# Nano-technology

## Introduction

- The word “**nano**” comes from a Greek word that means “**Dwarf**”
- $1nm=10^{-9}m$

### Definition

- **Nano-science** is the study of phenomena and manipulation of materials at atomic, molecular and macro-molecular scale, where properties differ significantly from those at larger scale.
- **Nano-technologies** are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer.
- **Nanotechnology** is a process that builds controls and restructures that are the size of atoms and molecules.
- **Nano-particle** is defined as the small object that acts as a whole unit in terms of transport and properties.

### Concept

- The idea of nanotechnology was for the first time introduced in 1959 by the physicist **Richard Feynman**.
- The term nanotechnology was first used in 1974 by **Norio Taniguchi**
- Nano-particle is ultrafine unit with dimensions measured in nanometers. Nano-particle exists in the nature and can be created artificially.
- Nano-particles are having the following properties
  - They are highly mobile in free state
  - They have enormous surface areas
  - They may exhibit the quantum effects
- Nano-technology is based on two main approaches
  1) **Bottom up approach**: Materials and devises are built from molecular components and which assemble themselves chemically by molecular recognition
  2) **Top down approach**: Nano objects are constructed from large entities without atomic level control

## Nano scale effects

- Two principal factors cause the properties of nano-material to differ significantly from other materials
  1) **Increased relative surface area**
  2) **Quantum effects**

1) **Increase relative surface area:**
   - Nano-scale materials have far larger surface areas than similar masses of larger area
   - As surface area per mass of material increases, greater amount of material can come into contact with surrounding materials, thus affecting reactivity.

| Size of the cube | Number of cubes | Collective surface area |
|---|---|---|
| 1m | 1 | 6 $m^2$ |
| 0.1m | 1000 | 60 $m^2$ |
| 0.01m | $10^6$ | 600 $m^2$ |
| 0.001m | $10^9$ | 6000 $m^2$ |
| $0.0^{-9}$m=1nm | $10^{27}$ | $6\times10^{-9}$ $m^2$ |

Quantum size effect = Electronic properties of solids are altered with reduction in particle size

- When particle sizes of solid matter in visible scale are compared to what can be seen in a regular optical micro-scope, there is a little difference in the properties of the particle.
- When the particles are created with nano dimensions the material properties change significantly from those at larger scales
- Melting point, fluorescence, electrical conductivity, magnetic permeability and chemical reactivity change as a function of size of the particle
- Materials reduced to nano-scale can show different properties compared to that they exhibit in macro-scale enabling unique application.

  **Example:**

  -Opaque substances become transparent (copper)
  -Stable materials turn combustible (aluminium)
  -Solids turn into liquids at room temperature (gold)
  -Insulators become conductors (silicon)

# Nano-pesticides, Nano-fertilizers and Nano-sensors

## Definition:

**Nano-pesticides**

- Nano-pesticides are defined as any formulation that includes elements of nm size range and/or claims novel properties associated with these small size range
- Nano-pesticides are plant protection chemicals, in which either the active ingredient or the carrier molecule is developed through nanotechnology
- The major aim in the development of nano-pesticides is to lessen the environmental hazards of a pesticide active ingredient through improving the efficacy of a chemical
- The size of a nanoparticle generally ranges 1-100 nanometer and a nanometer is one billionth of a meter. When the size gets this small, particles reach a very large surface area and thus more volume of pesticides get contact with the pests.

## Formulations of Nano-pesticides

- Nano-pesticides are formulated according to their intended purpose as formulations improving solubility, slow release of active ingredients, prevent degradation etc.
- Some foremost nano-formulations are:
  - **Nano-emulsions:** In this formulation active ingredient of the chemical is dispersed as nanosized droplets in water, with surfactant molecules confined at the pesticide-water interface
  - **Nano-suspension:** Nano-suspensions, also termed as nano-dispersions, are formulated by dispersing the pesticide as solid nanosized particles in aqueous media
  - **Polymer based nano-particles:** Polymer-based pesticide nanocarriers are majorly deployed in the slow and controlled release of active ingredients to the target site
  - **Nano-encapsulation:** This confines the hydrophobic or hydrophilic active ingredient, surrounded by a polymer coating or membrane.
  - **Nanospheres:** These are homogeneous vesicular structures, in which the bioactive ingredient is uniformly dispersed throughout the polymer matrix.
  - **Nanogels:** These are also known also hydrogel nanopartciles. These are formulated by cross linking of polymeric particles having hydrophilic groups
  - **Nano-fibres:** Nano-fibres are developed through electrospinning, thermal induced phase separation

