



NANOYOU Teachers Training Kit in nanoscience and nanotechnologies

# Chapter 4 – Fundamental “Nano- effects”

Module 1- Fundamental concepts in nanoscience and nanotechnologies

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## Contents

What happens at the nanoscale? .....	4
<i>A different kind of small</i> .....	5
<i>Physics at the nanoscale</i> .....	6
<i>Chemistry at the nanoscale</i> .....	7
<i>Molecules as devices</i> .....	9
Unique material properties at the nanoscale.....	9
<i>Surface properties</i> .....	9
<i>The importance of surface atoms</i> .....	11
<i>Shape also matters</i> .....	11
<i>Surface energy</i> .....	12
<i>Reactions where surface properties are very important</i> .....	13
<i>Catalysis</i> .....	13
<i>Detection</i> .....	14
Electrical properties.....	15
<i>Quantum confinement and its effect on material electrical properties</i> .....	15
<i>Nanomaterial with exceptional electrical properties:</i> .....	16
Optical properties .....	16
<i>Interaction of light with matter</i> .....	17
<i>Colour generation from nanoparticles and nanostructures</i> .....	18



NANOYOU Teachers Training Kit – Module 1– Chapter 4

<i>Colour in metal colloids (surface plasmons)</i> .....	19
<i>Colour in semiconducting nanocrystals (quantum dots)</i> .....	20
<i>From white to transparent materials</i> .....	21
Magnetic properties .....	21
Mechanical properties.....	23
<i>Improving existing materials</i> .....	23

## Chapter 4: Fundamental “nano-effects”

Nanoscience is often referred to as “the science of small”. The question we address in this chapter is: why does size matter? What is so special about nano-sized materials? How are their properties different from those of “conventional” bulk materials? Here we do not provide a complete review of the topic, which would involve an in-depth review of quantum physics. Rather, we highlight some fundamental aspects of nanoscience that are essential to understand the exceptional properties of nanomaterials. Rather than focusing on the theory behind these effects we focus on **the implications that these effects have on materials properties**.

### What happens at the nanoscale?

The macroscopic physical properties of a substance (melting point, boiling point, conductivity etc.) are determined by studying a pure sample in quantities big enough to be measured under normal laboratory conditions. One mole of any material contains  $6.022 \times 10^{23}$  molecules; one mole of water for instance weighs 18 gr. Therefore when the boiling point of one mole of water is determined, in reality the value which is obtained represents an average value based on the behaviour of billions and billions of molecules of water; we assume that the result should be true for any size of group of water molecules. This is not correct for many materials: as the size of the material is reduced, and the nanoscale regime is reached, it is possible that the same material will display totally different properties (different melting point, conductivity etc). This is because matter at the nanoscale no longer follows Newtonian physics but rather quantum mechanics.

**In other words, the properties of materials can be size-dependent.** This might be a rather new concept to bring into the classroom as conventionally the properties of a substance (solid, liquid or gas) are related to the atoms and molecules that make up the substance and the way they are connected to one another (chemical bonds). Size is not normally mentioned as a key factor. Students will probably expect a piece of gold to be golden in colour however big or small it is. This is correct at the macro and micro-scale level; but at the nanoscale things start to change dramatically, due to quantum effects. Precisely gold can be used as a prime example: a colloid of gold nanoparticles is no longer “golden” but ruby red in colour (**Figure 1**).



**Figure 1.** Dependence of colour on gold size. (Image source: L. Filippini, iNANO, Aarhus University, Creative Commons ShareAlike 3.0)

**TIP TO TEACHER:** the concept that a material can have properties that are size dependent can be illustrated through “macro” analogies. For instance a glass half-filled with water sounds differently from a glass totally filled with water. In this analogy, the quantity (volume) of the water determines the sound that is emitted. Similarly, a guitar string under more or less tension will sound differently.

### A different kind of small

Materials that belong to the “nanoscale” are made at least of clusters of atoms and molecules, not single atoms: for example 3.5 atoms of gold or 8 hydrogen atoms lined up in a row are one nanometre long. A glucose molecule is about 1 nm in size.

Nanomaterials represent a “different kind of small” compared to other “small” objects that a student might be familiar with. Nanomaterials are not as small as electrons or single atoms, and are bigger than “very small objects”, like a cell or bacterium, that a student can probably think of. Nanostructures are at the confluence of the smallest human-made objects (e.g., latest-generation transistors) and the largest molecules of living things (e.g., DNA, proteins). **Nanomaterials are intermediate in size between isolated atoms and molecules, and bulk materials. At this scale matter shows exceptional properties.**

Thanks to their unique properties, nanomaterials offer two exciting possibilities:

- Nanomaterials can be used to improve current materials or create new ones that have exceptional properties.
- As nanomaterials have dimensions in the range of the largest molecules found in the natural world, it is possible to integrate them and interact actively with them in a device.

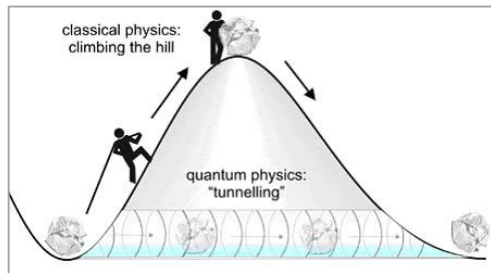
The fabrication and utility of a range of nanomaterials are further discussed in **Chapter 5 of Module 1 (“Overview of Nanomaterials”)**.

