

16. GREEN CHEMISTRY AND NANOCHEMISTRY

Can you recall ?



1. What do you mean by environment?
2. Which are the factors affecting the environment?
3. What is pollution? Which are the types of pollution?
4. Why it occurs?

16.1 Introduction

Chemistry plays an important role to improve the quality of our life. Unfortunately, due to this achievement our health and global environment are under threat. Also, due to increase in human population and the industrial revolution, energy crises and environmental pollution are highlighted major global problems in the 21st century. To minimize the problems of energy crises and pollution, we have to adapt **green chemistry**.

Do you know ?



Paul T. Anastas (Born on May 16, 1962) is the director of Yale university's Center for green chemistry and green engineering. He is known as father of green chemistry.

Green Chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and environment. The concept of green chemistry was coined by **Paul T. Anastas**.

Definition : Green Chemistry is the use of chemistry for pollution prevention by environmentally conscious design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

To reduce the impact of energy crises, pollution and to save natural resources, we

need to implement 12 principles of green chemistry enunciated by Paul Anastas wherever possible.

16.2 Sustainable development : Green chemistry plays an important role in sustainable development. We can achieve sustainable development by adapting the twelve principles of green chemistry. **Sustainable development** is development that meets the needs of the present, without compromising the ability of future generations to meet their own need. Sustainable development has been continued to evolve as that protecting the world's resources.

16.3 Principles of green chemistry :

1. Prevention of waste or by products :

To give priority for the prevention of waste rather than cleaning up and treating waste after it has been created.

Illustration : To develop the zero waste technology (ZWT). In terms of ZWT, in a chemical synthesis, waste product should be zero or minimum. It also aims to use the waste product of one system as the raw material for other system. For example : 1. bottom ash of thermal power station can be used as a raw material for cement and brick industry. 2. Effluent coming out from cleansing of machinery parts may be used as coolant water in thermal power station.

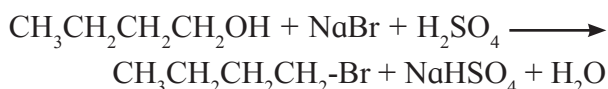
2. Atom economy : Atom economy is a measure of the amount of atoms from the starting materials that are present in the useful products at the end of chemical process. Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal.

Illustration : The concept of atom economy gives the measure of the unwanted product produced in a particular reaction.

% atom economy =

$$\frac{\text{Formula weight of the desired product}}{\text{sum of formula weight of all the reactants used in the reaction}} \times 100$$

For example : conversion of Butan-1-ol to 1 - bromobutane



% atom economy =

$$\frac{\text{mass of (4C + 9H + 1Br) atoms}}{\text{mass of (4C + 12H + 5O + 1Br + 1Na + 1S)atoms}} \times 100$$

$$= \frac{137 \text{ u}}{275 \text{ u}} \times 100$$

$$= 49.81 \%$$

3. Less hazardous chemical synthesis :

Designed chemical reactions and synthesis routes should be as safe as possible. So that we can avoid formation of hazardous waste from chemical processes.

Illustration : Earlier DDT (Dichlorodiphenyl trichloroethane) was used as insecticide and which was effective in controlling diseases like typhoid and malaria carrying mosquitos. It was realized that DDT is harmful to living things. Nowadays benzene hexachloride (BHC) is used as insecticide. One of the γ -isomer (gamma) of BHC is called gammexane or lindane.

4. Designing Safer Chemicals : This principle is quite similar to the previous one. To develop products that are less toxic or which require less toxic raw materials.

Illustration : In Chemical industries workers are exposed to toxic environment. In order to prevent the workers from exposure to toxicity, we should think of designing safer chemicals.

For example : Adipic acid is widely used in polymer industry. Benzene is the starting material for the synthesis of adipic acid but benzene is carcinogenic and benzene being volatile organic compound (VOC) pollutes air. In green technology developed by Drath and Frost, adipic acid is enzymatically synthesised from glucose.

5. Use Safer solvent and auxiliaries :

Choose the safer solvent available for any given step of reaction. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

Illustration : The main aim behind this principle is to use green solvents. For example, water, supercritical CO_2 in place of volatile halogenated organic solvents, for example, CH_2Cl_2 , CHCl_3 , CCl_4 for chemical synthesis and other purposes. Solvents as chemicals that dissolve solutes and form solutions, facilitate many reactions. Water is a safe benign solvent while dichloromethane is hazardous. Use of toxic solvent affects millions of workers every year and has implications for consumers and the environment as well. Many solvents are used in high volumes and many are volatile organic compounds. Their use creates large amounts of waste, air pollution and other health impacts. Finding safer, more efficient alternatives or removing solvents altogether is one of the best ways to improve a process or product.

6. Design for energy efficiency : Chemical synthesis should be designed to minimize the use of energy. It is better to minimize the energy by carrying out reactions at room temperature and pressure.

This can be achieved by use of proper catalyst, use of micro organisms for organic synthesis, use of renewable materials, ... ,etc.

Illustration : The biocatalyst can work at the ambient condition. Similarly, in chemical synthesis, refluxing conditions require less

energy, improving the technology of heating system, use microwave heating, , etc.

7. Use of renewable feedstocks : The perspective of this principle is largely toward petrochemicals. Use chemicals which are made from renewable (plant based) sources rather than other (for example : Crude Oil).

Illustration : Overexploitation of nonrenewable feed stocks will deplete the resources and future generation will be deprived. Moreover, use of these nonrenewable resources puts burden on the environment.

