

nano and materials

Materials are of huge importance to our everyday lives – so much so, that historical ages are not known by key time periods, but rather by the dominant materials used at the time e.g. Stone Age, Iron Age. Advances in technology and society have always been associated with the development of a new range of materials. In this module, materials will be discussed with respect to the current 'Nano Revolution'. Carbon based nanomaterials will be covered, including graphene and carbon nanotubes. Students will be introduced to the properties and uses of these, and additional nanomaterials, that are impacting and revolutionising products in our everyday lives in the areas of structures, clothing, medicine and electronics.

Learning Outcomes

In this module, students will:

- Develop an appreciation of the range of materials with which nanoscientists work.
- Understand some of the properties of these materials, including graphene and carbon nanotubes.
- Be able to identify a range of industries in which nanomaterials can be applied.
- Develop an awareness of nanotechnology in everyday life.

Wilson Staff

teachers' notes

SYLLABUS LINKS

JC Science

→ Carbon

LC Biology

 \rightarrow Use of Microscope

LC Physics

- Conductors
- \rightarrow Insulators
- → Semi-Conductors

LC Chemistry

- → Chemical Bonding (including octet rule)
- → Van Der Waals Forces
- \rightarrow Carbon
- Shapes of covalent molecules
- \rightarrow Delocalised ring of electrons
- \rightarrow Benzene structure

NCCA Proposed LC Revisions (2011)

- Allotropes of carbor
- → Incorporation of nanotub in polymers

Why study materials?

Materials are important in all aspects of life. By studying materials science, new more advanced products can be created, potentially with greater efficiency and at a lower cost. Novel products within electronics and medical devices may help improve the quality of everyday life. Just think about how the mobile phone has changed in recent years!

Choosing a material

Our choice of material for a particular product will depend on the function of the final product and the properties of the material. Building bricks would be suitable for constructing a house because they are strong. However, they are not suitable for making cars. Neither is polystyrene, because although it is lighter, it is not robust enough to ensure safety. Silver is a better conductor of electricity than copper. However, copper wire is most commonly used for electric wires, because silver is more expensive. Our choice of materials needs to balance cost and performance.

Why study Nanoscience?

At the nanoscale, material properties differ from the properties of the bulk material. Reasons for these differences include greater surface area to volume ratio and the random motion of particles (Brownian motion). Physical and chemical properties can be different, e.g. chemical reaction rates and colour. The more we understand about the properties of materials at the nanoscale, the more likely we are to be able to choose the most appropriate nanomaterials to create new products that exploit these properties.

Diamond and Graphite

STRUCTURE — Diamond and graphite are allotropes (different forms of the same element) of carbon. These allotropes arise due to carbon's ability to form different types of bonds. In diamond, the central carbon atom bonds to 4 different carbon atoms. In graphite, the central carbon atom bonds to 3 different carbon atoms.

In diamond, a 3-dimensional structure is formed by the bonding pairs of electrons repelling each other to form a tetrahedron like structure. In diamond, carbon forms 4 single bonds.

DELOCALISED BONDING IN GRAPHITE — In graphite, the central carbon atom bonds to 3 different carbon atoms. This suggests that a double bond is in the structure to obey the octet rule (a chemical rule of thumb that states that atoms tend to combine in such a way that they each have eight electrons in their outermost shells). However, the lengths of the bonds have been found to be identical and are intermediate between a double bond and a single bond. This bonding is the same type of bonding that is present in benzene.

The double bond is not confined to particular atoms but is shared by the carbons. This 'delocalised' double bond makes the carbon atoms more strongly bonded to each other. For simplicity, the carbons can be considered to be bonded together by strong single bonds.

The bonds in graphite repel each other to be as far away from each other as possible. This repulsion causes the carbons in graphite to form a 2-dimensional structure called trigonal planar (one atom at the centre and three atoms at the corners of a triangle).