## Physics at the nanoscale

Nanomaterials are closer in size to single atoms and molecules than to bulk materials, and to explain their behaviour it is necessary to use quantum mechanics. **Quantum mechanics** is a scientific model that was developed for describing the motion and energy of atoms and electrons. As quantum mechanics concepts are normally included in a secondary science (physics or chemistry) school curriculum, they are not described here in detail. Here we provide just a **brief summary** of the most salient quantum effects, together with other **physical properties that are relevant at the nanoscale**:

- Due to the smallness of nanomaterials, their mass is extremely small and gravitational forces become negligible. Instead **electromagnetic forces** are dominant in determining the behaviour of atoms and molecules.
- **Wave-corpucle duality of matter**: for objects of very small mass, such as the electron, wavelike nature has a more pronounced effect. Thus electrons exhibit wave behaviour and their position is represented by a wave (probability) function.
- One of the consequences is a phenomenon called **tunnelling**. Classical physics states that a body can pass a barrier (potential barrier) only if it has enough energy to “jump” over it. Therefore, if the object has lower energy than that needed to jump over the energy barrier (the “obstacle”), in classical physics, the probability of finding the object on the other side of the barrier is null. In quantum physics a particle with energy less than that required to jump the barrier has a **finite probability** of being found on the other side of the barrier. Figuratively, one can imagine that the particle passes into a “virtual tunnel” through the barrier (**Figure 2**). It should be noted that in order to have a tunnel effect the “thickness” of the barrier (i.e., energy potential) must be comparable to the wavelength of the particle and therefore this effect is observed only at nanometre level. So in simple words, electron (or quantum) tunnelling is attained when a particle (an electron) with lower kinetic energy is able to exist on the other side of an energy barrier with higher potential energy, thus defying a fundamental law of classic mechanics. **Tunnelling is the penetration of an electron into an energy region that is classically forbidden.**

Tunnelling is a fundamental quantum effect and it is the base of a very important instrument for imaging nanostructured surfaces called the **Scanning Tunnelling Microscope (STM)**. The same instrument can be used a nanofabrication tool (movement of single atoms). The operation principle and capabilities of the STM are discussed in **Chapter 6 of Module 1 “Characterisation Methods”**.



**Figure 2:** Schematic representation of tunnelling. (Image credit: Copyright Max Planck Institute for Quantum Optics).

- **Quantum confinement.** In a nanomaterial, such as a metal, electrons are confined in space rather than free to move in the bulk of the material.
- **Quantisation of energy.** Electrons can only exist at **discrete energy levels**. Quantum dots are nanomaterials that display the effect of quantisation of energy.
- **Random molecular motion.** Molecules move due to their kinetic energy (assuming the sample is above absolute zero). This is called random molecular motion and is always present. At the macroscale this motion is very small compared to the sizes of the objects and thus it is not influential on how the object moves. At the nanoscale, however, these motions can be of the same scale as the size of the particles and thus have an important influence on how they behave. One example of a random kinetic motion is the Brownian Motion.
- **Increased surface-to-volume ratio.** One of the distinguishing properties of nanomaterials is that they have an increased surface area. This characteristic is described in more depth in the next session.

### Chemistry at the nanoscale.

We said that a nanomaterial is formed of at least a cluster of atoms, often a cluster of molecules. It follows that **all types of bindings that are important in chemistry are also important in nanoscience**. They are generally classified as:

- **Intra-molecular bonding** (chemical interactions): these are bondings that involve changes in the chemical structure of the molecules. They include: ionic bonds, covalent bonds and metallic bonds;

- **Intermolecular bonding** (physical interaction): these are bondings that do not involve changes in the chemical structure of the molecules. They include ion-ion and ion-dipole interactions; Van der Waals interactions; hydrogen bonds; hydrophobic interactions; repulsive forces (such as steric repulsions).

It is assumed that the description of chemical and physical bonds is part of the secondary science school curriculum, so here we highlight some chemical and physical interactions that often used to describe the properties of nanomaterials.

Nanomaterials often arise from a number of molecules held together or large molecules that assume specific three-dimensional structures through intermolecular bonding (**macromolecules**). Therefore nanoscience also deals with **supramolecular chemistry** (i.e., the chemistry that deals with interactions among molecules), which is just a subarea of the general field called “chemistry”. In these macromolecules intermolecular bonding often plays a crucial role.

- Intermolecular bondings, such as **hydrogen bonding** and Van der Waals bonding are weak interactions, but in a large number they can have a total energy that can be quite large. Think for instance of the structure of DNA (which has a cross-section of 2 nm): the two helices are held together by numerous hydrogen bonds. This point becomes particularly relevant in nanoscience, where materials can have very large surface areas and consequently small forces can be applied to very large areas.

#### **HANDS ON ACTIVITY**

*A very simple demonstration to show how small forces become important on large surfaces is to take 2 big books made of thin paper (like a phonebook or Yellow Pages) and gradually lay one page of the first book over a page of the second book alternately. When only a few pages are overlapped, it is very easy to take the two books apart; you just need to pull. As the number of pages interconnected increases, it becomes harder to pull the two books apart. After a certain number of pages it is no longer possible to separate the 2 books by hand! The interaction between the pages is due to weak forces (electrostatic and Van der Waals). When the surface area is big, these weak forces result in a very strong interaction!*

- Intermolecular bondings often hold together macromolecules (such as proteins) in specific three-dimensional structures with which **precise biological functions** are associated. Disruption of these interactions in a protein irreversibly affects its 3D structure (quaternary structure) and leads to a total loss of function (*protein denaturation*).



- One type of intermolecular bonding that is particularly significant in nanoscience is the **hydrophobic effect**. This is a process which is basically driven by entropy and which has a major role in biological materials. In simple words it is the property by which non-polar molecules (e.g. oil) tend to form aggregates of like molecules in water. **TIP TO TEACHER:** Students will be familiar with the hydrophobic effect. A simple example is oil drops in water.

### Molecules as devices

In nanoscience macromolecules are often considered as “devices” that for instance can trap or release a specific ion under certain environmental conditions (pH etc). A biological example of such a macromolecule is ferritin. Therefore in nanoscience and nanotechnologies, where molecules can themselves be devices, **bonds may also be device components**. One area of study is for instance the use of molecules as **molecular switches, actuators and electronic wires**. This is further discussed in **Chapter 4 of Module 2: “Applications of Nanotechnologies: ICT”**.

