Application of Nanotechnology in Crop Pest Management

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Amar Singh, Ajay Kumar Sood, Ashwani Kumar Basandrai
Ranbir Singh Rana, Somya Hallan, Diksha Sinha
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CAAST, NAHEP, ICAR-WORLD BANK PROJECT ON PROTECTED AGRICULTURE AND NATURAL FARMING CSK HPKV, PALAMPUR, HIMACHAL PRADESH

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Preface

Food safety and environmental protection are parallel pillars of sustainable agriculture. Agriculture needs to innovate and modernise the technology to meet the increased food demands of the world for sustaining the expanding population along with maintaining environmental sustainability. In this context, nanotechnology is an emerging arena with the aim to deliver products with reduced phytotoxicity, improved shelf-life and healthier greener environmental impact. Nano particles may have immense uses for plant disease and insect-pest management. The nano particles may be used alone as protectants or as nano carriers for pesticides in precise disease and pest diagnosis through nano-sensors. Nano particles have several potential benefits. However, it is still less explored area and very few nano particle-based products have been commercialized for agricultural application in general and plant protection in particular. Moreover, this field is less explored in India for pest management as compared to other industries. Hence, to harness the potential of nano technology for plant protection, it is pertinent to understand the basis and gaps in research to facilitate the development of plant protection nano-products commercially.

Keeping this in view, a training-cum-webinar on '**Application of Nanotechnology in Crop Pest Management'** was organized on 14-15, October 2022 under the auspices of Centre for Advanced Agricultural Science and Technology (CAAST) on Protected Agriculture and Natural Farming (PANF)` under ICAR-NAHEP at CSKHPKV, Palampur. The main objective of the event was to create an understanding amongst the postgraduate students, faculty, researchers and extension personnel of SAUs and ICAR institutes about the issues and concerns pertinent to understanding and application of nano technology in pest management. Moreover, it was an endeavour to ignite the young brains to understand application of nano technology to meet plant protection needs and to take up research and developmental initiatives to harness the benefits of this novel technology. The training was conducted in online and offline hybrid mode. In all, 162 participants from 7 states covering 15 SAUs and ICAR institutes participated in it. Fifty candidates attended the training in off line mode and six learned experts shared their knowledge and experience to further augment the quality of research in the thematic area.

The effort has been done to compile the lectures in a book comprising six chapters featuring the concepts and applications of nano technology in crop pest management. The aspects comprised: Basic concept of nanotechnology in agriculture and plant protection; Development and role of nano-pesticide in pest diagnosis and management; and Future prospects of nano-pesticides. This book is expected to be of great significance to the students and of course to the teachers and researchers engaged in application of nano technology in crop protection.

It is our immense pleasure to express deep sense of gratitude and sincere thanks to Prof. H.K. Chaudhary, Hon'ble Vice Chancellor, CSKHPKV, Palampur,

and Dr. R.C. Agrawal Hon'ble Deputy Director General (Education), ICAR, our patrons, for their consistent and sustainable leadership, kind support, guidance and constant encouragement. Our heartfelt thanks are due to Dr. (Mrs.) Anuradha Agrawal for her keen interest, active co-operation and ever willing help in successful conduct and completion of the training programme. Cooperation received from Deans and Directors of the university as well as Head of Department of Plant Pathology and Department of Entomology is sincerely acknowledged. The successful conduct and completion of the webinar is due to timely delivery of the lectures by able experts and submission of the write up which could be transformed in the form of present book for the benefit of stakeholders. Various committees and project staff especially Er. Shakiv Pandit and Dr. Sachin Kaushal made tireless efforts to make the training-cum-webinar a great success and their contribution is gratefully acknowledged for their efforts in successful execution of various training related activities.

The financial help rendered by ICAR through World Bank funded project 'Centre for Advanced Agricultural Science and Technology (CAAST) on Protected Agriculture and Natural Farming (PANF)' under ICAR-NAHEP at CSKHPKV, Palampur is gratefully acknowledged.