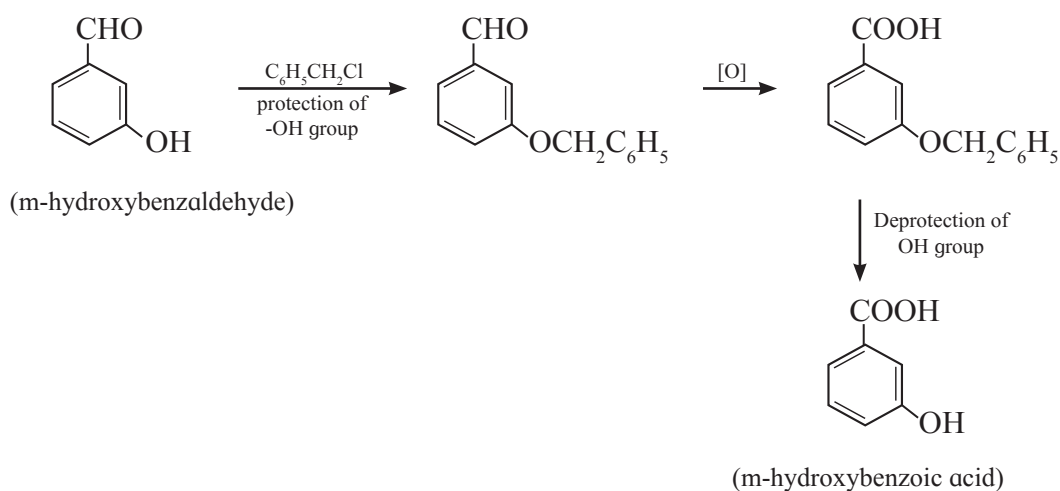
On the other hand, use of renewable resources for example agricultural or biological product ensures the sharing of resources by future generation. This practice generally does not put much burden on environment. The products and waste are generally biodegradable.

8. Reduce derivatives : [Minimization of steps]

A commonly used technique in organic synthesis is the use of protecting or blocking group. Unnecessary derivatization (for example installation / removal of use of protecting groups) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

Illustration : In organic synthesis, we need very often protection of some functional groups. Finally, we again need their deprotection. It is explained in the following example of synthesis of m-hydroxybenzoic acid from m-hydroxy benzaldehyde.

Obviously, in such cases, atom economy is also less. The green chemistry principle aims to develop the methodology where unnecessary steps should be avoided, if practicable biocatalytic reactions very often need no protection of selective group.



9. Use of catalysis : Use of catalyst in the chemical reaction speeds up its rate. Catalyst helps to increase selectivity, minimize waste and reduce reaction times and energy demands.

Complete the chart

| Reaction | Name of Catalyst used |
|---|-----------------------|
| 1. Hydrogenation of oil (Hardening) | |
| 2. Haber's process of manufacture of ammonia | |
| 3. Manufacture of HDPE polymer | |
| 4. Manufacture of H ₂ SO ₄ by contact process | |
| 5. Fischer-Tropsch process (synthesis of gasoline) | |

Do you know ?

Does plastic packaging impact the food they wrap ?



Phthalates leach into food through packaging so you should avoid microwaving food or drinks in plastic and not use plastic cling wrap and store your food in glass container whenever possible. Try to avoid prepackaging, processed food so that you will reduce exposure to harmful effect of plastic.

10. Design for degradation : Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative or environmentally persistent.

Illustration : The aim behind this principle is that the waste product should degrade automatically to clean the environment. Thus, the biodegradable polymers and pesticides are always preferred. To make separation easier for the consumer an international plastic recycle mark is printed on larger items.



Use this chart to sort plastic materials in daily life

11. Real-time Analysis Pollution Prevention:

Analytical methods need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

Illustration : Analytical methodologies should be developed or modified, so that continuous monitoring of the manufacturing and processing units is possible. This is very much important for the chemical industries and nuclear reactors.

12. Safer chemistry for Accident prevention:

We need to develop chemical processes that are safer and minimize the risk of accidents.

Illustration : The substances to be used in a chemical reaction should be selected in such a way that they can minimize the occurrence of chemical accidents, explosions, fire and emission. For example, if the chemical process works with the gaseous substances, then the possibility of accidents including explosion is relatively higher compared to the system working with non volatile liquid and solid substances.

16.4 The role of Green chemistry : The green chemistry approach recognizes that the Earth does have a natural capacity for dealing with much of the waste and pollution that society generates, it is only when that capacity is exceeded that we become unsustainable.

To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.

Green chemistry helps to reduce capital expenditure, to prevent pollution. Green chemistry incorporates pollution prevention practices in the manufacture of chemicals and promotes pollution prevention and industrial ecology. Green chemistry is a new way of looking at chemicals and their manufacturing process to minimize any negative

environmental effects. Right now the green chemistry revolution is beginning and it is an exciting time with new challenges for chemists involved with the discovery, manufacture and use of chemicals.

Green chemistry helps to protect the presence of ozone in the stratosphere essential for the survival of life on the earth. Green chemistry is useful to control green house effect (Global warming). So we should think about save environment and save earth.

Can you recall ?



1. What are the shapes of a bacillus and coccus? (Refer to chapter from Biology, Std. XI)
2. Which instrument is used to observe the cells ? (Refer to chapter 5 from Biology, Std. XI)
3. What is the size range of molecules of lipids and proteins ?