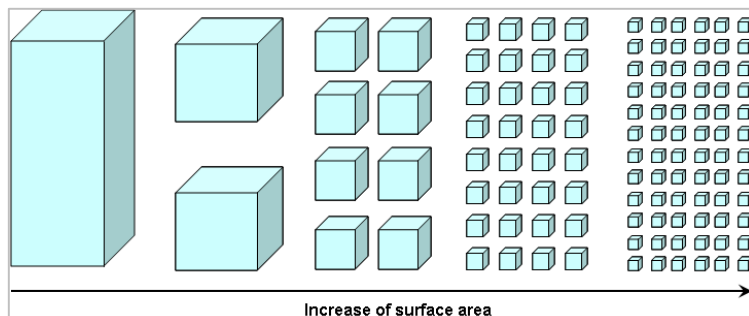
## Unique material properties at the nanoscale

### Surface properties

Regardless of whether we consider a bulk material or a nanoscale material, **its physical and chemical properties depend on a lot on its surface properties**. Surfaces perform numerous functions: they keep things in or out; they allow the flow of a material or energy across an interface; they can initiate or terminate a chemical reaction, as in the case of catalysts. The branch of science that deals with the chemical, physical and biological properties of surfaces is called **surface science**. In this context the term **interface**, rather than surface, is often used, to emphasise the fact that it is a boundary between two phases: the material and the surrounding environment (liquid, solid or gas).

If a bulk material is subdivided into an ensemble of individual nanomaterials, the total volume remains the same, but the **collective surface area is greatly increased**. This is schematically shown in **Figure 3**.

## NANOYOU Teachers Training Kit – Module 1– Chapter 4



**Figure 3.** Schematic drawing showing how surface-to-volume increases as size is decreased. Image not to scale. (Image source: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0)

The consequence is that the surface-to-volume ratio of the material – compared to that of the parent bulk material – is increased.

**TIP TO TEACHER:** A very simple example to mention in class is granular sugar and caster sugar. Caster sugar is finer, stickier (more surface absorption) and in water dissolves faster.

How would the total surface area increase if a cube of  $1\text{ m}^3$  were progressively cut into smaller and smaller cubes, until it is formed of  $1\text{ nm}^3$  cubes? **Table 1** summarises the results.

Size of cube side	Number of cubes	Collective Surface Area
1 m	1	$6\text{ m}^2$
0.1 m	1000	$60\text{ m}^2$
0.01 m = 1cm	$10^6 = 1\text{ million}$	$600\text{ m}^2$
0.001 m = 1mm	$10^9 = 1\text{ billion}$	$6000\text{ m}^2$
$10^{-9}\text{ m} = 1\text{ nm}$	$10^{27}$	$6 \times 10^9 = 6000\text{ Km}^2$

**USEFUL VIDEO #1: CUTTING CHEESE VIDEO.** A simple and fun video to watch that shows the increase in surface area as a material is cut into progressively smaller cubes can be seen at:  
<http://community.acs.org/nanotation/NanoTubePlayer/tabid/131/Videoid/101/Small-Can-Be-Big-A-French-Cheesy-Perspective.aspx> (In English).

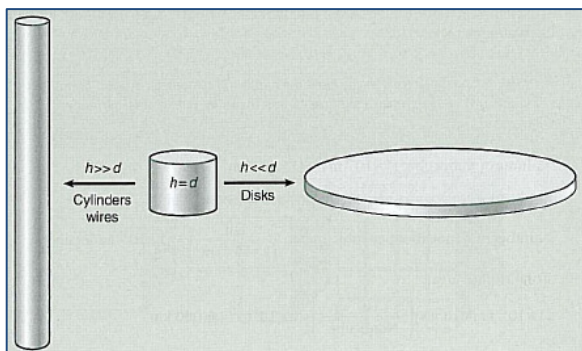
## The importance of surface atoms

In surface science the chemical groups that are at the material interface determine its properties. Properties like catalytic reactivity, electrical resistivity, adhesion, gas storage and chemical reactivity depend on the nature of the interface. **Nanomaterials have a significant proportion of atoms existing at the surface.** This has a profound effect on reactions that occur at the surface such as such as **catalysis** reactions, **detection reactions**, and reactions that, to be initiated, require the physical adsorption of certain species at the material's surface.

**USEFUL VIDEO #2: MENTOS IN DIET COKE VIDEO.** This video shows the effect of putting a Mentos into a bottle of diet coke. The effect is linked to the surface roughness of the mentos and to the chemistry of its coating. Even if this effect is not necessarily a "nano-effect", the video well illustrates the connection between surface properties and physical behaviour. The effect happens only with a mint Mentos – with a glazed (fruit) Mentos it doesn't, a sign that the effect is due to surface chemistry/topography. See: <http://dsc.discovery.com/videos/mythbusters-diet-coke-and-mentos.html> (in English).

The fact, that in a nanomaterial a larger fraction of the atoms is at the surface influences some physical properties such as the **melting point**. Given the same material, its melting point will be lower if it is nano-sized. Surface atoms are more easily removed than bulk atoms, so the total energy needed to overcome the intermolecular forces that hold the atom "fixed" is less and thus the melting point is lower.

## Shape also matters



**Figure 4.** The ratio between  $h$  and  $d$  determines whether a shape is like a wire or a disc. Shape influences surface area.

Given the same volume, **the extent of the surface area depends on the shape** of the material. A simple example is a sphere and a cube having the same volume. The cube has a larger surface area than the sphere. For this reason in nanoscience not only the size of a nanomaterial is important, but also its

shape. **Figure 4** illustrates this concept. In the section "catalysis" an example is given of a nanomaterial whose properties are determined not only by size but also by shape.