Editiors

Vice- Chancellor
CSK Himachal Pradesh Agricultural University
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FOREWORD

As we enter the third millennium with more than six billion people, we are confronted with an hercules task of providing environmental and food security to the increasing population, especially in the developing countries. This calls for reorientation of strategies to minimize the use of external inputs in agriculture and depend more on effective and eco-friendly approaches to sustain food production without causing imbalance in ecosystem. United Nations sustainable development goals require transition to a more sustainable future by implementing novel techniques to increase agricultural productivity through sustainable agriculture and nanotechnology has great potential to fulfil this goal. In crop protection, there is greater emphasis on nano-pesticides, nano-herbicides, agrochemical encapsulated smart nano-carriers and nano-biosensors with an aim to minimize inputs and enhance the efficiency of agro-chemicals thereby offering means to maintain the long-term development of agro-ecosystems.

Keeping this in view, a training-cum-webinar was organized on the topic, “Application of Nanotechnology in Crop Pest Management” on 14-15, October, 2022 under the aegis of ICAR-NAHEP-CAAST-PANF at CSKHPKV, Palampur. In all, 212 participants from seven States, covering fifteen SAUs and ICAR institutes, participated in the webinar in on-line/off-line mode. The event brought together six highly accomplished experts with diversified backgrounds across the country who have pondered upon the break through in research towards nano-drivern shift in crop protection practices.

I appreciate the efforts of Dr R S Rana and his team who have compiled these contributed lectures in a book form with the title “Application of Nanotechnology in Crop Pest Management”. Certainly, the book will serve as an important document for the stakeholders viz. students, teachers and researchers engaged in nano-technology in crop protection and will ignite the interest among the students to explore this new emerging field.

Prof. HK Choudhary

FOREWORD

Academic excellence in Agricultural Higher Education system in India is the need of the day. It may be attained by enhancing professional competence of faculty and to create world class infrastructure and laboratory facilities for the Post Graduate students of the State Agricultural Universities. ICAR has embarked upon an ambitious step to fulfil this objective by launching ICAR, National Agricultural Higher Education Project (NAHEP) jointly with the support from World Bank and Government of India. Under this prestigious project, the CSK Himachal Pradesh Krishi Vishvavidyalaya, Palampur was sanctioned the Centre for Advanced Agricultural Science and Technology (CAAST) on Protected Agriculture and Natural Farming (PANF) during 2019-20 with financial outlay of Rs.1891.05 lacs. The university is indebted to ICAR for this. The project has been instrumental in augmenting the institutional capacity for globally competitive professionals in protected and natural farming. It has strengthened the Higher Agricultural Education System (post-graduation) to enhance the quality of human resources, equipped with skill and entrepreneurship in PANF to meet future challenges and has become the knowledge leader on it. The project has also the mandate to study the new endeavours pertaining to theme and improve the teaching and learning process. The project will help to strengthen linkage between university and international research institutes, ensuing greater possibility for the students to be entrepreneurs and generate employment.

The importance of natural farming is evidenced by its adoption by a large number of farmers in the country. In Himachal Pradesh, a huge number of women farmers have adopted natural farming. Natural farming has great mitigation potential of climate change also.

The present book entitled, '**Application of Nanotechnology in Crop Pest Management'** has been compiled based on the lectures delivered by various experts during the national training-cum- webinar on 'Application of Nanotechnology in Crop Pest Management' under the auspicious of ICAR-NAHEP-CAAST-PANF by the Department of Plant Pathology and Department of Entomology. I appreciate the efforts of Dr Ashwani Kumar Basandrai (Consultant), Dr Ajay Sood and Dr. Amar Singh (CPI, Crop Protection) and the entire team for compiling and editing this useful publication and congratulate them. I am highly indebted to

Dr. HK Chaudhary, Honorable Vice Chancellor for his evergreen support. On behalf of CSKHPKV Palampur, I am highly grateful to Dr RC Agrawal, DDG (Edu) cum National Director, NAHEP, ICAR and National Coordinator, Dr Anuradha Agrawal for their constant encouragement and monitoring of the project activities for its successful execution.

