NANOYOU Teachers Training Kit in Nanoscience and Nanotechnologies

Chapter 3 – History of Nanotechnologies

Module 1- Fundamental concepts in nanoscience and nanotechnologies

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Chapter 3: History of Nanotechnologies

This chapter aims to provide some historical background to nanotechnologies. A very valid question that students might bring up in class, and that we attempt to answer, is "When was nanotechnology invented?" As we have mentioned in Chapter 1, nanotechnologies are an evolution of other materials engineering disciplines (like thin film technology). The term is really an "umbrella term" that covers disciplines that have very old historic roots. What is even more fascinating is that now scientists have the tools to study ancient artefacts and discover that in many cases these were made using nanoparticles! **Nanotechnologies are around us in Nature (Chapter 2) and in history!**

Feynman's speech

The concept of nanotechnology is attributed to Nobel Prize winner Richard Feynman who gave a very famous, visionary speech in 1959 (published in 1960) during one of his lectures, saying "The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom". At the time, Feynman's words were received as pure science fiction. Today, we have instruments (see below) that allow precisely what Feynman had predicted: creating structures by moving atoms individually.

Scanning Tunnelling Microscope

The development of nanotechnologies has been enabled by the invention of two analytic tools that have revolutionised the imaging (and manipulation) of surfaces at the nanoscale. These are the Scanning Tunnelling Microscope (STM) and the Atomic Force Microscope (AFM). The STM and the AFM are capable of imaging surfaces with **atomic resolution**.

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The operation principle of the STM and AFM and their use for surface imaging and surface manipulation are described in **Chapter 6 of Module 1 ("Characterisation methods")**.

Both instruments were invented by Binning and his co-workers from IBM Zürich. Binning, Rohrer and Ruska (all from IBM Zürich) were awarded the **Nobel Prize in Physics in 1986** for the invention of these

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amazing tools, which practically **opened the doors of the nanoworld to scientists**. With the advent of the STM scientists were given the tool not only to image surfaces with atomic resolution, but also to move individual atoms. The STM is the first step in realising Feynman's vision of atom-by-atom fabrication.

Coloured glass

Metal colloids (metal nanoparticles dispersed in a medium) are the best example of nanotechnology throughout ancient, medieval and modern times. In **Chapter 4** we reviewed how metal nanoparticles possess optical properties (i.e., different colours) that are related to surface plasmons. The size and shape of the metal nanoparticles influence their visible colours! There are numerous artefacts that have notable colour effects precisely because they are made with metal colloids:

- One of the most fascinating is a **piece of Roman glasswork**, the *Lycurgus cup*, dating from the fifth century. This magnificent cup, housed at the British Museum, depicts King Lycurgus dragged into the underworld by Ambrosia. When illuminated from the outside, the cup appears green. When illuminated from the inside, the cup appears ruby red except for the King, who looks purple. The reason for this dichroism was unknown until detailed SEM analysis of the cup was performed in 1990. It was found that it was due to the presence of nanosized particles of silver (66.2%), gold (31.2%) and copper (2.6%), up to 100 nm in size, that were embedded in the glass. Light absorption and scattering by these nanoparticles determines the different colours.

- The beautiful **stained glass windows produced in medieval times**, and visible in numerous churches, are made of a composite of glass and nano-sized metal particles. The "ruby-red" glasses often seen are a mixture of glass with ultrafine (nanosized) gold powder. The "purple of Cassius" is a colloidal mixture of gold nanoparticles and tin dioxide in glass.

- **Chinese art history** is also filled with examples of nanotechnology. For instance, the Chinese porcelain known as *famille rose* contains gold nanoparticles 20-60 nm in size.

Faraday's studies on gold colloids

If we look into the history of science, gold colloids have been the subject of research since the mid 19th century! It was actually **Michael Faraday who was the first to conduct systematic studies on the**

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properties of metal colloids, in particular made of gold. In 1857 Faraday presented during his lecture at the Royal Society of London a purple colour slide, stating that it contained “gold reduced in exceedingly fine particles, which becoming diffused, produce a ruby red fluid…the various preparations of gold, whether ruby, green, violet or blue…consist of that substance in a metallic divided state”.

Faraday postulated correctly about the physical state of colloids; he also described how a **gold colloid would change colour (turning blue) when salt is added**.


EXPERIMENT

This effect is shown in **Experiment C in the NANOYOU Experiment module.** Teachers have an opportunity to link this experiment with some concepts of science history.

In the early twentieth century Gustav Mie presented the ***Mie theory***, to which we still refer, which is a mathematical treatment of light scattering that describes the relationship between metal colloid size and the optical properties of solutions containing them.