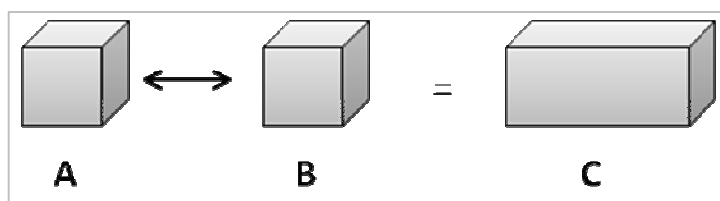
## Surface energy

Atoms and molecules that exist at the surface or at an interface are different from the same atoms or molecules that exist in the interior of a material. This is true for any material. Atoms and molecules at the interface have enhanced reactivity and a greater tendency to agglomerate: **surface atoms and molecules are unstable**, they have **high surface energy**.

**TIP TO TEACHER:** A simple example to use in class to demonstrate the concept of “high surface energy” is to coat some ping pong balls with Velcro (putting the two sides on different balls). If you place the balls in a plastic bag and shake, the balls will stick together. If normal balls are used, no attachment occurs.

As pointed out in the previous section, nanomaterials have a very large fraction of their atoms and molecules on their surface. On the other hand a fundamental chemical principle is that “systems of high energy will strive to attain a state of lower energy, by whatever means possible”. So how is it possible to have nanomaterials? Nature is abundant with nanomaterials (proteins, DNA etc). **Nanomaterials are inherently unstable**, therefore there are various methods that nanomaterials adopt to **minimise their inherent high surface energy**.

One of the ways of reducing surface energy for nanoparticles is **agglomeration**. Surface energy is an additive quantity. The surface of 10 identical nanoparticles is equal to the sum of the surface energy of each individual nanoparticle. If these were to agglomerate, and become one large particle, the overall surface energy would be reduced. The concept is illustrated in **Figure 5**. If a generic surface energy value  $\gamma$  is associated with each lateral surface of cube A, then its total surface energy is  $6\gamma$ . The same applies to cube B. Therefore the total surface energy of both cubes, A and B, separated, is  $2 \times (6\gamma) = 12\gamma$ . The total surface energy of the parallelepiped C, on the other hand, is  $10\gamma$ .



**Figure 5.** Surface energy of two separate cubes is higher than the surface energy of the two cubes agglomerated.

*Nanoparticles have a strong intrinsic tendency to agglomerate. To avoid that, surfactants can be used. This also explains why when nanoparticles are used in research and industry they are often immobilised*

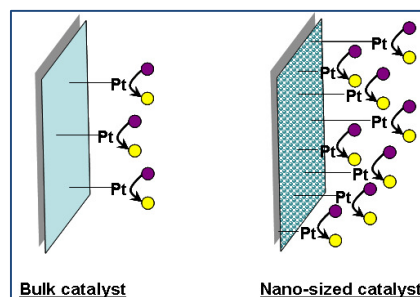
on a solid support or mixed within a matrix. Even in commercial products that claim to contain nanoparticles (such as sunscreens) microscope images show that they are actually present in the form of agglomerates of  $> 100$  nm dimensions.

### Reactions where surface properties are very important

In this last section we review briefly two reactions: catalysis and detection, where the surface properties of the material are particularly important, and we highlight what nanoscience can do to improve their outcome.

### Catalysis

A catalyst is a substance that increases a chemical reaction rate without being consumed or chemically altered. Nature's catalysts are called enzymes and are able to assemble specific end-products, always finding pathways by which reactions take place with minimum energy consumption. Man-made catalysts are not so energy efficient. They are often made of metal particles fixed on an oxide surface, working on a hot reactant stream (to reduce a phenomenon called 'catalyst poisoning' which occurs when species dispersed in the atmosphere, such as CO, occupy the active sites of the catalysts). One of the most important properties of a catalyst is its **active surface** where the reaction takes place. The 'active surface' increases when the size of the catalysts is decreased: the smaller the catalyst particles, the greater the ratio of surface-to-volume (as illustrated above). The higher is the catalysts' active surface, the greater is the surface reactivity. Research has shown that the **spatial organisation of the active sites in a catalyst is also important**. Both properties (nanoparticle size and molecular structure/distribution) can be controlled using nanotechnology. Hence, this technology has great potential to expand catalyst design with benefits for the chemical, petroleum, automotive, pharmaceutical and food industries. **The use of nanoparticles that have catalytic properties will allow a drastic reduction of the amount of material used, with resulting economic and environmental benefits.**



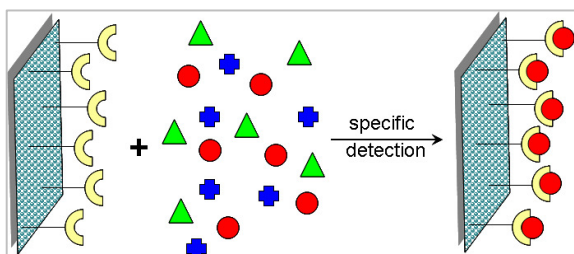
**Figure 6.** Schematic representation of the increased active surface of a nano-sized catalyst (right) compared to a bulk catalyst. (Image credit: L. Filippini, iNANO, Aarhus University, Creative Commons ShareAlike 3.0)

Catalysis and its importance in environmental and energy applications are discussed in **Chapters 2 and 3 of Module 2 (“Applications of nanotechnologies: Environment” and “Applications of Nanotechnologies: Energy”)**. **Figure 6** illustrates the effect of nanostructuring on a catalyst surface.

A good example of how nanoscience can impact the development of catalytic materials is that of gold. Bulk gold is a noble metal: it is stable, non-toxic, and resistant to oxidation and chemical attack. For these reasons it is widely used in jewellery. On the other hand **nanoscale gold particles can catalyse chemical reactions**. It has been found that finely dispersed gold nanoparticles on oxide supports are catalytically very active. In many cases the catalytic activity and selectivity of dispersed gold nanoparticles exceed those of the commonly used transition metal catalysts such as Pt, Rh, and Pd. This is an exciting result because metals like Pt and Pd (commonly used in catalysis such as automobile catalytic converters) are toxic and are also very rare metals, hence very expensive.