## Advantages of Nano-pesticides

- Improved solubility of active ingredients
- Better stability of formulation
- Slow release of active ingredient
- Improved mobility
- Higher surface area
- Uniform leaf coverage
- Improve pesticide utilization
- Nano-formulations improve adhesion of droplets to plant surface
- Eco-friendly approach

# Nano-fertilizers

## Definition

- Nano-fertilizers are nutrient carriers of Nano-dimensions capable of holding bountiful of nutrient ions due to their high surface area and release it slowly and steadily that commensurate with crop demand
- Nutrient use efficiencies of conventional fertilizers hardly exceed 30-35 %, 18-20 % and 35-40 % for N, P and K respectively. The data remain constant for the past several decade

- Nano particles have extensive surface area and capable of holding abundance of nutrients and release it slowly and steadily such that it facilitates uptake of nutrients matching the crop requirement without any associated ill effects of customized fertilizer inputs.
- Encapsulation of fertilizers within a nano particle is one of these new facilities which are done in three ways :
  - The nutrient can be encapsulated inside nanoporous materials
  - Coated with thin polymer film
  - Delivered as particle or emulsions of nano scales dimensions
- In addition, nanofertilizers will combine nano devices in order to synchronize the release of fertilizer-N and -P with their uptake by crops, so preventing undesirable nutrient losses to soil, water and air via direct internalization by crops, and avoiding the interaction of nutrients with soil, microorganisms, water, and air.
- Types of nano devices available are:
  - Nano-porous zeolites
  - Controlled release nano fertilizers

## Advantages related to transformed formulation of conventional fertilizer using technology

| Desirable Properties | Examples of Nano fertilizers-Enabled Technologies |
|---|---|
| Controlled release formulation | So-called smart fertilizers might become reality through transformed formulation of conventional products using nanotechnology. The Nano structured formulation might permit fertilizer intelligently control the release speed of nutrients to match the uptake pattern of crop. |
| Solubility and dispersion for mineral micronutrients | Nano sized formulation of mineral micronutrients may improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation and increase the bio-availability. |
| Nutrient uptake efficiency | Nano structured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production, and save fertilizer resource. |
| Effective duration of nutrient release | Nano structured formulation can extend effective duration of nutrient supply of fertilizers into soil |
| Loss rate of fertilizer nutrients | Nano structured formulation can reduce loss rate of fertilizer nutrients into soil by leaching. |

# Nano-sensors

## Definition and Types

- Nano-sensors are any biological, chemical or surgical sensory points used to convey information about nanoparticles to the macroscopic world.
- Different types include
  - Sensors using semi-conductor nanowire detection elements
  - Semi-conducting carbon nano tubes
  - Carbon nanotubes and nanowires detect bacteria and viruses
  - Nanocantilevers

# Nano-biosensors

## Introduction

- Nanobiosensor is a modified version of a biosensor which may be defined as a compact analytical device/ unit incorporating a biological or biologically derived sensitized element linked to a physico-chemical transducer
- Nanosensors with immobilized bioreceptor probes that are selective for target analyte molecules are called nanobiosensors.
- A nanobiosensor is usually built on the nanoscale to obtain process and analyze the data at the level of atomic scale
- Their applications include detection of analytes like urea, glucose, pesticides etc., monitoring of metabolites and detection of various microorganisms / pathogens.