Van Der Waals Forces

The electrons that form a bond are free to move in the molecule. At a certain time, a pair of electrons may be closer to one atom than the other. This causes one atom to appear to be temporally negative and the other to appear to be temporally positive. This temporary change can cause a charge to be induced in another molecule nearby, causing the molecule to be attracted. This attraction is known as the Van Der Waals interaction. Van Der Waals forces are very weak. A covalent bond requires more than 400 times the amount of energy to break compared to Van Der Waals Forces.

3-Dimensional (3-D) and 2-Dimensional (2-D) structures

3-D structures are those which if continued to be built up would have length, width and height. Diamond is a 3-D structure. 2-D structures are those which if continued to be built up, would have length and width but not height. Graphite is a 2-D structure. In the 2-D structure of graphite, the height of the carbon is ignored as it remains constant. Graphite forms a 3-D shape in the macro world, by the layering of graphite sheets, one on top of another.

PROPERTIES

- Diamond is very hard and difficult to chip or break. This is because the carbon atoms in diamond are tightly bonded to each other in all directions a large number of covalent bonds have to be broken to 'chip' the diamond.
- Graphite e.g. pencil lead is soft. The graphite sheets are weakly bonded to the layer above and below by Van Der Waals Forces. These bonds are very easy to break, allowing sheets of graphite to be easily removed, causing graphite to appear soft.
- Diamond behaves as an insulator. This is because all of the outer electrons in diamond are involved in bonding, there are no 'free' electrons.
- Graphite behaves as an electrical conductor. This is because the electrons in the delocalised double bond are not confined to a particular atom.

What is Graphene?

Graphene is a single layer of graphite and consists of a sheet of carbon atoms, just one atom thick. The existence of a single graphite sheet prior to 2004 had been doubted and was expected to be unstable. However, when graphene was first isolated using scotch tape and a graphite crystal in 2004, it was found to be very stable. This work by 2 Russian scientists, Andre Geim and Konstantin Novoselov, based at the University of Manchester, earned them the Nobel Prize in Physics, 2010.

PROPERTIES OF GRAPHENE

- Graphene is very strong as the bonding between the carbon atoms is reinforced by the partial double bond nature. It is one of the strongest materials tested, measurements have shown that graphene has a breaking strength 200 times greater than steel.
- Graphene is an excellent conductor of electricity it is a very promising candidate for future electronic applications.
- Graphene is also impermeable, not even a helium atom can penetrate the sheet.

SUGGESTED TIMING

Lesson Plan

→ 80 minutes class with activities; additional 40 minute class with option for a further single class.

Introduction Teacher activity → 5 minutes

Powerpoint presentation Slides 1–15 (Diamond, Graphite, Graphene) Teacher activity → 30 minutes

Worksheet questions 1–9 Student activity → 15 minutes

Activity 1 (model building) / Experiment 1 _{Student activity}

 \rightarrow 30 minutes

Remaining powerpoint Slides: 16–28 (carbon nanotubes and other nanomaterials) _{Teacher activity} Begin research for Worksheet Q12

Student activity → 40 minutes

Presentation to class on research (Worksheet Q12) Student activity → 40 minutes

APPLICATIONS OF GRAPHENE

- In 2010, IBM scientists demonstrated the world's fastest transistor, made using graphene. The speed was possible because of the higher speed at which electrons in graphene move compared to electrons in silicon. Graphene could be used to replace the silicon chip in the next generation of communication devices.
- Due to graphene's high electrical conductivity and high optical transparency, it is an ideal candidate for transparent conducting electrodes, required for such applications as touchscreens, liquid crystal displays, organic photovoltaic cells, and organic light-emitting diodes (OLED). Researchers have found that graphene could replace indium-based electrodes in OLED. The use of graphene instead of indium not only reduces the cost but eliminates the use of metals in the OLED, which may make devices easier to recycle.
- Graphene may be used in sensors for gases or diseases. Due to its impermeability, graphene may be ideal as a sensor, sensitive to even one molecule. Graphene could be coated with a thin layer of certain polymers, which absorbs molecules. The molecule absorption introduces a local change in electrical resistance of graphene, allowing detection of single molecules, thus making very sensitive sensors.
- Due to its great strength, graphene could potentially be used as a reinforcing material for composites, from day to day household plastics to building materials.
- According to researchers from the University of Texas in Austin, a single layer
 of graphene may be used to create a thin metamaterial cover to suppress the
 scattering from a passive object, thus making an invisibility cloak!