## Detection

The detection of a specific chemical or biological compound within a mixture represents the basis for the operation of numerous devices, like chemical sensors, biosensors and microarrays. [These devices will be described in more detail in **Chapter 1 of Module 2 (“Application of nanotechnologies: Medicine & Healthcare”)**]. As with catalysis, a detection reaction occurs at the material interface. The rate, specificity and accuracy of this reaction can be improved using nanomaterials rather than bulk materials in the detection area. The higher surface to volume ratio of nanomaterials increases the surface area available for detection with a positive effect on the rate and on the limit of detection of the reaction. In addition, nanomaterials can be designed to have specific surface properties (chemical or biochemical), tailored at a molecular level. This way, the active sites on the material surface can act as “locks” to detect specific molecules (the “keys”). **Figure 7** illustrates this concept. Scaling down using nanomaterials allows **packing more detection sites into the same device**, thus allowing the detection of multiple analytes.

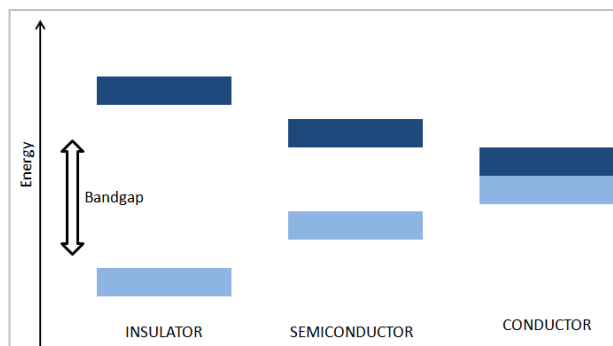


**Figure 7.** Schematic representation showing the specific detection of an analyte within a mixture by "receptor" sites in a nanomaterial. (Image credit: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0)

This scaling-down capability, together with the high specificity of the detection sites obtainable using nanomaterials, will allow the fabrication of super-small “**multiplex detection devices**”, that is, devices that can test and detect more than one analyte at the time.

### Electrical properties

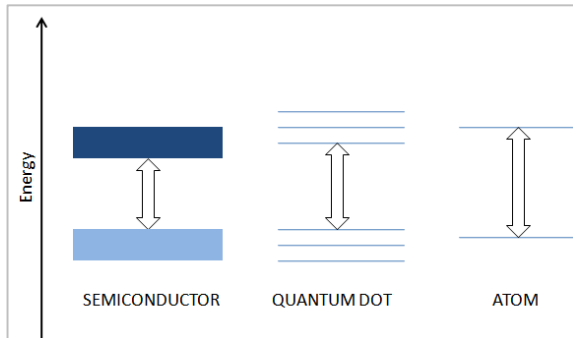
There are three categories of materials based on their electrical properties: (1) conductors, (2) semiconductors, and (3) insulators. The energy separation between the valence band and the conduction band is called  $E_g$  (bandgap). The ability to fill the conduction band with electrons and the energy of the bandgap determine whether a material is a conductor, a semiconductor or an insulator. In conducting materials like metals the valence band and the conduction band overlap, so the value of  $E_g$  is small: thermal energy is enough to stimulate electrons to move to the conduction band. In semiconductors, the bandgap is a few electron volts. If an applied voltage exceeds the bandgap energy, electron jump from the valence band to the conduction band, thereby forming **electron-hole pairs** called **excitons**. Insulators have large bandgaps that require an enormous amount of voltage to overcome the threshold. This is why these materials do not conduct electricity (**Figure 8**).



**Figure 8.** Schematic illustration of the valence and conduction bands in the three kinds of materials, insulator, semiconductor and conductor. (Image credit: L. Filippini, iNANO, Aarhus University, Creative Commons ShareAlike 3.0)

### Quantum confinement and its effect on material electrical properties

**Quantum confinement causes the energy of the bandgap to increase** as illustrated in **Figure 9**. Also, at very small dimensions when the energy levels are quantified, the band overlap present in metals disappears and is actually transformed into a bandgap. **This explains why some metals become semiconductors as their size is decreased.**



**Figure 9.** The image compares the energy of the bandgap (arrow) in a bulk semiconductor, in a quantum dot and in an atom. As more energy states are lost due to the shrinking size, the energy bandgap increases. (Image credit: L. Filippini, iNANO, Aarhus University, Creative Commons ShareAlike 3.0)

The increase of bandgap energy due to quantum confinement means that more energy will be needed in order to be absorbed by the bandgap of the material. Higher energy means shorter wavelength (blue shift). The same applies for the wavelength of the fluorescent light emitted from the nano-sized material, which will be higher, so the same blue shift will occur. This thus gives a **method of tuning the optical absorption and emission properties of a nano-sized semiconductor over a range of wavelengths by controlling its crystallite size**. The optical properties of nano-sized metals and semiconductors (quantum dots) are described in a dedicated section of this Chapter (Optical properties).

### Nanomaterial with exceptional electrical properties:

Some nanomaterials exhibit electrical properties that are absolutely exceptional. Their electrical properties are related to their unique structure. Two of these are **fullerenes and carbon nanotubes**. For instance, carbon nanotubes can be conductors or semi-conductors depending on their nanostructure. These materials are discussed in **Chapter 5 of Module 1 (“Overview of nanomaterials”)**. Another example is that of **supercapacitors**, which are materials in which there is effectively no resistance and which disobey the classic Ohm’s law.

### Optical properties

Some nanomaterials display very different optical properties, such as colour and transparency, compared to bulk materials. In this section we discuss the reason for this behaviour and provide some examples. Before going into detail, some fundamentals are reviewed.



