2.3 NANOMATERIALS

Nanoparticles

The physical and chemical properties of bulk materials are usually expected to remain the same whatever their size. However, if the particle size of a substance does become very small, then their properties can markedly change. This is particularly noticeable if the particle size approaches the nano scale.

Nano particles are defined as those between 1 and 100 nm. Typical examples are the C_{60} molecule, the buckyball, which is just over 1nm in diameter and nanotubes which are 1.3 nm in diameter but up to millimetres in length.

This range of particles is often considered as being a bridge between the macro world of bulk materials and the atomic and molecular world. They exhibit novel and potentially very useful properties. Through nanotechnology this has led to the development of many new substances, structures and devices.

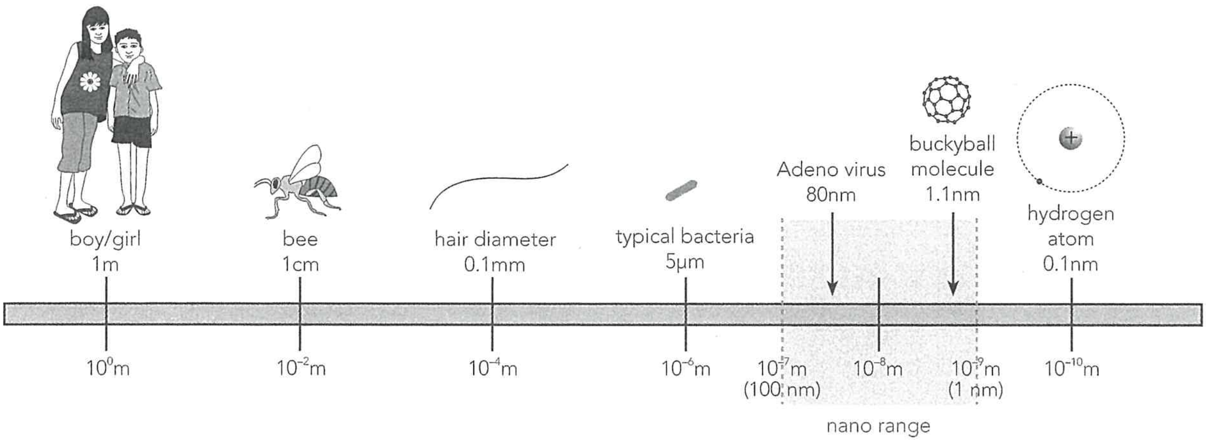


***Figure 2.1** The nanoparticle range. The C_{60} molecule is just over one nanometer in size and one of the smallest nanoparticles. A nanotube is a similar size in diameter but can be very long, up to 1mm or so.*

Question 2.9

(a) How many nanometers are there in each of the following

(i) 1.0 m ________________

(ii) 1.0 mm ________________

(iii) 1.0 µm ________________

(b) A soccer ball is approximately 22 cm in diameter. In comparison, the van der Waals diameter of a C_{60} molecule or buckyball is approximately 1.1 nm.

Calculate the factor by which the soccer ball is larger in terms of:

(i) diameter ________________________________

(ii) volume ________________________________

Note: for a sphere $V = \frac{4}{3}\pi r^3$

The effect of surface area

As particles become smaller their relative surface area to volume increases. This affects the properties of materials since much of their chemistry occurs at the surface. While for particles larger than, say a micron, the percentage of their atoms at the surface is very small; for particles in the nano range this becomes quite significant. The increased surface area leads to materials with some unusual properties and generally more reactive in nature.

