

Nanotechnology in Soil Science

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“There is plenty of room at the bottom” – Richard Feynman

27.1. Introduction

Nanotechnology is the understanding and control of matter of sizes roughly in the range of 1 to 100 nanometers. If one of the dimensions is in this range, it is considered a nanoparticle. Bulk materials when reduced to the nanoscale show some properties (melting point, physical strength, surface area, penetration power, electric conductance, optical effect, magnetism etc.) which are different from what they exhibit on a macro scale enabling unique applications. These materials can be either natural or engineered. At nanoscale, gravity would become less important, whereas surface tension and van der Waal forces would become more important.

Nanotechnology is a cocktail (**Fig. 27.1**) that brings together researchers from Chemistry, Physics, Biology and Engineering. Nanoscience has brought about a revolution in different fields by helping develop process and products that are hardly possible to evolve through conventional methods. The nanotechnology aided applications for example; nano-nutrients, nano-pesticides, insect repellants, nano-sensors, nano-magnets, nano-films, nano-filters etc. have the potential to change agricultural production by allowing better management and conservation of inputs.

27.2. Scope of Nanotechnology

Applications of nanoparticles are many fold. Its high surface area to volume ratio provides high reactivity as well as its small size provides better penetration into soil and plants. There are many sectors in which nanotechnology has been leaving its mark. Some of the important scopes have been shown in **Figure 27.2**. The nanomaterials and its functions are shown in **Table 27.1** and the nanotechnology developed so far under soil and water is shown in **Table 27.2**.

27.3. Historical Developments in Nano-science and Nanotechnology

The idea of nanotechnology dates back to the medieval period where gold nanoparticles were used to impart various colours in glass (**Fig. 27.3**). The first observations and size

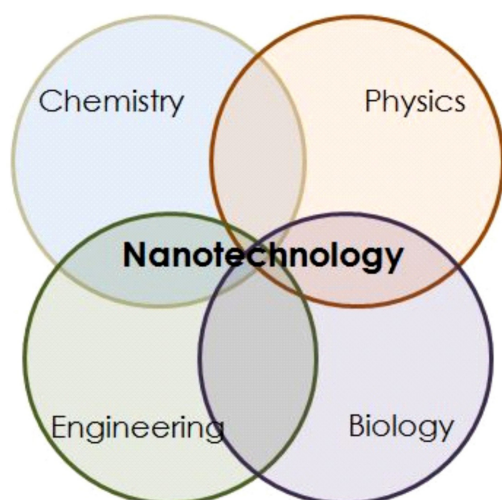


Figure 27.1. Fields involved in nanotechnology

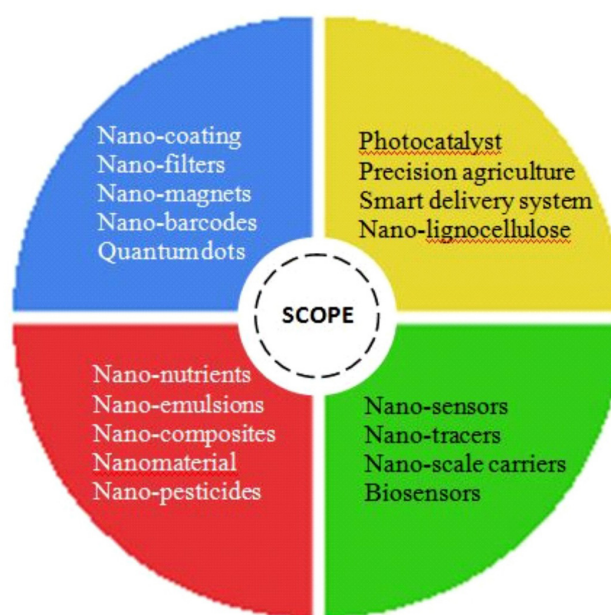


Figure 27.2. Scope of nanotechnology

Table 27.1. Nanomaterials and their functions

Nanomaterial	Function
Carbon nanotubes	Seed germination
Nanonutrients	Plant/animal/human nutrition
Nanopesticides	Plant protection
Nanoscale carrier	Efficient delivery of fertilizer, pesticides, herbicides
Nanosensors	To detect nutrients and contaminants
Nanochips/smart machines	For machinery and tracing
Nanocellulose	Light weight material
Identity Preservation and Tracking	To promote quality
DNA nanovaccines and Gene delivery	For treatment
Nano barcode technology	As ID tags for multiplex analysis
Photocatalysis	TiO ₂ , ZnO, SnO ₂ , ZnS etc. (oxidizing agent)

Table 27.2. Application of nanotechnology under soil and water

Application area	Probable type of technology
Soil	<ol style="list-style-type: none"> 1. Nanozeolites for soil conservation and slow release of fertilizers 2. Nanomagnets for removal of soil contaminants 3. Nanoparticles for more release of enzymes by activation of plants and microbes 4. Nanoparticles for enhanced release of polysaccharides by microbes for soil aggregation, moisture retention and carbon build-up 5. Nanosensors for automation
Water	<ol style="list-style-type: none"> 1. Nanosensors, polymers, clays, zeolites for contaminant detection 2. Nanomembranes for purification, desalination, detoxification 3. Nanomolecules for robust water tanks and to prevent leakage 4. Nanosensors for water flow detection 5. Nanozeolites for efficient release of water



Figure 27.3. The stunning Lycurgus cup reveals a brilliant red when light passes through its sections of glass containing gold-silver alloyed nano-particles

measurements of nanoparticles were made during the first decade of the twentieth century in 1914 by Richard Adolf Zsigmondy, who was the first to use the term nanometer for characterizing a particle size of $1/1,000,000^{\text{th}}$ of a millimeter; he developed the first system classification based on particle size in nanometer range. But the foundation of nano-science was established by Nobel Laureate Richard Feynman who first saw nanotechnology as a vital science and emphasized on its advancement. He introduced the idea of nanotechnology by delivering his famous talk entitled “There’s plenty of room at the bottom”. Although he did not use the term “nanotechnology”, he suggested that it will eventually be possible to manipulate atoms and molecules to create “nanoscale” machines. Due to lack of technological developments, although scientists had been studying nanoscience phenomena for many decades, they could not develop materials in the nanoscale size range. The term “nanotechnology” was coined in 1974 in a paper published by Norio Taniguchi of the University of Tokyo. Taniguchi approached nanotechnology from the “top-down” approach. The term “nanotechnology” was introduced to the world in 1986 by Eric Drexler in his book “Engineer of Creation” (Figure 27.4).

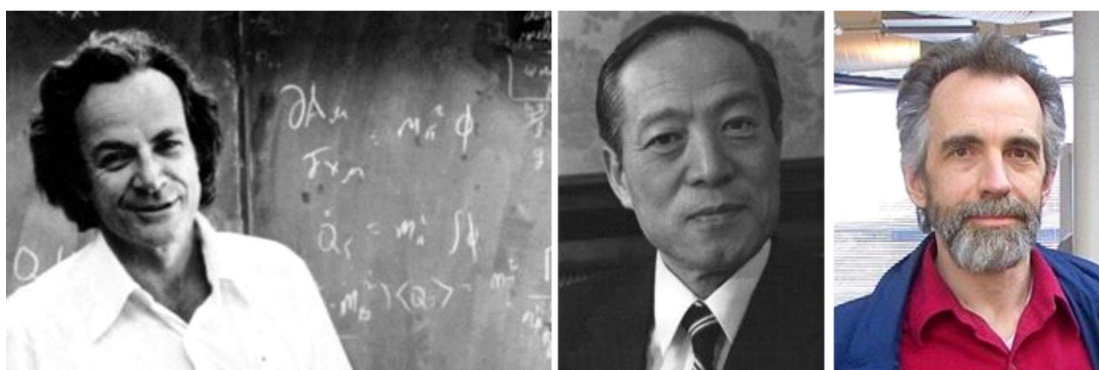


Figure 27.4. (from the left) Richard Feynman, Norio Taniguchi and Eric Drexler

The nanotechnology research accelerated with the discovery of fullerenes in 1985 by Harold Kroto, Robert F. Curl and Richard Smalley for which they were jointly awarded Nobel Prize in chemistry in 1996. Fullerenes are a family of carbon with 60 to 120 atoms forming a hollow cage like structure. These forms of carbon were different from rest of the allotropes of carbons namely, diamond, graphite and amorphous carbon. These advancements regarding fullerenes led to the discovery of, what we know now as carbon nano-tubes (CNTs) which find widespread application in solar cells and agriculture.

27.3.1. Chronological Development in Nanotechnology

- 1857: Gold colloid of nano-size was synthesized by Michael Faraday
- 1915: W. Ostwald wrote a book 'World of Neglected Dimensions' in German
- 1931: E. Ruska and M. Knoll developed first electron microscope
- 1951: E. Muller developed field Ion microscope which enabled the imaging of atoms from the tip of metallic samples.
- 1959: R. Feynman delivered his talk 'There is plenty of room at the bottom'
- 1968: A.Y. Cho and J. Arthur developed Molecular Beam Epitaxy technique for layer by layer growth of materials
- 1970: L. Esaki demonstrated quantum size effect (QSE) in semiconductors
- 1980: A.I. Akimov showed QSE in CdS and CdSe particles dispersed in glass, triggering the research on nanoparticles
- 1981: G. Binning and H. Rohrer developed scanning tunnelling microscope (STM) by which atomic resolution could be obtained.
- 1985: R.F. Curl, H.W. Kroto and R.F. Smalley synthesized sixty atom carbon molecules, later named 'Fullerene'
- 1989: D.M. Elgler wrote letters 'IBM' using xenon atoms
- 1991: S. lijima discovered 'carbons naotubes'
- 1999: C.A. Mirkin developed 'Dip Pen Lithography'
- 2000: D.M. Elgler devised 'Quantum Mirage' using Fe atoms on copper substrate; President Clinton announced U.S. National Nanotechnology Initiative
- 2011: First programmable nanowire circuits for nanoprocessors. DNA molecular robots learn to walk in any direction along a branched track mechanical manipulation of silicon dimers on a silicon surface.

In the Indian scenario, a larger emphasis has been to initiate nanotechnology. In the ancient time, Indian craftsmen used unique smelting techniques to manufacture the Damascus blades which led to nanotisation giving them a unique long-lasting edge. Wootz also had a high percentage of carbon, which was introduced by incorporating wood and other organic matter during fabrication. India, for ages, was a leading exporter of this steel which was used to make Persian daggers which were quite popular in Europe centuries ago (Indian craftsmen, artisans used nanotech 2000 years ago). Recently under 10th five-year plan (2002-2007), the Indian government has spent Rs. 1000 million for nanotechnology. Currently Department of Biotechnology (DBT), Department of Science and Technology (DST), Council of Scientific and Industrial Research (CSIR), Science and Engineering Research Council (SERC) and Indian Council of Agricultural Research (ICAR) invested huge funds to create and promote nano science and nanotechnology in different sections including agriculture.

27.4. Concept and Basics of Nano-Science and Nanotechnology

Nanoscience is the investigation of matter at a scale which is intermediate between 'bulk matter', described by Newtonian Physics and 'atomic matter' (atoms, electrons etc.) described by Quantum Physics. The exceptional properties of matter at the nanoscale have prompted scientists to 're-invent' the way materials are engineered and produced. It is opening up exciting new opportunities in many different fields.

Bulk materials possess continuous macroscopic physical properties. The same applies to micron-sized material (*e.g.*, a grain of sand). But when particles assume nano-scale dimension, the principles of classical Physics are no longer capable of describing their behaviour (movement, energy, etc). At these dimensions, quantum mechanics principles apply. The same material (*e.g.*, gold) at the nanoscale can have properties (*e.g.*, optical, mechanical, electrical, etc.) which are very different from the properties the material has at the macro scale (bulk). There are three important "nano" terms to consider while trying to understand the increasing news coverage and scientific developments in the field of nanotechnology. These terms are:

27.4.1. Nanoscale

Nano scale objects have at least one dimension (height, length, depth) that measures between 1 and 999 nano meters (1-999 nm). The nano meter scale is expressed as "the Feynman (Φ nman) scale" after his great contribution and notation is " Φ ".

One Feynman (Φ) = 1 Nanometer (nm) = 10 Angstroms (\AA) = 10^{-3} Micron (μ) = 10^{-9} Meter (m).

A nanometer (nm) is a unit of length in the metric system, equal to one billionth of a meter. The name combines the SI prefix *nano-* (from the Ancient Greek *nanos*, "dwarf") with the parent unit name *meter* (from Greek *metrin*, "unit of measurement"). The nanometer is often used to express dimensions on the atomic scales. The nanometer appears to be supplanting the other common unit for atomic scale dimensions, the angstrom, which is equal to 0.1 nm. The nanometre scale is conventionally defined as 1 to 100 nm (**Figure 27.5**). The size range is set normally to be minimum 1nm to avoid single atoms or very small groups of atoms being designated as nano-objects (**Figure 27.6**). Therefore nanoscience and nanotechnologies deal with at least clusters of atoms of 1nm size. The upper limit is normally 100 nm, but this is a "fluid" limit; often objects with greater dimensions (even 200 nm) are defined as nanomaterials. The reason why the "1 to 100 nm range" is so novel is that the definition itself focuses on the effect that the dimension has on a certain material. The insurgence of a quantum phenomenon in a particular material occurs within this range.

