphite on some transition metal carbide surfaces *Surf. Sci.* **287/288** 609
- [40] Nagashima A, Nuka K, Itoh H, Ichinokawa T and Oshima C 1993 Electronic states of monolayer graphite formed on tic(111) surface *Surf. Sci.* **291** 93
- [41] Ebbesen T W and Hiura H 1995 Graphene in 3-dimensions: towards graphite origami *Adv. Mater.* **7** 582
- [42] Affoune A M, Prasad B L V, Sato H, Enoki T, Kaburagi Y and Hishiyama Y 2001 Experimental evidence of a single nano-graphene *Chem. Phys. Lett.* **348** 17

- [43] Roscoe C and Thomas J M 1967 The identification and some pseudo-chemical consequences of non-basal edge and screw dislocations in graphite *Proc. R. Soc. Lond. A* **297** 397
- [44] Seibert K, Cho G C, Kütt W, Kurz H, Reitze D H, Dadap J I, Ahn H, Downer M C and Malvezzi A M 1990 Femtosecond carrier dynamics in graphite *Phys. Rev. B* **42** 2842
- [45] Ohashi Y, Koizumi T, Yoshikawa T, Hironaka T and Shiiki K 1997 Size effect in the in-plane electrical resistivity of very thin graphite crystals *TANSO* 235
- [46] Lu X, Huang H, Nemchuk N and Ruoff R S 1999 Patterning of highly oriented pyrolytic graphite by oxygen plasma etching *Appl. Phys. Lett.* **75** 193
- [47] Lu X, Yu M, Huang H and Ruoff R S 1999 Tailoring graphite with the goal of achieving single sheets *Nanotechnol.* **10** 269
- [48] Krishnan A, Dujardin E, Treacy M M J, Hugdahl J, Lynum S and Ebbesen T W 1997 Graphitic cones and the nucleation of curved surfaces *Nature* **388** 451
- [49] Dujardin E, Thio T, Lezec H and Ebbesen T W 2001 Fabrication of mesoscopic devices from graphite nanodisks *Appl. Phys. Lett.* **79** 2474
- [50] Gan Y, Chu W and Qiao L 2003 STM investigation on interaction between superstructure and grain boundary in graphite *Surf. Sci.* **539** 120
- [51] Zhang Y, Small J P, Pontius W V and Kim P 2005 Fabrication of electric-field-dependent transport measurements of mesoscopic graphite devices *Appl. Phys. Lett.* **86** 073104
- [52] Zhang Y, Tan Y-W, Stormer H L and Kim P 2005 Experimental observation of the quantum Hall effect and Berry's phase in graphene *Nature* **438** 201
- [53] Bunch J S, Yaish Y, Brink M, Bolotin K and McEuen P L 2005 Coulomb oscillations and Hall effect in quasi-2d graphite quantum dots *Nano Lett.* **5** 287
- [54] Bockrath M, Cobden D H, McEuen P L, Chopra N G, Zettl A, Thess A and Smalley R E 1997 Single-electron transport in ropes of carbon nanotubes *Science* **275** 1922
- [55] Tans S J, Verschueren A R M and C Dekker 1998 Room temperature transistor based on a single carbon nanotube *Nature* **393** 49
- [56] Martel R, Schmidt T, Shea H R, Hertel T and Avouris Ph 1998 Single- and multi-wall carbon nanotube field-effect transistors *Appl. Phys. Lett.* **73** 2447
- [57] Dresselhaus M S and Dresselhaus G 1981 Intercalation compounds of graphite *Adv. Phys.* **30** 139
- [58] Shenderova O A, Zhirnov V V and Brenner D W 2002 Carbon nanostructures *Critical Rev. Solid State Mater. Sci.* **27** 227
- [59] Braga S F, Coluci V R, Legoas S B, Giro R, Galvão D S and Baughman R H 2004 *Nano Lett.* **4** 881
- [60] Simpson C D, Brand J D, Berresheim A J, Przybilla L, Räder H J and Müllen K 2002 Synthesis of a giant 222 carbon graphite sheet *Chem.—Eur. J.* **8** 1424
- [61] Berry M V and Geim A K 2007 Of flying frogs and levitrons *Eur. J. Phys.* **18** 307  
See also Berry M V and Geim A K 2007 *Phys. World* p 28
- [62] Geim A K, Dubonos S V, Grigorieva I V, Novoselov K S, Zhukov A A and Shapoval S Y 2003 Microfabricated adhesive mimicking Gecko foot-hair *Nature Mater.* **2** 461
- [63] Venables J A, Spiller G D T and Hanbuckenn M 1984 Nucleation and growth of thin-films *Rep. Prog. Phys.* **47** 399
- [64] 'Andre Geim - Nobel Lecture' Nobelprize.org.  