The financial assistance by the ICAR, NAHEP and World Bank Project to bring out this publication is gratefully acknowledged

Dr Ranbir Singh Rana
(Principal Investigator)

1. Synthesis, characterization techniques and applications of nano-materials

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Abstract: Nano materials are unique class of materials with special physical, chemical and biological properties, by virtue of which they inherit varied practical applications. The nano materials can be organic or inorganic-based as well as composite. Synthesis methodology plays an important role to decide and control the size and surface area of nano particles. The nano particles are synthesized following bottom-up or top-down approaches. In the recent years, biosynthesis of nano particles using microbes, bacteria, fungi, plant extracts, etc. is gaining momentum and the resultant products are non-toxic and biodegradable. The biological methods for the synthesis of nano particles are simple, easy and possess unique and enhanced properties and find its way in biomedical applications. Technological advancements in the field of nano technology have the significant potential to produce products with considerable better functionalities. Nano materials and nano material-based composites have applications in various fields i.e. medicine (diagnosis and drug delivery), as catalyst, sensor and biosensors, in fuel cell applications, electronic devices, water treatment, agriculture, construction industry etc. Presently, nano materials have become important constituents in various products like scratch-resistant paints, surface coatings, electronics, cosmetics, environmental treatment processes, sports items, sensors, energy storage devices, power magnets, longer-lasting medical implants etc.

Introduction

Nano materials have gained high impact due to their unique physical, chemical and biological properties and various practical applications (Baig et al., 2021; Jeevanandam et al., 2018). Materials having their dimensions between 1 to 100nm are referred to as nano materials. Human beings identified asbestos nanofibers 4500 years ago. Chemical processes have been used about 4000 years ago by ancient Egyptians to synthesize PbS nano particles for hair dyes. These materials have natural origin and are produced by different natural processes like wildfires, weathering, volcanic eruption etc. (Sharma et al., 2020). Nano materials show different physio-chemical properties in comparison to bulk materials (Kolahalam et al., 2019). The concept of nano technology was proposed by Richard Feynman in 1959 and gave the idea of developing machines to the molecular level (Wu & Yu, 2017). The term 'nano technology' was first used by Norio Taniguchi in 1974. Nano technology involves the synthesis, creation, characterization and application of nano materials. The term 'nano' is a Greek word which means dwarf or very small with value equal to one thousand millionth of a meter (10^{-9} m). Nano materials have varied application in electronic devices, food industry, cosmetics, medicines, environment, sports and batteries (Bayda et al., 2020). The nano materials can be categorized on basis of their size into

a) Zero dimensional in which all three dimensions are in nanoscale (quantum dots)
b) One-dimensional in which any one dimension is outside the nanoscale (quantum wires)
c) Two-dimensional in which any two dimensions are outside the nanoscale
d) Three-dimensional in which none of the dimension is in nanoscale

1. Terms related to nano materials:

The terms related to nano materials are debateable and explicit. Researchers use these terms according to the requirement due to the lack of exact definitions. It is difficult to find out single definition to the terms related to the nano materials. Some of the definitions related to nano materials are given in Table 1.1.

