8.1 Carbon lattices

Diamonds are highly valued in our society. Diamonds are a form of pure carbon, but they are not the only form that carbon can take. **Graphite**, charcoal, **graphene** and **fullerenes** are also made entirely from carbon but their properties are very different from those of diamond. Scientists have found many exciting uses for these other forms of carbon. As the properties of these forms of carbon are quite different, it is not surprising that their chemical structures are also different.

ABUNDANCE AND PROPERTIES OF CARBON

Carbon is a fascinating element for many reasons. Carbon:

- is a vital component of all living systems
- is the 11th most abundant element in the universe
- has three isotopes: ^{12}C (98.9% abundant), ^{13}C (1.1% abundant) and ^{14}C (traces)
- has one of the highest melting points of any element. It undergoes **sublimation**, changing from a solid state directly to a gas state at temperatures above 3550°C
- is a non-metal, but a number of forms can conduct electricity
- can form single, double and triple covalent bonds with several other elements
- can form large molecules and lattice structures by bonding to itself.

ALLOTROPES

Some elements can exist with their atoms in several different structural arrangements called **allotropes**, that give them different physical forms. In different allotropes, the atoms are bonded to each other in different, specific ways. This gives them significantly different properties from other allotropes of the same element.

Oxygen forms allotropes. Oxygen gas consists of diatomic molecules with the formula O_2. Each oxygen atom in this arrangement is bound to one other oxygen atom. Ozone is another molecule containing only oxygen. Ozone molecules have the formula O_3 and consist of a central oxygen atom bound to two other oxygen atoms. Figure 8.1.1 shows the structure of these two molecules. As both contain only oxygen atoms, they are both allotropes of oxygen. The rest of this section will focus on the different allotropes of carbon.

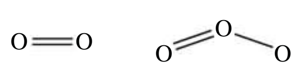


FIGURE 8.1.1 Oxygen and ozone are two molecules that contain only oxygen atoms.

FIGURE 8.1.2 Diamond is the hardest naturally occurring substance.

FIGURE 8.1.3 Natural graphite is soft and black.

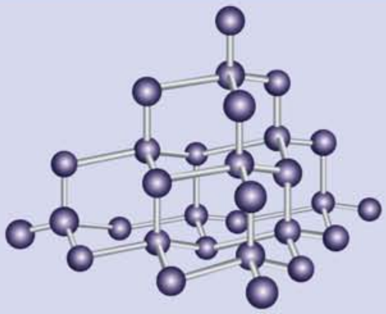
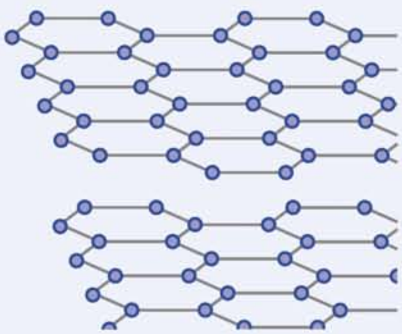
> Allotropes are different forms of the same element.

ALLOTROPES OF CARBON

Diamonds (Figure 8.1.2) might be a 'girl's best friend' but it is unlikely that graphite (Figure 8.1.3) will ever be held in the same esteem. Both of these minerals are made of the same single element—carbon. Graphene and fullerenes are new materials that are also allotropes of carbon.

Table 8.1.1 summarises some information about the structure, properties and uses of the three most common allotropes of carbon: diamond, graphite and amorphous carbon.

TABLE 8.1.1 Comparison of properties of some of the allotropes of carbon

Allotrope	Structure	Properties	Uses
Diamond	 Covalent network lattice, each carbon surrounded by four other carbon atoms in a tetrahedral arrangement	• Very hard • Sublimes • Non-conductive • Brittle	• Jewellery • Cutting tools • Drills
Graphite	 Covalent layer lattice, each carbon bonded to three other carbons, one delocalised electron per carbon atom	• Conductive • Slippery • Soft • Greasy material	• Lubricant • Pencils • Electrodes • Reinforcing fibres
Amorphous carbon	Irregular structure of carbon atoms. Many varieties exist with many different, non-continuous packing arrangements	• Conductive • Non-crystalline • Cheap	• Printing ink • Carbon black filler • Activated charcoal • Photocopying

Diamond

Diamond is the hardest naturally occurring substance known.

