

GRAPHITE TO GRAPHENE: FROM A MINERAL TO AN ADVANCED TECHNOLOGICAL MATERIAL

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Carbon is one of a small number of elements that occur in the “native” state. The two most dominant naturally occurring forms of carbon are graphite and diamond, and these could hardly be more different in their properties: diamond is the hardest known natural material, whereas graphite is one of the softest (see Hazen et al. 2013 for a review of carbon mineralogy). Maybe for some, “diamonds are a girl’s best friend”, but I would argue that “graphite is one of society’s most useful minerals”. The focus of this article is on graphite and, more particularly, on the closely related material *graphene*. And graphene is important because of its extraordinary properties and potential range of applications.

THE GRAPHITE STORY

In nature, graphite occurs mostly in metamorphic rocks. Graphite’s unique properties have led mankind to use it for thousands of years. Natural graphite was used in decorating pottery as early as the Neolithic Age. In historical times, perhaps as early as AD 1500, a very large graphite deposit was found in the Borrowdale area of the England’s Lake District (Cumbria, UK). This graphite had many important uses, including being formed into smooth refractory cannonball moulds during the reign Queen Elizabeth I (1558–1603). Not surprisingly, the production of Borrowdale graphite was strictly controlled by the “Crown” (government).

In the years since the Elizabethan period, graphite continued to have a range of uses. In particular, it has been used in refractories, batteries, steelmaking, brake linings and lubricants. One of the most important uses of graphite, beginning in the 16th century, was as the “lead” in pencils (the term *lead* being used at a time when graphite was believed to be a form of native lead). Initially, all pencils were made with England’s natural graphite and production was associated with the Borrowdale deposits. The “invention” of the pencil made a significant contribution to education and knowledge transfer for over six centuries. It is an intriguing precursor to our own age of communications based on electronic devices using materials such as graphene.

GRAPHENE, SCOTCH TAPE AND NOBEL PRIZES

The name “graphite” (from the Greek meaning “writing stone”) was coined by the famous German mineralogist Abraham Gottlob Werner in 1789. With the development of X-ray diffraction in the early 20th century, the crystal structure of graphite (and, hence, the structure of the “graphene layer”, see below), was determined by the distinguished Irish-born crystallographer, John Desmond Bernal (see Bernal 1924).

Graphite’s structure (FIG. 1) is of multiply stacked sheets of carbon atoms, each atom in a 3-fold coordination to its adjacent carbon atoms in a hexagonal pattern. Bonding within these sheets is very strong, but bonding between these sheets is very weak (van der Waals-type bonding). This allows the sheets to be easily separated by cleaving and, hence, why graphite can be used as pencil “lead”. *Graphene* is the name given to a material comprised of just a single sheet of the type of carbon atoms found in graphite (FIG. 1). There are also other “crystalline” arrangements of carbon atoms not found as minerals, such as those where graphene-type sheets roll up to form tubes (“carbon nanotubes”) or large numbers of carbon atoms to form sphere-like structures known as fullerenes: a well-known example is buckminsterfullerene which is otherwise known as a “bucky ball”) (FIG. 1).

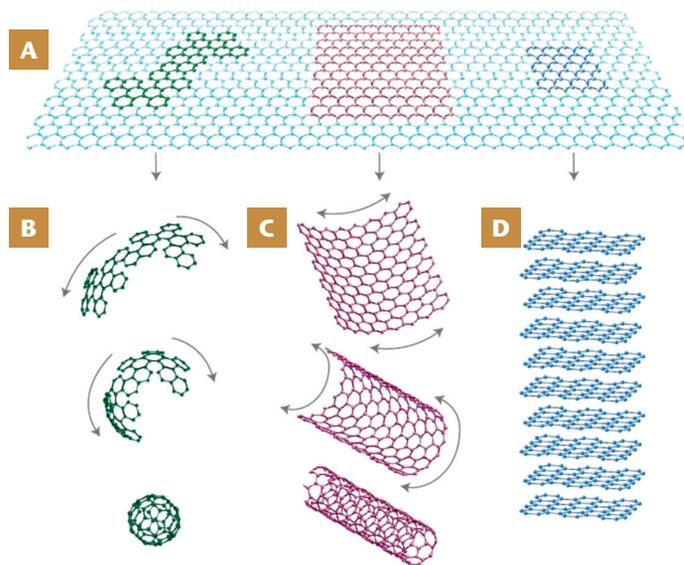


FIGURE 1 (A) A single layer of hexagonally arranged carbon atoms, each strongly bonded to three other carbon atoms to form a single sheet of graphene. (B) Folding of part of a single graphene sheet to form a ball, as in a fullerene (e.g., buckminsterfullerene, or “bucky ball”). (C) Folding of part of a single graphene sheet to form a carbon nanotube. (D) The stacking of graphene sheets as found in graphite. The bonding between these sheets is very weak, making cleavage very easy and enabling the physical separation of a single “graphene layer”. FROM GEIM AND NOVOSELOV (2007), USED WITH PERMISSION OF SPRINGER NATURE.

Although graphene had been theorized for many years, it was only first observed under the electron microscope in 1962. Then in 2004, two physicists at the University of Manchester (UK), Andre Geim and Konstantin Novoselov, succeeded in isolating graphene and characterising its properties. They found that by attaching Scotch Tape (also known as Sellotape) to a piece of graphite it was possible to peel away a single layer of the graphite so as to isolate a graphene sheet (Novoselov et al. 2004, 2005). This was a result of one of the Manchester physicists’ so-called “Friday night experiments” where free range was given to speculative investigations. This imaginative approach to science certainly paid dividends: Andre Geim and Konstantin Novoselov were awarded the 2010 Nobel Prize for physics. Andre Geim had previously been awarded a so-called Ig Nobel prize (given in recognition of a “wacky” piece of research) for his experiments on the levitation of live frogs in a strong magnetic field. He is the only scientist ever to be awarded both prizes. Techniques such as scanning tunnelling microscopy are now being used to study graphene at an atomic resolution (FIG. 2) (Zan et al. 2012).