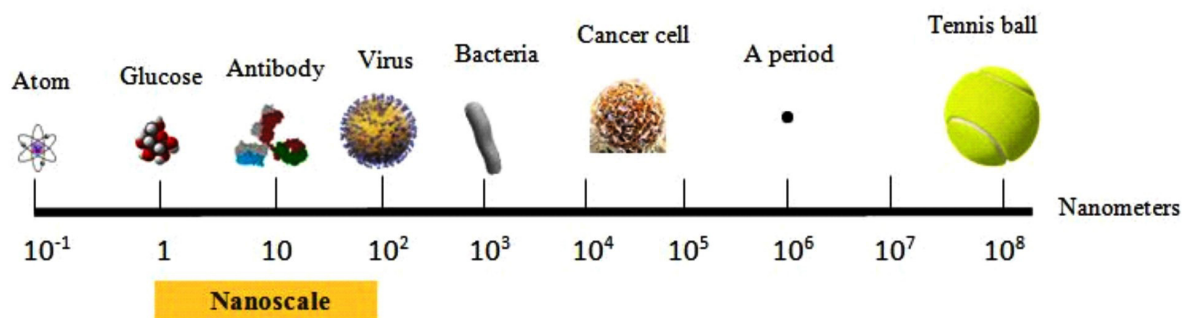


Figure 27.5. The Nanoscale

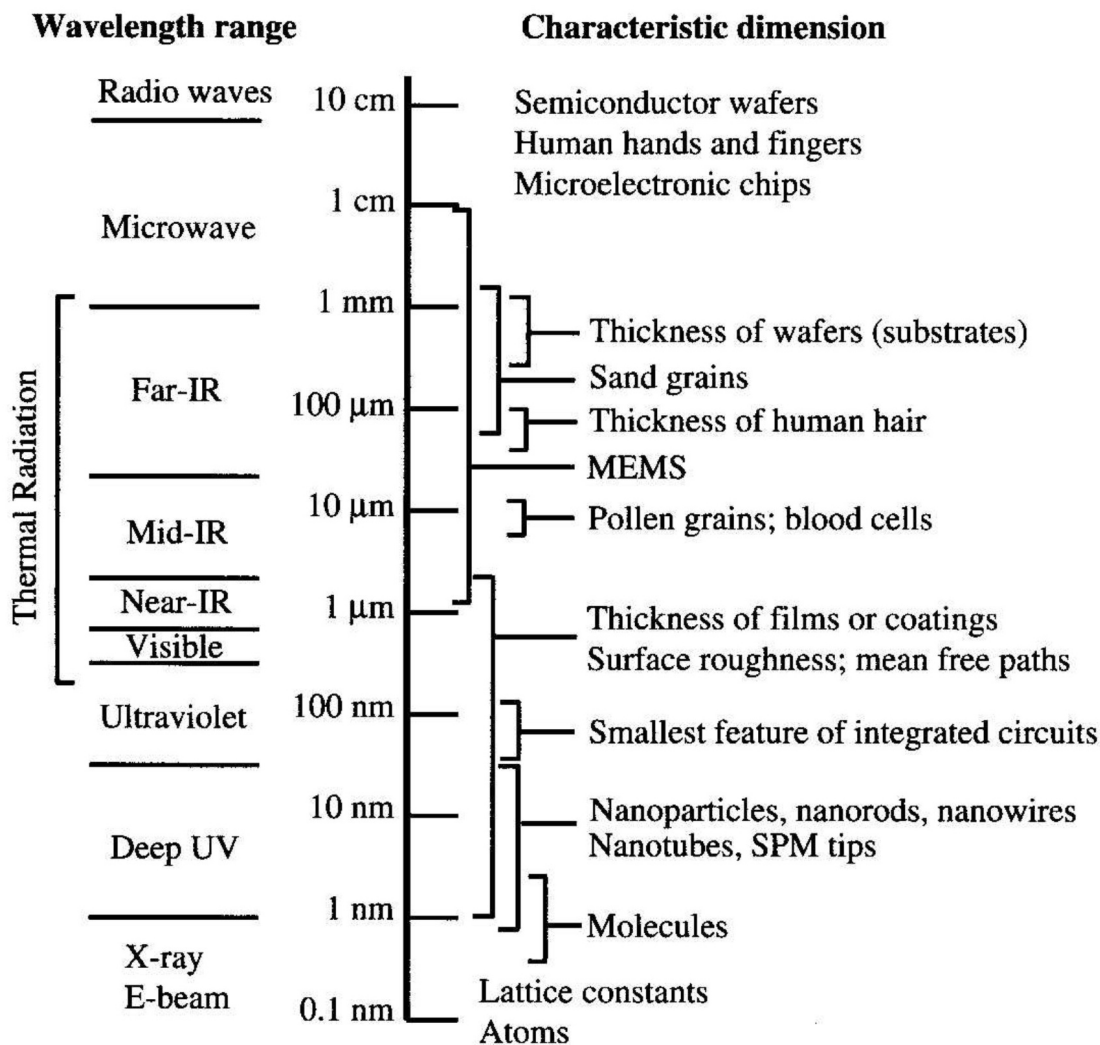


Figure 27.6. Scale of macroparticles to nanoparticles

27.4.2. Nanoscience

Nanoscience is the science of observing, measuring, and understanding the properties behavior, functionality and phenomena of nano-sized objects due to the influence of small dimensions. A common misconception is that nanoscience is just colloid science renamed. This is not the case. Colloids are generally defined as being between 1 and 1000 nm in size; nominally, therefore, nanoparticles are only within the smallest 10% of that range. In nanoscience, one studies the thermodynamic, mechanical, electrical, structural, optical, and/or chemical property variations as a function of the physical size and shape of the material.

27.4.3. Nanotechnology

The prefix 'NANO' derived from the Ancient Greek word $\acute{\alpha}\nu\acute{\alpha}\nu\acute{o}$ and later the Latin word *nanus*, both meaning "DWARF" and 'technology' is the application of practical sciences to industry or commerce. In short, nanotechnology depicts the application of nano scale materials and properties to solve a problem or serve a purpose.

Nanoparticles fall into three major types *viz.* (i) Naturally occurring, (ii) incidental, and (iii) engineered. Examples of naturally occurring nanoparticles include sea spray,

mineral composites, volcanic ash, viruses. A result of man-made industrial processes, incidental nanoparticles include cooking smoke, diesel exhaust, welding fumes, industrial effluents, sandblasting. Engineered nanoparticles comprise of any manufactured particles with nanoscale dimensions. Examples include metals, quantum dots, buckyballs/nanotubes, sunscreen pigments, nanocapsules.

27.4.4. What's Different About a Nanoparticle?

There are various reasons why nanoscience and nanotechnologies are so promising. First, at the nanometer scale, the properties of matter, such as energy, change. This is a direct consequence of the small size of nanomaterials, physically explained as quantum effects. The consequence is that a material (*e.g.*, a metal) when in a nano-sized form can assume properties which are very different from those when the same material is in a bulk form. For instance, gold, although inert in the bulk form, when broken into particles in the 10-100 nm range, becomes a highly effective catalyst. Aluminium foils come in handy to wrap sandwiches and keep them warm, but as a nanoparticle aluminum becomes an integral ingredient of explosive mixtures. Carbon atoms can be arranged into nanotube structures that are stronger than steel. Properties like electrical conductivity, colour, strength and weight change when the nanoscale level is reached. The same metal can become a semiconductor or an insulator at the nanoscale level. The second exceptional property of nanomaterials is that they can be fabricated atom-by-atom, with a process called bottom-up. The information for this fabrication process is embedded in the material building blocks, so that these can self-assemble in the final product (**Figure 27.7**). Finally, nanomaterials have an increased surface-to-volume ratio compared to bulk materials. This has important consequences for all those processes that occur at a material surface, such as catalysis and detection. For a spherical particle the ratio of surface area ($A=4\pi r^2$) to volume ($V= 4/3 \pi r^3$) is inversely proportional to the particle radius r according to equation [27.1]:

$$A/V = 3/r \quad \dots[27.1]$$

As a particle becomes smaller, its surface area becomes an increasingly larger component of its overall form. Given that atoms at surfaces have distinct bonding and reactivity characteristics from bulk atoms, it is expected that a particle of nanometer range will behave differently from a particle even at micron scale.

27.4.5. Properties of Nanoparticles

The nanoparticles (NPs) have extremely high specific surface areas for their volume and that a significant proportion of atoms on NP occur at surfaces, which in turn lead to higher reactivity of nanoparticles. Increased strength, increased heat resistance, melting points of nano materials decrease for clusters smaller than a few hundred angstroms. For example, the melting temperature of gold decreases approximately by a factor of two

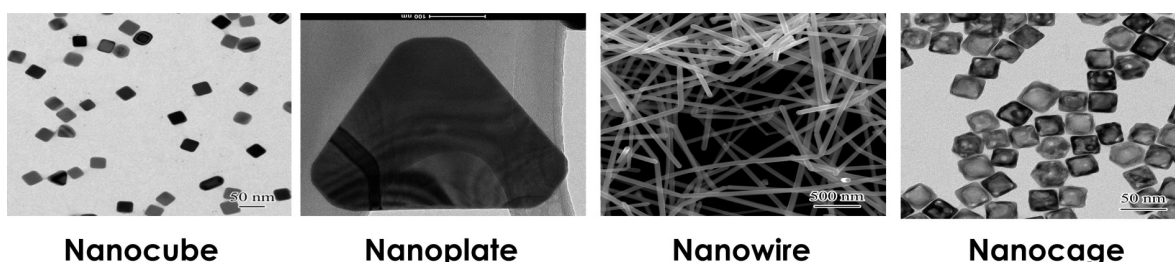


Figure 27.7. Different types of nanoparticle fabrications obtained by manipulation of matter

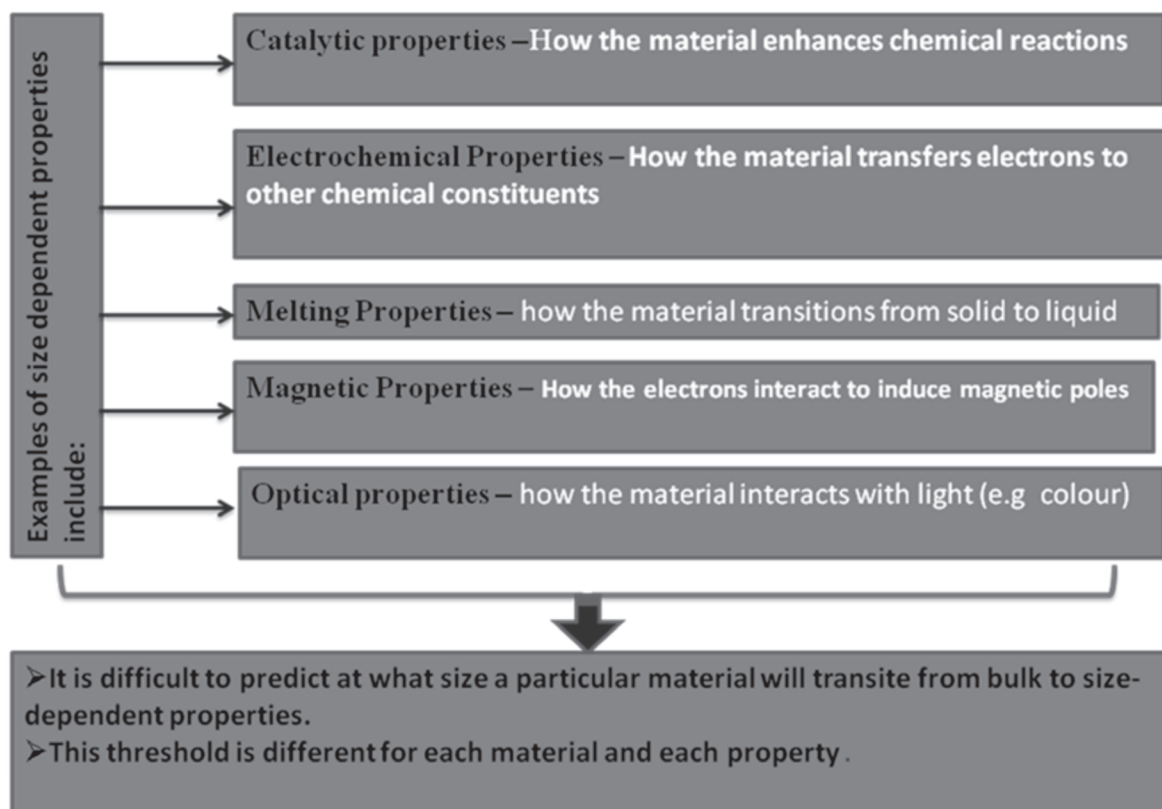


Figure 27.8. Size dependency of nanoparticles

when the cluster size is reduced from 10 nm to 2 nm. Magnetic properties (Figure 27.8) of nanoclusters are also very much different from that of the corresponding bulk material. For example, nanoclusters of certain materials like Pd, Na, K and Rh are ferromagnetic, where as in bulk form, these elements are paramagnetic. Superparamagnetism is a phenomenon that arises from the small size of nanoclusters.