Table 1.1 Terms related to nanomaterials

Term	Definition	Reference
Nanotechnology	It refers to the development of materials, devices by controlling the shape and size of matter at nanoscale.	Kreyling et al., (2010)
Nanoscale	A scale between 1 to 100nm.	Jeevanandam et al.(2018)
Nanomaterials	The material in which one or more dimensions of a particle are in size ranging from 1 to 100nm.	Baig et al.(2021)
Nanoparticles (Nps)	Particle with all the dimensions in nano range.	Baig et al. (2021)
Aspect ratio	Ratio of length (major axis) and width (minor axis) of nanoparticle.	Murphy & Jana (2002)
Nanosphere	Nanoparticle with aspect ratio of 1.	Murphy & Jana (2002)
Nanorods	In which both the axis has different lengths with aspect ratio greater than 1 but less than 20.	Murphy & Jana (2002)
Nanowires	These are similar to nanorods with higher aspect ratio.	Murphy & Jana (2002)
Nanofibers	The fibres with diameter in nanometre i.e. ranging between 10 to 100 nm and two dimension is in nano range while the third dimension is significantly larger.	Soltani et al. (2020)
Nanotubes	Nanoscale tube like structured material.	Venkataraman et al. (2019)
Nanocomposites	Multiphase material having one dimension of at least one phase in nano-range.	Baig et al. (2021)

2. Types of nano materials

2.1. Inorganic nano materials

Inorganic based nano materials include different metal and metal-oxide nano materials. Reducing or oxidizing/precipitating agents are added during the synthesis of metal and metal oxide nano particles, respectively and their surface, optical, thermal and electrical properties differ from their original bulk components in many ways (Rastogi et al., 2017).

2.1.1 Metal based nanoparticles: Metal-based NPs are synthesized using metals either through destructive or constructive ways. Pure metal nanoparticles are formed using metal precursors. Shape, facet and size affect the synthesis of metal precursors (Ijaz et al., 2020) and metal-based inorganic nanomaterials are silver (Ag), gold (Au), aluminium (Al), cadmium (cd), copper (Cu), iron (Fe), zinc (Zn) and lead (Pb) nanomaterials (Anonymous, 2021). Constrained surface plasmon resonance (SPR) gives these nanoparticles their distinctive opto-electrical properties (Aziz et al., 2019).

2.1.2 Metal oxide-based nanoparticles: Various metal oxide-based nano materials are zinc oxide (ZnO), copper oxide (CuO), magnesium aluminium oxide ($MgAl_2O_4$), titanium oxide (TiO_2), cerium oxide (CeO_2), iron oxide (Fe_2O_3), silica oxide (SiO_2) etc. (Makvandi et al., 2020). Metal oxide nanoparticles have the unique optical characteristics such as UV absorption, colour absorption in the visible spectrum and photo-luminescence (Rafiq et al., 2022).

2.1.3 Ceramic nano particles: Ceramic NP s are prepared from both metal and non-metals. The main constituents of ceramic nano particles include metal and metalloid oxides, carbides, phosphates and carbonates such as calcium, titanium, silicon etc. They have wide range of uses and offer a lot of advantageous characteristics such as excellent heat resistance and chemical inertness (Thomas et al., 2015). These characteristics make them useful in photocatalysis, imaging applications, photo-degradation of dyes and chemical processes (Bhardwaj et al., 2021). There are many methods to produce ceramic nano particles including co-precipitation (PPT) in reverse micelles, sol-gel chemistry, micro-emulsion, hydrothermal or solvo-thermal, template, bio-mimetic synthesis, chemical vapour deposition (CVD), surface derivatization and many more (Sigmund et al., 2006).

2.2 Carbon-based nano materials

Carbon nanomaterials, with remarkable and unique optical, chemical, mechanical and thermal capabilities, have a great potential in a numerous cutting-edge applications including electronics, batteries, capacitors, waste water treatment, heterogeneous catalysis, and medical field (Onyancha et al., 2022). Carbon-based nano materials comprise fullerenes, graphene and its derivatives, carbon nanotubes, nanodots, nanodiamonds etc. (Bhattacharya et al., 2016).

