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Nanochemistry in the New Leaving Certificate Chemistry Syllabus

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New Leaving Certificate Chemistry Syllabus

The draft revised leaving certificate syllabus in chemistry was approved for consultation by stakeholders in February 2011 [1]. Overall the development of the syllabus was welcomed by educators, particularly in the area of ‘Nano’ [2]. Section 2.6 of the draft syllabus, on the technological applications of chemistry, specifically relates to the topics of nanoscience, nanochemistry and nanotechnology, as shown in figure 1.

Students learn about	Student should be able to
2.6 Technological applications of chemistry	<ul style="list-style-type: none">• Discuss the terms : nanoscience, nanochemistry and nanotechnology• Describe and discuss how incorporation of carbon nanotubes into polymer composites can alter the mechanical properties of these composites• Describe/discuss the electronic properties and potential applications of carbon nanotubes

Figure 1. Specific ‘Nano’ topics highlighted in the draft revised Leaving Certificate syllabus in chemistry [1].

The aim of this article is to provide a brief overview of nanoscience, nanochemistry and nanotechnology and to highlight the importance of incorporating these relatively new, interdisciplinary topics into the science Leaving Certificate syllabus.

What is Nano?

Nano, Greek for ‘dwarf’ means one billionth. *Nanoscience* is therefore the study of atoms and molecules on a nanometre length scale (“nm”) and *nanochemistry* is the utilisation of synthetic approaches to make nanoscale materials with different size, shape, composition, surface structure, charge and functionality. However, the concept of nanoscience is not new; Chemists will tell you that they have been working in nanoscience for hundreds of years. For example, the orange, purple, red and greenish colours seen in the stained glass windows in many churches, such as those in the Honan Chapel at University College Cork (UCC), is due to the incorporation of different sized gold nanoparticles within the glass [3, 4].

What is new about current nanoscience and nanochemistry is the focus on developing new and improved products from this knowledge, *i.e.* *nanotechnology*, and the emergence of new instruments which allow materials to be imaged and manipulated. For example, early scientists first spotted living bacteria with a light microscope, whilst current researchers in nanoscience often use electrons, not light, to image and investigate the properties of

nanomaterials. For example, a transmission electron microscope (TEM) can see objects that are thousands of times smaller than a light microscope and hundreds of thousands of times smaller than can be observed by the human eye. The resolution of many TEM instruments is typically around 0.1 nm, which is the typical resolution between 2 atoms in a solid. The ability to synthesise, visualise and manipulate matter at the nanoscale potentially allows future researchers to build and change the structure of everyday things, from cancer cells to computers, improving our standard of living.

At the nanoscale, interactions between atoms often result in different properties that are not observed at larger length scales. For example, as mentioned above gold nanoparticles display different colours, melting points and chemical properties depending on their size which is not found for a gold “bar” held as gold reserves by central banks. The reason for this difference is that the interaction of gold atoms in the gold bar average out, influencing the overall properties and appearance of the object. However, a red, 10 nm sized gold nanoparticle, can be thought of as a tiny object, free from the averaging effects of countless numbers of atoms. Hence the growing interest in ‘nano’ is due to advances in science and engineering which have allowed new approaches for synthesising, positioning, connecting and imaging nanomaterials with controlled shape, composition and structure for use in the macroscopic real world.

Why Nano?

One great thing about nanoscience is that it is interdisciplinary. In research laboratories throughout the world, chemists, physicists and medics work with engineers, computer scientists, biologists to determine the applications and development of nanotechnologies. Many companies, *e.g.* pharmaceutical industries, computer manufacturers, healthcare companies, have nanotechnology research programmes, which will not only financially benefit these companies but will improve our standard of living, due to advances in nanotechnology which are expected over the next decade. The ability to engineer the surfaces of nanomaterials will lead to products with better mechanical, wetting, chemical resistant and optical properties, *e.g.* anti-graffiti or anti-fouling coatings, biocompatible implants, faster and more energy efficient transistors in microelectronic circuits, anti-bacterial wound dressings, super lightweight materials, novel drugs, improved water purification, cell phones with longer battery life *etc* [5].