27.4.5.1. Brownian Motion

Brownian motion may be defined as the random motion of particles suspended in a fluid (a liquid or a gas) resulting from their collision with the quick atoms or molecules in the gas or liquid. Brownian motion is a very important phenomenon in predicting the behaviour of nanoparticles. The three dimensional mean transfer distance (Δx) by the Brownian motion can be stated as equation [27.2], where D_B and Δt is Brownian diffusion coefficient and time, respectively. The Brownian diffusion coefficient in eq. [27.2] can be stated as eq. [3] where k is Boltzmann constant, T is the absolute temperature, μ is the viscosity of media and dp is particle size. From eq. [27.2] and eq. [27.3], it is clear that the Brownian motion increases as the particle size decreases. Thus, nano particles have very high chances to make an approach and collision with other nano particles whatever the media is. Since van der Waals attractive force also works amongst the nanoparticles, the generation of potential barrier among nano particles is necessary to prevent strong aggregations.

$$\Delta x = \sqrt{6D_B \Delta t} \quad \dots[27.2]$$

$$D_B = kT/(3 \pi \mu dp) \quad \dots[27.3]$$

27.4.5.2. Derjaguin, Landau, Verwey and Overbeek (DLVO) Theory

The theory describes the force between charged surfaces interacting through a liquid medium and explains the aggregation of aqueous dispersions quantitatively. It combines the effects of the electrostatic repulsion due to the double layer of counterions and the van der Waals attraction. According to the DLVO theory, the stability of a colloidal suspension is based on the net balance of two forces *viz.* a universal attractive van der Waals force which acts to bind particles together and the electrostatic repulsion which prevents aggregation. High ionic strength compresses the electrical double layer and the magnitude of the repulsive barrier decreases whereby van der Waals attraction dominates. Therefore, the net interaction potential becomes purely attractive at long and short-range leading to nanoparticle agglomeration. But in dilute electrolyte solutions, the counterion clouds that charge-compensate the charged surface of nanoparticles extend far from the particle surface making the double-layer interaction a long-range interaction. Since the van der Waals attraction is relatively weak at long-range, electrostatic repulsion dominates and a stable nanoparticle suspension results.

27.4.5.3. 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. Quantum confinement is responsible for the increase of energy difference between energy states and band gap. Phenomenon is tightly related with the optical and electronic properties of the materials. The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude as the wavelength of the electron wave function. When materials are this small, their electronic and optical properties deviate substantially from those of bulk materials. A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle. During this state, the bandgap remains at its original energy due to a continuous energy state. However, as the confining dimension decreases and reaches a certain limit, *typically in nanoscale*, the energy spectrum turns to be discrete. As a result, the bandgap becomes size-dependent. This ultimately results in a blue shift in optical illumination as the size of the particles decreases.

27.4.5.4. Quantization of Energy

Electrons can only exist at discrete energy levels. Quantum dots are nanomaterials that display the effect of quantization of energy.

27.4.5.5. Random Molecular Motion

Molecules move due to their kinetic energy. 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.

There are many other factors which play a crucial role in deciding the behaviour of nanoparticles, the most important being the zeta potential and pH.

27.4.5.6. Zeta Potential (ZP) and pH

When a particle is suspended in liquid the surrounding of the particle exists as two parts; an inner region called the Stern layer where the ions are strongly bound and an outer

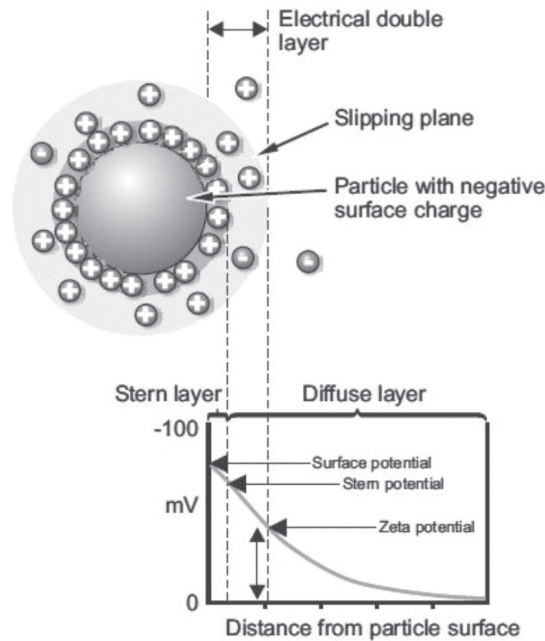


Figure 27.9. Zeta Potential of a particle with negative surface charge

diffuse region where they are less firmly attached as shown in **Figure 27.9**. When a particle moves, ions within the boundary move with it but any ions beyond the boundary do not move with the particle. This boundary is called the surface of hydrodynamic shear or the slipping plane. The potential on this surface is called the zeta potential. Higher zeta potential will impart stability to nanoparticles in suspension due to repulsion among the particles whereas low zeta potential leads to coagulation. As a general rule, the stability as per ZP (in milli volts) is given as:

$$-30 \text{ mV} > \text{ZP} > +30 \text{ mV}$$

This suggests that the value of ZP can attain either positive or negative values when the solution attains more positive ions (H^+) or more negative ions (OH^-), respectively. This is where pH comes into picture. It plays a crucial role in maintaining the zeta potential and hence the stability of the nanoparticles and therefore, a wise person would always report the pH corresponding to the measured ZP.

Zeta potential can be measured using the principle of Electrophoresis wherein an electric field is applied across the sample and the particles suspended in it move to the electrodes with the opposite of velocity (m s^{-1}) of the particle and the applied electric field (V m^{-1}) is the electrophoretic mobility (U_E) of the particle. When we obtain the electrophoretic mobility we use this to find the zeta potential of the particle using Henry's equation given below as equation [27.4].

$$U_E = \frac{2\varepsilon_r\varepsilon_0\zeta f(ka)}{3\eta} \quad \dots[27.4]$$

where, ε_r is the dielectric constant of the dispersion medium; ε_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2$); ζ is the zeta potential; η is the viscosity, $f(ka)$ is the Henry's function.

Electrophoretic determinations of zeta potential are most commonly made in aqueous medium and moderate electrolyte concentration. The $f(ka)$ in this case is 1.5, and is

referred to as the *Smoluchowski approximation*. Therefore calculation of zeta potential from the mobility is straightforward for systems that fit the Smoluchowski model, i.e. particles larger than about 0.2 microns (μ or μm) dispersed in electrolytes containing more than 10^{-3} molar salt. For small particles in low dielectric constant media $f(ka)$ becomes 1.0 and allows an equally simple calculation. This is referred to as the *Huckel approximation*. Non-aqueous measurements generally use the Huckel approximation. Fortunately, a particle size analyzer (PSA) which uses the above principle to measure the zeta potential gives its value right away avoiding the headache of going into all the calculations.

27.5. Synthesis of Nanoparticles (NPs)

Atoms and molecules are the basic building block of construction of every object. It is the way in which it is constructed which determines its properties. Nanoparticles can be constructed by a variety of methods. Two approaches (Figure 27.10) are generally involved in the generation of nanoparticles:

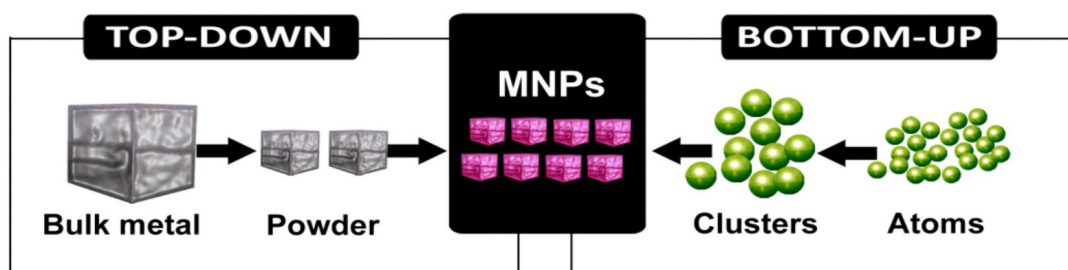


Figure 27.10. Approaches of nanoparticle synthesis

27.5.1. Top-Down Approach

It is an approach advanced by Richard Feynman; it is based on miniaturizing techniques like machining, templating and lithographic techniques. It involves division of a larger solid (Bulk) into smaller portions (Nanoparticles). In nature, these methods aren't cheap and quick to manufacture and are slow and not suitable for large scale production. Various methods like milling/attrition, chemical methods, photo-lithography, electron beam lithography, X-ray lithography, etc. are used in top-down approach.

27.5.2. Bottom-Up Approach

Bottom-Up approach was pioneered by Jean-Marie Lehn; it is based on gradual addition of atoms and molecules. It involves condensation of atoms/molecules in gas phase or in solution phase allowing them to grow in size until they reach the nanoscale size. In this approach, fabrication cost of the nanoparticles is much less. Methods for bottom-up approach are sol-gel processing, chemical vapour deposition, plasma spraying synthesis and molecular condensation.

An essential feature for the nanoparticle synthesis is the preparation of particles of specific size and shape. Different sizes and shapes of nanoparticles have a considerable impact on the nanoparticle properties as stated before. In order to eliminate the inter-particle interactions, nanoparticles often need to undergo many processes. The distance between the particles in the matrix must also be controlled.

The generation of nanoparticles in solid or gas phase is usually called physical methods, whereas methods which are often carried out in solution phase are chemical

methods. Synthesis of nanoparticles using biological sources is known as biological methods.

27.5.3. Methods Involved for Production of Nanoparticles

Nanoparticles can be synthesized by physical, chemical, physico-chemical (Aerosol) and biological methods.

27.5.3.1 Physical Methods

(a) *Grinding* — The particles which have natural deposits can easily be prepared in nanoform by physical methods after removing the impurities and subsequent grinding by ball mill or pot mill (**Figure 27.11**). For example, P nanoparticles can be prepared physically from rock phosphate after removing the impurities and then grinding by ball mill and pot mill to obtain 28 nm and 70 nm sizes, respectively.



Figure 27.11. Ball mill (left) and pot mill (right)

(b) *Thermal evaporation* — The base materials are heated at its vapor point or above. The evaporation causes the vaporized base material to deposit on the cooler portion of the substrate.

(c) *Sputtering*: It is the removal of atomized material from a solid due to energetic bombardment of its surface layers by ions or neutral particles (**Figure 27.12**).

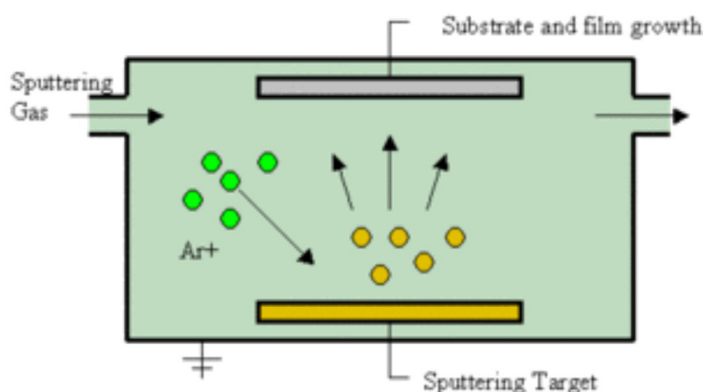


Figure 27.12. Sputtering

(d) *Pulsed Laser Deposition Technique*: It takes place in three stages. Firstly, the laser beam is focused on surface of target (**Figure 27.13**), which heats them up to evaporation temperature. In second stage, the emitted materials move towards the surface. Finally, the quality of the thin film is determined. This thin film is then carried out through many minor processes to completion.

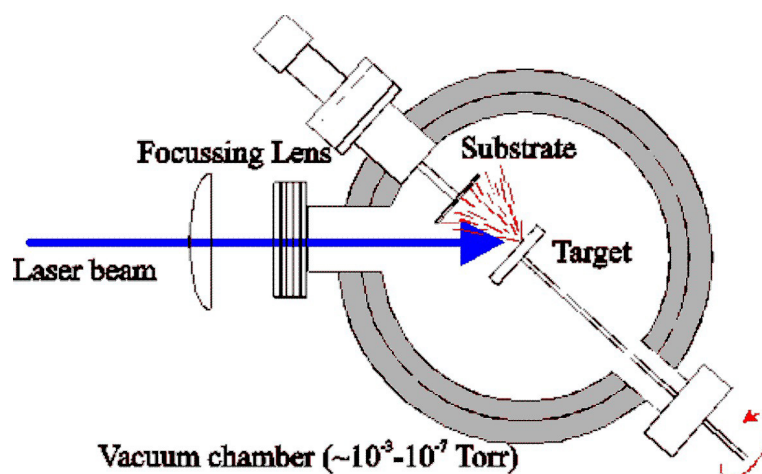


Figure 27.13. Laser Deposition Technique

27.5.3.2. Chemical Methods

Chemical synthesis is a very powerful method *i.e.* complex molecules can be made from simple reagents.

(a) *Sol-gel Techniques* — The sol-gel process involves initially a homogenous solution of one or more selected alkoxides which act as an organic precursor for silica, alumina, zirconia, etc. Reaction is initiated and the pH is controlled using a catalyst. It takes place in four stages.

1. *Hydrolysis*: The (-OR) groups are replaced by (-OH) groups.
2. *Condensation*: The formation of dimer, trimer is involved along with release of water or alcohol.
3. *Growth and agglomeration*: As the number of bonds increase, they start forming a network and a gel is formed upon drying. Larger particles are produced at higher temperatures.

(b) *Co-precipitation* — Co-precipitation involves simultaneous occurrence of nucleation, growth, coarsening and agglomeration processes (Figure 27.14). It leads to formation of a large number of small particles. The products are insoluble as they are formed under high supersaturation.

(c) *Microwave synthesis* — Microwave radiation is used for heating the source which improves the yield, leads to uniform reaction, and can lead to alternative pathways. Examples include Acicular magnetite, goethite, etc.

(d) *Microencapsulation* — Nanoparticles which can act as an active ingredient can be encapsulated inside a micron-sized matrix or coating using the technique of microencapsulation. This method is useful in controlled release of NPs when and where necessary.

(e) *Hydrothermal methods* — In a sealed vessel, solvents are brought to temperatures above their boiling points by increasing the pressure by heating it. The chemical reactions performed under such conditions are called solvo-thermal process, and if water acts as a solvent, it is known as hydrothermal processing.

(f) *Poly vinyl pyrolidene (PVP) method* — It is a solution phase synthesis of many colloidal particles. The hydroxyl group of the PVP is an appropriate reductant for aqueous synthesis of nanoparticles made of palladium, platinum, silver and gold.