Diamond does not contain small, discrete (individual) molecules. Instead, the carbon atoms bond to each other to form a continuous three-dimensional structure called a **covalent network lattice**. There are no weak intermolecular forces present, only strong covalent bonds. This is what gives diamond its strength.

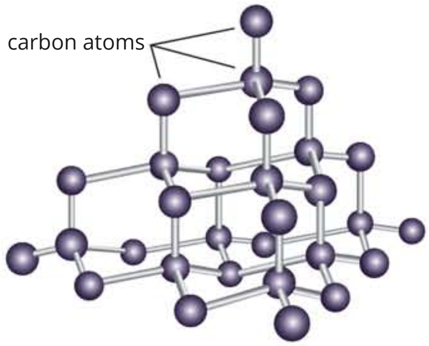


FIGURE 8.1.4 The structure of diamond showing each carbon atom with four single covalent bonds to neighbouring atoms.

> Diamond is made up of carbon atoms that bond with four neighbouring carbon atoms forming a covalent network lattice. This structure makes diamond extremely hard.

In general, substances that have a network lattice structure have very high melting points or decomposition temperatures. They are also very hard because the atoms are held firmly in fixed positions in the lattice.

As you saw in Chapter 7, when an atom has four electron pairs in its outer shell, the electron pairs position themselves as far away from each other as possible in a tetrahedral shape. In the covalent network lattice for diamond shown in Figure 8.1.4, you can also see that individual atoms within diamond form single covalent bonds to four other carbon atoms in a tetrahedral arrangement.

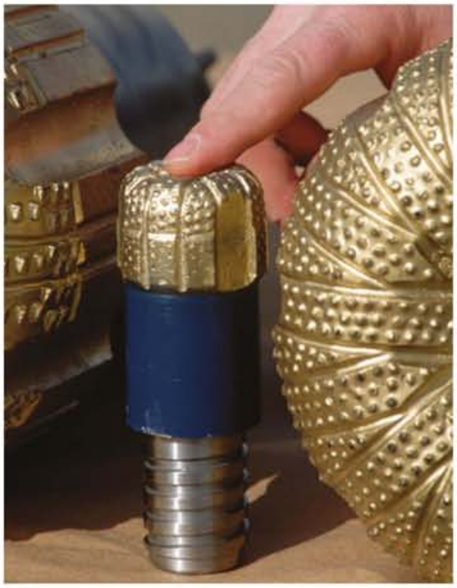


FIGURE 8.1.5 Diamond-tipped drills used to drill through rock in the fracking industry.

The structure of diamond is directly related to its properties.

- Single covalent bonds between carbon atoms are strong bonds. The entire structure of a diamond consists of a continuous network of these bonds, making diamond very hard and rigid.
- There are no small molecules in diamond, so there are no weak forces between the atoms. There are only strong covalent bonds between carbon atoms and this makes the sublimation point very high (about 3500°C).
- The rigidity means that diamonds are brittle and break rather than bend.
- Diamond does not conduct electricity because it does not contain any charged particles that are free to move.
- Because the atoms in diamonds are held together very strongly, the thermal conductivity is extremely high. It is five times greater than that of copper, leading to some specialty electronic uses where diamond is used to transfer heat away from some important electrical components.

The crystalline appearance of diamonds and their high refractive index make them sparkle and has made them extremely popular as jewellery, but the hardness of diamond also lends itself to industrial uses. Many industrial cutting and drilling tools for working with tough materials are diamond tipped. The drill tips in Figure 8.1.5 are used to drill through rock in the fracking industry. They contain small pieces of diamond that improve the hardness and durability of the tool.

CHEMFILE

Impact diamonds

'We are speaking about trillions of carats', trumpeted the 2012 headline from the British *Daily Mail*. It was in reference to a 100 km meteorite crater, the Popigai Crater, in Russia that could supply world markets with diamonds for 3000 years. The now closed Mirny mine, shown in Figure 8.1.6, is also in Russia. This open-cut mine is over 500 metres deep and has yielded diamonds worth more than $20 billion since 1951.

