Chapter 16
Introducing Graphene

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16.1 Historical

Graphene was first widely popularized following the publication of Geim and Novoselov, then working at the University of Manchester in the UK, reporting the isolation of individual sheets of graphene on a silica wafer using a very simple method involving peeling off layers of it from highly ordered pyrolytic graphite (HOPG) using cellophane adhesive tape (also called "micromechanical cleavage" or the "Scotch® tape method") [461, 462] in 2004. The name *graphene* itself was formalized by IUPAC (the International Union of Pure and Applied Chemistry) in 1995 [463] to avoid the use of other synonyms such as "graphite layers," "carbon layers," "carbon sheets," and "carbon exfoliates," although it was used by Mouras et al. [464] in 1987. Geim and Novoselov received the Nobel Prize in Physics in 2010 for their work on graphene [465].

However, as with all "discoveries" and "research," there is evidence that graphene was synthesized, observed, and even recognized much earlier than the above-cited work of Geim and Novoselov. For example, Boehm et al. reported on the adsorption properties of "very thin carbon sheets" in 1962, clearly recognizing what they were studying as individual sheets of graphite; they also first reported in detail the production of reduced graphene oxide (closely resembling graphene) from graphene oxide [466–468]. The term *graphene* was used by Mouras et al. in 1987, also to describe individual sheets of graphite [464]. As early as 1859, Brodie is said to have recognized graphene structurally in reduced graphite oxide [2067]. Wallace recognized graphene and discussed its structure theoretically in

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1947 [470]. And Ruess and Voigt appear to have presented transmission electron micrograph (TEM) images of few-layer graphene (“highly lamellar carbon” according to their description) in *1948* [471]. Oshima and Nagashima produced “Ultra-thin epitaxial films of graphite and hexagonal boron nitride on solid surfaces” in 1997 [472]; however, in these films, the graphene appeared to be bonded to the substrates rather than free standing as in the later Geim/Novoselov product. Jang et al. [473] filed a US patent describing “nanoscaled graphene plates” in 2002, which was issued in 2006, in which medium-scale synthesis of graphene was described. (To their credit, however, Geim and Novoselov demonstrated an extremely facile and reproducible method of synthesizing it, thus opening windows to the detailed study of its theoretical and experimental properties and applications.)

Other work of historical importance for the record and preceding the above-described seminal work of Geim and Novoselov includes that of Enoki et al., who used high temperatures (>1600 °C) to convert “nano-diamonds” into nm-scale regions of graphene atop highly ordered pyrolytic graphite (HOPG) in 2001 [474].

16.2 Basics of Graphene

Here are some basic parameters and properties of graphene that may serve to usefully orient the reader:

- *C-C bond distance* of about 1.42 Å.
- *Thickness* about 3.35 Å (this is close to the interplanar spacing in 3-D graphite).
- *Weight per unit area* about 0.77 mg/m^2.
- *Specific surface area* of about 2600 m^2/g (similar to that of activated carbon and significantly larger than that of CNTs).
- *Mechanical properties – tensile strength*, *Young’s modulus,* and *fracture toughness*:
  - Pure, defect-free graphene has a calculated *tensile strength* of about 130 GPa and a *Young’s modulus* of about 1035 GPa. These values have also been experimentally measured in very small samples [475]; they may be compared with those for standard stainless steel, of about 1.5 GPa and about 200, respectively. On the other hand, the Young’s modulus for graphite along the basal plane only is also about 1000 GPa [476].
  - However, very few as-synthesized samples are defect-free, and so their tensile strength and Young’s modulus do not approach these calculated numbers; and very few samples of graphene are large enough for their exceptional strength to be utilized in any practical manner. Nevertheless, such values have been used to accord superlative predictions to graphene, e.g., that a 1 m^2 sample of graphene could “support up to 5 kg, but weigh only 0.77 mg, 1/10,000 of the weight of standard office paper of the same size” or that, in analogy to CNTs, it could be used to construct “an elevator to space.”

  - Conversely, pure, defect-free graphene is very brittle: it has a *fracture toughness* of about 4 MPa/m$^{1/2}$ vs. about 20–50 MPa/m$^{1/2}$ for most metals [477].