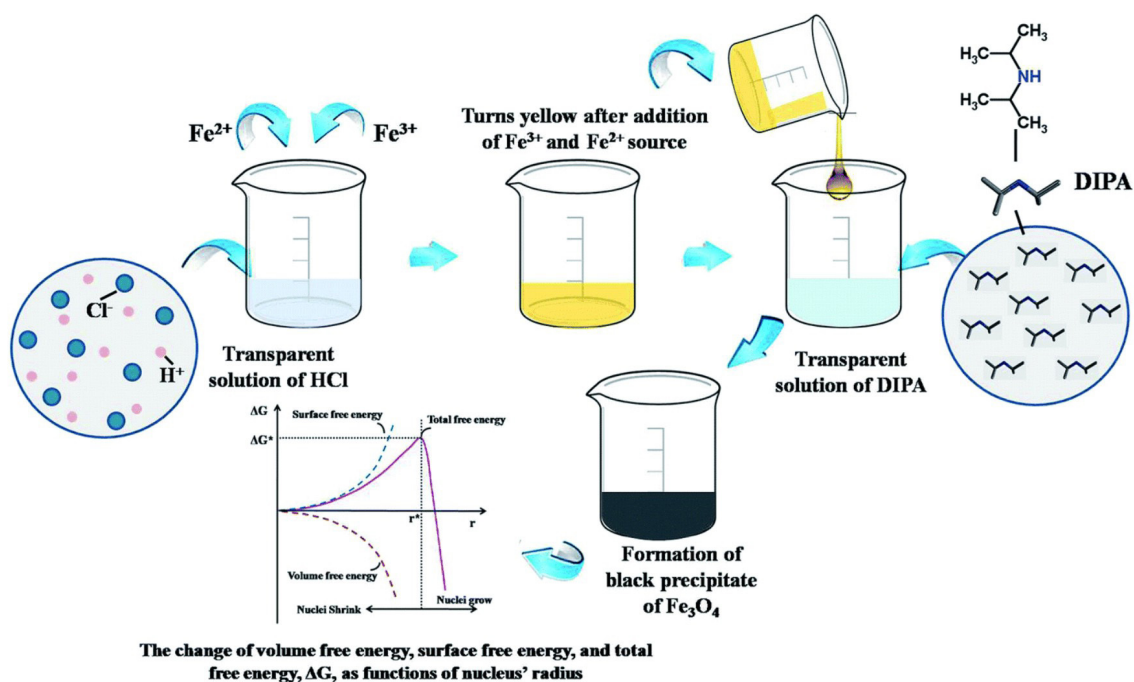


Figure 27.14. Co-precipitation technique

(g) *Sonochemistry* — Sonochemistry (Figure 27.15) uses high-frequency sound waves to power chemical reactions. The ultrasound leads to formation of highly reactive radical species, forming tiny bubbles which collapse quickly, thus generating a chemical reaction.

27.5.3.3. Aerosol Methods (Physico-chemical)

An aerosol is defined as a mixture of solid or liquid particles suspended in air or other gaseous environment. Aerosol can vary in size and composition, and can be natural or manmade. The original synthesis pathways employed by Gleiter and coworkers entailed evaporation of a metal into a low density gas where the vapours formed nanoparticles by homogeneous nucleation.

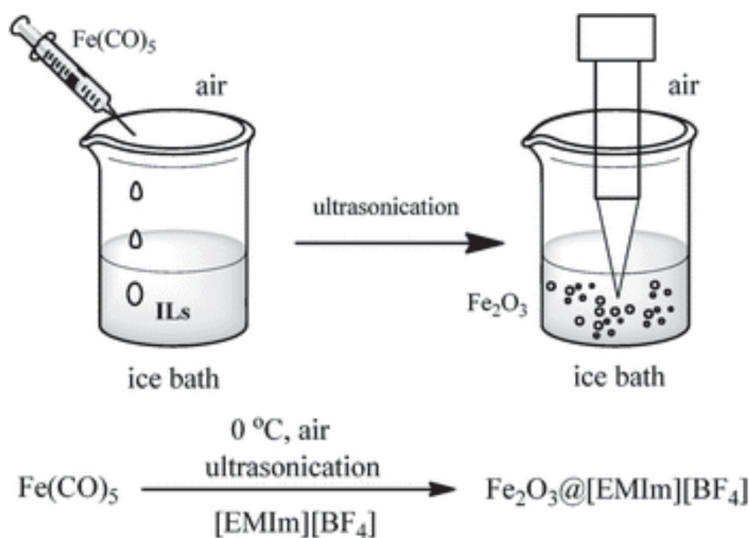


Figure 27.15. Ultrasonication

Aerosol is a metastable suspension of particles in a gas, therefore to ensure expression of nanoparticle properties, large quantities are needed to be synthesized carefully under controlled conditions (Figure 27.16). Aerosol methods are preferred over physical and chemical methods due to their ability to satisfy the demands of high product purity, improved composition and less environmental hazards. There are five different aerosol techniques used for nanoparticle production: (i) Furnace method: (> 100 nm); (ii) Flame method: (suitable precaution) TiO_2 ; (iii) Electro spray: 1 g per year; (iv) CVD (Chemical vapour deposition) method; and (v) PVD (Physical vapour deposition) method. Electro spray is the most accurate method for nanoparticle production but it is the slowest among all the methods.

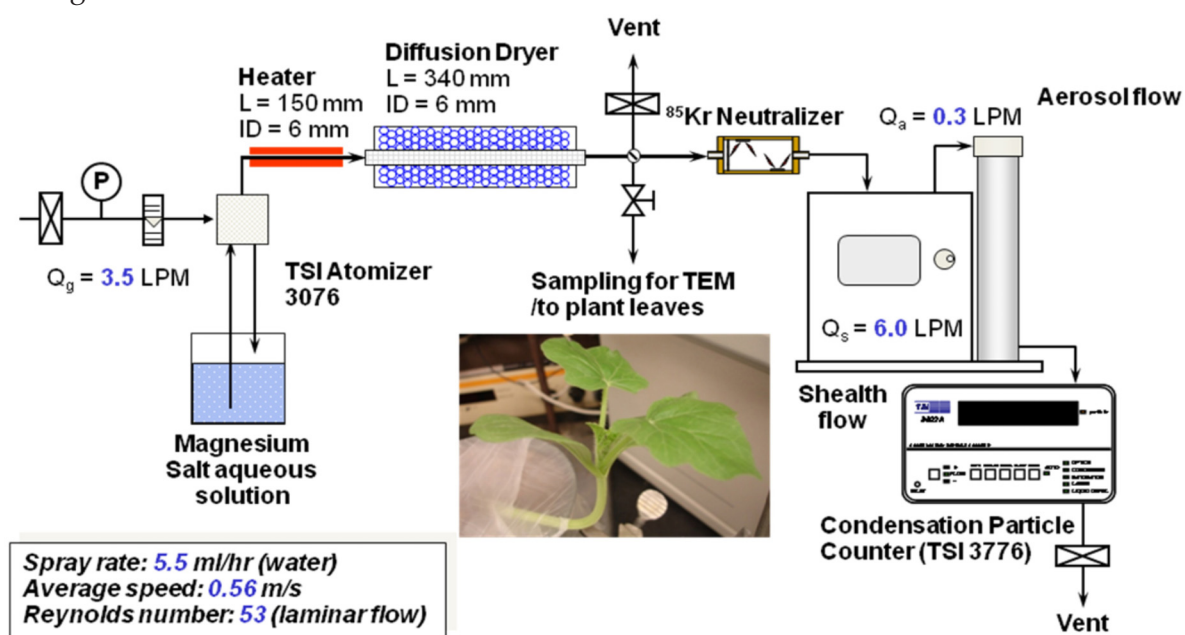


Figure 27.16. Aerosol method for physico-chemical synthesis of nanoparticles

27.5.3.4. Biological Methods

Biological methods are a safe and ecologically-sound approach for nanoparticle fabrication as an alternative for physical, chemical and aerosol methods. There are various means of biological synthesis of nanoparticles where selected microbial proteins are used to break down salts into their respective nano forms (Figure 27.17).

- Use of bacteria* — *Bacillus megaterium* JCT 13 produces phosphorus nanoparticles from tTri calcium phosphate
- Use of fungi* — Fungi have been a key element in biological synthesis of nanoparticles, giving a wide variety of nanoparticles than bacteria. For example: *Aspergillus oryzae* TFR-9 produces Zn, P, Ag, Au, Fe and Ti nanoparticles. Fungi secrete large amount of proteins giving high productivity and yield as compared to bacteria.
- Use of plants* — *Azadirachta indica* produces silver nanoparticles.
- Use of biomolecules (Proteins)* — Proteins (32 and 33 kDa weight group) can be used for production of Mg, Zn and Fe nanoparticles from their respective oxide salts.
- Use of herbs* — *Desmodium triflorum*, which is a wild branched slender diffused herb with trifoliolate leaves, which can be found in grasslands, forests, agricultural lands, has been used to synthesize silver nanoparticles. More studies showed that these nanoparticles exhibit good antibacterial performance against pathogens.

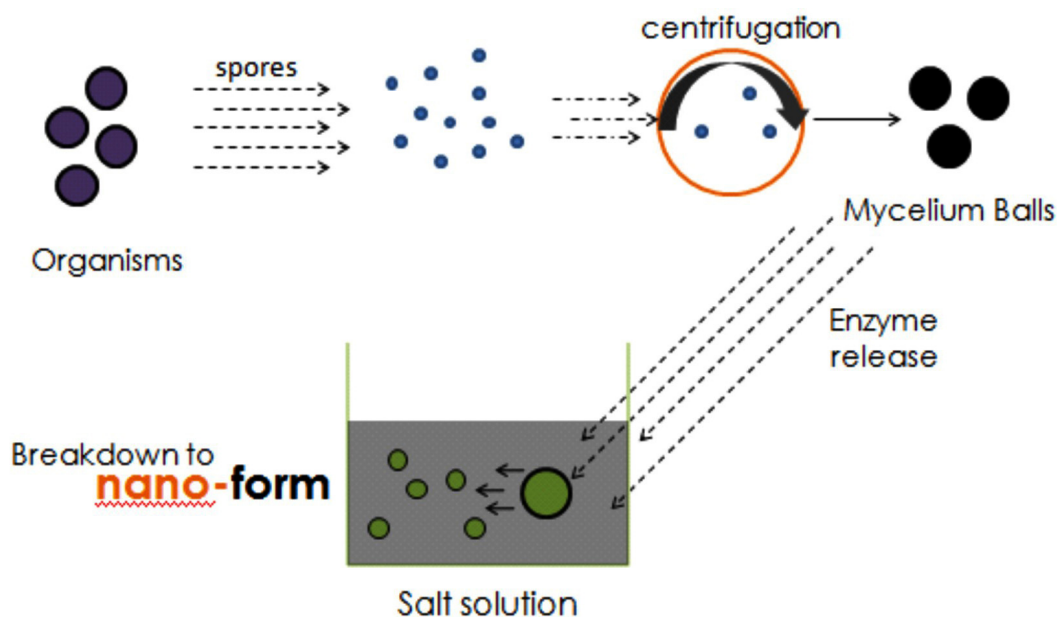


Figure 27.17. Biosynthesis of nanoparticles from fungal protein

f) *Microwave-assisted biosynthesis* — In this technique, microwave-assisted anti-malignant plant leaf of guava is used for synthesis of stable poly-shaped gold nanoparticles. This method has reduced the effort required in synthesis using micro-organisms and has improved the productivity manifold times.

27.6. Characterization of Nanoparticles (NPs)

The properties of nanoparticles depend upon a variety of parameters such as particle size, surface area, porosity, solubility, aggregation, zeta potential, wettability, etc. These properties must be analyzed properly for proper manufacture of the nanoparticles. There are various instruments which can be used to understand the characterization parameters in nanoparticles, these include:

27.6.1. Particle Size Analyzer (PSA)

This technique is used to determine the particle size distribution along with the behavior of complex fluids. In this method, the light hits the nanoparticles and is scattered in all directions (Figure 27.18). Larger particles scatter more light than smaller particles. The

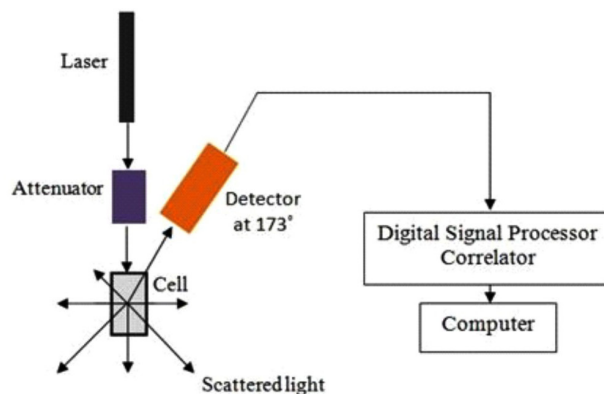


Figure 27.18. Particle Size Analyzer and the principle involved

reason for this is that the area of contact for the larger particle is more. This scattered light undergoes either destructive or constructive interference by the surrounding particles, and these fluctuations give rise to information about the movement of these scatterers. This fluctuation arises due to the fact that the particles in solution undergo Brownian movement.

Dynamic Light Scattering (DLS) measures the time-dependent fluctuations in the scattering intensity to determine the translational diffusion coefficient (D) and subsequently the hydrodynamic diameter (D_H) from the Stokes-Einstein equation [27.5].

$$D = \frac{kT}{3\pi\eta D_H} \quad \dots[27.5]$$

where, k is the Boltzmann constant, T is the absolute temperature (in K) and η is the viscosity

The concentration of particles determines how hard it is to scatter the given solution, lower the concentration; more difficult it is to reproduce the results (Figure 27.19). This technique also measures the zeta potential of the solution, which determines the degree of aggregation of nanoparticles. The higher the zeta potential, lesser is the aggregation.