16.5 Introduction to nano chemistry : From clothes, sunglasses you wear to computer hard drives and even cleaning products, nanotechnology plays a big role in the manufacture of many materials. We have been using Lasers in DVD, CD players for a long time which contain nanosize components. Look at Fig. 16.1 which shows comparative scales from macro-materials to atoms.

Also observe another Fig. 16.2 which depicts the materials in nature, as well as devices that are man made. In both figures some objects like tennis ball (Fig. 16.1), ant, human hair (Fig. 16.2) we can see with our own eyes whereas bacteria, virus, red blood cell, we can not observe with naked eye. These are known as nanomaterials.

a. What is nanoscience ?

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales where properties differ significantly from those at a larger scale.

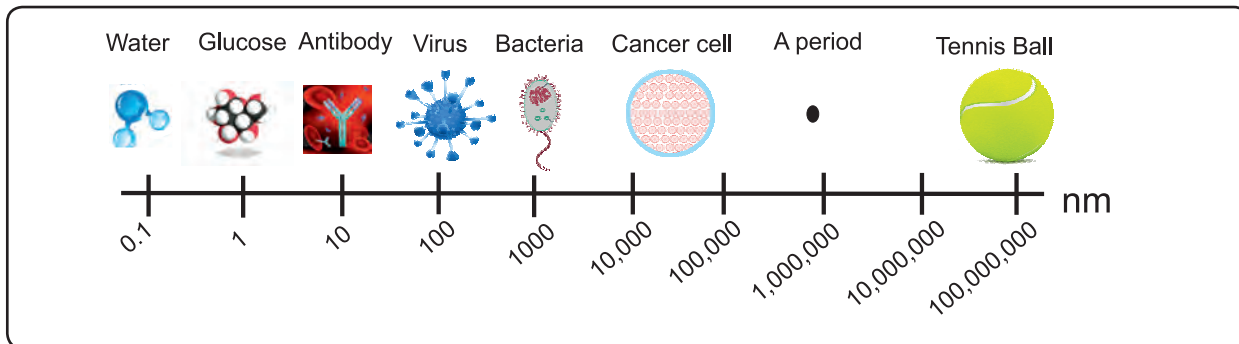


Fig. 16.1 Macro-materials to atoms

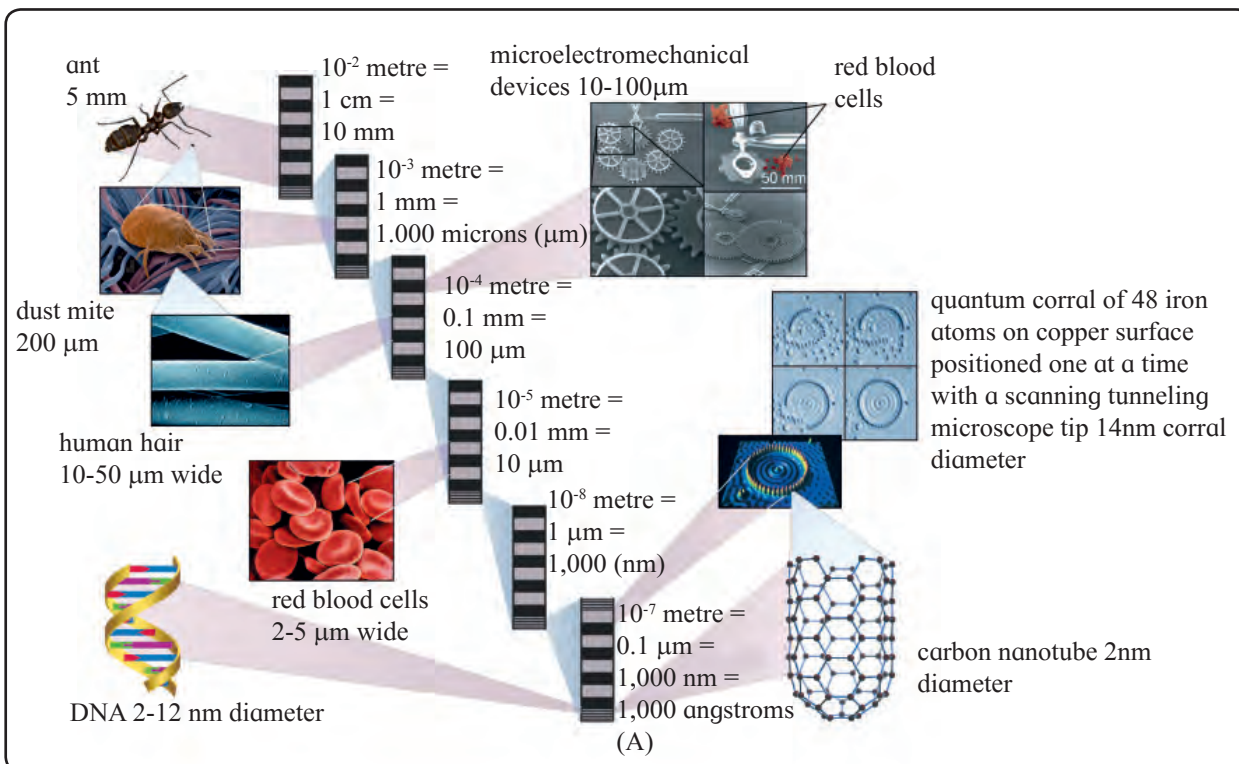


Fig. 16.2 Scale of nanomaterials

b. How do we define nanotechnology ?

Nanotechnology is the design, characterization, production and application of structures, device and system by controlling shape and size at nanometer scale.

c. Why Nano ?