- Many forms of graphene are produced using *graphene oxide* **(GO)**, which is relatively easy to synthesize from graphite, as the starting material. GO is then reduced. The reduction is however rarely 100% complete. Thus, the resulting *reduced graphene oxide* **(RGO)** frequently possesses not only impurities (such as remnants of catalysts, if used in the reduction process) but also some still-oxidized sites, frequently in the form of -C = O or –COOH groups. Nevertheless, many researchers still use RGO in their work and believe their findings extend to pure graphene.
- In addition to single sheets of graphene, i.e., monolayers, graphene as studied in the laboratory also comes in forms such as *bilayer* or *few-layer*, *nanoribbons*, and even *quantum dots*.
- Pure, defect-free graphene has an *electrical conductivity* of about 3.6×10^8 S/m or about 6 X that of Cu or Ag.
- Pure, defect-free graphene has a *thermal conductivity* of 2000–4000 W/m^2 K. These values are typical for suspended monolayers, with the higher values typical of purer samples [477].

Figure 16.1 below shows the basic structure of graphene. Figure 16.2 illustrates the "Scotch® tape" method of fabricating sheets of single-layer graphene from highly ordered pyrolytic graphite (HOPG). Figure 16.3 shows a TEM image of one of the first free-standing graphene films ever produced, in 2007.

16.3 Toxicology of Graphene

While graphene is widely recognized to have much less toxicity than CNTs, it does still present some issues in this regard, especially with the potential of being incorporated into consumer products and in medical applications [486–489].

It is believed that the toxicity of graphene and graphene oxide (GO, including reduced graphene oxide, RGO) is mainly attributable to the *mechanical* damage of the cell membrane of bacteria due to the sharp edges of the nanosheets [490, 491]. - Hydrazine-reduced GO nanosheets were reported to be more toxic to the bacterial cell, possibly due to residual hydrazine. In in vitro mammalian cell line experiments, the cytotoxic effect of GO was found to be dose and time dependent, even at a concentration of less than 20 μg/mL. Above 50 μg/mL, GO appears to severely affect the cell survival rate and induce apoptosis in the human fibroblast cell line. Similar cytotoxic effects have also been observed in other cell lines such as MGC803, MCF-7, MDA-MB-435, and HepG2. Experimental data also demonstrate that GO enters into the cytoplasm of the cell and is found to be present in subcellular compartments such as in the lysosomes, mitochondria, endoplasm, and