FIGURE 8.1.6 The Mirny diamond mine is over 500 metres deep.

It is thought that the impact of a large meteorite created enough heat and pressure in the Popigai Crater to make diamonds. Russian scientists are reported to have known of this deposit since 1971, but kept details hidden until supplies from other sources began to run out. Diamonds formed from a meteorite strike, like those in Figure 8.1.7, are referred to as 'impact diamonds'. They can be almost as large as a 20-cent coin, and are prized for their extreme hardness.

FIGURE 8.1.7 High-quality 'impact diamonds' can be almost the size of a 20-cent coin.

Graphite

Graphite is a very different form of carbon. As you can see in Figure 8.1.8, the carbon atoms in graphite are in layers. There are strong covalent bonds between the carbon atoms in each layer. However, there are weak dispersion forces between the layers. As a consequence, it is hard in one direction but quite slippery and soft in another direction. The structure of graphite is referred to as a **covalent layer lattice**.

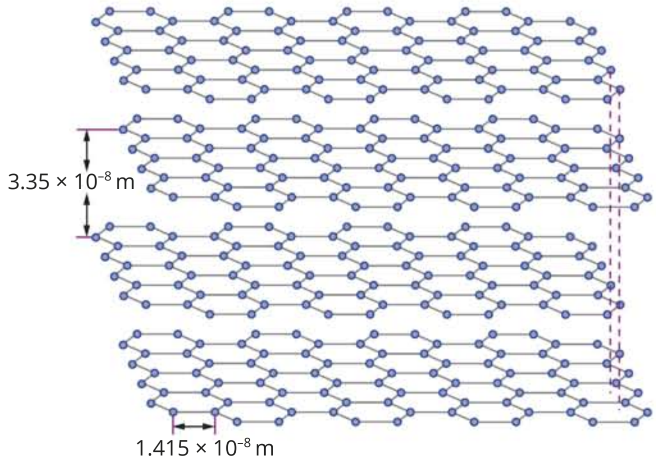


FIGURE 8.1.8 Graphite has a covalent layer lattice structure. The carbon atoms within each layer are covalently bonded to each other. Weak dispersion forces exist between the layers.

The covalent layer lattice structure of graphite also explains some of its other properties.

- The strong covalent bonds between the atoms in each layer explain graphite's resistance to heat. Graphite sublimes at a temperature of about 3600°C.
- Each carbon atom is bonded to three other carbon atoms. The fourth valence electron from each atom is able to move within the layer. The electrical conductivity of graphite is due to these delocalised electrons.

The conductivity of graphite makes it suitable for applications such as battery electrodes where conductivity is required but a metal is not suitable.

In graphite, each carbon atom is covalently bonded to three other carbon atoms. The layered network structure contains delocalised electrons. Bonds within the layers are strong but bonds between layers are weak dispersion forces.

Graphite can also be used as a lubricant. The weak dispersion forces between layers allow these layers to slide over each other and to reduce the friction between moving parts, such as in locks or machinery.

Graphite is also used as an additive to improve the properties of rubber products and it can be woven into a fibre. This helps to reinforce plastics. Figure 8.1.9 shows spun graphite fibre, which can be used to make strong composite materials such as those used in tennis racquets, fishing rods and racing car shells.