However, nanotechnology is not all about the future. Manufacturers are currently utilising nanoscience and nanochemistry to enhancing old products, which go beyond products available from bulk materials. For example transparent sunscreens, such as those manufactured by Nanophase Technologies [6], contain nanosized particles of zinc oxide (ZnO) or titanium dioxide (TiO₂). The high surface areas of the nanosized particles provide improved deflection of the sun’s harmful UV radiation, compared to the larger particles which were present in earlier bright white sunscreen products. Other examples include stain-resistant trousers and ties produced by companies like Nanotex [7]. Transistors in computers are already below 100 nm, which has allowed electrical devices, such as mobile phones, to become smaller and more powerful [8]. The cosmetic industry has been among the first adaptors of nanotechnology through the use of engineered nanoparticles to enhance the performance of their products, *e.g.* to improve the feel and texture of face creams as well as providing UV protection to the skin [9]. Nanomaterials in cosmetics have also been reported to help increase the penetration of active materials into the skin.

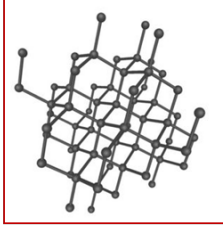
Whilst it is easy to imagine all kinds of new materials, devices and products that can be manufactured using nanochemistry, some projects are unlikely to, or will never, materialise. For example, life-threatening nanoscale robots ('nanobots'), described by Eric K. Drexler in his book '*Engines of Creation: The Coming Era of Nanotechnology*' [10], that could replicate using nanoscience to build objects one atom at a time. Another example comes from Michael Crichton's book '*Prey*' in which he describes a deadly cloud of nanomachines which escape from a laboratory, with the intention of wiping out mankind [11]. Add such writings to media hype and you end up with a lot of misinformation on what nanoscience may lead to in the future, rather than what could never happen based on the laws of chemistry, physics and biology. For example, using molecular chemistry to build nanobots would be extremely difficult and involve controlling the positioning of atoms in three dimensions, which would involve controlling the motion of each and every atom within the structure. Nanobots made from organic molecules are also likely to find themselves being devoured by bacteria whilst large amounts of time, synthetic processing and resources would be required to produce nanobots from inorganic materials (such as sand).

Smart Materials From Carbon

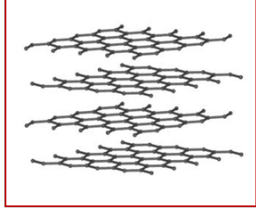
Nearly every industry, *e.g.* energy, electronics, biomedical, will benefit from nanotechnology through the processing and chemical synthesis of new materials. Many applications are just waiting for the right nanomaterial to be created, for examples materials for energy efficient solar cells. To understand how nanomaterials might be used, we need to understand not only how they are synthesised but what are their structures. Carbon is a common element of choice for use in nanotechnologies as it offers a wide range of properties, which include [12]:

- the formation of strong covalent bonds with other carbon atoms, resulting in the formation of allotropes of carbon with different physical and chemical properties, *e.g.* graphite and diamond. Figure 1 and table 1 show different allotropes of carbon, including some of their physical properties.
- bonding with a range of other atoms, *e.g.* oxygen, nitrogen, sulphur, silicon to make a range of organic and inorganic materials with a range of different properties.
- the ability to form covalent bonds with four other atoms at a time, which is more bonds than most atoms can form, allowing the formation of chains of atoms and hence the formation of materials with different properties.

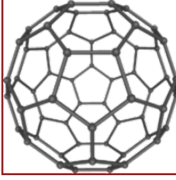
Allotropes of carbon have different covalent bonding arrangements



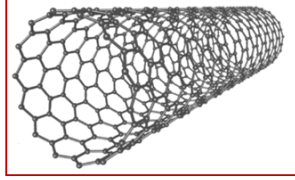
diamond



graphite



buckyball



nanotube

- Carbon atoms form covalent bonds by sharing outer shell electrons with each other
- Diamond, graphite, buckyballs and carbon nanotubes all have different covalent arrangements of carbon atoms
- The differing covalent arrangements of carbon atoms lead to the different properties of carbon allotropes

Figure 1. Different allotropes of carbon [13].