### Characteristics of ideal biosensor

- Highly specific for the purpose of the analyses i.e. a sensor must be able to distinguish between analyte and any 'other' material.
- Stable under normal storage conditions.
- Specific interaction between analytes should be independent of any physical parameters such as stirring, pH and temperature.
- Reaction time should be minimal.
- The responses obtained should be accurate, precise, reproducible and linear over the useful analytical range and also be free from electrical noise.
- The nanobiosensor must be tiny, biocompatible, nontoxic and non-antigenic.
- Should be cheap, portable and capable of being used by semi-skilled operators.

## Constituents of Nanobiosensors

- A typical nanobiosensor comprises of 3 components; biologically sensitized elements (probe), transducer and detector

1) The biologically sensitized elements (probe) including receptors, enzymes, antibodies, nucleic acids, molecular imprints, lectins, tissue, microorganisms, organelles etc., which are either a biologically derived material or bio-mimic component that receives signals from the analytes (sample) of interest and transmits it to transducer. And such nano-receptor may play a vital role in the development of future nanobiosensors.
2) The transducer acts as an interface, measuring the physical change that occurs with the reaction at the bioreceptor/sensitive biological element then transforming that energy into measurable electrical output.
3) The detector element traps the signals from the transducer, which are then passed to a microprocessor where they are amplified and analyzed; the data is then transferred to user friendly output and displayed/stored

## Types of Nanobiosensors

- **Mechanical Nanobiosensors**: Nanoscale mechanical forces between biomolecules provide an exciting ground to measure the biomolecular interaction. This helps in the development of minute, sensitive and label free biosensors
- **Optical Nanobiosensors:** Optical biosensors are based on the arrangement of optics where beam of light is circulated in a closed path and the change is recorded in resonant frequency when the analyte binds to the resonator
- **Nanowire Biosensors:** Nanowire biosensor is a hybrid of two molecules that are extremely sensitive to outside signals: single stranded DNA, (serving as the 'detector') and a carbon nanotube, (serving as the transmitter). The surface properties of nanowires can be easily modified using chemical or biological molecular ligands, which make them analyte independent, This transduces the chemical binding event on their surface into a change in conductance of the nanowire with extreme sensitivity, real time and quantitative fashion.
- **Ion Channel Switch Biosensor Technologies:** The Ion Channel Switch (ICS) is based on a synthetic self-assembling membrane that acts as a biological switch for detecting the signals i.e. the presence of specific molecules by triggering an electrical current
- **Electronic Nanobiosensors:** Electronic nanobiosensors work by electronically detecting the binding of a target DNA that actually forms a bridge between two electrically separated wires on a microchip
- **Viral nanobiosensors:** Virus particles are essentially biological nanoparticles. Herpes simplex virus (HSV) and adenovirus have been used to trigger the assembly of magnetic nanobeads as a nanosensor for clinically relevant viruses
- **Nanoshell Biosensors:** Positioning gold nanoshells are used in a rapid immunoassay for detecting analytes within complex biological media without any sample preparation
- **PEBBLE Nanobiosensors:** Probes Encapsulated by Biologically Localized Embedding (PEBBLE) nanobiosensors consist of sensor molecules entrapped in a chemically inert matrix by a microemulsion polymerization process that produces spherical sensors in the size range of 20 to 200 nm. These nanosensors are capable of monitoring real-time inter- and intra-cellular imaging of ions and molecules.

### Role of Nano-Biosensors in Agriculture

Presently, nanomaterial-based biosensors exhibit fascinating prospects over traditional biosensors. Nanobiosensors have marked advantages such as enhanced detection sensitivity/ specificity and possess great potential for its applications in different fields including environmental and bioprocess control, quality control of food, agriculture, bio defence, and, particularly, medical applications. But here we are concerned with the role of nano biosensor in agriculture and agro-products. Some of the potential applications of nanobiosensors are listed below:

- As Diagnostic Tool for Soil Quality and Disease Assessment
- As an Agent to Promote Sustainable Agriculture
- As a Device to Detect Contaminants and Other Molecule
- As Tool for Effective Detection of DNA and Protein

# Use of Nano-technology in Agriculture

## Introduction

- Agriculture has always been the backbone of the developing countries
- Nanotechnology is now emerging and fast growing field of science which is being exploited over a wide range of scientific disciplines including Agriculture
- A smarter way for sustainable agriculture appears to be nanotechnology