Miniaturised electronics

Youngsters are surrounded by electronic devices – computers, mobile phones, portable electronic games, etc. It is really amusing to see their reaction when we show them pictures of the first mobile phones that were introduced in the 1980s! We (and even more they) take for granted the miniaturisation of electronic devices, and are used to expecting even more every year or so. The evolution of this miniaturisation has been enabled by the tremendous advances in the semiconductor industry and the ability to produce smaller and smaller integrated circuits (ICs). The “core” of ICs is the transistor – every chip is made of numerous transistors that act like gates for the flow of electrons: they can be in the open or closed mode. Just to give an idea, in 1965, 30 transistors populated a chip; in 1971, 2,000 populated it, and today there are about….40 million! This exponential growth was actually predicted in 1965 by Gordon E. Moore (one of the founders of Intel). Moore predicted that the “complexity of integrated chips” would double every 18 months. At the time he was a visionary…but indeed Moore’s law proved to be right. The data density of computer chips has increased in the last years at the predicted pace, doubling every 18 months.

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TIP TO TEACHER: Ask your students to go home and collect information on old computers or laptops owned by their parents, friends or relatives. Ask them to record when they were purchased (approximate date of production), and what was the data storage capacity (hard disc capacity). Make an overall table with the information collected by all the class. Is Moore's law confirmed?

The history of integrated chips is, in a sense, the history of nanotechnology. The **first transistor invented in 1947** was a bulk, macro object (**Figure 1**). To keep up with the demand for miniaturisation, the dimensions of the transistor have been reduced considerably in the last 20 years. In the year 2002, the nanosize was reached and a single transistor was 90 nm. As of today (end of 2009) a single transistor in an Intel Core 2 Quad processor is 45 nm.

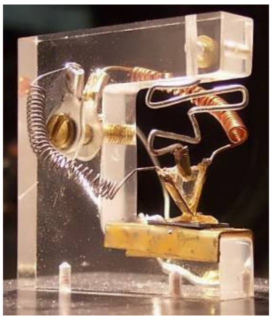

Figure 1. Replica of the first bipolar Transistor. This replica was photographed at the Nixdorf-Museum, Paderborn, Germany. (Image credit: Wiki Commons, Creative Commons Attribution ShareAlike 3.0)

If they were to keep pace with Moore's law, transistors would have to be as small as 9 nm by 2016. This dimension is below the fabrication capabilities of the latest-generation tools used in the microelectronics industry. Moreover at this dimension, electrons would be able to "jump" the gate just with their own thermal energy. Numerous novel approaches are under investigation to realise workable transistors of this size. These include molecular electronics and quantum computing – both are examples of true nanotechnologies.

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The fabrication techniques used in the microelectronics industry are reviewed in **Chapter 6 of this Module ("Fabrication techniques")**. The future evolution of computing and the impact of nanotechnologies are discussed **in Chapter 4 of Module 2 ("Applications of Nanotechnologies: ICT").**

The GMR effect

Numerous popular electronic products, such as the iPod, have components that use an effect called Giant Magnetoresistance (GMR). In simple terms, the electrical resistance of structures made of **very thin layers of magnetic and non-magnetic metal**s can change by an unexpectedly large amount in the

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presence of an applied magnetic field. The effect was discovered independently by Albert Fert and Peter Grunberg in 1988, and for its discovery they shared the **2007 Nobel Prize in Physics**. When the prize was announced, the Swedish Academy of Science wrote:

"GMR technology may also be regarded as one of the first major applications of the nanotechnology that is now so popular in a very diverse range of fields".

The GMR effect is a true nano-effect! GMR is used in the latest-generation memory devices like the MRAM. The details of the GMR effect are described **in Chapter 4 of Module 2 ("Applications of Nanotechnologies: ICT").**

Advanced materials

The **history of material engineering** is full of examples of nanomaterials! Often these were produced inadvertently, and not characterised at the nanoscale since the analytic tools were not available. For instance, the process of **anodising** was first patented in the early 1930s. This represents one of the most important processes used in industry to protect aluminium from corrosion. It consists of depositing a thin protective oxide layer on the aluminium surface. The inventors of this technique were not aware that the **protective layer is actually a nanomaterial** last generation memory devices last generation memory devices – the anodic layer is composed of hexagonally close-packed channels with diameters ranging from 10 to 250 nm or greater.

Other familiar examples are: nanoparticles that are found in the rubber component of automobile tires; titanium dioxide pigment found in some latest-generation sunscreens; components in computer chips; numerous synthetic molecules used in current drug compositions; thin hard coatings used in industry.

There are many nanomaterials that have a long history; we cannot review them all here, so we will limit the discussion to two examples.

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Fullerenes and carbon nanotubes

In 1985 R.E. Smalley, H.W. Kroto and R.F. Curl discovered a new form of the element carbon: the *buckyball*, a molecule consisting of 60 atoms of carbon (C_{60}) assembled in a form similar to a football. The researchers were then able to develop a method to synthesise and characterise this new nanomaterial. The existence of C_{60} had actually been predicted by Eiji Osawa of Toyohashi University of Technology in a Japanese magazine in 1970. This new **allotrope of carbon** was officially named Buckminsterfullerene in honour of Buckminster Fuller, an architect famous for his geodesic dome design. Shortly after the discovery in 1985, various others fullerenes were discovered.