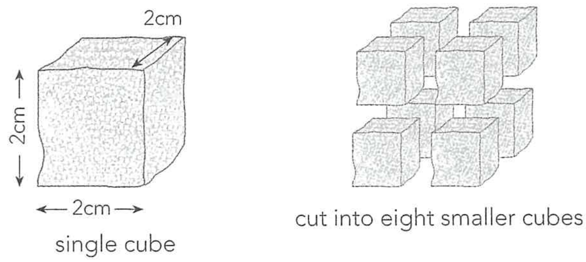


***Figure 2.2** The effect of particle size and relative surface area. When a sugar cube is cut into eight smaller cubes the total surface area doubles. This of course will increase the rate of dissolution. How much greater would the total surface area be if we could cut the sugar cube into cubes of only 1 mm sides? What if they were only 1 nm sides?*

Worked Example

2.1 A sugar cube measuring 2.0 cm × 2.0 cm × 2.0 cm as shown in Figure 2.2 is cut into 8 smaller and equal cubes. Assuming no loss of material calculate (a) the surface area of the original cube, (b) the total surface area of the 8 smaller cubes and (c) the factor by which the surface area changed.

(a)	Surface area of large cube	=	(6) × (2 × 2)	=	24 cm^2
(b)	Surface area of 8 smaller cubes	=	(8) × (6) × (1 × 1)	=	48 cm^2
(c)	Change in surface area	=	48/24	=	2

The surface area has doubled.

Question 2.10

Suppose the sugar cube shown above in Figure 2.2 could be further subdivided into very small cubes with 1.0 mm sides. Assume no loss of material.

(a) Determine how many 1.0 mm cubes there would be. ____________________

(b) Calculate the total surface area of the smaller cubes. ____________________

(c) By what factor does the total surface area differ from the original?

____

(d) What would this factor be if the cubes were nano cubes with sides of 1.0 nm only?

____

____

2.4 NANOTECHNOLOGY

As we have seen earlier nanoparticles have relatively high surface areas and hence a large percentage of their atoms or molecules can more readily interact. Their small particle size also results in unexpected and unique properties which are quite different to those of bulk materials. For example gold nanoparticles melt at a much lower temperature and appear red in solution. Some others such as zinc oxide nanoparticles are great absorbers of ultraviolet radiation; clay nanoparticles impart greater strength to polymers and titanium dioxide nanoparticles can create self-cleaning surfaces.

Nanotechnology makes use of these special properties of nanoparticles in creating many new products and techniques that are used in everyday life and industry. These include the use of such things as special coatings and smart surfaces, antimicrobial dressings and filters, stronger materials utilising nanoparticle additives and automotive catalytic converters.

Nanotechnology is a very large field of study and developments are ongoing in such areas as – drug therapy delivery systems, antimicrobial filters and dressings, nanocomposites offering lighter and stronger materials, computer chips and mass storage systems, solar cells and more efficient fuels and batteries . The possibilities are huge and diverse.

Below we take a brief look at a few of the more common and current examples which are the result of nanotechnology.

Sunscreens

A very common example of nanotechnology in action is the use of zinc oxide nanoparticles in some sunscreen lotions. These particles are excellent absorbers of ultra-violet light but unlike their bulk counterparts they create a transparent layer. This transparency is due to the fact that the zinc oxide nanoparticles being used are much smaller than the wavelength of visible light. Hence visible light is able to pass between the nanoparticles with very little being reflected.

The resulting sunscreens are very popular since they are very effective and importantly, also less visible. They are also cheaper to produce since smaller amounts of zinc oxide are actually needed.

Nanoparticles of zinc oxide and titanium dioxide are used in a similar way in paints and plastics. They absorb ultraviolet light and so help prevent the early breakdown of these materials when exposed to the sun.

Special surfaces and coatings

Nanoparticles can be used in a variety of ways to create special surfaces or alter the surfaces of materials such as fabrics in a useful way. Self-cleaning surfaces and stain resistant fabrics are two common examples.

A self-cleaning surface, on say window glass, can be achieved by coating it with a thin layer, typically 40 nm thick, of titanium dioxide nanoparticles. Several properties of these particles are helpful in achieving the desirable features of this surface.

Firstly, as with the invisible sunscreens discussed above, the particles used are so small as to reflect very little visible light. This makes the self-cleaning film transparent. Also, the coating causes photocatalysis to occur which assists in the chemical breakdown of any organic material on the glass. In addition, when water wets the glass the nanoparticles prevent water from forming droplets but rather a thin layer which flows and washes off the dirt.