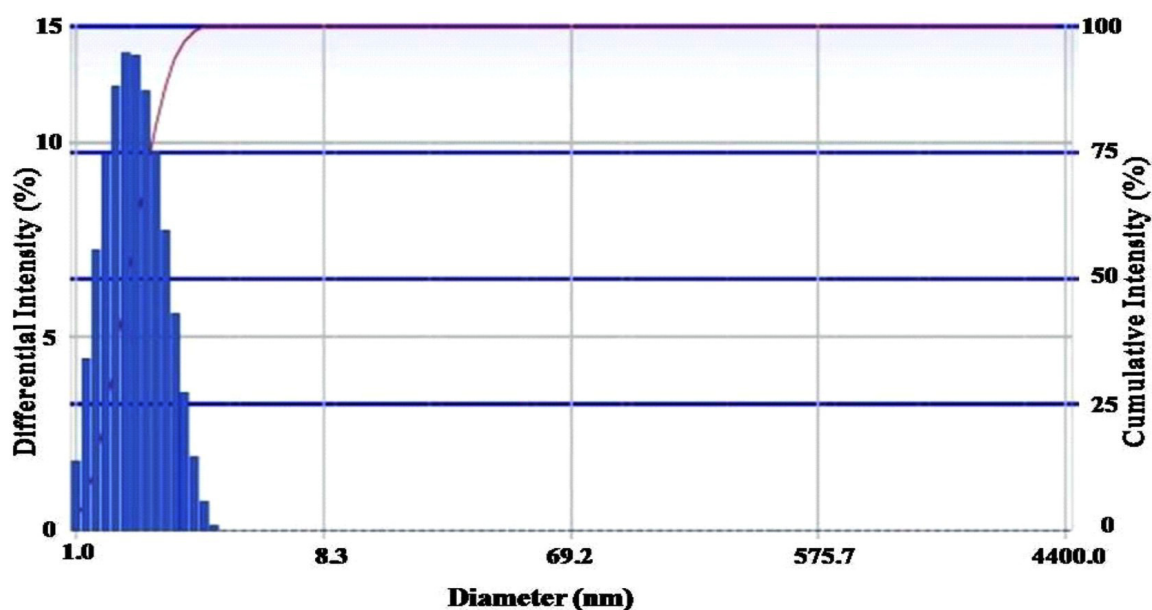


Figure 27.19. Intensity size distribution for biosynthesized Mg nanoparticles obtained from PSA

27.6.2. Ultraviolet and Visible (UV-VIS) Absorption Spectroscopy

It is an absorption spectroscopy which uses ultraviolet and visible light to differentiate the desired nanoparticles (Figure 27.20). When the light is incident on the required particles, transition from ground state to excited state takes place, giving readings of the transition wavelengths. This method has an advantage due to its wide range of wavelengths in the electromagnetic spectra.

Spectroscopy gives both, qualitative as well as quantitative results, *i.e.* the maximum wavelength of the bulk gives us information about the structure and the intensity of absorption gives us the number of particles absorbing light. There are many types of spectrometers like single beam, double beam and multiple channel spectrometers.

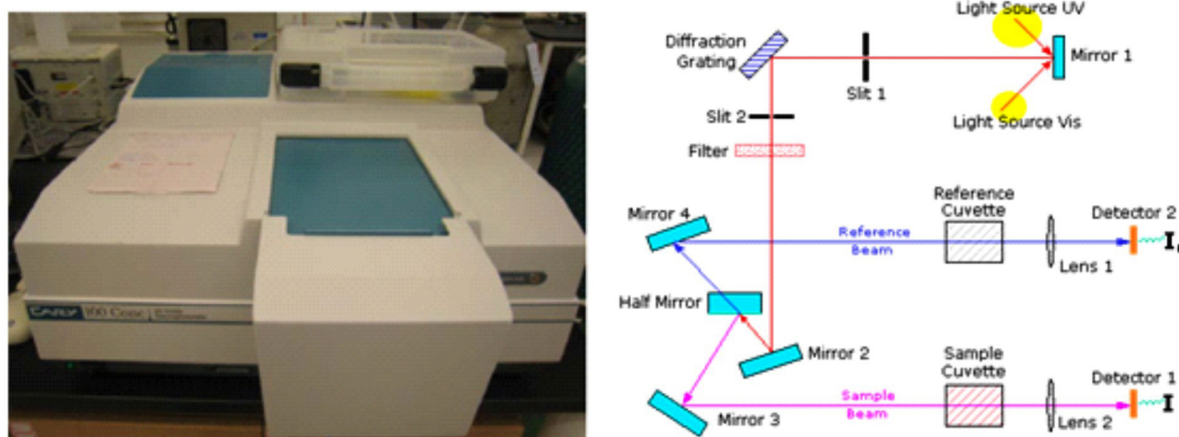


Figure 27.20. UV-Vis Spectroscopy (left) and the principle involved (right)

27.6.3. Transmission Electron Microscopy (TEM)

It is a microscopy technique which transmits a beam of electrons through an ultra-thin specimen, which interacts with the beam. An image is formed of the particle (Figure 27.21) with the help of electrons, which is then magnified and focused on a fluorescent screen which is then detected. It provides with the 3-dimensional measurements of the nanoparticles along with their composition.

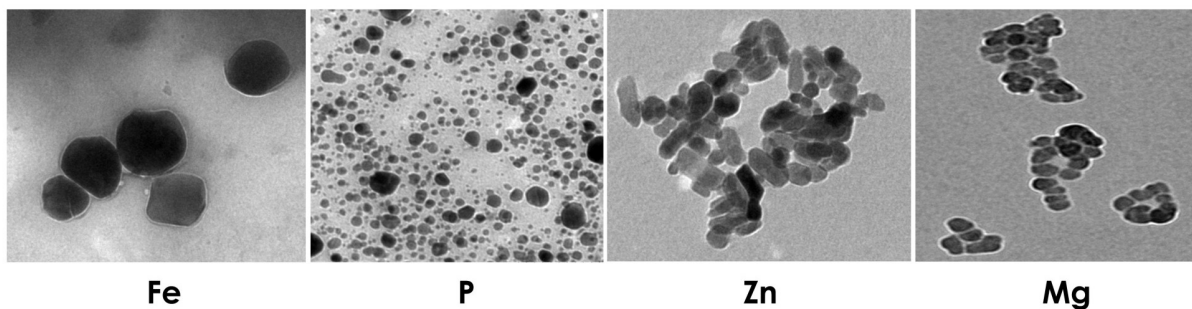


Figure 27.21. Transmission electron microscopy and images obtained from it

The TEM specimen holder allows the rotation of sample by a desired angle to obtain a proper image. The material preparation is a tedious task which makes it a time-consuming process along with low output result. It also has a very low analysis region to be explored.

27.6.4. Scanning Electron Microscopy (SEM)

It is an electron microscopy technique which uses a high energy beam of electrons in a raster scan pattern imaging the sample's surface. This produces signals which reconstruct the sample using information provided like topography, composition, conductivity, etc. The SEM produces variety of signals like secondary electrons, X-rays, light and many more. The first SEM image was produced by Max Knoll in 1935. The SEM gives information on surface structure of the particle (**Figure 27.22**). While using SEM, the sample must be solid and must fit in the experiment chamber.

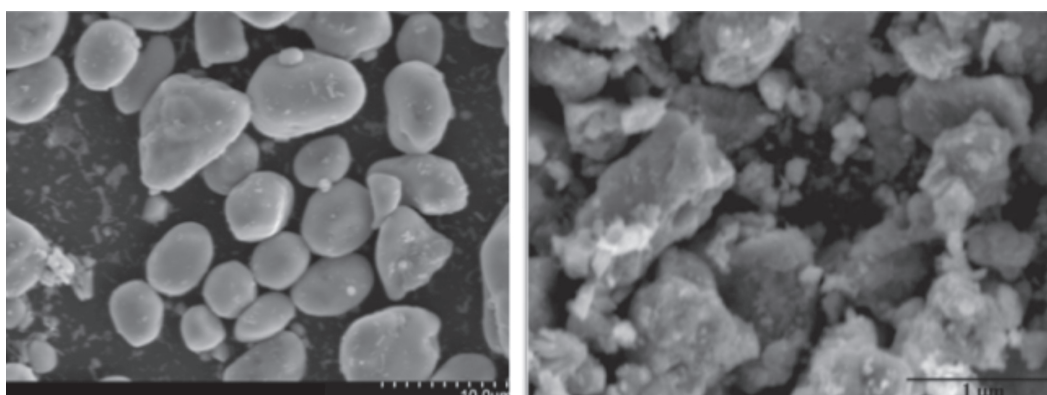


Figure 27.22. Scanning electron microscopy images of silver (left) and zinc (right)

27.6.5. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a very high resolution type of scanning probe microscopy. The precursor of AFM was a scanning tunneling microscope. The AFM is one of the most accurate tools for nanoparticle analysis with precise imaging, measurement and manipulation of nanoparticles. The forces inside the nanoparticles like mechanical contact force, van der Waals force, magnetic, electrostatic and chemical bonds are measured by this technique. Due to their high resolution, the 3-dimensional picture (**Figure 27.23**) of the particle is very beautiful as well as detailed with structural

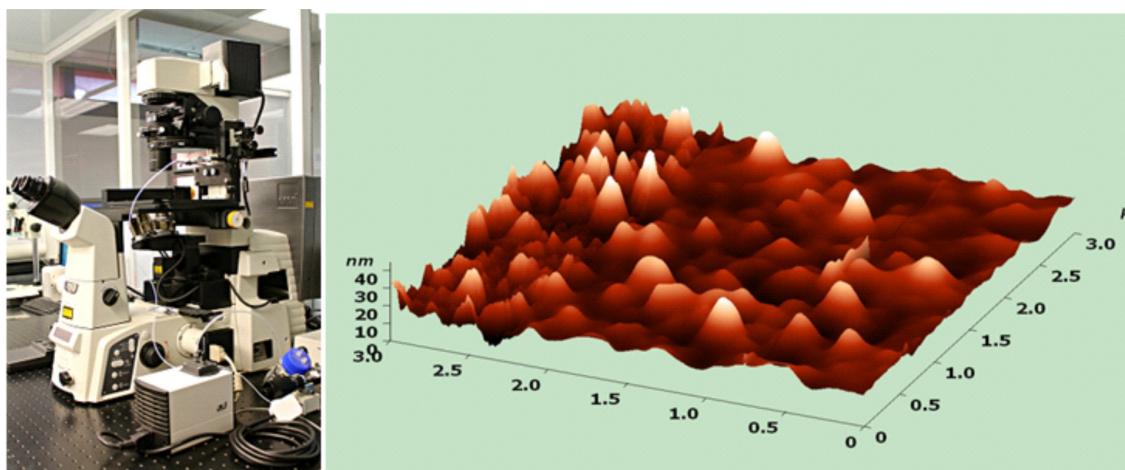


Figure 27.23. Atomic force microscopy (left) and 3-D AFM image of nitrogen NP (right)

information. The nanoparticles analyzed by this technique are either rigidly attached to a solid structure or possess weak adhesion forces with the substrate.

27.6.6 Fourier Transform Infrared (FTIR) Spectroscopy

It is a technique in which the target is analyzed by placing it in front of an infrared beam. The main motive in this method is to determine the chemical functional groups present in the sample. Different functional groups absorb different IR frequencies. At temperatures above zero Kelvin, when the frequency of vibration of atoms equals the IR frequency, the radiation is absorbed by the molecule. The radiation is then mathematically converted to nanoparticle's structure using Fourier Transform.

Fourier transform infrared spectroscopy (**Figure 27.24**) is usually better than other methods as it is a non-destructive, environment-friendly technique; it has good speed and more reliable outputs. It is also mechanically easy to operate providing precise measurement without requiring any external calibrations. Further, it gives an indication which functional group is involved in breaking down or absorption of particles.

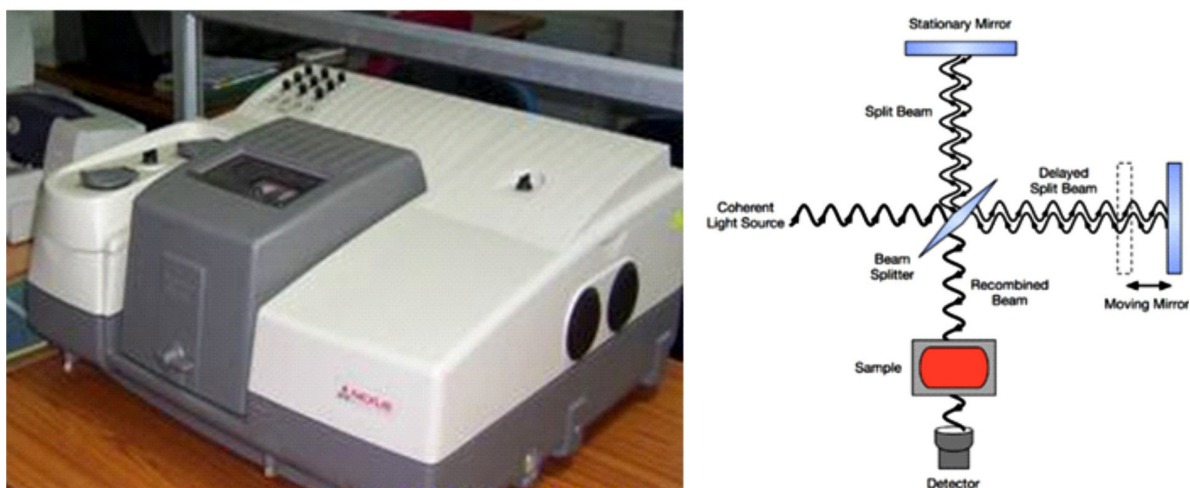


Figure 27.24. Fourier transform infrared spectroscopy (left) and principle involved (right)

Sometimes energy dispersive X-ray (EDX) spectroscopy is attached with the SEM, TEM or AFM which provides information on purity of the particle (**Figure 27.25**).