Why aren't we already using graphene in devices?

Graphene is tricky to make, and even trickier to handle. The process of separating it from graphite, where it occurs naturally, is difficult and will require some technological development before it is economical enough to be used in industrial processes. However, some progress has been made with this.

In CRANN, Professor Jonathan Coleman published a paper in 2009, outlining a method to take graphite and separate it into its individual graphene sheets. They stopped them sticking back together by coating each sheet with soap molecules! This resulted in the production of billions of soap-coated graphene sheets dissolved in water. Electron microscopy allowed the researchers to observe the individual carbon atoms, confirming that they had made graphene. Because of its high yield and throughput, this method is ideal for producing graphene in industrial quantities.

ACTIVITIES

Worksheet

→ Worksheet questions 1–11 can be used together with the PowerPoint presentation. They are designed to facilitate students to think about the properties of materials, and reinforce learnings from the presentation. Students can begin research to Question 12 in class and use another period to present their findings. Answers to all the questions can be found by reading the Teachers' Background Material provided.

Classroom / Lab Activities

⇒ The Activity sheets provided outline how students can build models of graphite, diamond and carbon nanotubes, which will help them in visualising the structure and bonding. In addition, there is an experiment to determine the conduction properties of graphite.

Other 'super' materials

In February 2011, a team of scientists, led by Professor Jonathan Coleman, Principal Investigator at CRANN, and colleagues at the University of Oxford, discovered a way of splitting layered materials resulting in a whole family of new nanomaterials which have exceptional properties. Their research was published in the prestigious journal, *Science*.

With just 1 mg of material, billions and billions of one-atom-thick 'nanosheets' can be made from a wide variety of exotic layered materials. There are over 150 of these novel materials – such as Boron Nitride, Molybdenum Disulfide, and Tungsten disulfide – that have the potential to be metallic, semi-metallic or semiconducting depending on their chemical composition and how their atoms are arranged. These 'nanosheets' have chemical and electronic properties which are well suited for applications in new electronic devices, super-strong composite materials, energy generation and information storage. In particular, this research represents a major breakthrough towards the development of efficient thermoelectric materials. The thermoelectric effect is when a temperature change results in electric potential or vice versa.

Other Forms of Carbon

Besides graphite (graphene) and diamond, there are other forms of carbon such as the Fullerene family, of which Buckyballs and carbon nanotubes are members. A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube.

Carbon Nanotubes

Nanotubes are a form of carbon with a cylindrical structure. The walls consist of a oneatom thick sheet of carbon and thus can be imagined as a graphene sheet rolled up. By imagining the sheet rolled in 3 different directions, we can picture the three different types of nanotubes – armchair, zigzag and chiral nanotubes. Although nanotubes resemble rolled up graphene, they cannot really be made that way. A chemical process called chemical vapour deposition (CVD) is a common method for the commercial production of carbon nanotubes.

The armchair configuration is a conductor of electricity, while zigzag and chiral nanotubes are semi-conductors. The difference in conductivity is due to the path taken by the electrons. Electrons find it easier to flow in the armchair configuration than the other formations.

Nanotubes have a large strength to weight ratio. The bonding in nanotubes is the same bonding found in graphene, making nanotubes very strong. However they are very light, making them the ideal material for reinforced composites.