Fabrics which are stain resistant or water repellent are now a reality through the use of polymer coatings containing suitable nanoparticles such as carbon nanotubes. The effect of the coatings is to produce very tiny nano sized bumps or hairs on the surface of the fabrics fibres. These prevent the water from soaking through but instead rolling off and taking any dirt with it.

This is sometimes referred to as the "lotus effect" since the leaves of lotus plants have similar characteristics. Manufacturers that produce a range of these fabrics have taken the cue from nature in using nanoparticles to mimic particular plant surfaces. Importantly, due to nanoparticles being so small, they do not affect the look or feel of the fabrics.

Nanocomposite Materials

Materials can be made lighter and stronger through the addition of suitable nanoparticles or simply by arranging the atoms of the element to form desirable nanostructures. These materials differ from normal composites in that the reinforcing phase, that is the nanoparticles added, have a high aspect ratio (much greater in length than width) and very high surface area to volume ratio.

This means that the addition of only small amounts of nanoparticles, say as little as one percent by weight, can markedly affect the properties of the resulting material. The concentration, type and shape of nanoparticles used can differently affect the final properties of the material created. This includes their melting point, strength, stiffness, durability, thermal and electrical conductivity, catalytic action and so on.

Hence a wide variety of useful nanomaterials are now available. Car manufacturers for example use carbon nanocomposites to create bumpers that are much lighter and more resistant to scratches and dents. A nanoflex alloy (carbon and iron) is widely used for the manufacture of sporting goods due to its high strength, hardness and formality. Special purpose composites are continually being developed such as sponge like silica surfaces which can trap toxic metals like lead and mercury in water.

A selection of nano-consumer products and the nanoparticles used is shown below.

PRODUCT DESCRIPTION	NANOPARTICLE/S USED
Antibacterial towels, garments	Ag
Auto paint finish	Ceramic
Auto sealants	SiO_2
Carbon fibre tennis racquet	C nanotubes
Ceramic filters	Ceramics, Ag
Computer processor chip	Cu, Si
Flash memory stick	Si
Fuel catalyst	CeO
Fullerene face cream	C_{60}
Golf clubs	C, Fe, Ti
Racing bicycles alloy frame	Al_2O_3, C
Stain resistant clothing	C nanotubes
Self cleaning window spray	TiO_2
Sunscreen lotion	ZnO

Table 2.1 A selection of nano-consumer products and the nanoparticles used. There are literally thousands of new and improved products which are the result of nanotechnology. A great variety of materials are used as nanoparticles. A convenient website which lists the myriad of nano-consumer products on the market and the companies producing them is **www.nanotechproject.org/cpi.**

Medical Applications

Nanotechnology in the medical field has resulted in many important and often lifesaving applications. These applications, in such areas as medical research, diagnostics and treatment, are both numerous and diverse. They range from the simple use of antibacterial bandages to the use of sophisticated diagnostic tools for the better imaging and screening of patients.

Some other commonly used applications include cancer therapy, controlled drug delivery, sunscreens, antioxidants, bone growth, dental ceramics and bio-composites.

The most exciting application in biomedicine is the use of nanoparticles for targeted drug delivery. This is an area of active research with different methods being tested to find, for example, a way that nanoparticles can be used to specifically target cancer cells.