[http://www.nobelprize.org/nobel\\_prizes/physics/laureates/2010/geim-lecture.html](http://www.nobelprize.org/nobel_prizes/physics/laureates/2010/geim-lecture.html)
- [65] Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stormer H L, Zeitler U, Maan J C, Goebinger G S, Kim P, Geim A K 2007 Room-temperature quantum Hall effect in graphene *Science* **315** 1379
- [66] Chen J-H, Jang C, Adam S, Fuhrer M S, Williams E D and Ishigami M 2008 Charged-impurity scattering in graphene *Nature Phys.* **4** 377
- [67] See for example: Fradkin E 1986 Critical behavior of disordered degenerate semiconductors: I. Mondels, symmetries, and formalism *Phys. Rev. B* **33** 3257
- [68] Miao F, Wijeratne S, Zhang Y, Coskun U C, Bao W and Lau C N, 2007 Phase-coherent transport in graphene quantum billiards *Science* **317** 1530
- [69] Danneau R, Wu F, Craciun M F, Russo S, Tomi M Y, Salmilehto J, Morpurgo A F and Hakonen P J 2008 Shot noise in ballistic graphene *Phys. Rev. Lett.* **100** 196802
- [70] Chen J-H, Jang C, Xiao S, Isigami M and Fuhrer M S 2008 Intrinsic and extrinsic performance limits of graphene devices on SiO<sub>2</sub> *Nature Nanotechnol.* **3** 206
- [71] Abanin D A *et al* 2011 Giant nonlocality near the dirac point in graphene *Science* **332** 328
- [72] Bolotin K I, Sikes K J, Jiang Z, Klima M, Fundenberg G, Hone J, Kim P and Stormer H L 2008 Ultrahigh electron mobility in suspended graphene *Solid State Commun.* **146** 351–5
- [73] Castro E V, Ochoa H, Katsnelson M I, Gorbachev R V, Elias D C, Novoselov K S, Geim A K and Guinea F 2010 Limits on charge carrier mobility in suspended graphene due to flexural phonons *Phys. Rev. Lett.* **105** 266601
- [74] Geim A K 2009 Graphene: status and prospects *Science* **324** 1530
- [75] Young A F and Kim P 2009 *Nature Phys.* **5** 222
- [76] Stander N, Huard B and Goldhaber-Gordon D 2009 Evidence for Klein tunneling in graphene p–n junctions *Phys. Rev. Lett.* **102** 026807
- [77] Schedin F, Geim A K, Morozov S V, Hill E W, Blake P, Katsnelson M I and Novoselov K S 2007 Detection of individual gas molecules adsorbed on graphene *Nature Mater.* **6** 652
- [78] Zhou S Y, Gweon G-H, Fedorov A V, First P N, de Heer W A, Lee D-H, Guinea F, Castro A H Neto and Lanzara A 2007 Substrate-induced bandgap opening in epitaxial graphene *Nature Mater.* **6** 770
- [79] Yavari F, Kritzinger C, Gaire C, Song L, Gullapalli H, Borca-Tasciuc T, Ajayan P M and Koratkar N 2010 Tunable bandgap in graphene by the controlled adsorption of water molecules *Small* **6** 2535
- [80] Nair R R, Blake P, Grigorenko A N, Novoselov K S, Booth T J, Stauber T, Peres N M R and Geim A K 2008 Fine structure constant defines visual transparency of graphene *Science* **320** 1308
- [81] Blake P *et al* 2008 Graphene-based liquid crystal device *Nano Lett.* **8** 1704
- [82] Wang F, Zhang Y, Tian C, Girit G, Zettl A, Crommie M and Shen Y R 2008 Gate-variable optical transitions in graphene *Science* **320** 206
- [83] Chen Y P and Yu Q 2010 Graphene rolls off the press *Nature Nanotechnol.* **5** 559
- [84] Obraztsov A N 2009 Chemical Vapour deposition making graphene on a large scale *Nature Nanotechnol.* **4** 212
- [85] Ismach A, Druzgalski C, Penwell S, Schwartzberg A, Zheng M, Javey A, Bokor J and Zhang Y 2010 Direct Chemical vapor deposition of graphene of dielectric surfaces *Nano Lett.* **10** 1542
- [86] Bae S *et al* 2010 Roll-to-roll Production of 30-inch graphene films for transparent electrodes *Nature Nanotechnol.* **5** 574
- [87] Wang X, Zhi L and Muellen K 2008 Transparent, conductive graphene electrodes for dye-sensitized solar cells *Nano Lett.* **8** 323

- [88] Zhu Y, Sun Z, Yan Z, Jin Z and Tour M M 2011 Rational design of hybrid graphene films for high-performance transparent electrodes *ACS Nano* **5** 6472
- [89] Yang N, Zhai J, Wang D, Chen Y and Jiang L 2010 Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells *ACS Nano* **4** 887
- [90] Lee J M *et al* 2010 Vertical pillar-superlattice array and graphene hybrid light emitting diodes *Nano Lett.* **10** 2783
- [91] Meyer J C, Girit C O, Crommie M F and Zettl A 2008 Imaging and dynamics of light atoms and molecules on graphene *Nature* **454** 319