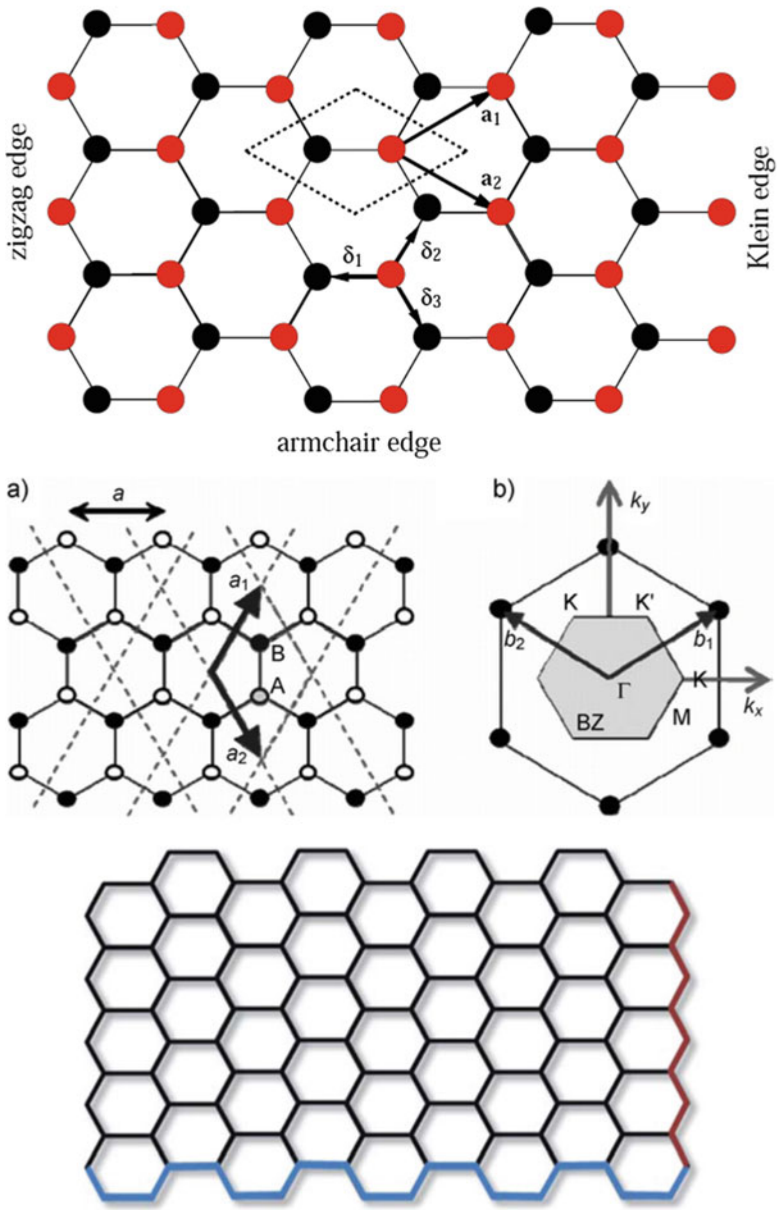

Fig. 16.1 Basic geometry of graphene lattice and the corresponding reciprocal lattice (After Refs. [478–480], reproduced with permission)

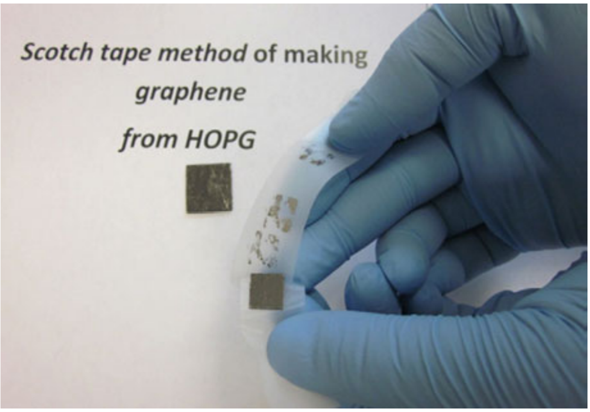

Fig. 16.2 Illustration of the “Scotch® tape” or mechanical exfoliation method of fabricating sheets of single-layer graphene from highly ordered pyrolytic graphite (HOPG) (After Ref. [481], reproduced with permission)

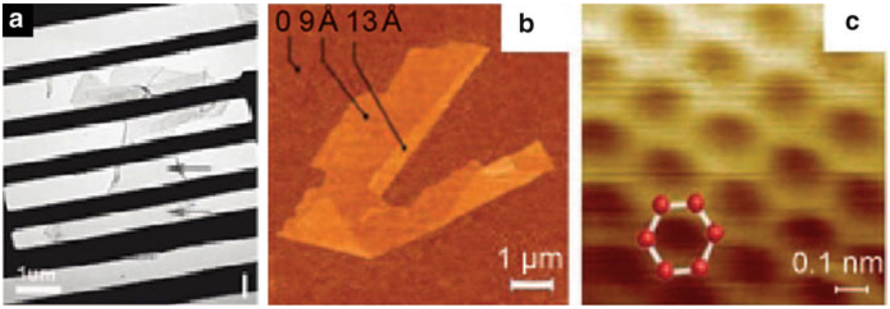

Fig. 16.3 Images of graphene: (**a**) TEM image of one of the first free-standing graphene films ever produced, in 2007. After Ref. [482], reproduced with permission. (**b**) AFM image of single-layer graphene. The folded edge exhibits a relative height of approximately 4 Å, indicating that it is single layer. (**c**) High-resolution STM image (After Refs. [483–485], reproduced with permission)

even nucleus. One hypothesis has been that GO attaches to the cell membrane and induces downregulation of the adhesion-associated gene [490, 491].

On the other hand, other studies have shown that forms of graphene, including graphene nanoribbons, have little or no toxicity up to a concentration of about 50 µg/mL, interpreted by the fact that they do not alter the differentiation of human bone marrow stem cells toward osteoblasts or adipocytes, although they do penetrate or pierce cell membranes and thus enter the interior or cells [486–489].

