

# Graphene prehistory

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## Abstract

After the 2010 Nobel Prize recognized the research breakthrough reported by our group in a 2004 paper, I feel that, as my contribution to the proceedings of the Nobel symposium held earlier in 2010, it is both appropriate and important to review pre-2004 scientific literature and acknowledge early ideas. With the benefit of hindsight, I also try to analyze why our first graphene paper has attracted so much interest.

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

Before 2004, I had never worked on anything remotely relevant to graphene. In fact, I believe that our *Science* paper [1] was my first publication that contained the word ‘carbon’ or ‘graphite’. The reasons and circumstances of how this work started are discussed in detail in my Nobel lecture [2]. In short, the initial idea was to make films of graphite ‘as thin as possible’ and investigate their electronic properties. In hindsight, this idea was stimulated by (i) my background knowledge about the electric field effect in metals and semimetals; (ii) general interest generated by carbon nanotube research; and (iii) casual reading of reviews and papers about graphite. These stimuli were acknowledged in the *Science* paper. The first review of the earlier literature that was relevant specifically to graphene was provided in our 2007 progress article [3]. Since then, I updated my conference presentations whenever a historically important paper came to light. This is the first opportunity for me to update the history chapter in writing by adding several new references that came to light in the last three years. Furthermore, my recent call for further historical insights [4] was answered by a number of researchers and, for completeness, I want to acknowledge their early ideas and contributions, too.

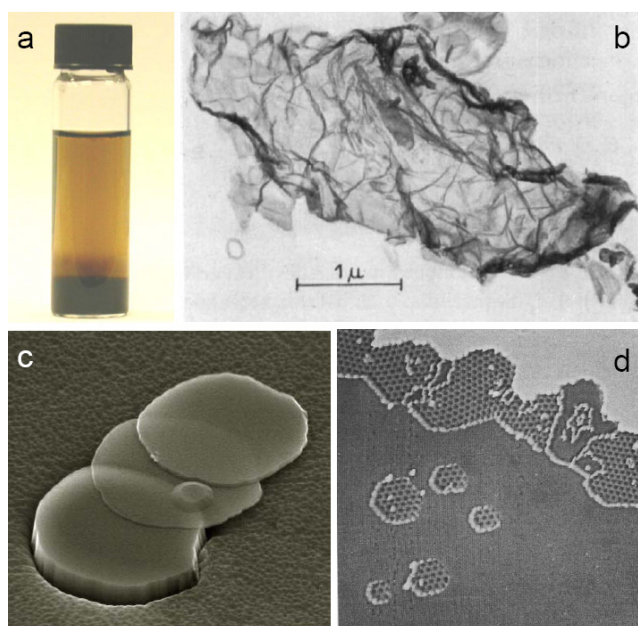
## 1. Early incarnations of graphene

Looking back at graphene’s history, let me start with the observation made by the British chemist Benjamin Brodie [5]. In 1859, by exposing graphite to strong acids, he obtained what he called ‘carbonic acid’ (figure 1(a)). Brodie believed that he discovered ‘graphon’, a new form of carbon with a molecular weight of 33. Today we know that he observed

a suspension of tiny crystals of graphene oxide, that is, a graphene sheet densely covered with hydroxyl and epoxide groups [6]. Over the next century, there were quite a few papers describing the laminated structure of graphite oxide, but the next crucial step in graphene history was the proof that this ‘carbonic acid’ consisted of floating atomic planes. In 1948, G Ruess and F Vogt used transmission electron microscopy (TEM) and, after drying a droplet of a graphene-oxide suspension on a TEM grid, they observed creased flakes down to a few nm in thickness [7]. These studies were continued by the group of Ulrich Hofmann. In 1962, he and Hanns-Peter Boehm looked for the thinnest possible fragments of reduced graphite oxide and identified some of them as monolayers [8] (figure 1(b)).