Allotrope	Hardness	Tensile Strength	Conducts Heat	Conducts Electricity
Coal	+	+	+	No
Graphite	++	++	+++++	+++++
Diamond	+++++	Not Known	+++	No
Buckyballs	+++++	++++	+	+
Carbon Nanotubes	++++++	+++++	+++++	++++++

Table 1. A comparison of the properties of different carbon allotropes [13].

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure and can exist as either single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). A SWNT has a single cylinder, whereas a MWNT consists of multiple concentric nanotube cylinders, as shown in figure 2.

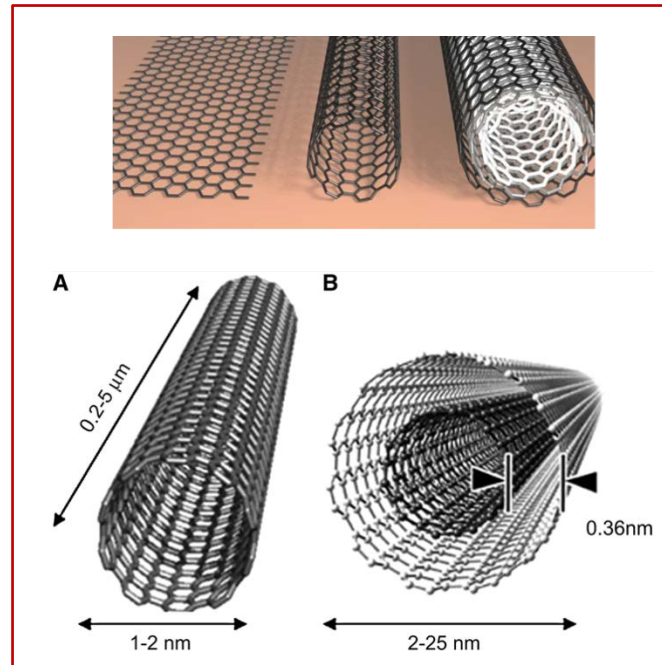


Figure 2. Conceptual diagrams of (A) a SWNT and (B) a MWNT, formed from a graphene sheet.

The discovery of single and multi-walled CNTs has had one of the greatest impacts in nanoscience and nanotechnology, as they have unparalleled strength and high thermal and electrical conductivities, making them ideal building blocks for a wide range of applications [15]. This article will highlight some of the properties of SWNTs, as they have been the most widely researched. SWNTs have been found to conduct heat as well as diamond and are two hundred times stronger than steel, at one sixth of the weight. Depending on their structure, SWNTs can also have outstanding electrical properties. As nanotubes are composed of carbon, chemists are able to bond other atoms or molecules to their surfaces creating new nanomaterials for use with biological systems or as composite materials.

Depending on the angle which a graphene sheet is rolled up, called a roll-up vector, the electrical properties of SWNTs can be changed dramatically. Nanotubes having a helical twist in their structure have semiconducting properties, while achiral tubes are metallic. The structure of metallic ‘zig-zag’ and ‘armchair’ tubes, as well as chiral semiconducting SWNTs are shown in figure 3.