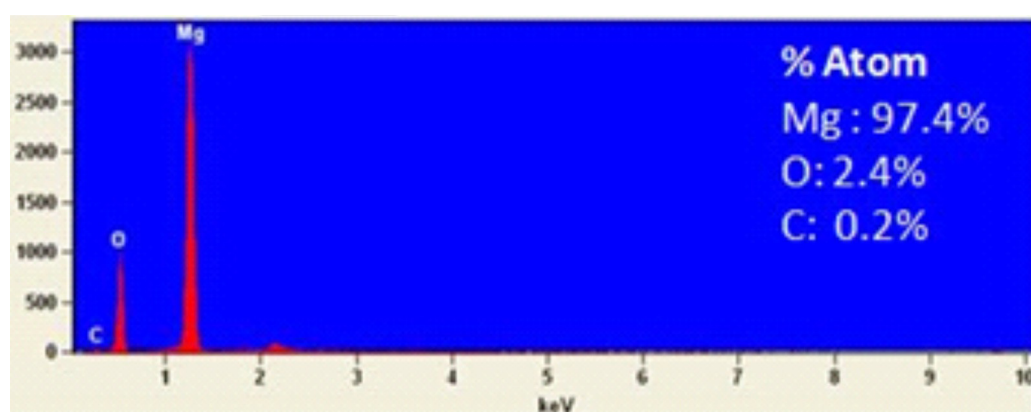


Figure 27.25. Typical EDX of biosynthesized magnesium nanoparticle

27.6.7. X-Ray Diffraction (XRD)

X-ray diffraction or crystallography is a method of determining the arrangement of atoms within a nanoparticle (Figure 27.26). The X-ray beam strikes the crystal and diffracts into different directions. From the diffraction angles and intensities of these beams, we can get a 3-dimensional picture of the atoms inside the nanoparticles. Diffraction only occurs when Bragg's Law is satisfied.

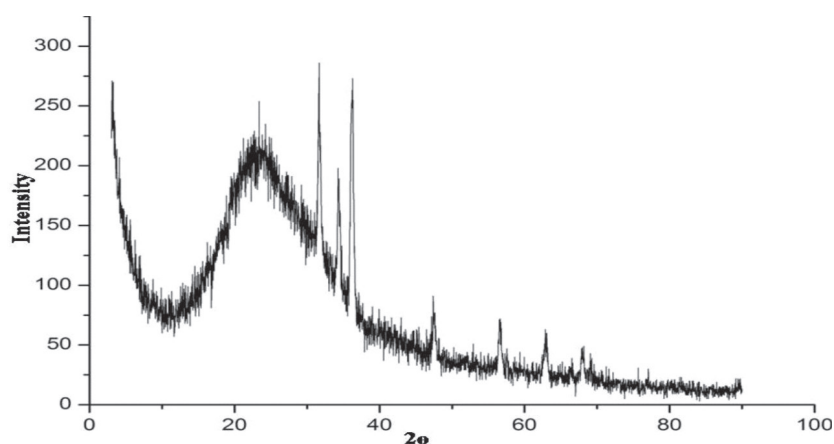


Figure 27.26. X-ray Diffraction image of biosynthesized zinc nanoparticle

There are many methods through which crystals of nanoparticles can be created like hanging drop method, sitting drop method, microdialysis, etc. When the X-ray pattern is recorded, the relative peaks are formed by the mathematical interpretation of the data and the peak provides us with the 3-dimensional structure.

27.6.8. Lithography

Lithography is a technique for defining useful shapes on the surface of a semiconductor wafer. It was invented in 1798 by Alois Senefelder in Germany. There are many lithographic techniques, like photolithography, electron beam lithography, X-ray lithography etc. which are developed by using different lens systems, radiation exposures, but all of them follow a basic and common approach. This technique is used to transfer previously determined pattern on a surface and is a crucial technique in fabrication of nanoparticles.

27.6.9. Ultrasonication

Sonication uses sound energy to agitate particles, breaking intermolecular interactions. It is also used to initiate many chemical reactions. It can be used to remove dissolved gases from liquid. It disperses the nanoparticles in liquid, which breaks the particle agglomeration, e.g. metal oxides, nanoclays and carbon nanotubes. The concentration of solution also plays a crucial role in this method.

27.6.10. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

It is a highly sophisticated technique which uses plasma to dissociate ions contained in a sample. These ions are then extracted from the plasma and analyzed in mass spectrometer for detection. This technique is highly sensitive and capable of detection of nanoparticles (metals/non-metals) with extremely low concentration of order 10^{-12} g (pg). The coupling

of plasma with mass spectrometer provides us with an insight structure of nanoparticle but at the same time increases the complexity.

27.7. Estimation and Measurement of Nano-particles in the Soil

Method of estimation for engineered NP in soil system is still in its infancy. But the methods developed for aquatic colloids could be used for the determination of engineered NP such as microscopic methods (electron microscopy, atomic force microscopy), size fractionation [ultra filtration, field-flow fractionation (FFF) or centrifugation] and chromatography (size-exclusion or gel-permeation chromatography). The following methods may be used to measure the nanoparticle concentration in a colloidal suspension:

27.7.1. TEM Image Analysis

Accurate gravimetric measurement using analytical balances may not be practical in the submicrogram range, as this is approaching the sensitivity limit for most instruments. Hence indirect methods, such as TEM image analysis provides approximate concentration. To obtain a TEM image, a fixed volume of a particle colloid sample is deposited on a TEM grid. The particles are counted per unit of the grid after drying. In this way, a typical TEM image, containing up to several thousand particles, should accurately represent the full sample batch. This is a labour-intensive and expensive method.

27.7.2. ICP-MS Method

A direct and simple inductively coupled mass spectroscopy (ICP-MS) method was developed for the determination of gold nanoparticles. Assuming a spherical shape of the gold nanoparticle and a density with a uniform face-centered cubic gold nanoparticle, the average of gold atoms for each gold nanoparticle can be calculated by the following equations [27.6.1 and 27.6.2]:

$$N_{\text{at}} = N_A \pi r D^3/6M \quad \dots[27.6.1]$$

$$N_{\text{at}} = N_A \pi r D^3/6M \quad \dots[27.6.2]$$

where N_A is the Avogadro number (6.023×10^{23}), r the density ($1.93 \times 10^{-20} \text{ g nm}^{-3}$), D diameter in nm and M atomic weight (197 g mol^{-1}). Considering an average gold nanoparticle of 15 nm, the average of gold atoms is 1.04×10^5 gold atoms/nanoparticle. Finally, dividing the gold atoms/L by the number of gold atoms/nanoparticle is obtained to a number of 4.40×10^9 gold nano particles/L.

27.7.3. Quartz Crystal Microgravimetry (QCM) Method

The quartz crystal microbalance (QCM) is a nanogram resolution mass sensing technique based on the piezoelectric effect. It may be applied to accurately quantify NP concentrations in size selected colloidal suspensions in a low boiling point solvent. By depositing a fixed volume of the NP colloidal solution on crystal surface and determining the dry residue mass after solvent evaporation, the nanoparticle concentration is measured and expressed as mass per unit volume.

27.8. Fate and Behavior of the Metal-based Nano-particles in Soil

27.8.1. Soil Nanoparticles

Soil matrix consists of particles of different size fractions, such as the colloidal fraction, clay fraction, silt fraction, sand fraction, and gravel and each fraction has specific properties and roles within this matrix. The smallest fraction or "ultrafine" fraction in

soils always gets special importance as this fraction governs the soil physical and chemical properties, such as cation exchange capacity, anion exchange capacity, soil water holding capacity, tortuosity, particle aggregation, etc. Over the wide range of colloid particle sizes, the largest particles have the greatest percentage mass, but the smaller particles have the greatest number and percentage of total surface area. Because of its large surface area, large percentage of surface atoms with unbalanced charge, large number of surface functional groups per unit of mass the ultrafine fraction dramatically change the physicochemical properties of soil. Recently significant amounts of different NPs have been produced for use in different field of studies and more research and developmental work is necessary as these nanoparticles in one way or another, will be deposited or discarded into the soil.

27.8.2. Natural Nanoparticles

Naturally-present colloids and macromolecules in soils are nanoparticulate and microparticulate clays, organic matter, iron oxides and other minerals play an important role in biogeochemical processes. Generally nanoparticles are present in soil in two broader categories like nano-minerals and mineral NPs. Nano-minerals are defined as the minerals that only exist in this size range, *e.g.*, certain clays and Fe and Mn (oxyhydr) oxides whereas mineral NPs are defined as minerals that can also exist in larger sizes, *e.g.*, most known minerals. The formation of natural nanoparticles that are present in volcanic dust, most natural waters, soils, and sediments, has been governed by the different soil, geological, and biological processes. Nanosheets, nanorods and nanoparticles are the three classes of natural nanoparticles present in the soil system. Nanosheets in the form of thin coatings are commonly present on surfaces of primary minerals of the soil matrix. Nano-sheets may also occur in the form of thin platelets, which promote accelerated and intensive dissolution of existing minerals and subsequent precipitation of neophases. Nanorods are formed as a result, intense dissolution of primary soil minerals, such as feldspars and mica, which initially occurred, and were followed by precipitation of goethite, sodalite, and other secondary phases. The NPs may also be formed in soils as a result of biotic processes.

27.8.3. Manufactured Nanoparticles

In the near future, anthropogenic nanoparticles are being and will be produced for its application in different fields. Several manufactured nanoparticles are of now being heavily used by the industries, for example, ZnO-nanoparticles are being used in solar cell device as the photoelectrode; fullerene nanoparticle is being used in electronic, optic, medical, and cosmetic applications; Ag-NPs are integrated into consumer and medical products; cerium dioxide (CeO₂) NPs are being used as a catalyst in the automotive industry; TiO₂-NPs are being used in cosmetics, sunscreens, paints and coatings. It is almost certain that significant amounts of the MNP will be deposited in the soil environments.

27.8.4. Behaviour of Nanoparticles in the Soil

The characteristic behaviour of nanoparticles in soils is still obscure. Advanced techniques and equipments are to be developed to conduct studies of the reactions that occur at the or in the nano-pores within soil matrices. Because of the diversity of nanotechnology applications, NPs may enter the environment through many pathways. The sources of NPs to the environment are complex, consisting of both point and diffuse releases. During

industrial production and transportation, accidental spills may occur. Emissions to the atmosphere may result in deposition to soils and waters from various sources (e.g., waste incineration). Further deliberate additions to the environment may occur via the use of NPs in soil and water remediation technologies and agriculture (e.g., as fertilizers). The major source of NP deposition onto land is currently through the disposal of wastewater treatment plant (WWTP), sewage sludge, where NPs that are released from consumer products into wastewaters may partition into sewage sludge during the wastewater treatment process. The NPs that are present in soils may undergo transformations, such as growth, dissolution, aggregation, and aging, changing the micro or nano environment surrounding the individual soil NPs. The NPs may interact in different ways with an array of minerals of the soil solid phase, and a variety of soil solution aqueous species. Because of these transformations and interactions, the extent and timescale of processes and reactions that control the fate of nutrients and contaminants may also change. A number of key processes are likely to affect the fate and bioavailability of nano-particles in the soil environment as depicted in **Figure 27.27**.

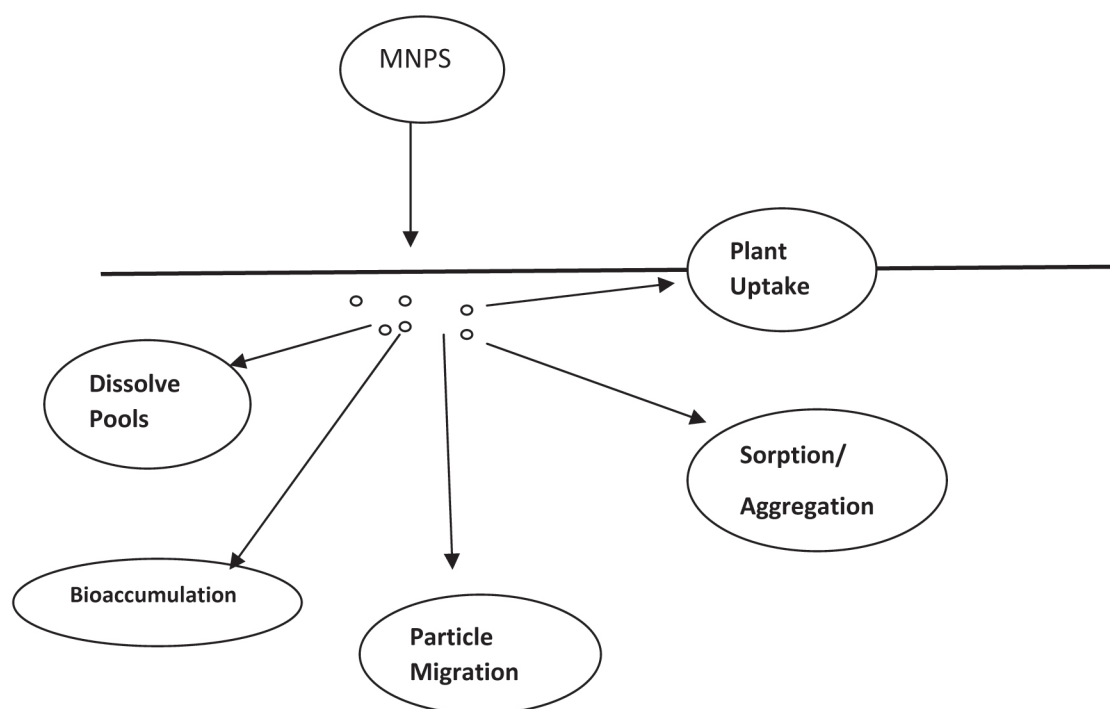


Figure 27.27. Fate of nanoparticles in soil matrix

27.8.4.1. Stability

The stability of NP is a function of their surface energy and NPs are more stable when they possess a low surface energy. For example, the surface energies of small rutile particles are higher than those for anatase particles of a similar size, consistent with anatase being the more stable phase of nanocrystalline TiO_2 . Manufactured metal-based NPs possess a number of key characteristics that are believed to exert important controls on their environmental behaviour, fate, and ecotoxicity. These include physical characteristics, particularly size and shape, and chemical characteristics such as the acid–base character of the surface and the aqueous solubility of the metal. These characteristics in turn will determine the extent to which metal-based NPs undergo transformations that will control their fate, behaviour, and ecotoxicity in the environment. Such processes will include aggregation/ agglomeration, sorption to surfaces, and dissolution to the ionic

metal. Soil represents a relatively complex medium for the understanding of the physicochemical behaviour of manufactured NPs. In comparison with the dissolved phase, in which behaviour can be understood largely in terms of particle stability against aggregation, soils present a solid matrix with which NPs may interact, as well as an aqueous phase, which may contain appreciable amounts of natural colloidal/ particulate material.