The nanometer scale : ‘Nano’ in Greek means dwarf but in actual case ‘nano’ is even smaller than dwarf. Conventionally, the nanometer scale is defined as 1-100 nm. One nanometer is one billionth of a meter. (that is 1nm = 10⁻⁹m).

The materials we see around us are bulk materials that possess macroscopic physical properties. Grain of sand that is micron-sized

material also possesses same bulk properties. But material synthesized at nanoscale (1nm - 100nm) possesses unique optical, structural, thermal, catalytic, magnetic and electrical properties. These properties change as a function of size and are very different from their bulk materials.

d. What is a nanomaterial ?

The nanomaterial is a material having structural components with atleast one dimension in the nanometer scale that is 1-100 nm. Nanomaterials are larger than single atoms but smaller than bacteria and cells. These may

be nanoparticles, nanowires and nanotubes according to dimensions. Nanostructured materials may be large organic molecules, inorganic cluster compounds and metallic or semiconductor particles.

What are zero, one and two dimensional nanoscale system ?

i. Zero-Dimensional Nanostructures : For example, Nanoparticles.

A zero dimensional structure is one in which all three dimensions are in the nanoscale.

ii. One-Dimensional Nanostructures : For example, Nanowires and Nano rods.

A one dimensional nanostructure is one in which two dimensions are in the nanoscale.

iii. Two-Dimensional Nanostructures : For example, Thin films.

A two-dimensional nanostructure is one in which one dimension is in the nanoscale.




| Nanomaterial Dimension | Nanomaterial Type | Example |
|-------------------------------|---|---|
| All three dimensions < 100 nm | Nanoparticles, Quantum dots, nanoshells, nanorings, microcapsules |  |
| One dimension < 100 nm | Nanotubes, fibres, nanowires |  |
| Two dimension < 100 nm | Thin films, layers and coatings |  |

Fig. 16.3 Illustration of zero, one, two dimensions

e. Definition of Nanochemistry : It is the combination of chemistry and nanoscience. It deals with designing and synthesis of materials of nanoscale with different size, shape, structure and composition and their organization into functional architectures. Nanochemistry is used in chemical, physical,

materials science as well as engineering, biological and medical applications.

Do you know ?



A very highly useful application of nanochemistry is 'medicine'. A simple skin care product of nanochemistry is sunscreen. Sunscreen contains nanoparticles of Zinc oxide, (ZnO) and Titanium dioxide, (TiO₂). These chemicals protect the skin against harmful UV (ultraviolet) rays by absorbing or reflecting the light and prevent the skin from damage.

Internet my friend



Find out similar applications in medicine related to wounds, healing process. Also find out applications of TiO₂ and ZnO in other areas.

16.6 Characteristic features of Nanoparticles

: What makes the science at nanoscale special is that at such a small scale, different laws dominate over those that we experience in our everyday life.

16.6.1 Colour : It is an optical property that is different at nanoscale. Elemental gold as we know, has nice shining yellow colour. However, if you had only 100 gold atoms arranged in cube, its colour would be red.

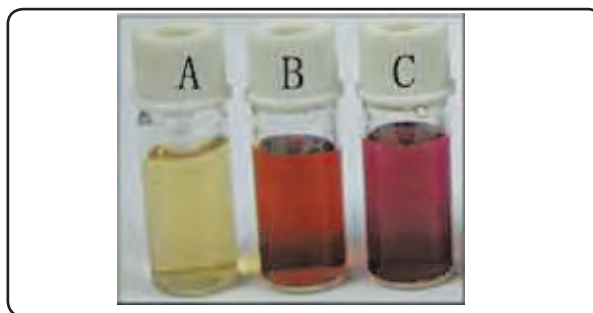


Fig. 16.4 Formation of gold nanoparticles solution

16.6.2 Surface area : High surface-to-volume ratio is a very important characteristic of nanoparticles. If a bulk material is sub divided into a group of individual nanoparticles, the total volume remains the same, but the

collective surface area is largely increased. With large surface area for the same volume, these small particles react much faster because more surface area provides more number of reaction sites, leading to more chemical reactivity. Explanation of increase in surface area with decrease in particle size.

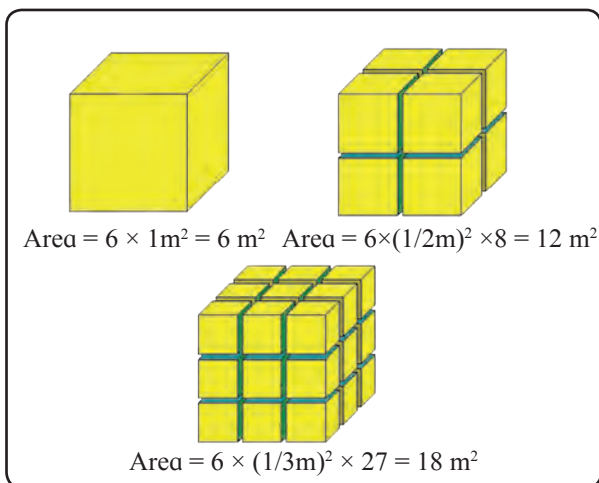


Fig. 16.5 : Surface area of nanoparticles

Fig. 16.5 shows the surface areas when a cube of 1m^3 were progressively cut into smaller cube until cube of 1nm^3 formed.

16.6.3 Catalytic activity : Due to increase in surface area with decrease in particle size, nanomaterial-based catalysts show increased catalytic activity. Usually they are heterogeneous catalysts that means catalysts are in solid form and the reactions occur on the surface of the catalyst. Nanoparticle catalysts can be easily separated and can be recycled. Example, Pd, Pt metal nanoparticles used in hydrogenation reactions.