Many potential applications have been proposed for carbon nanotubes, including conductive and high-strength composites, energy storage and energy conversion devices, sensors and nanometre-sized semiconductor devices. Some of these applications are now realised in products, e.g. lightweight windmill blades, bicycle components and concrete infused with carbon nanotubes.

Buckyballs

Buckyballs are members of the fullerene family. They are made up of 60 carbon atoms, arranged in a dome like structure. The structure is similar to the stitching on old footballs, comprising of hexagons and a number of pentagons. Their proper name is 'Buckminsterfullerene' and it is named after the architect, R. Buckminster Fuller, who designed the dome-like structure originally. Many of these domes have been replicated around the world. Spaceship Earth at Disney World's Epcot Center in Florida is 80.8 meters (265 ft) wide and is the only self-supporting geodesic sphere in existence!

The diameter of the buckyball is approximately 1 nm. The bonding is similar to the bonding in graphene, and buckyballs conduct electricity very well because of this bonding.

The dome like structure can be used to house atoms and small molecules. Research is taking place to use buckyballs as a drug delivery system – either by inserting the drug inside the buckyball or attaching it to the outside.

Other nanomaterials

- Nanowires e.g. silver could be used in flexible electronic display panels like e-paper. CRANN in collaboration with Hewlett Packard is researching the use of silver nanowires in the development of transparent electrodes. These materials may be used in future displays such as flat panel TV screens and electronic paper. The average diameter of silver nanowires is in the order of 100 nm, with a length of 5 – 60 µm.
- Nanoparticles e.g. zinc and titanium have made suncreams 'invisible'. Zinc nanoparticles in suncreams have an average size of approximately 35 nm.

Potential toxicity of zinc and other nanoparticles

There have been scientific studies to investigate the potential toxicity of zinc oxide. Scientists report that further research should be done. Safety is something that credible scientists take seriously, and indeed an important part of scientific research is to adhere to strict health and safety guidelines. Some international agencies that are funding nanoscience research are now requiring parallel studies to be conducted concerning toxicology. It is important to note that the relationship between dose and its effects on the exposed organism is of high significance in toxicology i.e. the amount of exposure to the substance needs to be considered. All substances are toxic under certain conditions.

References (accessed July 2011)

- Different forms of carbon: www.nisenet.org/catalog/programs/forms-carbon
 - Nano in products: www.nanoandme.org/nano-products/ cosmetics-and-sunscreen/
- Carbon nanotubes and their applications: www.understandingnano.com/nanotubes-carbon.html
- Graphene Loudspeakers: www.physorg.com/news/2011-07korean-graphene-transparent-loudspeakers.html
- Graphene transistors: www-03.ibm.com/press/us/en/ pressrelease/29343.wss
- www.understandingnano.com/graphene-applications.html
 Graphene as an invisibility cloak:
- www.nanowerk.com/spotlight/spotid=21931.php • Coleman, J.N. et al. Two-Dimensional Nanosheets Produced
- by Liquid Exfoliation of Layered Materials. Science, 4 Feb 2011: Vol. 331, No 6017, pp. 568-571
- Concrete infused with carbon nanotubes: www.news.medill. northwestern.edu/chicago/news.aspx?id=154964
- Buckyballs: www.understandingnano.com/buckyballsfullerenes.html

experiment

Aim

To determine the conductive properties of graphite.

Materials

- Battery
- Connecting wires
- Filament bulb
- Pencil lead

Method

- Remove one inch of graphite from pencil.
- Connect battery to filament bulb using wire.
- Connect filament bulb to graphite using wire.

- Connect graphite to battery using wire (the circuit is now closed).
- Record the result.

Predicted Results

The filament bulb should light, showing that graphite conducts electricity.

Possible Errors

Check connections are secure and ensure battery is of appropriate voltage (9 V).