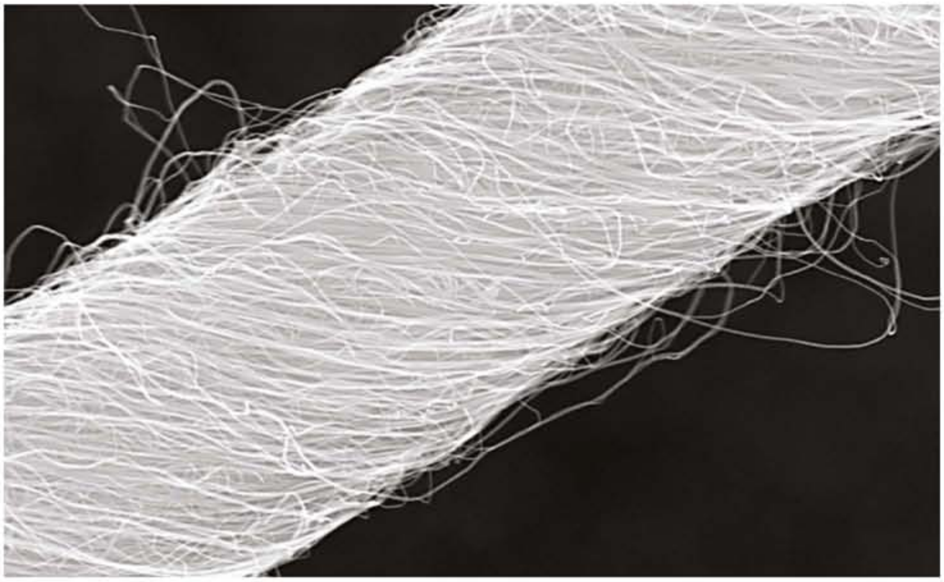


FIGURE 8.1.9 Graphite fibre can be used to reinforce plastics.

CHEMFILE

Black-lead pencils

In 1564, a very pure deposit of graphite was discovered in England. The graphite was so stable that it could be cut into thin, square sticks that could be used for writing. String was wrapped around the graphite to make the first pencils. Later the string was replaced with wood (Figure 8.1.10).

The pencils were so effective that during the Napoleonic Wars, the English were considered to have a technological advantage, because their pencil-written communications were far more effective than the French equivalents. Napoleon commissioned a French inventor, Nicholas-Jacques Conte, to develop an alternative to pure graphite. The mixtures of clay and powdered graphite that he designed are the basis for the 'lead' in modern pencils.

FIGURE 8.1.10 An early pencil that consisted of a strip of graphite placed between pieces of wood.

Amorphous forms of carbon

Charcoal (Figure 8.1.11) and carbon black (Figure 8.1.12) are examples of **amorphous** carbon that has no consistent structure. It contains irregularly packed, tiny crystals of graphite and other non-uniform arrangements. Lumps of charcoal are produced for use as a fuel, while carbon black is used to make printer toner ink.

FIGURE 8.1.11 Lumps of charcoal are produced for use as a fuel.

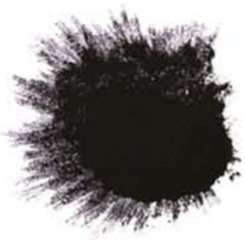


FIGURE 8.1.12 Carbon black is used in printer toner ink.

Amorphous carbon can be formed from the **combustion** of wood and other plant matter when there is a limited supply of air. There are several other types of amorphous carbon, including soot, which can be seen in Figure 8.1.13, being emitted from an industrial chimney. The distinctions between the different forms of amorphous carbon are blurred.

FIGURE 8.1.13 Soot is emitted from an industrial chimney.

Each form of amorphous carbon has its uses and some have been used by society for centuries. Since the Middle Ages it has been common to produce charcoal in ovens. Figure 8.1.14 shows a number of beehive-shaped ovens that were used to produce charcoal from timber. These ovens were built between 1876 and 1879.

FIGURE 8.1.14 These ovens in Nevada, USA, were built between 1876 to 1879 to make charcoal.

Uses of carbon black

Carbon black is a refined type of amorphous carbon in which the particle size is more uniform. Most carbon black is used to reinforce rubber products such as tyres and hoses, causing their black appearance. The surface interaction between the fine carbon particles and the rubber molecules increases the strength and toughness of the product.

Many printer and photocopier toners contain carbon black particles mixed with a binder polymer and other additives. More than 9 million tonnes of carbon black is used annually worldwide.

Uses of activated charcoal

Charcoal can be 'activated' by heating it to high temperatures in the presence of an inert gas. Activated charcoal particles are so porous that it is estimated that a 1-gram sample has a surface area similar to that of an Australian Rules football oval. Figure 8.1.15 shows a microscope image of activated charcoal.

FIGURE 8.1.15 A microscope image of activated charcoal shows that it contains many pores and hollows.