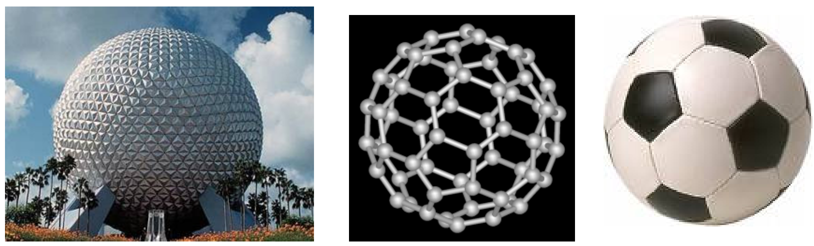

Figure 2. (Left to right): a geodesic dome designed by architect Buckminster Fuller, the structure of a C60 and a soccer ball.(Images credit: Wiki commons images, Creative Commons

In 1996, Kroto, Curl, and Smalley were awarded the **1996 Nobel Prize in Chemistry** for their roles in the discovery of this class of compounds.

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The properties and applications of fullerenes and their parent nanomaterial carbon nanotubes are described in detail in **Chapter 5 of Module 1 ("Overview of Nanomaterials").**

Liquid crystals

Liquid crystals were first accidently discovered in 1888 by Friedrich Reinitzer, a botanical physiologist who was working in the Institute of Plant Physiology at the University of Prague. Reinitzer was conducting experiments on a cholesterol based substance (cholesteryl benzoate) and trying to determine the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck

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by the fact that this substance seemed to have two melting points. He found a first melting point at 145.5°C, where the solid crystal melted into a cloudy liquid. This "cloudy intermediate" existed up to 178.5°C, where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. At first Reinitzer thought that this might be a sign of impurities in the material, but further purification did not bring any changes to this behaviour. He concluded that the material had two melting points, but asked his colleague Otto Lehmann, a German physicist who was an expert in crystal optics, for help in understanding this unexpected behaviour. They isolated and analysed the "cloudy intermediate" and reported seeing crystallites. Lehmann then conducted a systematic study of cholesteryl benzoate and other solids that displayed the double melting behaviour. He became convinced that the cloudy liquid had a unique kind of order. It could sustain flow like a liquid, but under the microscope appeared like a solid. In contrast, the transparent liquid at higher temperature had the characteristic disordered state of all common liquids. Eventually he realised that the cloudy liquid was a new state of matter and coined the name "liquid crystal," to emphasise that it was something between a liquid and a solid, sharing important properties of both. Not just a liquid, where molecules are randomly distributed, and not just a solid, where molecules are ordered in organised structures.

TIP TO TEACHER: the discovery of liquid crystals is a good example of how science often proceeds, i.e., with a discovery made by mistake that is then further investigated (rather than just dismissed as an error). In fact, many major scientific discoveries were made this way. An instructor may take this opportunity to illustrate to the class other scientific discoveries that were the result of an accidental discovery, followed by the studies of a long-sighted scientists who pursued understanding the scientific meaning of this "accident" (another great example is the discovery of penicillin).

The scientific community challenged the conclusions of Reinitzer and Lehmann, since at that time scientists knew only three states of matter: gas, liquid and solid. The general idea was that all matter normally had one melting point, where it turns from solid to liquid, and a boiling point where it turns from liquid to gas.

Nevertheless the work done by Lehmann was continued in the beginning of the 20th century, but liquid crystals were treated by the scientific community as a pure scientific curiosity. Only later did scientists realise that these materials were indeed a fourth state of matter and could actually have commercial use. In 1969, Hans Kelker succeeded in synthesising a substance that had a nematic phase at room temperature, the N-(4-Methoxybenzylidene)-4-butylaniline (MBBA) molecule. Later other chemically

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stable substances (cyanobiphenyls) with low melting temperatures were synthesised: these materials opened the doors to the use of liquid crystals in practical applications such as displays. Since these discoveries, research on these materials has increased and in **1991 Pierre-Gilles de Gennes received the Nobel Prize in Physics** "for discovering that methods developed for studying order phenomena in simple systems can be generalised to more complex forms of matter, in particular to liquid crystals and polymer".

Now we know that the peculiar properties of a liquid crystal depend on how external factors, such as electric field or temperature, change its phase, with a consequent rearrangement of its supramolecular nanostructure.

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Nowadays liquid crystals are used for many applications, mainly in the ICT sector, as in mobile phone displays. Liquid crystals are described in detail in **Chapter 5 of Module 1 ("Overview of Nanomaterials")** and their applications discussed in **Chapter 4 of Module 2 ("Application of nanotechnologies: ICT").**

EXPERIMENT

In **EXPERIMENT B of the NANOYOU Experiment Module** students prepare different types of liquid crystals that change phase with temperature and as a consequence change colour. The students can make a room thermometer with four different types of liquid crystals.

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