## Potential applications of Nanotechnology in Agriculture

- Increase the productivity using nanopesticides and nanofertilizers
- Improve the soil quality using nanozeolites and hydrogels
- Stimulate crop growth using nanomaterials
- Provide smart monitoring using nanosensors by wireless communication devises

## Nanotechnology in tillage

- Mechanical tillage practices improve soil structure and increase porosity leading to better distribution of soil aggregates and eventually modify the physical properties of soil.
- Nanomaterials usage increase soil pH and soil structure
- It also reduces mobility, availability and toxicity of heavy metals besides reducing soil erosion
- Nanoparticles in soil reduce cohesion and internal friction besides reducing the shear strength of the soil. Reduction in adhesion of soil particles allows easy crushing of lumps with less energy

## Nanotechnology in Seed Science

- Seed is nature's nano-gift to man. It is self perpetuating biological entity that is able to survive in harsh environment on its own.
- Nanotechnology can be used to harness the full potential of seed.
- Seed production is a tedious process especially in wind pollinated crops.
- Detecting pollen load that will cause contamination is a sure method to ensure genetic purity.
- Pollen flight is determined by air temperature, humidity, wind velocity and pollen production of the crop.
- Use of nanobiosensors specific to contaminating pollen can help alert the possible contamination and thus reduces contamination.
- The same method can also be used to prevent pollen from Genetically, modified crop from contaminating field crops.
- Novel genes are being incorporated into /seeds and sold in the market.
- Tracking of sold seeds could be done with the help of nanobarcodes that are encodable, machine - readable, durable and sub-micron sized taggants.
- Disease spread through seeds and many times stored seeds are killed by pathogens.
- Nano-coating of seeds using elemental forms of Zn, Mn, Pa, Pt, Au, Ag will not only protect seeds but used in far less quantities than done today.
- Technologies such as encapsulation and controlled release methods have revolutionized the use of pesticides and herbicides. Seeds can also be imbibed with nanoencapsulations with specific bacterial strain termed as Smart seed.
- It will thus reduce seed rate, ensure right field stand and improved crop performance.
- A smart seed can be programmed to germinate when adequate moisture is available.
- Coating seeds with nanomembrane, which senses the availability of water and allow seeds to imbibe only when time is right for germination, aerial broadcasting

of seeds embedded with magnetic particle, detecting the moisture content during storage to take appropriate measure to reduce the damage and use of bioanalytical nanosensors to determine ageing of seeds are some possible thrust areas of research.

- Carbon nanotubes (CNTs) can also be used as new pores for water permeation by penetration of seed coat and act as a passage to channelize the water from the substrate into the seeds. These processes facilitate germination which can be exploited in rainfed agricultural system.

## Nanotechnology in Water Use

- Water purification using nanotechnology exploits nanoscopic materials such as carbon nanotubes and alumina filters for nanofiltration
- It utilizes the existence of nanoscopic pores in zeolite filtration membranes, nanocatalysts and magnetic nanoparticles
- Carbon nanotube membranes and Nanofibrous alumina filters can remove almost all kinds of water contaminants including turbidity, oil bacteria, viruses and organic contaminants