Activated charcoal can adsorb impurities onto its porous surface. The impurities are trapped in the pores of the activated charcoal particles by weak attractive forces, such as dispersion forces. This makes activated charcoal useful as:

- water filters
- 'odour-eater' inserts in shoes
- a treatment for a drug overdose. Activated charcoal is pumped into the victim's stomach to adsorb the harmful drug molecules.

CHEMFILE

Production of biochar

Most scientists agree that rising levels of carbon dioxide in the atmosphere, which are a result of human activities, are causing global warming. One area of research at the CSIRO to help combat rising carbon dioxide levels is the production of **biochar**.

Biochar is a high-carbon, porous and fine-grained residue produced by placing biomass (plant and forest waste) in a trench and covering it with soil. The biomass is allowed to smoulder, burning very slowly in the absence of oxygen. The product of this process is carbon and not carbon dioxide.

Biochar can increase the fertility of soils and agricultural production, using waste that would otherwise have become carbon dioxide. Figure 8.1.16 shows farmers adding biochar to the soil in a field.

FIGURE 8.1.16 Biochar added to soil improves the soil by supplying carbon and trapping nutrients.

8.1 Review

SUMMARY

- Carbon can be found in the Earth's crust in the form of diamond, graphite or charcoal. The structures and properties of these allotropes are very different.
- In diamond, each carbon atom is covalently bonded to another four carbon atoms in a tetrahedral shape, forming a covalent network lattice structure. Diamond sublimes at a high temperature, is extremely hard and has a sparkling, crystalline appearance.
- In graphite, each carbon atom is covalently bonded to three other carbon atoms. The layered network structure contains delocalised electrons. Bonds within the layers are strong but bonds between layers are weak dispersion forces. Graphite is slippery, conducts electricity and sublimes at a high temperature.
- Amorphous carbon products, such as carbon black, soot and charcoal, are formed from the combustion of plant and animal matter in a limited supply of air. Amorphous carbon has no consistent structure.

KEY QUESTIONS

1 Why can carbon form so many different compounds?

2 **a** What is meant by the word *sublime*?
  b Explain why diamond and graphite only sublime at temperatures over 3500°C.

3 Explain the following properties of diamond and graphite in terms of their respective structures.
  a Hardness or softness
  b Ability or inability to conduct electricity

4 Explain the following in terms of the structures of graphite and diamond.
  a Graphite is used as a lubricant.
  b Diamond is often used as an edge on saws and a tip on drills.

8.2 Carbon nanomaterials

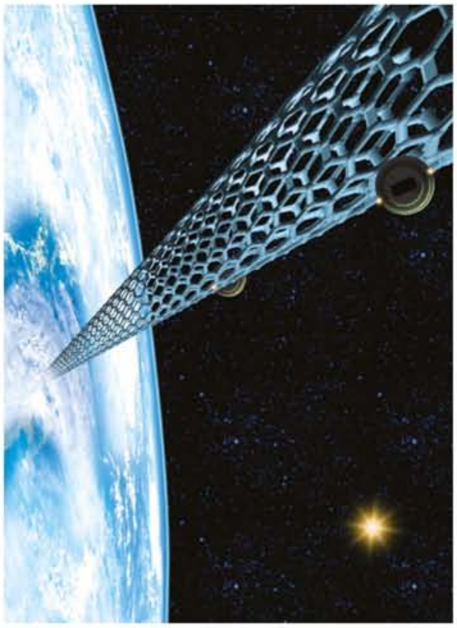


FIGURE 8.2.1 Artist's impression of a space elevator made of a carbon nanotube.

Imagine an elevator with a difference, an elevator into space. Rockets are costly and dangerous. Why not take an elevator ride instead? While this concept might sound like science fiction, scientists are considering this idea very seriously. Japanese company Obayashi has announced that they will have a space elevator up and running by the year 2050. The elevator would reach 96 000 km into space and use robotic cars powered by magnetic linear motors. The concept is only possible because of the properties of a recently discovered allotrope of carbon—carbon **nanotubes**. Figure 8.2.1 is an artist's impression of a space elevator, made of a carbon nanotube.