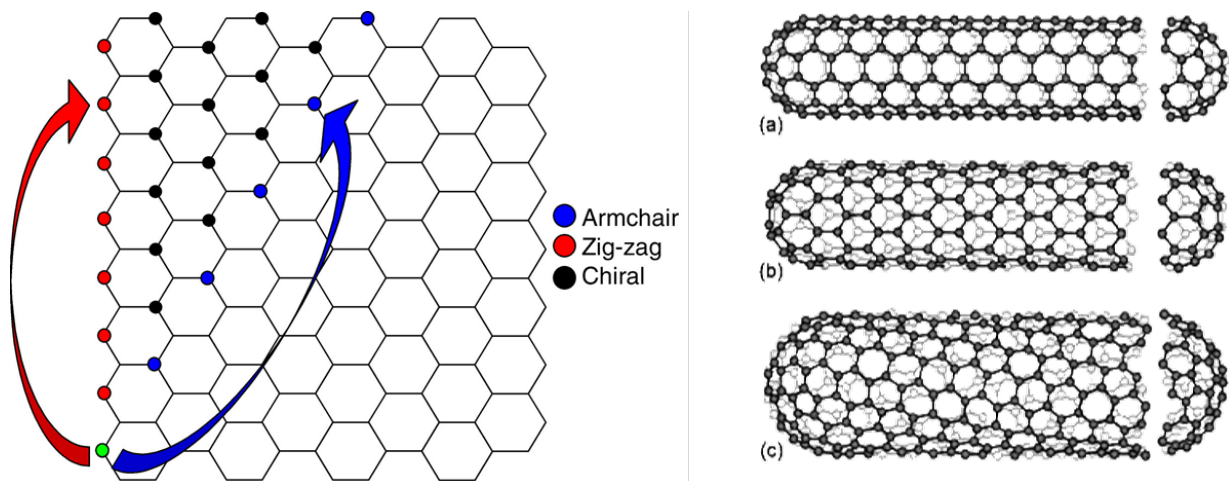


Figure 3. Graphic showing how a graphene sheet can be rolled to form different SWNT structures: (a) a metallic ‘zig-zag’ nanotube, (b) a metallic ‘armchair’ nanotube and (c) a chiral ‘semiconducting’ nanotube [3].

Ballistic electron transport (electrical conductivity without phonon and surface scattering) has been observed in metallic SWNTs, resulting in nanotubes with a higher electrical conductivity than copper. As a result of their electrical properties, helical carbon nanotubes have enabled the fabrication of the first nanotube transistors, a step towards molecular electronics.

Carbon Nanotube Chemistry

An issue with using SWNTs in commercial applications is their tendency to aggregate. To overcome this problem, a number of chemical approaches have been developed to modify nanotubes, allowing them to be solubilised in a range of matrices. Oxidation of CNTs using strong acid, *e.g.* nitric acid, opens up the ends of nanotubes and introduces carboxylate functionalities, imparting modest solubility of CNTs in polar solvents. Several chemical reactions have also been employed to graft molecular or polymeric species onto the surfaces of CNTs, for the application of these materials as chemical or biological sensors [15]. Sensors using SWNTs have are able to detect chemical vapours, *e.g.* nitrogen dioxide (NO_2) in explosives, at part per billion (ppb) concentration levels. However, one problem is that many molecules can interact with CNTs, so in order to ensure that CNT sensors detect the right chemical, chemists have successfully coated SWNTs with polymers that only allow certain molecules to reach the nanotube and blocks other species. For example, SWNTs coated with the polymer polyethyleneimine allows CNT sensors to detect NO_2 , but minimises their sensitivity to ammonia (NH_3). Conversely, coating CNTs with a polymer called Nafion, prevents NO_2 penetration but allows a CNT sensor to detect NH_3 . Figure 4 shows a range of application of both purified and functionalised SWNTs.

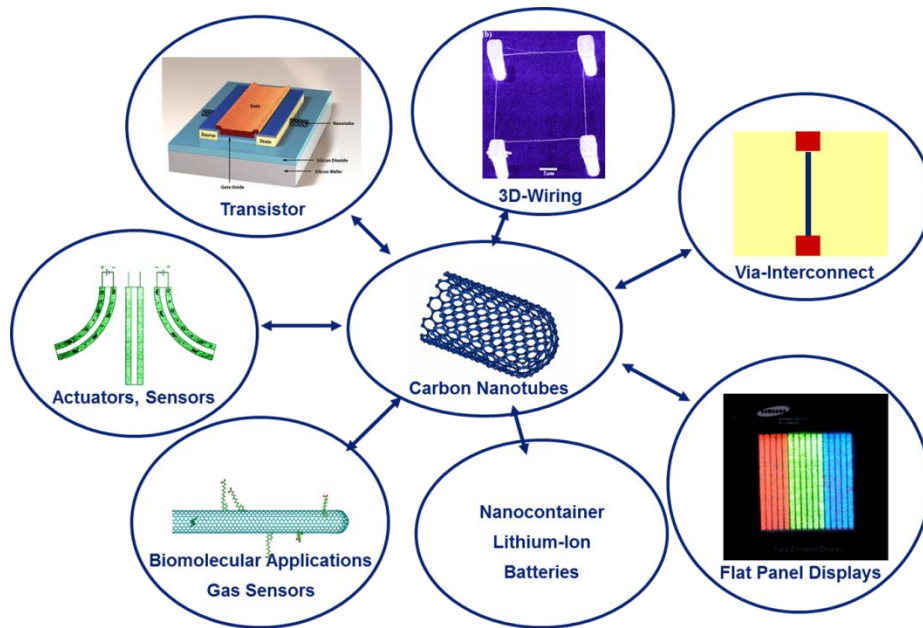


Figure 4. Some applications of purified and functionalised SWNTs [16].