- [92] Nair R R *et al* 2010 Graphene as a transparent conductive support for studying biological molecules by transmission electron microscopy *Appl. Phys. Lett.* **97** 153102
- [93] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 Graphene photonics and optoelectronics *Nature Photon.* **4** 611
- [94] Lee C, Wei X, Kysar J W and Hone J 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene *Science* **321** 385
- [95] Son Y-W, Cohen M L and Louie S G 2006 Energy gaps in graphene nanoribbons *Phys. Rev. Lett.* **97** 216803
- [96] Han M Y, Özyilmaz B, Zhang Y and Kim P 2007 Energy band-gap engineering of graphene nanoribbons *Phys. Rev. Lett.* **98** 206805
- [97] Özyilmaz B, Jarillo-Herrero P, Efetov D and Kim P 2007 Electronic transport in locally gated graphene nanoconstrictions *Appl. Phys. Lett.* **91** 192107
- [98] Liao L, Bai J, Cheng R, Lin Y-C, Jiang S, Huang Y and Duan X 2010 Top-gated graphene nanoribbon transistors with ultrathin high-k dielectrics *Nano Lett.* **10** 1917
- [99] Ponomarenko L A, Schedin F, Katsnelson M I, Yang R, Hill E W, Novoselov K S and Geim A K 2008 Chaotic dirac billiard in graphene quantum dots *Science* **18** 356
- [100] Ihn T *et al* 2010 Graphene single-electron transistors *Mater. Today* **13** 44
- [101] Lin Y-M, Dimitrakopoulos C, Jenkins K A, Farmer D B, Chiu H-Y, Grill A and Avouris Ph 2010 1 00-GHz transistors from wafer-scale epitaxial graphene *Science* **327** 662
- [102] Liao L, Lin Y-C, Bao M, Cheng R, Bai J, Liu Y, Qu Y, Wang K L, Huang Y and Duan X 2010 High-speed graphene transistors with a self-aligned nanowire gate *Nature* **467** 305
- [103] Lin Y-M *et al* 2011 Wafer-scale graphene integrated circuit *Science* **332** 1294
- [104] Hill E W, Geim A K, Novoselov K, Schedin F and Blake P 2006 Graphene spin valve devices *IEEE Trans. Magn.* **42** 2694
- [105] Cho S, Chen Y-F and Fuhrer M S 2008 Gate-tunable graphene spin valve *Appl. Phys. Lett.* **91** 123105
- [106] Hong A J *et al* 2011 Graphene flash memory *ACS Nano* **5** 7812
- [107] Abanin D A *et al* 2011 Giant nonlocality near the dirac point in graphene *Science* **332** 328
- [108] Schwierz F 2010 Graphene transistors *Nature Nanotechnol.* **5** 487
- [109] Jia X, Campos-Delgado J, Terrones M, Meunier V and Dresselhaus M S 2011 Graphene edges: a review of their fabrication and characterization *Nanoscale* **3** 86
- [110] Sprinkle M, Ruan M, Hu Y, Hankinson J, Rubio-Roy M, Zhang B, Wu X, Berger C and de Heer W A 2010 Scalable templated growth of graphene nanoribbons on SiC *Nature Nanotechnol.* **5** 727
- [111] Dössel L, Gherghel L, Feng X and Müllen K 2011 Graphene nanoribbons by chemists: nanometer-sized, soluble and defect-free *Angew. Chem. Int. Edn Engl.* **50** 2540
- [112] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J-H, Kim P, Choi J-Y and Hong B H 2009 Large-scale pattern growth of graphene films for stretchable transparent electrodes *Nature* **457** 706
- [113] Kim B J, Jang H, Lee S-K, Hong B H, Ahn J-H and Cho J H 2010 High-performance flexible graphene field effect transistors with ion gel gate dielectric *Nano Lett.* **10** 3464
- [114] Gwon H, Kim H-S, Lee K U, Seo D-H, Park Y C, Lee Y-S, Ahn B T and Kang K 2011 Flexible energy storage devices based on graphene paper *Energy Environ. Sci.* **4** 1277
- [115] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 Superior thermal conductivity of single-layer graphene *Nano Lett.* **8** 902
- [116] Wehling T O, Novoselov K S, Morozov S V, Vdovin E E, Katsnelson M I, Geim A K and Lichtenstein A I 2008 Molecular doping of graphene *Nano Lett.* **8** 173
- [117] Elias D C *et al* 2009 Control of graphene's properties by reversible hydrogenation: evidence for graphane *Science* **323** 610
- [118] Nair R R *et al* 2010 Fluorographene: a two-dimensional counterpart of teflon *Small* **6** 2877
- [119] Reina A, Son H, Jiao L, Fan B, Dresselhaus M S, Liu Z and Kong J 2008 Transferring and identification of single- and few-layer graphene on arbitrary substrates *J. Phys. Chem. C* **112** 17741
- [120] Reina A, Jia Z, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition *Nano Lett.* **9** 30