TiO_2 , ZnO are used in photocatalysis. Gold in bulk form is unreactive, but gold nanoparticles are found to be very good catalyst for various organic reactions.

Internet my friend

Find out various applications or use of gold nanoparticles.



16.6.4 Thermal properties : melting point

The melting point of nanomaterial changes drastically and depends on size. For example,

sodium clusters (Na_n) of 1000 atoms appeared to melt at 288 K while cluster of 10,000 atoms melted at 303 K and bulk sodium melts at 371K.

16.6.5 Mechanical properties

Mechanical strength : Nanosized copper and palladium clusters with diameter in the size range of 5-7 nm can have hardness upto 500% greater than bulk metal.

16.6.6 Electrical conductivity : Electrical conductivity is observed to change at nanoscale. For example, carbon nanotube can act as a conductor or semiconductor in behaviour.

16.7 Synthesis of nanomaterials

16.7.1 : There are two approaches to the synthesis of nanomaterials. Bottom up and Top down. Fig. 16.6 shows schematic illustration of the preparation methods of nanoparticles.

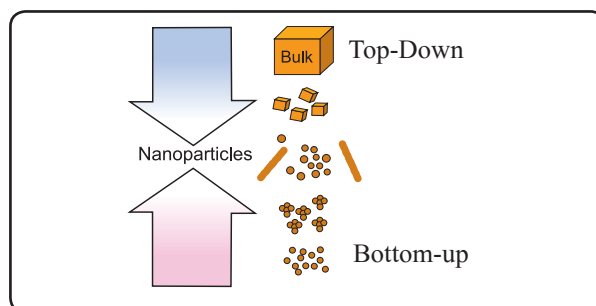


Fig. 16.6 : Schematic illustration of the preparation of nanoparticles

In the bottom up approach, molecular components arrange themselves into more complex assemblies atom by atom, molecule by molecule and cluster by cluster from the bottom. Example : synthesis of nanoparticles by colloidal dispersion.

In the top-down approach, nanomaterials are synthesized from bulk material by breaking the material. The bulk solids are dis-assembled into finer pieces until they are constituted of only few atoms.

16.7.2 Wet chemical synthesis of Nanomaterials : Sol-gel process : Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1-100nm. A gel is interconnected rigid network

with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer.

A sol-gel process is based on inorganic polymerization reactions. It is generally carried out at room temperature and includes four steps : hydrolysis, polycondensation, drying and thermal decomposition. This method is widely employed to prepare oxide materials.

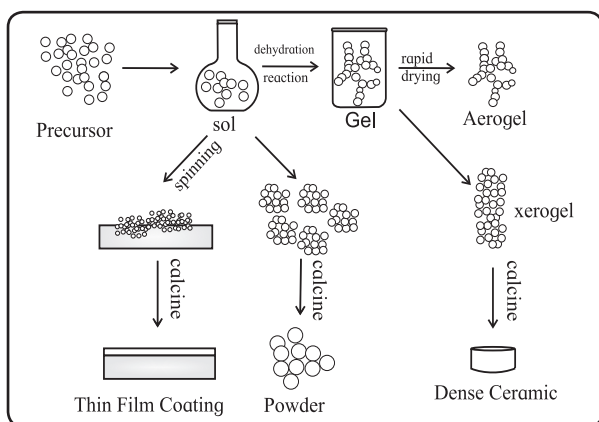
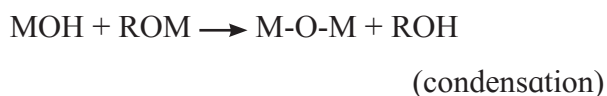
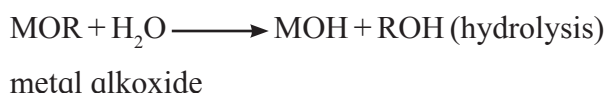


Fig. 16.7 : Schematic representation of sol-gel process of synthesis of nanoparticles

The reactions involved in the sol-gel process can be described as follows :



1. Formation of different stable solution of the alkoxide or solvated metal precursor.

2. Gelation resulting from the formation of an oxide or alcohol-bridged network (gel) by a polycondensation reaction.
3. Aging of the gel means during that period gel transforms into a solid mass.
4. Drying of the gel : In this step, water and other volatile liquids are removed from the gel network.
5. Dehydration : The material is heated at temperatures upto 800 °C.

16.7.3 Analysis or characterization of nanomaterials :

The synthesized material is analyzed by various analytical tools or techniques. The name of the technique and its use is described in the following Table 16.1.

16.7.4 Photographs of instruments

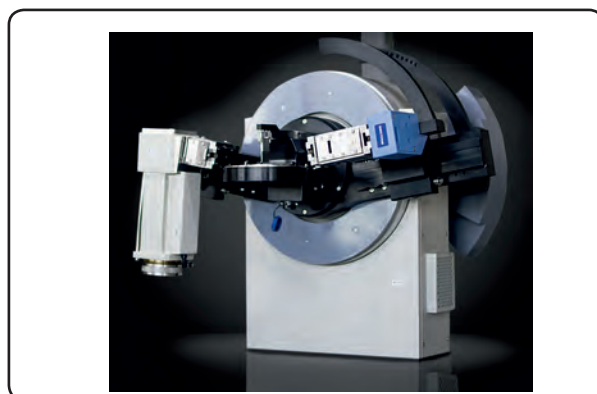


Fig. 16.8 Photograph of X-ray diffractometer

Table 16.1

| Name of Technique | Instrument used | Information |
|---|--|--|
| 1. UV-visible spectroscopy | UV-visible spectrophotometer | Preliminary confirmation of formation of nanoparticles |
| 2. Xray Diffraction (XRD) | Xray diffractometer | particle size, crystal structure, geometry |
| 3. Scanning electron microscopy | Scanning electron microscope (SEM) | Structure of surface of material that is morphology |
| 4. Transmission electron microscopy | Transmission electron microscope (TEM) | particle size |
| 5. FTIR Fourier transform infrared spectroscopy | Fourier transform infrared spectrophotometer | Absorption by functional groups, Binding nature. |