## Interaction of light with matter

The “colour” of a material is a function of the interaction between the light and the object. If a material absorbs light of certain wavelengths, an observer will not see these colours in the reflected light. Only reflected wavelengths reach our eyes and this makes an object appear a certain colour. For example leaves appear green because chlorophyll, which is a pigment, absorbs the blue and red colours of the spectrum and reflects the green.

In general light ( $I$ ) incident on a material can be transmitted ( $T$ ), absorbed ( $A$ ) or reflected ( $R$ ):

$$I = T + A + R$$

As the size of the materials is reduced, **scattering (S) of light** can also contribute to its colour (or transparency). Below is a short summary of each process:

- **Reflection (R)** occurs when a light strikes a smooth surface and the incident wave is directed back into the original medium. The reflected wave has same geometrical structure as the incident wave.

- **Absorption (A)** is a process that involves energy transformation. The energy levels of a substance determine the wavelengths of light that can be absorbed. It is a molecular phenomenon, dependent on the chemical identity and structure of the substance (not on the size of the molecules or clusters), and involves electronic transitions, vibrations and rotations. Chromophores and fluorephores are examples of organic materials that have specific electronic transitions.

- **Transmission (T)** is the ability of light to pass through a material; it is complementary to absorption. Transmission of light is what is left after reflection, scattering and absorption has occurred.

- **Scattering (S)** is the phenomenon that occurs when radiation hits a structure with dimensions comparable to the incident wavelength. Therefore it is a physical process that *depends on cluster size*, the index of refraction of the cluster and the index of refraction of the suspension medium. It is a physical interaction only – no energy transformations occur during scattering (as opposed to absorption), energy is simply redirected in many directions. The wavelength of the incoming light and that of the outgoing light are the same. After the light hits the clusters in the colloid and is redirected once, it can encounter another cluster and be re-directed again. This phenomenon is called **multiple scattering**. At the “macro” level the overall effect can be that light is sent back the way it came (back scattering) or moves forward in the same direction it was moving initially (front scattering). **Maximum**

**scattering occurs for wavelengths twice as large as the cluster size.** Therefore if the cluster is about 200 nm, than maximum scattering is observed at 400nm, which lies in the visible light range.

*The formula indicated above still holds if scattering occurs.* Scattering simply contributes to the “reflection” (back scattering) and “transmission” (front scattering) parts of the equation. Light that has been absorbed cannot be scattered.

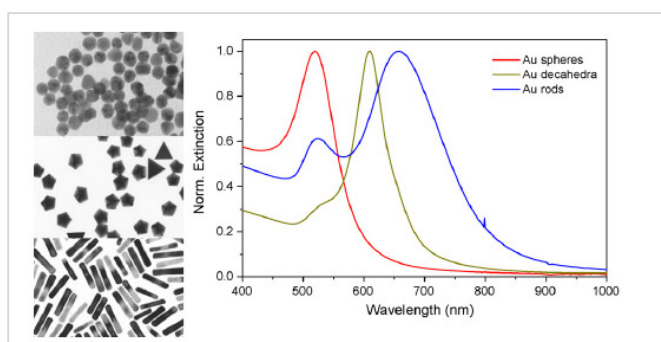
### Colour generation from nanoparticles and nanostructures

Nanomaterials in general can have peculiar optical properties as a result of the way light interacts with their fine nanostructure. Below is an overview:

Colour due to...	Example of nanomaterial
<b>Interference.</b> The colour is based on the constructive interference of light wavelengths as they interact with the nanomaterial	Butterfly wings (photonic crystals within). This example is described in <b>Chapter 2 of Module 1 “Natural Nanomaterials”</b> .  Liquid crystals (e.g., soap). the colours of liquid crystals are explained in detail in <b>Experiment B of the Experimental Module</b>
<b>Scattering.</b> The colours arises from the fact that different particle sizes scatter different wavelengths.	Colloids (milk).
<b>Surface plasmons.</b> This is a peculiar effect found in metal nanoparticles (described in the next session) responsible for the vivid colours of metal colloids.	Metal colloids (nano-gold)
<b>Quantum fluorescence.</b> The quantum confinement in nano-sized semiconductors leads to discrete energy levels from which energy can be emitted (fluorescence) after it has been absorbed by the semiconductor.	Semiconductor quantum dots (QDs)

## Colour in metal colloids (surface plasmons)

One of the distinguishing properties of **metal nanoparticles** in general is their optical properties, which are different from those of their bulk counterpart. This is due to an effect called **localised surface plasmon resonance**. In simple words, when light hits a metal surface (of any size) some of the light wave propagates along the metal surface giving rise to a surface plasmon – a group of surface conduction electrons that propagate in a direction parallel to the metal/dielectric (or metal/vacuum) interface. When a plasmon is generated in a conventional bulk metal, electrons can move freely in the material and no effect is registered. In the case of nanoparticles, the **surface plasmon is localized in space**, so it oscillates back and forth in a synchronised way in a small space, and the effect is called Localised Surface Plasmon Resonance (LSPR). When the frequency of this oscillation is the same as the frequency of the light that it generated it (i.e., the incident light), the plasmon is said to be in resonance with the incident light.



**Figure 10.** Transmission electron micrographs and UV—Vis spectra of gold nanoparticle colloids with various geometries: (top) spheres, (middle) decahedra and (bottom) rods. (Image credit: Reprinted from: Borja Sepúlveda et al., "LSPR-based Nanobiosensors", *Nano Today* (2009), 4 (3), 244-251, with permission from Elsevier).

The energy of LSPR's is **sensitive to the dielectric function of the material and the surroundings and to the shape and size of the nanoparticle**. This means that if a ligand, such a protein, attaches to the surface of the metal nanoparticle, its LSPR energy changes. Similarly, the LSPR effect is sensitive to other variations such as the distance between the nanoparticles, which can be changed by the presence of surfactants or ions. The LSPR effect has been observed not only on metal nanoparticles but also in nano-rings, voids in metal films and other nanostructures (**Figure 10**).