This remarkable observation received little attention until 2009–10. I have to mention that the 1962 identification relied on a relative TEM contrast, an approach that would not stand today’s scrutiny because the contrast strongly depends on focusing conditions [9]. For example, Rahul Nair and I tried but predictably failed to distinguish between monolayers and somewhat thicker flakes by using only their TEM contrast. Graphene monolayers were unambiguously identified in TEM 40 years after the 1962 paper, by counting the number of folding lines [10–12]. Nonetheless, the Boehm–Hofmann work should, in my opinion, stand as the first observation of graphene sheets because monolayers should have been present among the residue, and the idea was correct. Furthermore, it was Boehm *et al* who in 1986 introduced the term graphene, deriving it from the combination of the word ‘graphite’ and the suffix that refers to polycyclic aromatic hydrocarbons [13].

In addition to the TEM observations, another important line in pre-2004 graphene research was its epitaxial



**Figure 1.** Prehistory of graphene. (a) Graphene as probably seen by Brodie 150 years ago. Graphite oxide at the bottom of the container dissolves in water making the yellow suspension of floating graphene flakes. (b) TEM image of ultra-thin graphitic flakes from the early 1960s (reprinted with permission from [8]). (c) SEM image of thin graphite platelets produced by cleavage (similar to images reported in [26]). (d) STM of graphene grown on Pt (reprinted with permission from [18]). The image is  $100 \times 100 \text{ nm}^2$  in size. The hexagonal superstructure has a period of  $\sim 22 \text{ \AA}$  and appears due to the interaction of graphene with the metal substrate.

growth. Ultra-thin graphitic films and, sometimes, even monolayers were grown on metal substrates [14–18], insulating carbides [19–22] and graphite [23] (see figure 1(d)). The first papers I am aware of go back to 1970 when John Grant reported graphitic films on Ru and Rh [14] and Blakely *et al* [15] on Ni. Epitaxial growth on insulating substrates (SiC) was first demonstrated by van Bommel *et al* in 1975 [19] whereas Chuhei Oshima found other carbides allowing graphene growth (for example, TiC) [20]. The grown films were usually analyzed by surface science techniques that average over large areas and say little about the film's continuity and quality. Occasionally, scanning tunnelling microscopy (STM) was also used for visualization and local analysis.

Even more relevant were earlier attempts to obtain ultra-thin films of graphite by cleavage, similar to what we did in 2004. In 1990, Heinrich Kurz's group reported 'peeling optically thin layers with transparent tape' (read Scotch tape), which were then used to study carrier dynamics in graphite [24]. In 1995, Thomas Ebbesen and Hidefumi Hiura described few-nm-thick 'origami' visualized by atomic force microscopy (AFM) on top of HOPG [25]. Rod Ruoff and his colleagues [26] photographed thin graphite platelets in a scanning electron microscope (SEM) (figure 1(c)). In 2003, graphene monolayers were reported by Yang Gan who used STM for their cleavage on top of HOPG [27].

Finally, there were electrical studies of thin graphite films. Between 1997 and 2000, Yoshiko Ohashi succeeded in cleaving crystals down to  $\sim 20 \text{ nm}$  in thickness ( $\sim 60$  layers),

studied their electrical properties including Shubnikov–de Haas oscillations and, quite remarkably, observed the electric field effect with resistivity changes of up to 8% [28, 29]. Also, Ebbesen's group succeeded in growing micron-sized graphitic disks with thickness down to 60 layers and measured their electrical properties [30].

As for theory, let me make only a short note (for more references, see [3, 31]). Theoretically, graphene ('a monolayer of graphite') was around since 1947 when Phil Wallace first calculated its band structure as a starting point to understanding the electronic properties of bulk graphite [32]. Gordon Semenoff and Duncan Haldane realized that graphene could provide a nice condensed-matter analogue of  $(2+1)$ -dimensional quantum electrodynamics (QED) [33, 34] and, since then, the material served as a toy model to address various questions of QED (see, e.g. [35, 36]). Many of the theories became relevant to experiment well before 2004, when electronic properties of carbon nanotubes (rolled-up graphene ribbons) were investigated. A large amount of important theoretical work on graphene was done by Tsuneya Ando, and Millie Dresselhaus and co-workers (for examples, see [37–39]).