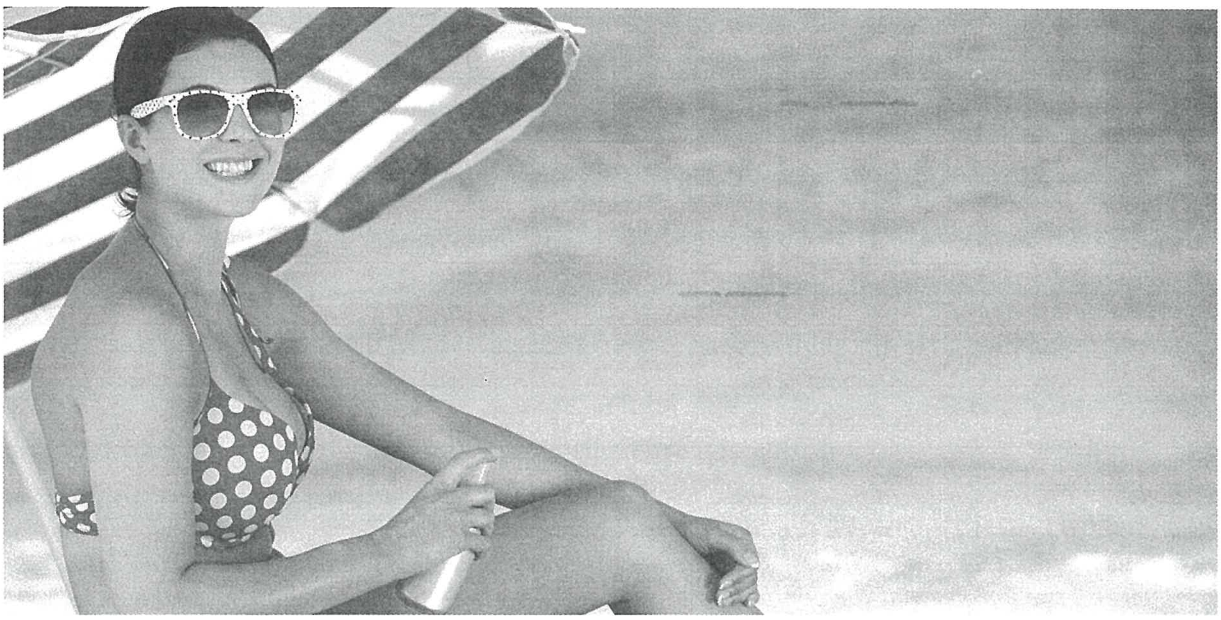
It may be possible to encapsulate drugs within suitable nanoparticles so that they can more effectively be delivered to diseased cells without affecting healthy cells. In this way it may be possible to target undesirable bodies such as virus cells or penetrate through difficult areas such as the blood-brain barrier in order to reach and treat brain tumors.

Safety Issues and Regulations

The use of nanoparticles has provided a great number of new and very useful products. However since their properties are often markedly different from those of bulk materials their use poses potential hazards to health and the environment. Nanoparticles are generally very reactive and catalytic. Their unique properties and in particular the way they react with living cells and the environment is under continual analysis.

The CSRIO carries out ongoing research into the health, safety and environmental aspects of using nanotechnologies in manufacturing. Their research aims to understand and minimise possible risks. For example, in its study of the use of nanoparticles in sunscreens its research poses such questions as: Do zinc oxide nanoparticles penetrate the skin? If so, to what extent and to what effect? What are any long term health effects and what is the long term fate of the nanoparticles in the environment? Research worldwide is undertaken by many scientific and industry bodies in order to better understand the benefits and risks associated with nanotechnology.

Regulations also exist, both internationally and nationally, to regulate the use of nanonaterials to avoid potential risks to health and safety. In Australia for example, the Therapeutic Goods Administration (TGA) regulates the use of many products including sunscreens. Only approved ingredients that have been assessed for safety can be included in these products. The TGA also requires that the efficacy of each product is tested to determine the sun protection factor (SPF) which is printed on the label.



Question 2.11

Zinc oxide nanoparticles are commonly used in the manufacture of some sunscreen lotions. Describe two properties of these nanoparticles that make them ideal for this use.

Question 2.12

Stain resistant and water repelling fabrics are produced by thinly coating their surfaces with a polymer layer containing carbon nanotubes.

(a) Describe the kind of surface this creates at the nanoscale level.

(b) How does this surface prevent staining?

(c) Why is this feature often referred to as the lotus effect?

Question 2.13

A thin coating of titanium dioxide (TiO_2) nanoparticles applied to glass creates a surface which wets more easily and prevents the formation of water droplets. The coating may also be photo-catalytic.

Briefly explain how this helps the glass surface to be self-cleaning.

Question 2.14

Nanocomposite materials can be made stronger by the addition of very small amounts of suitable nanoparticles, such as nanotubes, or ceramic platelets. Briefly discuss two useful properties of the nanoparticles used and how these help in creating stronger materials.

be recovered by filtration and the sugar by recrystallisation of the filtrate.