27.8.4.2. Aggregation and Agglomeration

Aggregation is defined as the association of primary particles by strong bonding, whereas agglomeration is defined as association by weak bonding caused by van der Waals forces. In the environment, physical forces (*e.g.*, Brownian motion, gravity, and fluid motion) and NP characteristics (*e.g.*, surface properties, particle size) will affect NP agglomeration and aggregation. The particles are constantly colliding with each other because of Brownian motion, and agglomeration will occur when the energy of either motion or attraction exceeds the energy of repulsion. Aggregation may result in the formation of particle flocks that are of sufficient size to sediment out of solution by gravity. The NP-aggregate size in solution depends on properties such as initial particle size and concentration.

27.8.4.3. Surface Coating

The chemistry of the medium will influence the electrostatic surface charge of the particles, thereby affecting agglomeration, aggregation rates and particle stability. In the absence of a surface coating, metal-based NPs have charged surfaces resulting from the presence of hydroxyl (–OH) groups that can take up and release protons, and can take up dissolved chemical species such as metal ions and ligands. Surface charging results in the formation of an electrical double layer, comprising the charged surface sites and a diffuse layer containing ions attracted from the solution to the particle surface in response to the charge. The electrical potential at the interface of the diffuse layer and the bulk solution (the zeta potential) can be measured, and its variation with solution chemistry can effectively be used as a surrogate for the variation in particle surface charge with solution chemistry. The zeta potential of uncoated metal or metal oxide particles typically decreases from positive values at low pH to negative values at high pH. As the pH approaches the iso-electric point, or the “point of zero charge,” where particle charge/zeta potential approaches zero, the aggregation rate will increase because of the lowering of the electrostatic repulsive forces between particles. A suspension of homogeneously charged particles will be stable when the magnitude of the zeta potential is greater than 30 mV. Classical colloid theory can be applied to metal and metal oxide NPs to help explain their stability. The Derjaguin, Landau, Verwey, and Overbeek theory considers stability as a function of the repulsive (*i.e.*, electrostatic) and attractive forces (*i.e.*, van der Waals) to which a particle is subjected. Although the Derjaguin, Landau, Verwey, and Overbeek theory has generally proved unsatisfactory for the quantitative prediction of colloid behaviour in complex natural environments, the conceptual framework that it provides for considering such behaviour can be useful in explaining trends in observed behaviour in such systems.

27.8.4.4. Dissolution

Some types of metal-based NPs are thermodynamically unstable and undergo chemical dissolution if kinetic restrictions are absent. Dissolution occurs when an ion detaches

from the particle and migrates through the electrical double layer into the solution. The dissolution behaviour of non-nanosized metals and metal oxides in soils may be of use in prioritizing NPs for study and in choosing which soil properties to consider that may influence their dissolution rates. Behaviour of the nanoparticles within the soil systems will be further complicated by the presence of the solid phase. Soil components such as clay particles or humic molecules, themselves having the charged surfaces, will influence the association of NPs with the solid phase. Such soil components may also form colloids in the aqueous phase, which will interact with NPs. For example, humic molecules desorbing into the aqueous phase may sorb to NP surfaces, and so influence the NP stability. All of these processes are themselves strongly influenced by overriding characteristics of the soil system, particularly the pH and the ionic strength of the aqueous phase. The NPs were found to quickly equilibrate between the aqueous and solid phases, and concentrations in the smaller than 1-mm fraction were stable. The aggregation rate of TiO₂-NPs in soil suspensions has been found to be negatively correlated with soil characteristics such as dissolved organic matter and clay contents, and positively correlated with the ionic strength, zeta potential, and pH. Nano particles are sorbed less strongly to soils of low ionic strength and high dissolved organic matter content. Assuming that bioavailability is related to the particle fraction suspended in the pore water and not the fraction associated with the soil matrix, these factors may be affecting the bioavailability of metal-based NPs in soils.

27.8.4.5. Ionic strength

The ionic strength of the medium affects the stability of the diffuse layer in the electrical double layer. An increase in the ionic strength will lead to a decrease in the electrical double layer thickness, which favours particle association and leads to increasing agglomeration. The effects of ionic strength on the aggregation of Ag-NPs (uncoated, citrate, and sodium borohydride-coated particles) have been observed for suspensions with pH higher than 7. This demonstrates that here the particles were stabilized by electrostatic repulsion, caused by the predominance of negative forms (*i.e.*, anions) in the medium and the negative charge of the particles.

27.8.4.6. Natural Organic Matter

Natural organic matter has the ability to stabilize engineered nanoparticles (ENPs). Fullerene was found to be stabilized in the presence of dissolved organic matter (DOM) in suspension. Generally, after release of the ENPs in soil solution, they may interact with DOM in particulate form and be suspended and transported rather than aggregate and deposit quickly. The DOM adheres to the surface of ENPs and modifies their surface physicochemical properties and enhances their stability.

27.8.4.7. pH

To understand the fate and behaviour of ENPs in soil, it is necessary to understand the effect of pH on ENPs suspension. pH is mainly responsible for governing the zeta potential of colloids (Figure 28). The colloidal system exhibits minimum stability or maximum coagulation, when pH is at point of zero charge (pzc). The colloid surface is positively charged when the pH is lower than the pzc value and the zeta potential will increase with decreasing pH below the pzc. Conversely, the colloid surface possesses positive charge at pH above pzc and the zeta potential will be more negative with increasing pH. Nanoparticles with low zeta potential tend to coagulate or flocculate, whereas higher

value of zeta potential will impart stability to the nano- particle suspension. The solubility of metal-based nanoparticles and their surface charges are governed by solution pH and consequently the electrostatic interactions between nanoparticles and between nanoparticles and porous media. Dissolved counter ions in solution determine the long range electrostatic interactions for electronically stabilized ENPs and hence decrease the stability and transport of ENPs in the porous media.

27.8.4.8. Zeta Potential

Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. If the dispersion pH is below 4 or above 8 there is sufficient charge to confer stability. However if the pH of the system is between 4 and 8 the dispersion may be unstable (**Table 27.3**). This is most likely to be the case at around pH 6 (the isoelectric point). Zeta potential value can be related to the stability of colloidal dispersions. The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles in dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, *i.e.*, the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate.

Table 27.3. Stability of nanoparticles in suspension with respect to zeta potential

Sl. No.	Zeta potential (mV)	Stability behavior of the colloid
1	from 0 to ± 5 ,	Rapid coagulation or flocculation
2	from ± 10 to ± 30	Incipient instability
3	from ± 30 to ± 40	Moderate stability
4	from ± 40 to ± 60	Good stability
5	more than ± 61	Excellent stability

27.8.4.9. Point of Zero Charge

The potential at the point of zero charge (pzc), describes the condition when the electrical charge density on a surface is zero. Point of zero charge (pzc) is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface. When the pH is lower than the pzc value, the system is said to be “below the pzc.” Below the pzc, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface is positively charged (attracting anions). Conversely, above pzc the surface is negatively charged (attracting cations /repelling anions). At pzc, the colloidal system exhibits zero zeta potential (*i.e.*, the particles remain stationary in an electric field) causes minimum stability (*i.e.*, exhibits maximum coagulation/ flocculation rate), maximum solubility of the solid phase and maximum viscosity of the dispersion (**Figure 27.28**). Dispersion is stable in the colloid –chemical sense when its particles remain permanently free. In dilute dispersions it is sufficient to consider only interactions between pairs of particles. In very concentrated systems it may be necessary to take also multi-particle interactions into account.

27.9. Applications of Nanotechnology in Soil Science

In today’s world, the nanotechnology is the upcoming revolution after the semiconductor revolution which has the potential to open doors to completely new applications in many

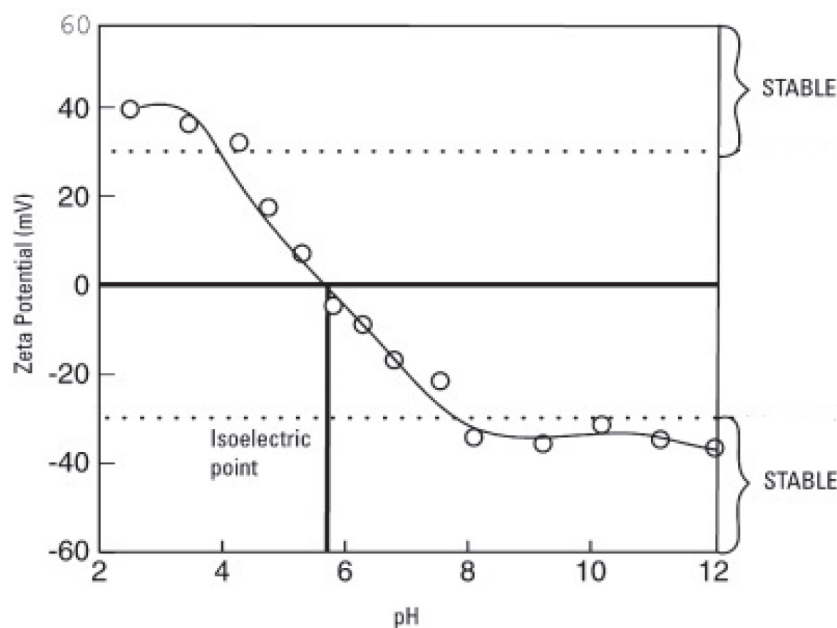


Figure 27.28. Stability of nanoparticles in suspension varies with respect to pH

fields such as agriculture, information technology, medical science, energy, food safety, transportation, etc. Some of the important applications in the field of Soil Science are discussed below:

27.9.1. Nano-fertilizers

Nano-fertilizer technology is very innovative. Significant increase in yields has been observed due to foliar application of nanoparticles as fertilizer (Figure 27.29). It was shown that 640 mg ha^{-1} foliar application of nano P gave 80 kg P ha^{-1} equivalent yield of clusterbean and pearl millet under the arid environment. Currently research is underway to develop nanocomposites to supply all the required essential nutrients in suitable proportions through smart delivery systems. Fertilizers encapsulated in nanoparticles will increase the uptake of nutrients. In the next generation of nano fertilizers the release of nutrients can be triggered by an environmental condition or simply at desired specific time.



Figure 27.29. Biosynthesized nanofertilizers

27.9.2. Biosensors

Nanotechnology is playing an increasingly important role in the development of biosensors (Figure 27.30). The sensitivity and performance of biosensors is being improved by using nanomaterials for their construction. The use of these nanomaterials has allowed the introduction of many new signal transduction technologies in biosensors. Portable instruments capable of analyzing multiple components are becoming available. The nanobiosensors are effective devices to detect the composition of the soil, *i.e.* the nutrients and also the toxic substances in the soil. In this way, we can plan techniques such that the composition of soil is suitable for the respective crops and the toxic substances such as metals are dealt with properly.

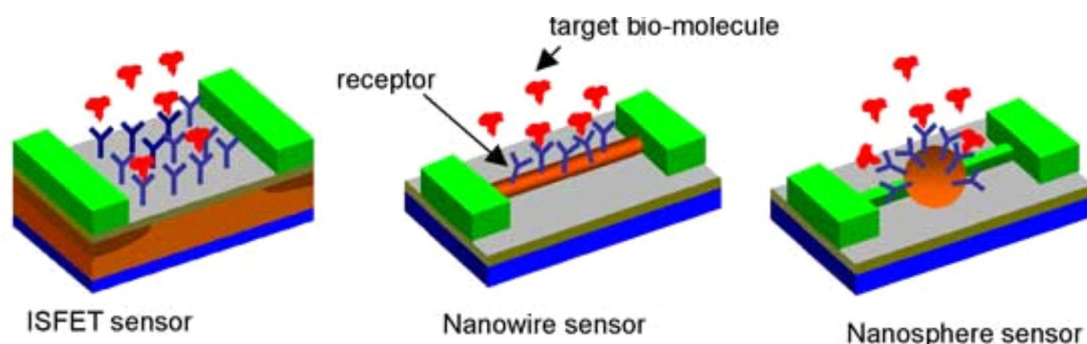


Figure 27.30. Biosensors

A microbial biosensor is an analytical device with a biologically integrated transducer that generates a measurable signal indicating the analyte concentration. This method is ideally suited for the analysis of extracellular chemicals and the environment, and for metabolic sensory regulation. These microbial sensors are integrated with many more micro/nanodevices to overcome the limitations like low sensitivity, poor selectivity and impractical portability.