Carbon Nanotube Composites

A composite is an engineered material composed of two or more components. Many of the outstanding properties of carbon nanotubes can be best exploited by incorporating them into some form of matrix, and the preparation of nanotube containing composite materials is now a rapidly growing research area. A commonly used method for preparing CNT/polymer composites has involved mixing nanotube dispersions with solutions of the polymer and then evaporating the solvents in a controlled manner. Much of the research undertaken to-date on the preparation of CNT/polymer composites has been driven by a desire to exploit the stiffness and strength of CNTs. Even where the interest has been focused on other properties, the ability of nanotubes to improve the mechanical characteristics of a polymer has often been a valuable added benefit. Composite materials containing conventional carbon fibres in a metal matrix, such as aluminium or magnesium, are used in a number of specialist applications. Such composites combine low density with high strength and modulus, making them particularly attractive to the aerospace industry. There is growing interest in the addition of CNTs to metal matrices. Significantly, a number of sports equipment manufacturers are supplying composite materials containing CNTs for lightweight, robust racquets, with larger ‘sweet spots’ for hitting a ball. For example, the badminton racquet manufacturer Yonex incorporates CNTs into their cup stack carbon nanotubes racquets. American baseball bat manufacturer Easton Sports has formed an alliance with the nanotechnology company Zyvex to develop baseball bats incorporating CNTs and Babolat have incorporated CNTs into their tennis racquets. The Swiss manufacturer bicycle BMC, were the first company to manufacturer a super light-weight bicycle frame (the ‘Pro-Machine’) incorporating CNTs, which was first tested out by the Phonak Cycling Team in the 2005 Tour de France (figure 5).



Figure 5. Images of strong but lightweight CNT composites used to in the production of bicycle frames (BMC) [17] and tennis racquets (Babolat) [18].

Nanoscience – The International Context

Many nanotechnology breakthroughs have already started to have an impact in the market place [19]. 2009 values for nanotechnology-enabled products were approximately worth €74 billion in the US and €206 billion worldwide. Trends suggest that the number of nanotechnology products and workers will double every three years, achieving a €2.5 trillion market with six million workers by 2020. Nanotechnology research and development has therefore become a socio-economic target in many countries. Industry giants such as Intel, IBM, Hewlett-Packard, DuPey, Pfizer, GSK and Eli Lilly are just a few companies with sites based in Ireland with interests in nanotechnology. The resources, processes and facilities many of these large companies already have in place should allow them to take advantage of nanotechnology discoveries to initially improve existing products, as well as developing new and innovative products.

As mentioned previously, nanotechnology is a multi-disciplinary research field. Chemists are working with physicists and biologists, who might work with engineers and computer scientists to model very specific chemical/physical interactions of a nanomaterial. This interconnectedness of nanotechnology is a big part of nanotechnology development. Both large and small companies developing commercial nanotechnologies are likely to have to develop partnerships and collaborations, not only between different industries but also between different companies and universities. Additionally, many of the tools required for developing future nanotechnologies, *e.g.* electron microscopes, are too expensive to purchase and maintain for many companies, particularly SMEs. However, in Ireland Government funded nanoscience research centres, such as the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN, www.crann.tcd.ie), based at Trinity College Dublin and the Tyndall National Institute (www.tyndall.ie) based at University College Cork, allow businesses to access and train their staff on state-of-the-art equipment required for nanoscience research at a reasonable cost. These nanoscience research centres also facilitate collaborations between industry and universities in Ireland to create and commercialise research outputs, as well as the development of new instruments and tools required for further nanotechnology growth.

Ireland Science Punching Above Its Weight!