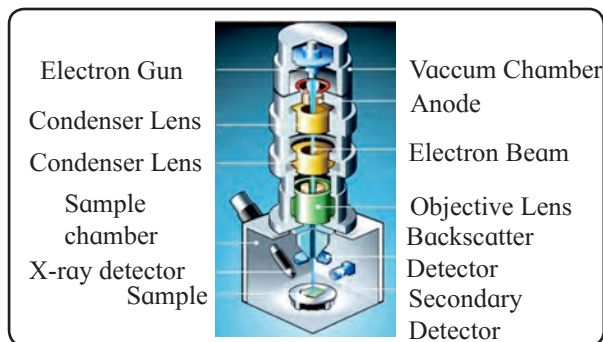


Fig. 16.9 Schematic diagram of scanning electron microscope



Fig. 16.10 Scanning electron microscope

16.8 History of nanotechnology :

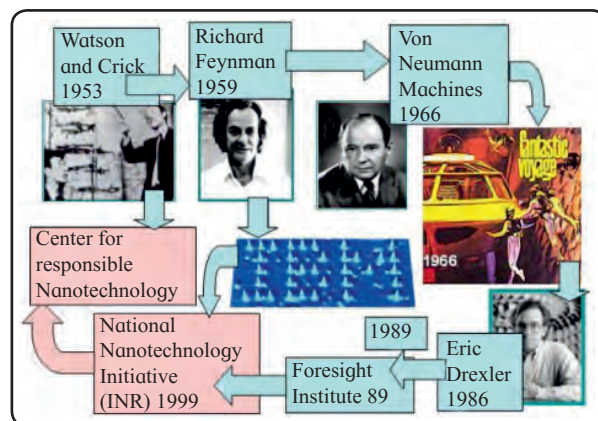


Fig. 16.13 : Scientists contributed to nanotechnology

Nanomaterials have been produced and used by humans for hundreds of years. However, understanding of certain materials as nanostructured materials is relatively recent. Due to the development of advanced tools that is sophisticated instruments, it has been possible to reveal the information at nanoscale.

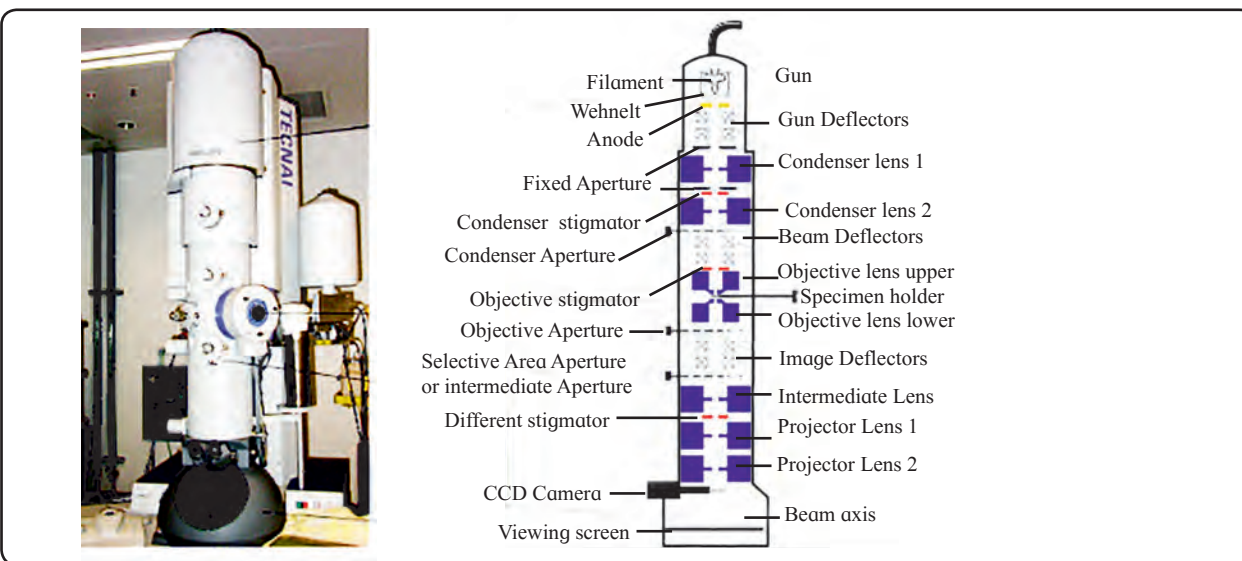


Fig. 16.11 Transmission electron microscope (TEM)