16.4 Basic Mechanical Properties of Graphene

The basic mechanical properties of graphene, reproduced here for convenience from earlier in this book, can be summarized as follows; many of the values cited for particular parameters apply, within a range of about ±20%, equally to monolayer, bilayer, and trilayer (but not > three layer) graphene [481]:

- Pure, defect-free graphene has a *calculated tensile strength* of about 130 GPa and a *Young's modulus* of about 1035 GPa. These values have also been *experimentally* measured in very small samples [492]; they may be compared with those for standard stainless steel, of about 1.5 GPa and about 200, respectively. On the other hand, the Young's modulus for graphite along the basal plane only is also about 1000 GPa [476].
- However, very few as-synthesized samples are defect-free, and so their tensile strength and Young's modulus do not approach these calculated numbers; and very few samples of graphene are large enough for their exceptional strength to be utilized in any practical manner. Nevertheless, such values have been used to accord superlative predictions to graphene, e.g., that a 1 m^2 sample of graphene could "support up to 5 kg, but weigh only 0.77 mg, 1/10,000 of the weight of standard office paper of the same size" or that, in analogy to CNTs, it could be used to construct "an elevator to space."
- Conversely, pure, defect-free graphene is very brittle: it has a *fracture toughness* of about 4 $MPa/m^{1/2}$ vs. about 20–50 $MPa/m^{1/2}$ for most metals [477].
- The *spring constant* of suspended graphene sheets, as determined according to Hooke's law, is in the region of 1–5 N/m [493].
- Other mechanical properties of graphene of note and their most recent reported values are as follows [494–496]: *second- and third-order elastic* stiffness of 340 and (-)690 N/m, respectively, *breaking stiffness* of 1 TPa (1000 GPa), and *intrinsic strength* of 130 GPa.

16.5 Hype on Graphene vs. CNTs Compared

Intense research and development on graphene are comparatively more recent on graphene as compared to CNTs, by approximately 10 years. As a result, as of this writing, there appears to be more promise and less "early disappointment" with regard to graphene's impact on science and commerce than with CNTs. A recent article in *Chemical and Engineering News*, the member publication of the American Chemical Society, gave a succinct account of the current status of graphene [497].

Nevertheless, and rather unfortunately, barring breakthroughs in economical, bulk production methods for highly pure, defect-free graphene in the near future, graphene appears to be on the same trajectory as CNTs in terms of expectation vs. realization, just delayed by a decade or so. As of this writing, about seven research papers are published *daily* on graphene, and more than 26,000 patents have been filed on subjects related to graphene, with a large proportion of these in East Asia [497]. The European Union recently launched an R&D initiative (similar to US initiatives on, e.g., the human genome) focusing on graphene with a budget of US $1.1 billion over 10 years [498]. There is even an exposition dedicated to graphene, denoted "Graphene & 2D Materials Europe," part of a larger, IDTechEx exhibit [499, 500].

With regard to commercial products or potential products, a very few have, as of this writing (2016), now made it to the market. A Spanish company started production of Li batteries incorporating graphene, with a claimed energy density about five times that of standard secondary Li batteries [501]. A New Jersey-based US company now offers RFID (radio frequency identification) tags with a bit of graphene in them to improve their high-temperature/high-pressure performance [502] as well as specialized antennae for cell phones (mobiles) that incorporate graphene and afford improved performance [503]. And there are other niche products already on the market as of this writing: some tennis rackets incorporating a bit of graphene (substituted for carbon fibers) to increase stiffness and reduce weight and a few conductive inks incorporating graphene [497].

In spite of all this development, however, as of this writing (2016), worldwide sales of graphene-related materials are about *US $30 million* [497]. Commercial products incorporating graphene can be counted on the fingers of one hand, as noted in the previous paragraph. The prediction that these sales will hit US $220 million in 2026 [497] seems, at least as of this writing, highly optimistic. And the expectation voiced by some in the initial, exciting years of graphene development, that graphene will replace Si in electronic circuits, seems, at this writing, or that it will appear in "low-cost touch interfaces for wearable electronic devices" [497] even more far removed, in this author's humble opinion.

16.6 Problems and Exercises

1. Briefly enumerate the major milestones in the historical discovery and development of graphene, starting with the year 1947.
2. Enumerate the defining, basic physical and structural properties of graphene, including such properties as C–C bond length, thickness, density, surface area, major mechanical properties, salient electrical properties, and salient thermal properties. Where relevant (e.g., for mechanical properties), compare graphene's values with those of other common materials (e.g., steel, copper).
3. Briefly outline the principle classes of methods of preparation of graphene. Under which class does the "Scotch® tape method" fall?
4. What is the principle mechanism of toxicity of graphene in vivo?
5. Briefly identify the known and established commercial applications of graphene as of 2016. Do the same as of your reading today.