Table 2 below shows Ireland's national science ranking in (nano)materials science between 2000-2010 based on Thomson Reuters Essential Science Indicators, and as reported in the Times Higher Education Supplement [20]. As expected, the number of materials science journal articles published by Irish Scientist (which incorporates research publications in the field of chemistry, physics and biology) in this period was lower than countries with large 'scientific populations', such as the US, Japan and England. However the impact of the research published by Irish scientists is significant. The number of citations per paper for Ireland, which is a measure of the number of times a research article is referred to by other researchers throughout the world and therefore a measure of 'research quality', was greater than for Germany, England, France and Japan. Out of the 81 nations listed in this study, Ireland was ranked 8th in the world, meaning that for a small country Ireland certainly does punch above its weight in nanoscience. Further investment in science education in schools is therefore essential to facilitate the training of future Irish nanoscientists. Only through investment in science will Ireland be able to improve its status as a world leader in nanotechnology and retain and attract further company investment into the country.

Rank	Country	Papers	Citations	Citations Per Paper
1	The Netherlands	4,881	58,477	11.98
2	US	67,902	774,556	11.41
3	Switzerland	4,713	51,436	10.91
4	Israel	2,321	25,146	10.83
5	Denmark	1,526	15,740	10.31
6	Singapore	5,183	52,000	10.03
7	Scotland	1,658	16,494	9.95
8	Ireland	1,351	12,468	9.23
9	England	19,752	182,130	9.22
10	Belgium	3,958	34,595	8.74
11	Austria	3,439	29,160	8.48
12	Germany	31,964	261,247	8.17
13	France	21,861	172,352	7.88
14	Sweden	5,995	46,747	7.80
15	Canada	11,023	81,115	7.36
16	Italy	10,344	75,541	7.30
17	Spain	11,073	80,196	7.24
18	Australia	7,475	53,616	7.17
19	Norway	1,333	9,318	6.99
20	Japan	50,155	335,049	6.68

Table 2. Ranking in materials science is by citations per paper among nations that published 1,000 or more papers during the period to reveal weighted impact [20].

Summary

Nanotechnology is the next big scientific and industrial wave and will impact all industries, from healthcare to the next generation of computers and communications. Presently, 10% of

all Irish exports are enabled by nanoscience, with the global nanotechnology market predicted to be worth €1.5 trillion by 2015. Nanotechnology already touches our society in many areas, economically, socially and ethically. With nanotechnology innovations creating new chemistries, materials and devices there will be an impact on both educational and workforce requirements. Education in this area is also necessary to remove potential economic barriers for the application of nanotechnologies into Irish industry.

While nanoscience, nanochemistry and nanotechnology are not necessarily thought of as topics for the high school classroom, introducing such cutting-edge topics into the leaving certificate syllabus is likely to provide a means to motivate student interest in science and engineering. The challenge of preparing a 'nanoeducated' workforce is dependent on the country's education system, which is currently limited to undergraduate and graduate programs at Universities, in unison with national research institutes. However, the importance of introducing the concepts of nanoscience at an earlier stage cannot be overstated. The introduction of nanochemistry into the leaving certificate syllabus will foster explorations in science at the nanoscale and provide connections between and among the sciences that will help students to develop an understanding of the relationships between disciplines. Implementation of nanoscience education into schools is a common process worldwide and Ireland cannot afford to delay any longer. The current 'crop' of high school students is Ireland's 21st century workforce in nanotechnology and hence education at this level is essential for Ireland's economic future.

Biography

Justin D. Holmes is Professor of Nanochemistry at University College Cork (UCC), Ireland. Since joining the Chemistry Department at UCC in October 1999, he has established an active research group in the synthesis, assembly and characterisation of nanoscale materials for electronic, energy, environmental and catalytic applications. He is Group Leader of the Materials Chemistry and Analysis Group at the Tyndall National Institute in Cork, which incorporates the Electron Microscopy and Analysis Facility (EMAF). Prof Holmes is also a Principal Investigator within the Centre for Adaptive Nanostructures and Nanodevices (CRANN), based at Trinity College Dublin (TCD), where he leads a research strand in the development of new materials for nanoscale electronic devices. He also holds an adjunct position within the School of Chemistry at TCD. Prof Holmes is co-founder and currently Chair of the Scientific Advisory Board for the UCC spin-out company Glantreo Ltd.

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