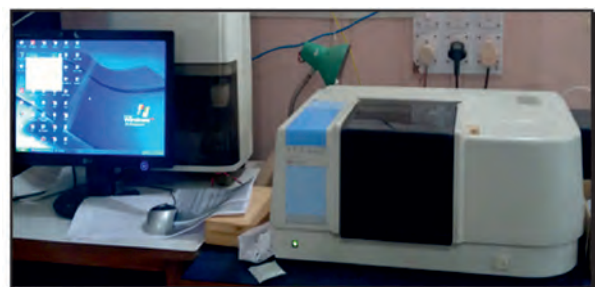


Fig. 16.12 FTIR spectrophotometer

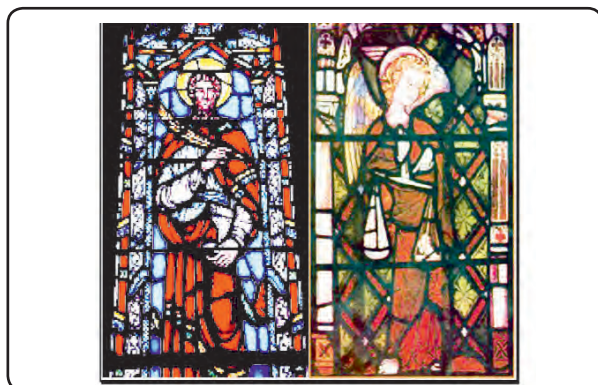


Fig. 16.14 Ruby red colour

a. Beautiful ruby red colour of some ancient glass paintings is due to gold and silver nanoparticles trapped in the glass matrix.

b. The decorative glaze or metallic film known as lustre found on some medieval pottery is due to certain spherical metallic nanoparticles.

c. Carbon black is a nanostructured material that is used in tyres of car to increase the life of tyre. (Discovery in 1900). Carbon nanotubes are made up of graphite sheets with nanosized diameter. They have highest strength.

d. Fumed silica, a component of silicon rubber, coatings, sealants and adhesives is also a nanostructured material.

Internet my friend

Find out more number of nanostructured materials in day to day used products.



Do you know ?

1. The term 'nanotechnology' was defined by Tokyo science University Professor, Nario Taniguchi in 1974.
2. Invention of Scanning Tunneling Microscope (STM) in 1980, led to the discovery of fullerenes in 1986 and carbon nanotubes a few years later.



Internet my friend

Collect the information about the scientists who discovered SEM, STM, TEM instruments.

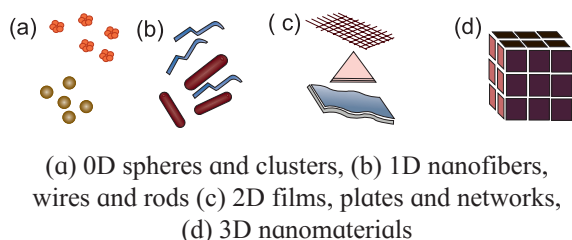
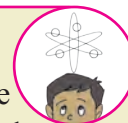


Fig. 16.15 Classification of nanomaterials

Can you think ?

Visualize the size effect : Size difference between the earth and an apple is equal to the size difference between atoms (30 nm) and an apple.



16.9 Applications of nanomaterials :

Nanochemistry has already contributed to number of innovative products in various disciplines because of their unique physical, chemical, optical, structural, catalytic properties and so on. Few applications are given below :

a. Nanoparticles can contribute to stronger, lighter, cleaner and smarter surfaces and systems. They are used in the manufacturing of scratchproof eyeglasses, transport, sunscreen, crack resistant paints and so on.

b. Used in electronic devices. For example, Magnetoresistive Random Access memory (MRAM)

c. Nanotechnology plays an important role in water purification techniques.

Water contains waterborne pathogens like viruses, bacteria. 1.1 billion people are without access to an improved water supply. The provision of safe drinking water is currently high priority. Recently, cost effective filter materials coated with silver nanoparticles (AgNps) is an alternative technology. (For example : water purifier) Silver nanoparticles act as highly effective bacterial disinfectant, remove E.Coli from water.

d. Self cleaning materials : Lotus is an example of self cleaning. The lotus plant (*Nelumbo nucifera*) although grows in muddy water, its leaves always appear clean. The plants' leaves are superhydrophobic. Nanostructures on lotus leaves repel water which carries dirt as it rolls off. Lotus effect is the basis of self cleaning windows.

Do you know ?

Sol-gel processes are used in the motor vehicle industry to produce water repellent coatings for wind screens or exterior mirrors.



16.10 Nanoparticles and Nanotechnology :

Advantages :

1. Revolution in electronics and computing.
2. Energy sector - nanotechnology will make solar power more economical. Energy storage devices will become more efficient.
3. Medical field :

Manufacturing of smart drugs, helps cure faster and without side effects. Curing of life threatening diseases like cancer and diabetes.

Disadvantages : Despite the possibilities and the advancements that the nanotechnology offers to the world, there also exist certain potential risks involved with the disadvantages of it.

Nanotechnology has raised the standard of living but at the same time, it has increased the pollution which includes air pollution. The pollution caused by nanotechnology is known as nano pollution. This kind of pollution is very dangerous for living organisms.

Nanoparticles can cause lung damage. Inhaled particulated matter can be deposited throughout the human respiratory tract and then deposit in lungs.

The characteristics of nanoparticles that are relevant for health effects are size, chemical composition and shape.