Alternative Method

Instead of using a filament bulb, an LED can be used.



worksheet

Name

Date			

1. If you were to build a house, what materials would you use? Discuss why. Would you use the same material to make the body of a car?

2. Would polystyrene be suitable for making the body of a car? Discuss your reasoning.

3. What else affects the choice of material? Silver is a better conductor of electricity than copper. However, copper wire is the most commonly used. Why do you think this is the case?

4. Why do we need to study materials at the Nanoscale?

5. List some differences between diamond and graphite.

6. What is the difference between diamond and graphite at the nanoscale that makes these materials so different?

7. Explain what happens at the nanoscale when you write with a pencil? What bonds are being broken?

8. Graphene is called 'a miracle material' because of its properties. What are some of the potential uses of graphene?

9. Why can graphene potentially be used as a sensor?

10. Can you work out the type of each nanotube from the picture?

11. What are some of the current and potential uses of carbon nanotubes?

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12. Nanomaterials are being used in sports, cosmetics and in medicine. Besides the examples given in the presentation, research a product that uses nanomaterials. Describe the science behind the product and present your findings to the class using a poster/oral presentation.

model building

Model building of these materials will help students understand their structures, and in the case of diamond and graphite, the bonding patterns. Model building of graphite will allow students to peel off layers and appreciate the weakness of Van Der Waals forces.

Title

Model Building of Graphite, Diamond and Carbon Nanotubes.

Materials

- Polystyrene packing pellets
- Tooth picks

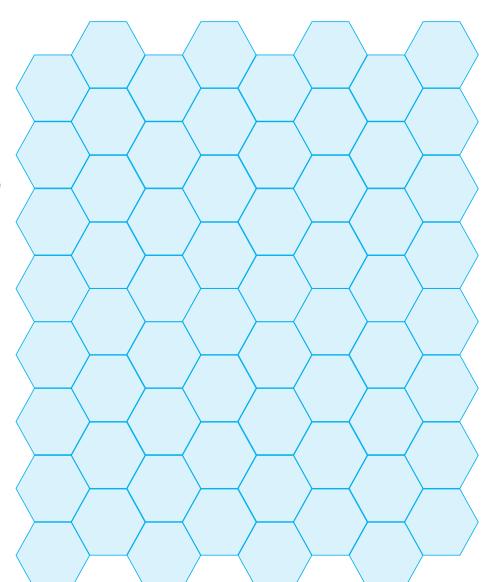
Method

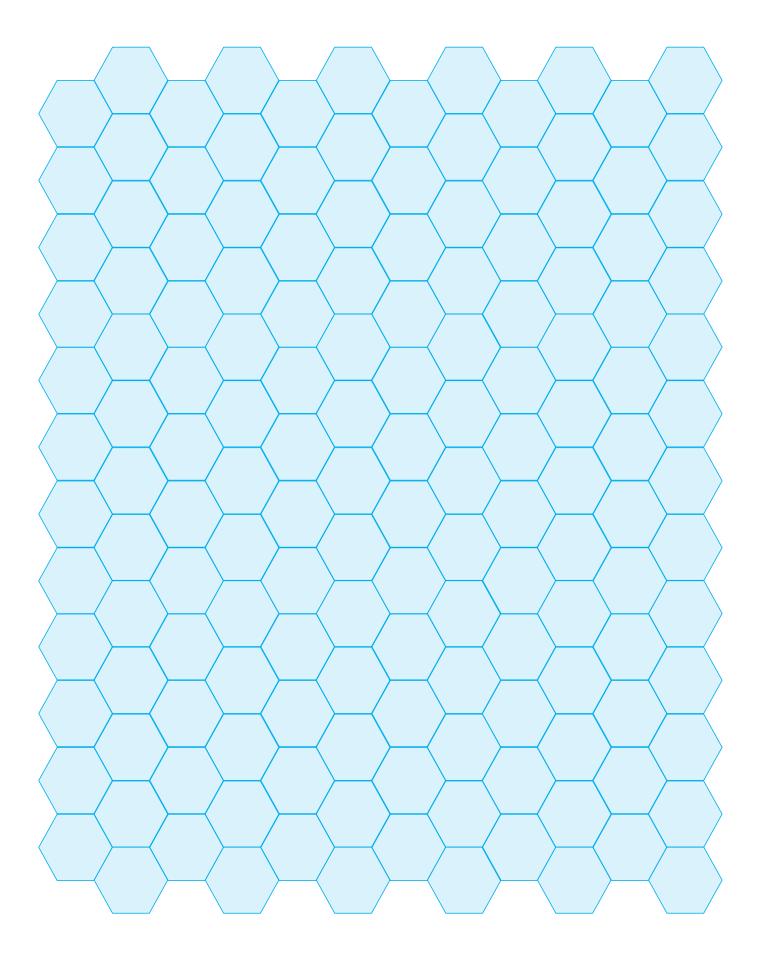
Polystyrene packing pellets and tooth picks are a good cheap way of making up the structures of diamond and graphite (graphene). Molecular model kits can also be purchased online from a lab ware supplier. Students should follow the diagrams in the sheets provided to replicate diamond and graphite.