To complete the history of graphene, let me also acknowledge some earlier ideas. Thomas Ebbesen and Hidefumi Hiura envisaged a possibility of graphene-based nanoelectronics in 1995 (as an example, they referred to nm ribbons made from graphene grown epitaxially on TiC) [25]. Even earlier, in 1970, Hans-Joachim Teuschler secured a patent that imagined field effect transistors employing 'pyrolytic graphite' instead of Si [40]. Also, it was pointed out to me by Rod Ruoff and Reginald Little that their pre-2004 papers discussed possibilities and mentioned an intention of obtaining isolated monolayers [26, 41]. Finally, the layered structure of graphite was known since the early days of x-ray crystallography, and researchers certainly have been aware of graphite being a deck of weakly bonded graphene planes for even longer. This property has been widely used to create a variety of intercalated graphite compounds [42] and, of course, to make drawings. After all, we now know that isolated monolayers can be found in every pencil trace, if one searches carefully enough in an optical microscope [43]. Graphene has literally been before our eyes and under our noses for many centuries but was never recognized for what it really is.

## 2. Beyond observations

One may find some of the cited ideas and historical papers irrelevant, but I tried my best to avoid any pre-2004 result, especially experimental, being overlooked. All the mentioned studies poked in the right direction, but there were no big surprises to spark a graphene gold rush. This is probably because the earlier experiments had one thing in common: they were observational. They observed ultra-thin graphitic films, and occasionally even monolayers, without reporting any of graphene's distinguishing properties. The few electrical and optical measurements cited above were done using thin films of graphite and could not assess the physics that graphene brought to the fore since 2004.

Our *Science* paper [1] provided a clear watershed. The article reported the isolation of graphene crystals large enough to do all sorts of measurements, beyond the observation in an electron microscope. The method of graphene isolation and identification, which we described in there, was so straightforward and accessible that even schoolchildren could probably do it. These results are widely considered to be important but, if we were to stop there, just with these observations, our work would only add to the previous literature and, I believe, disappear into oblivion, too. It is not the observation and isolation of graphene but its electronic properties that took researchers by surprise. Our measurements delivered news, well beyond the Scotch tape technique, which persuaded many researchers to join in the graphene rush.

First, the 2004 paper reported an ambipolar electric field effect, in which resistivity changed by a factor of  $\sim 100$ , that is thousands of times more than the few % changes observed previously for any metallic system. This amounted to a qualitative difference. To appreciate the exquisiteness of this observation, imagine a nanometre thick Au film. No matter what you do with such a film by physical means, it will remain a normal metal with the same properties. In contrast, properties of graphene can be altered by simply varying the gate voltage. We could tune graphene from a state close to a normal metal with electrons in concentration  $\sim 10^{21} \text{ cm}^{-3}$  to a metal with a similar concentration of holes, all the way through a 'semiconducting' state with few charge carriers.

Even more remarkably, our devices exhibited an astonishing electronic quality. Graphene was completely unprotected from the environment, as it was placed on a microscopically rough substrate and covered from both sides with adsorbates and a polymer residue. Still, electrons could travel submicron distances without scattering, flaunting all the elements outside. This level of electronic quality is completely counterintuitive. It contradicts the common wisdom that surface science requires ultra-high vacuum and, even then, thin films become progressively poorer in quality as their thickness decreases. Even with hindsight, such electronic quality is mystifying and, in fact, not fully understood so far.