Exercises

1. Choose the most correct option.

- The development that meets the needs of present without compromising the ability of future generations to meet their own need is known as
 - Continuous development
 - Sustainable development
 - True development
 - Irrational development
- Which of the following is γ -isomer of BHC?
 - DDT
 - lindane
 - Chloroform
 - Chlorobenzene
- The prefix 'nano' comes from
 - French word meaning billion
 - Greek word meaning dwarf
 - Spanish word meaning particle
 - Latin word meaning invisible
- Which of the following information is given by FTIR technique ?
 - Absorption of functional groups
 - Particle size
 - Confirmation of formation of nanoparticles
 - Crystal structure
- The concept of green chemistry was coined by
 - Born Haber
 - Nario Taniguchi
 - Richard Feynman
 - Paul T. Anastas

2. Answer the following

- Write the formula to calculate % atom economy.
- Name the γ -isomer of BHC.

- iii. Ridhima wants to detect structure of surface of materials. Name the technique she has to use.
- iv. Which nanomaterial is used for tyres of car to increase the life of tyres ?
- v. Name the scientist who discovered scanning tunneling microscope (STM) in 1980.
- vi. $1 \text{ nm} = \dots\text{m}$?

3. Answer the following

- i. Define (i) Green chemistry (ii) sustainable development.
- ii. Explain the role of green chemistry.
- iii. Give the full form (long form) of the names for following instruments.
 - a. XRD b. TEM. c. STM
 - d. FTIR e. SEM
- iv. Define the following terms :
 - a. Nanoscience
 - b. Nanotechnology
 - c. Nanomaterial
 - d. Nanochemistry
- v. How nanotechnology plays an important role in water purification techniques?

- vi. Which nanomaterial is used in sunscreen lotion ? Write its use.
- vii. How will you illustrate the use of safer solvent and auxiliaries ?
- viii. Define catalyst. Give two examples.

4. Answer the following

- i. Explain any three principles of green chemistry.
- ii. Explain atom economy with suitable example.
- iii. How will you illustrate the principle, minimization of steps ?
- iv. What do you mean by sol and gel? Describe the sol-gel method of preparation for nanoparticles.
- v. Which flower is an example of self cleaning ?

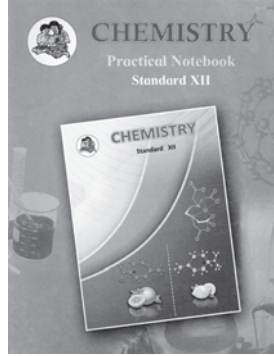
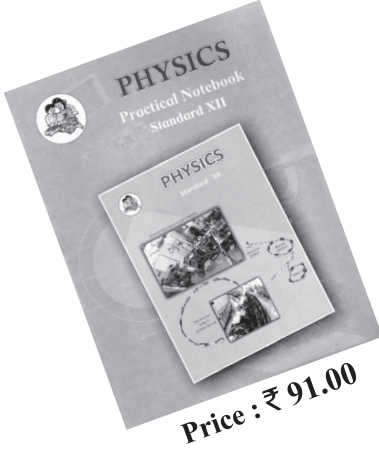
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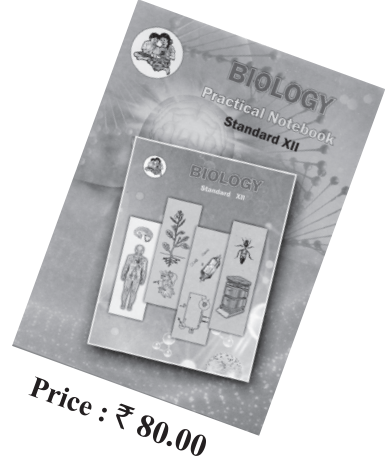
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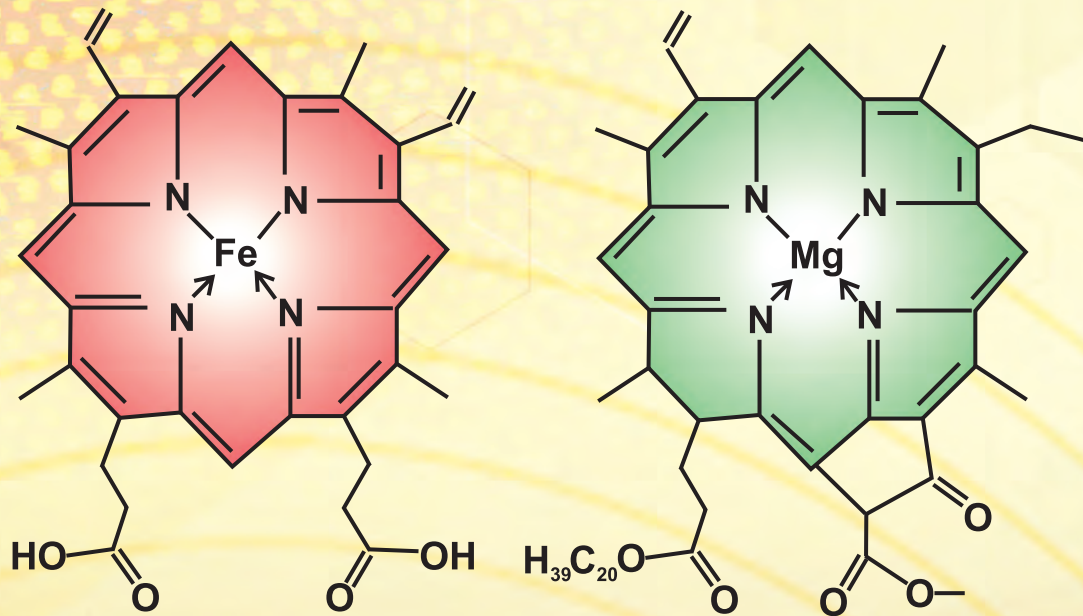
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