GRAPHENE, THE WONDER MATERIAL

The successful isolation of graphene revolutionized the worlds of research and of industry. For example, Manchester University now has two new buildings, one that houses the National Graphene Institute and the other housing the Graphene Engineering Innovation Centre (<https://www.graphene.manchester.ac.uk>), both involving multimillion dollar investments. In the 15 years following Geim and Novoselov’s discovery, thousands of articles, including review papers, were published on graphene. Just a few examples are those of Choi et al. (2010), Geim (2009), Geim and Novosolev (2007), Novoselov (2011) and Randviir et al. (2014). Graphene creates great interest because it has a whole range of unusual properties which, in turn, lead to numerous practical applications. The unique properties of this 2-D “crystal” include the following:

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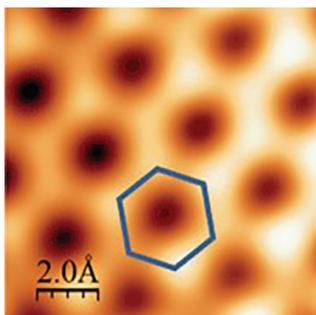


FIGURE 2 Scanning tunnelling microscope image of graphene showing atomic resolution of the hexagonal array of carbon atoms. FROM ZAN ET AL. (2012).

Electronic: Electrons move through the 2-D structure of graphene much more easily than through ordinary conductors. The charge carriers that conduct electricity move as though they are massless (at just three-hundredths of the speed of light).

Optical: Graphene is virtually transparent to visible light with an optical transparency of up to 97.7%.

Thermal: A high thermal conductivity ($5,000 \text{ Wm}^{-1}\text{K}^{-1}$) is also a characteristic of graphene.

Mechanical: The in-plane strength of graphene is two hundred times that of steel, even though it is the thinnest object ever discovered (being a 2-D crystal that is one atom thick). It also has an incredibly large specific surface area of $2,630 \text{ m}^2\text{g}^{-1}$.

APPLICATIONS AND POTENTIAL APPLICATIONS

The excitement about graphene amongst physicists and materials scientists is because of its potential for the development of new technologies. Just a few examples are given below.

Computers, Data Storage, and Solar Cells

The ease and speed with which charge carriers (such as electrons) move in graphene make it a likely candidate to succeed silicon in high-speed computer chips. High-speed graphene transistors are set to appear in consumer electronics. A related application concerns data storage where reducing the size, or increasing the capacity, of devices such as the USB flash drive could have similar impact for the consumer. Devices with about ten times the storage capacity of widely available 16GB USB flash drives have been developed, with prospects of storing a terabyte on a device the size of a flash drive and at a modest cost to the user.

A related aspect to that of data storage is concerned with energy storage. Graphene-based supercapacitors can deliver high electric currents over a short space of time. Applications to transport include electric cars, trains and, one day perhaps, electric aircraft. In the case of electric cars, the advantages are in the ability to more rapidly recharge the car battery and so be able to travel longer distances before needing to recharge again.

The combination of high conductivity, flexibility and almost perfect optical transparency also make graphene an attractive material for use in touch-screen displays and solar cells, especially as we develop ways of making ever-larger sheets of graphene.

Sensors and Filters

In contrast to applications of graphene associated with its electronic and optical properties, there are uses in the development of very sensitive sensors for gases and biomolecules. Detection of individual gas molecules adsorbed on graphene have been reported (Schedin et al. 2007). The operational principle is based on a change in electrical conductivity as a result of the adsorption of molecules onto the graphene surface. Good sensing properties have been shown, for example, towards NO_2 , NH_3 , CO

and dinitrotoluene (a volatile compound found in explosives). As well as gas sensing, there are biosensing applications, including examples of interest in medicine such as the detection of the neurotransmitters dopamine and serotonin. In contrast, graphene-based biosensors have been developed for the detection of human exposure to cadmium (Cd^{2+}), a toxic element found in industrial and mine wastes.

Sensitive detection of toxins in the human body or in the natural environment is one important application of relevance to environmental scientists: another is the actual cleaning-up of the environment. Here, graphene can also make a major contribution, such as in the decontamination of drinking water. The conventional water-filter membranes used in water purification are made from polymers that cannot handle the diverse mix of contaminants commonly found in polluted waters. Some of them either clog filters or allow contaminants to pass through, so they have to be separated out before the water is filtered. Graphene-based technology can produce clean drinking water, regardless of how dirty it is before treatment, in a single step. The system employs a film made from a thin layer of graphene that allows water to pass through microscopic nanochannels in its surface while stopping larger-molecule pollutants.

New Composite Materials

Graphene is often described as “the world’s strongest material”. It can be added to metals, plastics or other materials to make them stronger (or to produce a light-weight, but very strong, material). Graphene-enhanced composite materials can find uses in areas ranging from aerospace to building materials. Popular current examples include addition to materials used in sporting goods, such as running shoes and tennis racquets, to enhance their performance.

CONCLUSION

Thus, from the 16th century use of graphite as the “lead” in then-new pencil technology, to the current prospects of knowledge transfer in enhanced electronic devices employing graphene, we can say most emphatically ... mineralogy matters.

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