Diamond, graphite and amorphous carbon have long been recognised as allotropes of carbon. However, since the 1970s, scientists have discovered how to make a new range of carbon allotropes that are examples of **nanomaterials**.

You will remember from Chapter 1 that nanomaterials are particularly interesting because they have a very high surface area to volume ratio, leading to some unique or enhanced properties.

Fullerenes

In the late 1970s, while working at the Australian National University in Canberra, Dr Bill Burch discovered a new allotrope of carbon. This allotrope was made up of molecules containing a roughly spherical group of carbon atoms arranged in a series of pentagons and hexagons, similar to the shape of a soccer ball, as you can see in Figure 8.2.2.

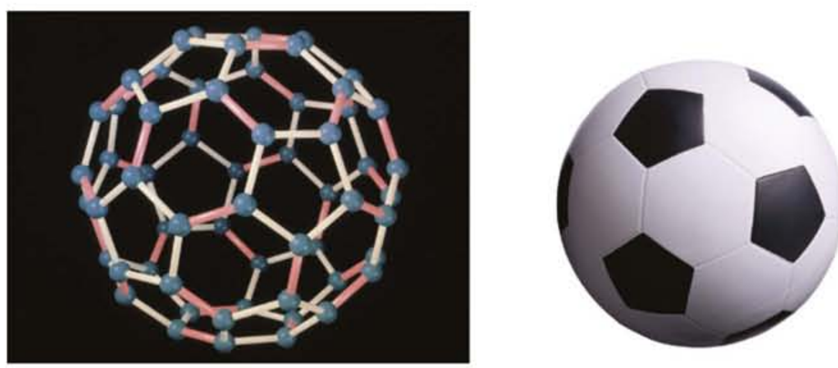


FIGURE 8.2.2 The structure of a fullerene has a similar pattern to the surface of some soccer balls.

Fullerenes are an allotrope of carbon where the atoms are arranged in a series of pentagons and hexagons.

Scientists have since found further variations of this molecule. These molecules have similar structures to the geodesic designs of architect Richard Buckminster 'Bucky' Fuller. They are called fullerenes, although they are more commonly referred to as **buckyballs**. Figure 8.2.3 shows the Biosphere in Montreal, Canada—a museum designed by Buckminster Fuller.

FIGURE 8.2.3 The Biosphere in Montreal, Canada, is a museum designed by Buckminster Fuller.

Fullerenes have three covalent bonds to each carbon atom and in some ways appear to be similar to graphite. This leaves delocalised electrons in the structure and the possibility of electrical conductivity. Although fullerenes were initially just a curiosity, scientists predict that they have significant potential in a number of fields such as composite materials and **photovoltaic cells** (solar panels). The most stable fullerene molecule involves 60 carbon atoms bonded into an approximately spherical shape that is known as buckminsterfullerene or C_{60}.

CHEMFILE

Fullerenes in flexible photovoltaic cells

Traditional photovoltaic cells (the solar panels you see on many rooftops) are made from highly refined and purified silicon crystals. Manufacturing these crystals is complex and the cells produced are rigid and brittle.

Research into fullerenes has led to alternative types of photovoltaic cells, known as polymer solar cells. Polymer solar cells (Figure 8.2.4) use alternate layers of fullerene molecules instead of silicon. The cell produced is lighter than conventional cells and offers the advantage of being flexible. A flexible cell could match the curved shape of a caravan roof or the cabin of a boat. The initial problem with these cells was their low efficiency. Research into fullerenes and other aspects of the cells continues to improve their efficiency.

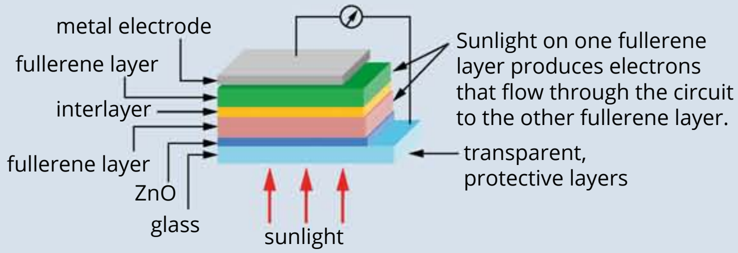


FIGURE 8.2.4 Polymer solar cells are constructed from transparent covering layers and alternate layers of fullerenes.