27.9.3. Smart Delivery of Nutrients

A smart delivery system for agriculture should consider the factors or combination of factors such as time controlled, specifically targeted, highly controlled, remotely regulated/pre-programmed and multifunction characteristics to avoid biological barriers for successful targeted release of required nutrients. The nanoscience has greatly impacted the conventional delivery systems by eliminating the limitations such as leaching, degradation by photolysis, hydrolysis and bio-instability in atmosphere. This results in repeated use of pesticides and insecticides causing higher cost of cultivation and environmental pollution. Nano-encapsulated agrochemicals should be designed in such a way that they possess all necessary characteristics like effective concentration, stability, solubility, time-controlled release in response to certain stimuli, enhanced targeted activity and less eco-toxicity with safe and easy mode of delivery thus avoiding repeated applications. There are various means through which this delivery system can be put to use.

27.9.3.1. Nano Herbicides

Herbicides are chemicals used to kill weeds especially when the moisture content in the soil is not as per required by the crop. Nano-herbicides (usually coated material) provide better penetration in the soil and allow slow and controlled release of active ingredients in reaching the targeted weed causing minimum environmental damage.

27.9.3.2. Nano Insecticides

The insecticides are also a concern for agricultural purpose as they induce death to insects and other pests that try to harm the crops. Nano insecticides like surface modified hydrophobic nanosilica have been put to use instead of conventional insecticides as they are safe for plants and cause less environmental pollution.

27.9.3.3. Nano Fungicides

Fungal pathogens are a major part of the pesticides which harm the crops hence fungicides are prepared to tackle them separately. The small size of nanoparticles puts them to use

in nano-fungicides as they penetrate easily and colonize the fungal spores which are a source of fungal pathogens. For example Ag-NPs are a common source of nano-fungicides but if used in very high concentration can produce chemical injuries in crops such as cucumber.

27.9.4. Rhizosphere Studies

Controlled foliar application of nanoparticles (P, Zn, Mg) as nutrients may trigger enzymes (Figure 27.31) and growth promoting substances to release through roots resulting influence on microbial population in the rhizosphere. Nanosensors can help in tracing particular microbial activity in the rhizosphere.

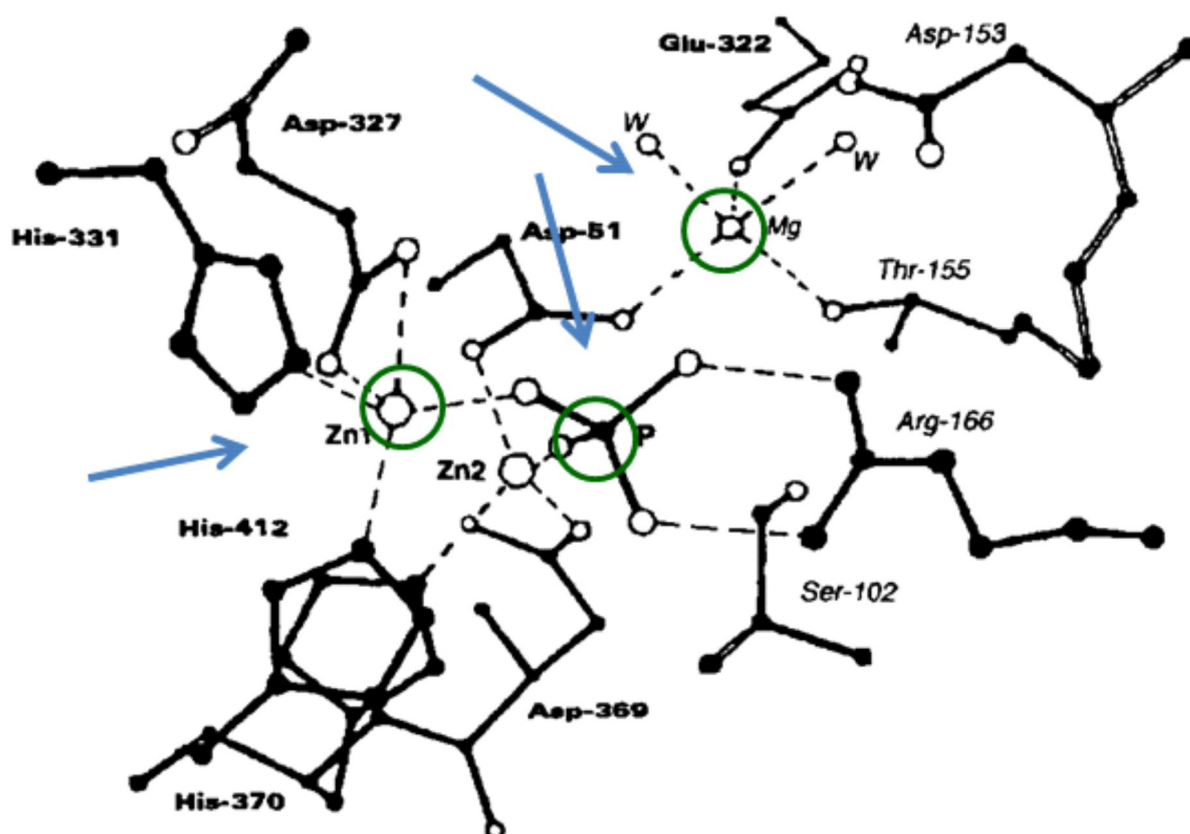


Figure 27.31. Triggering of enzymes by foliar application

27.9.5. Precision Farming

Precision farming is a farming management concept based on maximizing output (*i.e.* crop yields) while minimizing the input (*i.e.* fertilizers, pesticides, herbicides, etc.) through managing environmental variables and applying targeted actions. With the help of technologies like global satellite positioning system (GPS), remote sensing devices, we can determine whether the crops are growing at their maximum efficiency, and if not, determining the respective problems. Various factors like soil composition, weather, plant development, fertilizers used, chemicals and water provided, are analyzed such that the production costs can be minimized and production potentially increased. Nanotechnology provides with a variety of devices which can reduce the cost of precision farming manifolds. For example, nano-devices and sensors are developed which can penetrate the soil and can inform about the any environmental changes taking place so that we can act accordingly.

Nanosensors which utilize carbon nanotubes are small enough to trap and measure the level of proteins and small molecules in the soil. These nanodevices are capable of triggering an electrical or chemical response if the soil and environmental conditions change adversely.

27.10. Safety, Toxicity and Adaptation of NP's in the Soil and Aquatic Life

The ultra-small sizes make the nanoparticles of immense usefulness. But unfortunately the same characteristics cause several adverse effect and may represent significant hazards to environment, animals, human beings and plants when used non-judiciously. The possible hazards are:

- a) Nanoparticles as pesticides, fertilizers or other formulations, when airborne, may deposit on plant parts. They may plug the stomata and create a fine physical and toxic layer on stigma preventing pollen tube penetration. They may also enter the vascular tissues and impair translocation of water, minerals and photosynthate.
- b) Animals may inhale nanoparticles and resulting suffer from various ill-effects and disorders. The particles may also enter the blood stream.
- c) Nano-pesticides may reduce environmental contamination through the reduction in pesticide application rates but they may also create new kinds of contamination of soil and waterways due to enhanced transport, longer persistence and higher toxicity.
- d) Airborne nanoparticles present some specific hazards for human health. They may enter the body through the respiratory system. Due to the entry of nanoparticles in lungs and bloodstream, there is a possibility of inflammation, protein fibrillation and induction of genotoxicity.

Because of these risks, the use of nanotechnology in fertilizer and pesticide formulations has to be addressed very cautiously and this warrants mandatory need to critically analyze and examine the risks involved with the nano-formulations.

27.10.1. Safe Handling of Nanoparticles

During manufacture of nanoparticles, use of B2 biosafety cabinet is internationally recommended. While handling of nanoparticles one should wear mask and nitrile gloves as a precautionary measure. Nanoparticle in gaseous phase should be experimented in an unsealed environment to study its exposure. The laboratory used for nanoparticle studies should be extremely clean.

The dust particle concentration should not exceed 10^4 m^{-2} . Maintenance and upgradation of machinery used in processing and distribution of NPs should be taken care of. Cleaning up of spilled chemicals and waste materials containing nanoparticles should be a primary task as when exposed to environment, these waste products can enter the soil and kill the necessary microbes or invade the aquatic life causing them to extinct.

27.10.2. Risk Assessment Programme

There should be a planned programme which can be implemented in case the soil, atmosphere or aquatic life is exposed to the toxicity of the NPs. Various chemicals should be kept ready to counter the harmful effects of NPs. Moreover, the workers should also be given proper education and training in the handling of NPs. For example, workers

should be given respirators while spraying nano-fertilizers so that the airborne toxic substances from the NP's cannot affect them.

There should be an organization responsible for surveying and keeping check on all the ongoing research and industrial activities related to nanotechnology. In this way, the government can always keep a track on its upcoming applications as well as can ensure that the NP production is not exceeding a designated toxicity level.

27.11. Conclusion

Nanotechnology has greatly impacted the modern world. It has proved to be a gateway of new applications in agricultural as well as other fields. Due to their small size, nanoparticles act as an excellent catalysts in many chemical reactions taking place in industries. Their small size also allows them to penetrate into the soil and through the plants more readily making them extremely viable in the field of Soil Science. We have seen how nanotechnology extends its scope into foods, medicine, tissue engineering with optimized outputs.

The history of nanotechnology describes its presence decades ago among the ancient people using gold NPs to impart colours to glass and how many researchers mentioned it in their research, leaders described its application in their speeches and how this science is in transition of becoming a technology by efforts of many scientists who are vigorously digging in this field to make more from it.

Synthesis of NPs depends on various factors, for example, the medium in which they are prepared or the method used for its preparation, etc. Generally its synthesis is differentiated in four ways, physical, chemical, physico-chemical (aerosol) and biological methods. Apart from synthesis, the characterization of NPs is also a crucial task to perform. It determines the shape, size, chemical bonds, functional groups, electron alignment, etc. of NPs allowing us to replicate the NPs and also provide it with some modifications to make it more efficient. For example, nanoparticles are coated with different substances to prevent their decay or agglomeration in the soil.

Besides all its advantages, it has its limitations too. These NPs produce waste toxic materials which if contacted with soil and aquatic environment can cause contamination/pollution. These NPs also depend on environmental factors like temperature, pH, solubility, etc. hence if these factors are altered, it may alter the function of NPs. Apart from these there are many reasons which have limited the applications of nanotechnology. If these limitations are countered or overcome, then nanotechnology will become a revolutionizing technology of 21st and 22nd century.

Study Questions

1. Define nanoparticles. How are they different from mega particles? Why is there a need to go onto the nano scale?
2. Name three prominent scientists in the field of nanotechnology. Give their contribution.
3. Explain the types of nanoparticles
 - (a) based on their origin
 - (b) based on their shape
4. How does nanotechnology help in the development of Soil Science?
5. What are the methods used for synthesis of nanoparticles? Which method is the most accurate?

6. Expand the following acronyms of the following instruments used in Nanoscience research:
- AFM _____
 - TEM _____
 - SEM _____
 - ICPMS _____
 - QCM _____
 - FTIR _____
 - PSA _____
 - DLS _____
7. Define 'Quantum confinement'.
8. Write short notes on
- Nano-fertilizers
 - Biosensors
 - Precision farming
 - Smart delivery of nutrients
9. On a bright sunny day a certain research scholar was working in the laboratory with zinc oxide (ZnO) nanoparticles. The scholar was measuring the zeta potential (ZP) and was amazed to see the variation with addition of a few drops of 0.1 N NaOH. The variation of pH *versus* zeta potential is tabulated below:

ZP (mV)	35.4	27.1	13.5	7.7	2.9	-1.3	-4.2
pH	3.2	3.4	3.6	3.8	4.0	4.2	4.4

Based on the above observations, the scholar had the following queries in mind:

- What could be the possible explanation for the zeta potential to change from a positive value to a negative value?
 - Which pH range is suitable for storage of ZnO nanoparticles? Also which range of pH is most unstable?
10. What are the safety measures needed in the laboratory and field for handling of nano materials?
11. What are the possible hazards for non-judicious use of nanoparticles?
12. Name the instruments used for the characterization of nanoparticles. Explain the two most important instruments needed for day to day activity in nanotechnology laboratory.
13. Why is biological synthesis of nanoparticle more important for agricultural use?
14. Particles of size 2 μm are dispersed in water at 300 K containing high concentration of salts. When a steady electric field is applied across it, the velocity of the particles was observed to follow an equation which can be represented as

$$V = 8t^2 - 32t + 275$$

where V is the velocity in mm s^{-1} and t is time in seconds. Calculate the zeta potential in mV of the particles suspended in the solution. The properties of the dispersion medium are given as follows:

Temperature ($^{\circ}\text{C}$)	Dynamic viscosity ($\text{mm}^2 \text{s}^{-1}$)	Dielectric constant
20	1.00	80.4
25	0.89	78.3
30	0.80	76.5
35	0.72	74.8
40	0.65	73.1

15. Suppose the relation between particle size 'S' (in nm) and zeta potential 'Z' (in mV) is given as

$$10^{-5}S + 0.09 = Z$$

where z varies with time (in sec) as

$$Z = 0.4t^2 - 2t + 1$$

Given the information that the isoelectric point is where the net charge of the solution becomes zero; what will be the particle size 2 sec before reaching the isoelectric point? Give reasons for obtaining such a large size dimension.

16. Explain the DLVO theory for nanoparticle suspension stability.
17. Describe the properties of the nanoparticles.
18. Explain why nanoparticles are so special in the field of Science.
19. What is the fate of nanoparticles in soil system?
20. What is the effect of pH, ionic strength and natural organic matter on nanoparticles suspension?

References/Further Suggested Readings

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