## Nanotechnology in Fertilizers

- Fertilizers have played a pivotal role in enhancing the food grain production in India
- Despite the resounding success in grain yield, it has been observed that yields of many crops have begun to stagnate as a consequence of imbalanced fertilization and decline in organic matter content of soils.
- Excessive use of nitrogenous fertilizer affects the groundwater and also causes eutrophication in aquatic ecosystems.
- A disturbing fact is that the fertilizer use efficiency is 20-50 per cent for nitrogen and 10-25 per cent for phosphorus.
- Elimination of eutrophication and drinking water with possible build up of nutrients in soil is possible only by adoping nano fertilizers an emerging alternative to conventional fertilizers
- Additionally, nano-technology has improved nutrient use efficiency,and minimize costs of environmental protection.
- Slow-release of nano-fertilizers and nanocomposites are excellent alternatives to soluble fertilizers. Nutrients are released at a slower rate throughout the crop growth; plants are able to take up most of the nutrients without any waste.
- Slow release of nutrients in the environments could be achieved by using zeolites that are a group of naturally occurring minerals having a honeycomb-like layered crystal structure. Its network of interconnected tunnels and cages can be loaded with nitrogen and potassium, combined with other slowly dissolving ingredients containing hosphorous, calcium and a complete suite of minor and trace nutrients. Zeolite acts as a reservoir for nutrients that are slowly released “on demand.”
- Fertilizer particles can be coated with nanomembranes that facilitate slow and steady release of nutrients.
- The Nano-composites being contemplated to supply all the nutrients in right proportions through the “Smart” delivery systems also needs to be examined closely.
- Currently, the nutrient use efficiency is low due to the loss of 50-70% of the nitrogen supplied in conventional fertilizers.
- Encapsulation of fertilizers within a nanoparticle is one of these new facilities which are done in three ways
  a) the nutrient can be encapsulated inside nanoporous materials,
  b) coated with thin polymer film
  c) delivered as particle or emulsions of nanoscales dimensions

# Nanotechnology in Plant protection

- Persistence of pesticides in the initial stage of crop growth helps in bringing down the pest population below the economic threshold level and to have an effective control for a longer period. Hence, the use of active ingredients in the applied surface remains one of the most cost-effective and versatile means of controlling insect pests.
- To protect the active ingredient from the adverse environmental conditions and to promote persistence, a nanotechnology approach, namely "nano-encapsulation" can be used to improve the insecticidal value.
- Nanoencapsulation comprises nano-sized particles of the active ingredients being sealed by a thin-walled sac or shell (protective coating).
- Nanoencapsulation of insecticides, fungicides or nematicides will help in producing a formulation which offers effective control of pests while preventing accumulation of residues in soil.
- In order to protect the active ingredient from degradation and to increase persistence, a nanotechnology approach of "controlled release of the active ingredient" may be used to improve effectiveness of the formulation that may greatly decrease amount of pesticide input and associated environmental hazards.
- Nano-pesticides will reduce the rate of application because the quantity of product actually being effective is at least 10-15 times smaller than that applied with classical formulations, hence a much smaller than the normal amount could be required to have much better and prolonged management.
- Recently,clay nanotubes (halloysite) have been developed as carriers of pesticides at low cost, for extended release and better contact with plants, and they will reduce the amount of pesticides by 70-80%, thereby reducing the cost of pesticide with minimum impact on water streams.

# Nanotechnology in Weed Management

- Multi-species approach with single herbicide in the cropped environment resulted in poor control and herbicide resistance
- Continuous exposure of plant community having mild susceptibility to herbicide in one season and different herbicide in other season develops resistance in due course and become uncontrollable through chemicals
- Developing a target specific herbicide molecule encapsulated with nanoparticle is aimed at specific receptor in the roots of target weeds, which enter into roots system and translocated to parts that inhibit glycolysis of food reserve in the root system. This will make the specific weed plant to starve for food and gets killed
- In rainfed areas, application of herbicides with insufficient soil moisture may lead to loss as vapour so controlled release of encapsulated herbicides is expected to take care of the competing weeds with crops.
- Now a days, adjuvants for herbicide application are currently available that claim to include nanomaterials.
- Excessive use of herbicides leave residue in the soil and cause damage to the succeeding crops. continuous use of single herbicide leads to evolution of herbicide resistant weed species and shift in weed flora.
- For example, Atrazine, an s-triazine-ring herbicide, is used globally for the control of pre-and postemergence broadleaf and grassy weeds, which has high persistence (half life-125 days) and mobility in some types of soils. Residual problems due to the application of atrazine herbicide pose a threat towards widespread use of herbicide and limit the choice of crops in rotation.
- To remediate the atrazine residue from soil within a short span of time, application of silver modified with nanoparticles of magnetite stabilized with Carboxy Methyl Cellulose (CMC) nanoparticles recorded 88% degradation of herbicide atrazine residue under controlled environment found to be a potential remedy.