One of the consequences of the LSPR effect in metal nanoparticles is that they have **very strong visible absorption** due to the resonant coherent oscillation of the plasmons. As a result, colloids of metal nanoparticles such as gold or silver can display **colours which are not found in their bulk form**, like red, purple or orange, depending on the nanoparticles' shape, size and surrounding media. An example has



already been illustrated in **Figure 1**, which shows that a colloid of gold nanoparticles about 15nm in size is ruby red! The properties of metal nanoparticles make them useful in **sensing**.



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The applications of metal nanoparticles are discussed in **Chapter 5 of Module 1 (“Overview of Nanomaterials”)** and in **Chapter 4 of Module 2 (“Applications of Nanotechnologies: medicine and healthcare”)**.

### Colour in semiconducting nanocrystals (quantum dots)

As mentioned earlier, nanosized semiconductors have quantised energy states; therefore the CB and VB bands split up and become discretised. Charge transfer occurs between these discrete levels, so only wavelengths of a certain dimension are absorbed, and as a consequence emission is also monochromatic. Quantum confinement causes the energy of the bandgap to increase; therefore more energy is needed in order to be absorbed by the bandgap



**Figure 11.** Ten distinguishable emission colours of ZnS-capped CdSe QDs excited with a near-UV lamp. (Reprinted by permission of Macmillan Publishers from Macmillan Publishers Ltd: Nature Biotech. (2001) 19, 631-5, Copyright 2001).

of the material. Higher energy means shorter wavelength (blue shift). The same applies to the wavelength of the fluorescent light emitted from the nano-sized material, which will be higher, so the same blue shift will occur. Tuning the size of the semiconductor nanocrystal is a means to tune the bandgap, and therefore the wavelength absorbed/emitted by the crystal. As a result **the same material (e.g., CdSe) emits different colours depending on its size (Figure 11)**.

QDs are currently used as an **alternative to conventional dyes** in fluorescence microscopy and in other methods where dyes are used (e.g., dye-sensitised solar cells). QDs are also being studied as alternative light emitting sources.



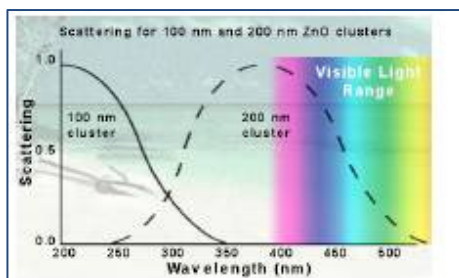
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The applications of semiconducting nanoparticles (quantum dots) are discussed in **Chapter 5 of Module 1 (“Overview of nanomaterials”)** and **Chapter 3 of Module 2 (“Applications of nanotechnologies: Energy”)** and in **Chapter 4 of Module 2 (“Applications of nanotechnologies: ICT”)**.

## From white to transparent materials

Scattering of visible light is responsible for the **white appearance of high-protection sunscreens**. Students will be familiar with these thick, white paste-like sunscreens that are often used on children and on adults with sensitive skin. These sunscreens contain **ZnO and TiO<sub>2</sub> clusters of about 200nm**. Visible light interacts with these clusters and all of its wavelengths are scattered: the combination of the visible spectrum is white; therefore the sunscreen appears white (as illustrated in the curve shown in **Figure 12**).

If the **dimensions of the cluster are reduced, for instance from 200nm to 100nm**, maximum scattering occurs around 200 nm and the curve is shifted towards shorter wavelengths, which are no longer in the visible light regime: the effect is that the same material (e.g., ZnO), now in smaller size (100nm), no longer appears white but transparent (**Figure 12**)



**Figure 12.** Scattering curves for 100nm and 200 nm ZnO clusters. (Image credit: reprinted from Nanosense Curriculum Series "Clear Sunscreens", Copyright 2005-2008 SRI International, Creative Commons Attribution ShareAlike 3.0).



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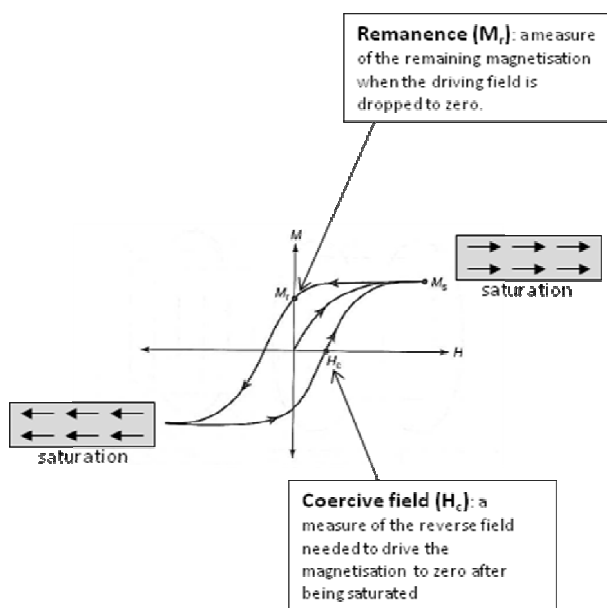
The different light scattering of bulk and nanosized ZnO and TiO<sub>2</sub> is exploited in latest-generation sunscreens which appear transparent rather than white. This and other applications including coatings for solar panels are discussed in **Chapter 5 of this Module 1 ("Overview of Nanomaterials")**.

## Magnetic properties


The magnetic properties of a magnet are described by its magnetisation curve. In general terms, the magnetisation curve of a ferromagnetic material is a plot of the total magnetisation of the sample versus the applied DC field with strength H, as illustrated in **Figure 13**.

Initially as H increases, M increases until a saturation point M<sub>s</sub> is reached. When H is decreased from the saturation point, M does not decrease to the same value it had before; rather, it is higher on the curve

of the decreasing field. This is called **hysteresis**. When the applied field  $H$  is returned to zero, the magnet still has a magnetisation, referred to as **remnant magnetisation**  $M_r$ . In order to remove the remnant magnetisation a field  $H_c$  has to be applied in the direction opposite to the field applied the first time. This field is called the **coercive field**.