In semiconductor physics, electronic quality is described in terms of charge carrier mobility  $\mu$ . Our *Science* paper reported few-layer graphene with room-temperature  $\mu \approx 10\,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . For a general reader, 10 000 may sound like just another number. To explain its significance, let us imagine that in 2004 we made devices, for example, from reduced graphene oxide, which exhibits  $\mu \sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  due to its irreversibly damaged crystal lattice [44]. In our second paper on graphene [45], we reported two-dimensional (2D) dichalcogenides with  $\mu \approx 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Despite these materials being one-layer thick, similar to graphene, there has been little interest in them, because nothing remarkable has so far been found in their properties. The reported ballistic transport over submicron distances was essential to spark the interest in graphene and to allow the observation of many effects reported both in 2004 and later. This would have been impossible if graphene exhibited  $\mu$  below approximately several  $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

If not for graphene's high quality and tunability, there would be no new physics and, therefore, no graphene boom

that delivered so many remarkable phenomena over the last six years. Our *Science* paper offered the first glimpse of what graphene really is in its new incarnation as a high quality 2D electronic system and beyond.

### 3. Immediately after

In early September 2004, before our *Science* paper was published, I received an e-mail from Paul McEuen. He wrote that he had heard rumors about our forthcoming paper and wanted to organize a session on ultra-thin graphite at the APS March meeting. As invited speakers, the e-mail suggested Philip Kim, Walt de Heer, Paul and me. The first two names were unfamiliar to me at that time. The session was not granted and I would probably have forgotten about this e-mail but, after our report was published in *Science*, papers from all three groups also appeared in rapid succession. It is appropriate to end this article with mentioning those independent contributions.

First, there appeared a paper from de Heer's group [46]. They reported three-layer graphene films grown on top of SiC [19] and measured their electrical properties. Some of their samples exhibited  $\mu$  up to  $\approx 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and showed nascent Shubnikov-de Haas oscillations. Resistivity changes of 2% were demonstrated by varying gate voltage at liquid-helium temperatures, small in comparison with the pre-2004 reports. The paper also repeated the idea of large-scale graphene-based nanoelectronics. As mentioned above, arrays of nanoribbon transistors made from graphene were discussed in 1995 and, in patent literature, speculations about transistors made from graphitic films go back as far as 1970. The really important news that de Heer's paper delivered was the feasibility of inch-scale graphene-on-SiC wafers. This facilitated many experiments that otherwise would be difficult or even impossible until recently, when other growth techniques were developed.

A paper from Paul McEuen's group came out second [47]. They cleaved graphite by sonication and visualized deposited fragments by AFM. Platelets down to  $\sim 10$  layers in thickness were reported, which were thinner than any other isolated graphite films studied before 2004. The electrical measurements revealed mobilities up to  $\sim 2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The paper did not report the electric field effect, probably because the devices had high contact resistance. However, due to the latter, they exhibited pronounced Coulomb blockade oscillations. After 2005, the group continued to study mostly carbon nanotubes but occasionally reported some spectacular results on graphene such as, for example, the observation that graphene monolayers were impermeable to gases, including helium [48].

Then appeared a paper from Philip Kim's group [49]. In fact, it was submitted earlier than the other two, in August 2004, but published nearly a year later. The report described electronic properties of ultra-thin graphite platelets (down to  $\sim 35$  layers), which were obtained by mechanical cleavage using a 'nanopencil' [43]. Their devices exhibited high  $\mu$  and, although the electric field effect was still relatively small, it could reach a factor of ten in high magnetic fields. Shubnikov-de Haas oscillations were measured and analyzed in a manner similar to that in our *Science* report.



Except for having the much thicker devices, Philip followed the same route as we took. How close his group was could be judged from the fact that, after adopting the Scotch tape technique, Philip started studying monolayers in early 2005. This allowed him to catch up quickly and, in mid 2005, our two groups submitted independent reports that appeared back-to-back in *Nature*, both describing the all-important observation of Dirac fermions in monolayer graphene [50, 51].

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