Graphene and nanotubes

Two other allotropes of carbon that are being heavily researched are nanotubes, which are regarded as being part of the fullerene family, and graphene.

Graphene

You have seen that graphite has a layered structure. Graphene is best described as a single layer of graphite (Figure 8.2.5). Graphene is a single layer sheet with the same arrangement as those stacked in graphite. It is a very new material and was first isolated in 2004.

Graphite is soft, due to the weak dispersion forces between its layers. Graphene is only a single layer and retains the electrical conductivity of graphite but it is an extremely strong and tough material.

Graphene has many potential uses. Graphene could:

- replace silicon as the basis for computer chips and circuits due to its high electrical conductivity
- be used in desalination plants. Water under pressure can pass through the thin layer but dissolved impurities cannot
- be used to construct electrodes where it is an advantage for an electrode to be a non-metal
- be used in organic photovoltaic cells
- be used to reinforce composite materials because of its strength.

An interesting feature of graphene is that, because it is a single layer, every carbon atom is available for reaction from two sides at any instant during a chemical reaction.

FIGURE 8.2.5 Graphene is a single layer sheet with the same arrangement as those stacked in graphite.

Nanotubes

'Nanotubes' are closely related to graphene. They are called nanotubes because they have a long, hollow structure with walls formed from graphene. The diameter of these cylinders is very small, around 1 nanometre (10^{-9} metre) wide, while they can be millions of times longer. They can be capped on the end of each cylinder by a half fullerene molecule as shown in Figure 8.2.6.

Nanotubes can be single-walled or multi-walled. A multi-walled nanotube has smaller tubes sitting inside larger tubes.

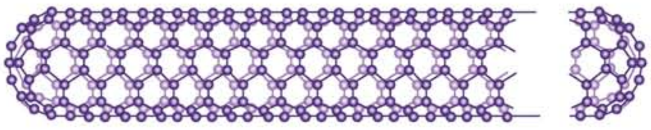


FIGURE 8.2.6 A carbon nanotube can be regarded as a sheet of graphene rolled into a cylinder and capped on the ends by half a fullerene molecule.

Scientists are interested in nanotubes because of their:

- unique strength
- electrical conductivity
- thermal conductivity
- strong forces of attraction to each other.

Nanotubes hold great promise in fields such as optics, nanotechnology and electronics. Their extraordinary strength and thermal and electrical conductivity suggest they may be useful as additives in various structural materials.

POTENTIAL OF CARBON NANOMATERIALS

Carbon nanomaterials offer huge gains in performance and properties over some other materials in current use and have a broad range of potential applications. The carbon–carbon bonds in these structures are very strong and there are no weak points in a single layer of graphene or a nanotube.

Carbon nanotubes are:

- up to 300 times stronger than steel. Rope made from nanotubes with a diameter of 1 cm could support a weight of over 1000 tonnes. Nanotubes are already being used in high-performance sporting equipment
- better conductors of electricity than silver. Since nanotubes are essentially 'wires' that are much narrower in diameter than metal wire, they offer the possibility for extreme miniaturisation of electrical circuits
- better thermal conductors than diamond. Nanotubes could be used to transfer heat away from electrical components
- stronger than Kevlar fibres. Stain-resistant nanofabrics that never require washing are already available. You could even carry water in the pockets of a vest made from this material
- capable of adsorbing more gas or impurities than activated charcoal.

Perhaps the best way to highlight the potential of nanomaterials is with two exciting examples.

Example 1. Volvo concept car

Volvo has embarked on a radical new design for an electric car that aims to harness the properties of nanomaterials. As shown in Figure 8.2.7, most of the steel in the car has been replaced with carbon nanotube sheets. These sheets have the advantage of lightweight strength but they can also serve as a giant battery for the car. Fullerenes are incorporated in the carbon sheets, allowing them to act as photovoltaic cells, supplying the energy needed to recharge and power the car.