**Figure 13.** Magnetisation hysteresis loop with the coercive field  $H_c$ , the remnant magnetisation  $M_r$ , and the saturation point  $M_s$  indicated. (Image credit: : L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0).

 The diverse **applications of magnets** require the magnetisation curves to have different properties. In general, for **soft magnetic materials** (e.g. those used in transformers and rotating electrical machinery) which are subject to rapidly alternating AC magnetic fields (so that they repeat the magnetisation curve many times), small or zero coercive fields are required to minimise the energy loss (in the form of heating) during operation. In the case of **permanent magnets** (hard magnets) used as part of high-field systems, large coercive fields are required and large hysteresis loops are sought, as well as high saturation magnetisations.

**Nanostructuring of bulk magnetic materials can be used to design the magnetisation curve of the material, leading to soft or hard magnets with improved properties.**

In general, the magnetic behaviour of a material depends on the structure of the material and on its temperature. In order to “feel” a magnetic field a material must have a nonzero net spin (transition metals). The typical size of classically expected magnetic domains is around  $1 \mu\text{m}$ . When the size of a



magnet is reduced, the number of surface atoms becomes an important fraction of the total number of atoms, surface effects become important, and quantum effects start to prevail. When the size of these domains reaches the nanoscale, these materials show **new properties due to quantum confinement**, like the giant **Magnetoresistance effect (GME)**. This is a fundamental nano-effect which is now being used in modern data storage devices. The effect of nanostructuring on magnetic materials is discussed in detail in **Chapter 5 of this Module 1 (“Overview of Nanomaterials”)**.

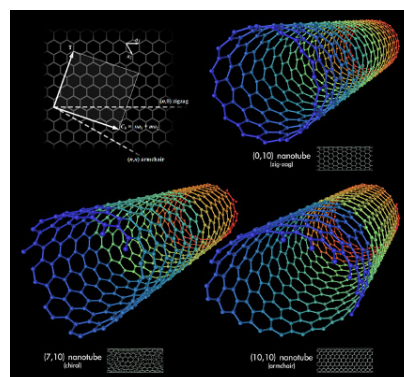


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The GMR effect and its application to the data storage devices are discussed in **Chapter 4 of Module 2 (“Applications of nanotechnologies: ICT”)**.

### Mechanical properties

Some nanomaterials have **inherent exceptional mechanical properties** which are connected to their structure. One such material is **carbon nanotubes**: these are extremely small tubes having the same honey-comb structure of graphite, but with different properties compared to graphite. They can be single-walled or multi-walled, as illustrated in **Figure 14**. Carbon nanotubes are 100 times stronger than steel but six times lighter!! The different structures, properties and potential applications of carbon nanotubes are reviewed in the next chapter, **Chapter 5 of this Module 1 (“Overview of Nanomaterials”)**.



**Figure 14.** Types of carbon nanotubes.  
Image credit: by Mstroeck on  
en.wikipedia, Creative Commons  
Attribution ShareAlike 3.0

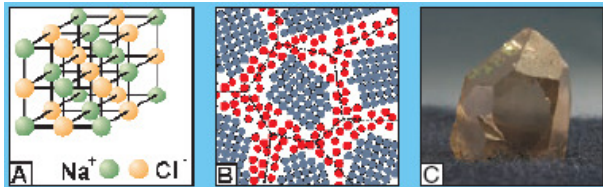
### Improving existing materials

Nanomaterials can also be used to **improve the mechanical properties of existing materials**. In this case nanocomposites are formed.

One example is **nanocrystalline materials**, which are polycrystalline (i.e., made of many crystals which are identical but connected without orientation) and defined as materials with grain sizes from a few nanometres up to 100 nm. In contrast, the grain size in industrial metallic materials is about 10,000 nm or greater. These materials generally show improved mechanical properties (toughness, hardness, etc.).



**Why is this so?** A polycrystalline material (illustrated in **Figure 15**) has large pockets of regularity (crystals) in a “sea” of atoms that are not ordered (amorphous region).



**Figure 15.** A). Structure of NaCl, where the vast majority of sodium and chlorine atoms are organized at a fixed distance from each other and always alternately (example of a single crystal). (B) Structure of a polycrystalline material like iron. Large pockets of regularity are seen in a “sea” of atoms that are not ordered. In Figure B, the blue atoms are organized in tiny single crystals, while the “sea” consists of the red atoms where there is no crystal lattice. (C) A SiO<sub>2</sub> crystal (quartz), which has the typical fracture surface of single crystals. (Reprinted from: “Nanoteknologi– 12 historier om den nyeste danske nanoforskning”, Copyright iNANO, Aarhus University).

Within the crystalline structures there can be defects (cracks or dislocations). If subjected to mechanical stress, the polycrystalline materials can fracture because these defects allow the crack to propagate. To impede the movement of cracks and dislocations tiny particles (nanoparticles) of another material can be added in the lattice. Nanocrystalline materials can have vastly improved mechanical, magnetic, electrical, and catalytic properties and greater corrosion resistance compared to conventional materials with large grains.



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**What can these materials be useful for?** Nanocrystalline materials are already used in the form of hard coatings to protect tools in industry, such as **cutting tools**, where they are making a great impact in improving tool performance and life span. **Nanoparticles added to a ceramic**, such as alumina, also increase its mechanical properties, and the same applies to the addition of **nanomaterials (such as carbon nanotubes) to polymers**. The possibility of using nanomaterials for improving the mechanical properties of materials involves both inorganic and organic (polymeric) composites. Both these type of **nanocomposites** are discussed in detail in **Chapter 5 of this Module 1 (“Overview of Nanomaterials”)**. These materials have a very broad spectrum of utility, ranging from improved metals to improved plastics.