2.8

(i) salt from water: salt will crystallise from solution.

(ii) water from salt: water evaporates, salt does not.

(iii) sand from water: sand is insoluble.

(iv) charcoal from salt: salt is soluble, charcoal is not.

(v) KNO_3 from NaCl: Differences in solubility, NaCl crystallises first.

(vi) blue dye from ink: selective adsorption of different components of ink.

(vii) alcohol from wine: different boiling points allow fractional distillation.

(viii) salt from sugar: differences in solubility.

2.9

(a) (i) 10^9 (ii) 10^6 (ii) 1000

(b) (i) $0.22\ m / 1.1 \times 10^{-9}\ m = 2.0 \times 10^8$ times larger

(ii) Volume of a sphere is proportional to its radius cubed.

Hence volume ratio $= (0.11)^3 / 0.55 \times 10^{-9})^3 = (2.0 \times 10^8)^3 = 8.0 \times 10^{24}$

Hence volume of the soccer ball is 8.0×10^{24} times larger than that of a buckyball.

2.10

(a) 2 cm = 20 mm hence

N° of cubes with 1 mm sides = $20 \times 20 \times 20 = 8000$

(b) Total surface area $= (8000) \times (6) \times (0.1\ cm \times 0.1\ cm)$

$= 480\ cm^2$

(c) Change in surface area = 480/24 = 20

The surface area is 20 times greater.

(d) For nanocubes of 1.0 nm sides; 2 cm = 2.0×10^7 nm

N° of cubes $= (2 \times 10^7) \times (2 \times 10^7) \times (2 \times 10^7) = 8 \times 10^{21}$

S.A. $= (8 \times 10^{21}) \times (6) \times (1.0 \times 10^{-7} cm \times 1.0 \times 10^{-7} cm)$

$= 48 \times 10^7\ cm^2$

Change in S.A. $= 48 \times 10^7/24 = 2 \times 10^7$ times

2.11

ZnO nanoparticles are good absorbers of harmful UV rays present in sunlight. They are also smaller than the wavelength of visible light. Hence light is able to pass between the particles creating a transparent effect.

2.12

(a) The carbon nanotubes create a surface with nano-size bumps and low surface energy.

(b) The higher surface energy of water prevents it from wetting the fabrics surface. Instead the water will bead into droplets, roll over the nano-sized bumps of the fabric, and carry any dirt along with it.

(c) Water and dirt also roll off the leaves of lotus plants. The nano-sized bumps on its surface prevent water from soaking it. This was the inspiration for the development of stain resistant and waterproof fabrics.

2.13

If water droplets form and then dry on glass, they leave water marks due to small amounts of dirt or impurities in them. The effect of the TiO_2 layer is to prevent droplets forming and so water runs off carrying any dirt along with it. The photo-catalytic properties of the TiO_2 layer also help to break down any organic material on the glass.

2.14

Nanoparticles used in nanocomposite materials have very high surface area to volume ratios. This markedly increases the interaction and bonding which occurs between the atoms and particles in the material. The added nanoparticles may also have a high aspect ratio, that is, they are thin and long. This further helps to bond and tie a great number of particles together.

Review Questions

1. (a) mixture (d) element
   (b) compound (e) mixture
   (c) mixture (f) compound.

2. **homogeneous mixture** e.g. salt solution, coffee drink, cordial.
   heterogeneous mixture e.g. concrete mix, sand and salt mixture, fruit cake mix.

3. (a) decantation and filtration
   (b) fractional distillation
   (c) dissolution and filtration
   (d) evaporation/crystallisation
   (e) evaporation/distillation.

4. (a) residue (f) crystallisation
   (b) decantation (g) filtration/crystallisation
   (c) mixture (h) evaporation
   (d) element (i) distillation
   (e) filtrate (j) solution.

5.

(a) 1.1 nm / 0.1 nm = 11

A buckyball is 11 times larger than a hydrogen atom.

(b) 5 μm / 80 nm = 62.5 ≈ 60

A typical bacteria is about 60 times larger than the Adeno virus.