Due to the complex structure of nanotubes and buckyballs, making models using polystyrene pellets is not recommended. However, model buckyballs can also be purchased online from a lab ware supplier.

An old style football containing pentagon and hexagon patches could also be used to show the molecular structure of buckyballs.

Teachers can demonstrate the structure of nanotubes by cutting the hexagonal pattern out from the patterned sheet provided and folding it in different directions to form the three different nanotube configurations which can be seen on the corresponding PowerPoint.





activity 1

Name	A
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Date	0

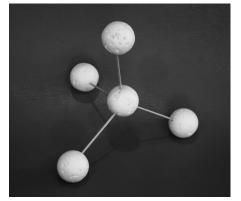
Aim

To make models of the nano-scale structures of diamond and graphite.

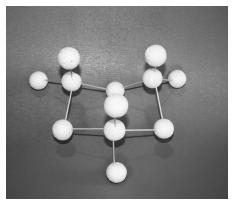
Materials

- Polystyrene pellets
- Toothpicks

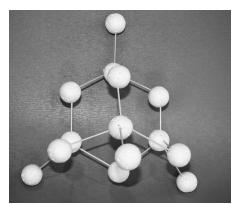
Method – Diamond



1 Using the Polystyrene pellets and tooth picks, make a tetrahedron structure

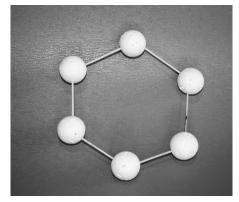


2 Extend the structure to form 3 Tetrahedrons linked together as shown.

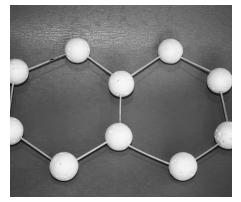


3 To complete the structure – create a tetrahedron for the top of model.

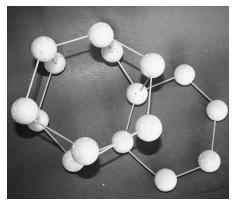
Method – Graphite



1 Using the Polystyrene pellets and tooth picks, make a hexagon structure.



2 Extend the structure to form 2 hexagons linked together as shown.



3 Repeat the above procedure and form the following structure.

experiment 1

Name

Date			

Results

Aim

To determine the conductive properties of graphite.

Materials

- Battery
- Connecting wires
- Filament bulb
- Pencil lead

Method

- 1 Remove one inch of graphite from pencil.
- 2 Connect battery to filament bulb using wire.
- **3** Connect filament bulb to graphite using wire.
- 4 Connect graphite to battery using wire (the circuit is now closed).
- 5 Record the result.

What can you conclude about the conductive properties of graphite from this experiment?