2.2.1 Fullerenes: After graphite and diamond, fullerene is the third allotropic form of carbon. It was discovered in 1985 by Harold W. Kroto, Robert F. Curl and Richard E. Smalley. Fullerene has an icosahedral symmetrically closed-cage structure which is made up of 20 hexagons and 12 pentagons, where each carbon atom is connected via sp^2 hybridization to three other carbon atoms. Fullerene is known as Buckminsterfullerene because of its resemblance to a structure designed by American architect Richard Buckminster Fuller. Fullerene is also known as buckyball because it is a molecule with 60 carbon atoms (C_{60}) arranged in the form of a soccer ball. Fullerene crystallizes as molecule structures and can be thought of as a zero-dimensional carbon structure, in contrast to the atom-based crystals of graphite or diamond which have atom configurations. The findings revolutionized the study of new carbon allotropes and nano-structured materials and the researchers were awarded the 1996 Nobel Prize in chemistry. Fullerenes act as electron-deficient alkene;therefore, react with entities that donate electrons. Its geodesic structure and electronic bonds give it its molecular stability. Excellent mechanical qualities allow fullerenes to withstand high pressures and maintain their original shape even after being exposed to pressures of more than 3000 atm. Fullerenes have numerous uses, but currently its most prominent use is being made in organic solar cells. It can also be used in medicine and pharmaceuticals as antibacterial agents and neuroprotective medications. Fullerenes are also anti-oxidants that interact with free radicals to prevent cell damage or its death (Siqueira & Oliveira, 2017).

2.2.2. Carbon nanotubes: Carbon nanotubes (CNTs) are flexible allotrope of carbon having cylindrical and long tube-like structure consisting of rolled up sheets of graphene. Carbon nanotubes (CNTs) are of two types i.e. single walled carbon nanotubes (SWCNTs) formed of single carbon atom layer with 3 nm diameter and multiwalled carbon nanotubes (MWCNTs) formed by several nanotubes joined together with diameter exceeding 100nm. MWCNTs have higher mechanical strength compared to SWCNTs due to the existence of multilayers of carbon atoms. CNTs are having better tensile strength and young's modules than the metals like iron, steel and other similar materials. CNTs are widely used in mechanical, chemical, electrical and biological technology with common applications in energy storage, electrochemical processes and vacuum electronics. CNTs can be made via hydrothermal processes and thermal methods including chemical vapour deposition (CVD) and plasma-based procedures like discharge and laser ablation. Out of all traditional techniques used to make CNTs, CVD is the most favoured since it can create CNTs in a variety of shapes including powder, straight, coiled etc. (Rao et al., 2021).

2.2.3 Graphene: Graphene is a fundamental building component of other graphitic forms such as fullerenes, graphite and carbon nanotubes (CNTs). Graphene is composed of single layer of carbon atoms in a densely packed honey comb two-dimensional lattice. It can be layered to create 3D graphite and rolled to create 1D CNTs. It can be wrapped into a spherical fullerene by adding pentagons. Thus, graphene can be considered as the origin of all graphitic materials (Zhang et al., 2013). Graphene has been actively explored in many sectors since its discovery in 2004 (Patel et al., 2019). Excellent mechanical stiffness and high thermal stability are of the unusual physical characteristics of graphene. Additionally, this carbon allotrope's electric characteristics are fundamentally distinct from those of three-dimensional materials. Wallace examined the electrical properties of graphene in 1947. Originally used the word “graphene” was used as “graphitic intercalation compounds” (GIC) in 1987 (Maiti et al., 2019).

2.3. Organic nanomaterials

Organic nanoparticles are typically defined as solid nano particles with diameter between 10nm to 1µm, and are made up of organic compounds, primarily lipids or polymeric substances. Due to its enormous potential in various industrial field i.e., electronics, photonics, conducting materials, sensors, medicine, biotechnology etc. such type of nano particles have experienced significant growth and in-depth research over the past decades (Brayner et al., 2013). Organic-based materials are formed from organic materials, eg. dendrimers, cyclodextrin, liposome and micelle. These nanoparticles are bio-degradable, non-toxic, and some like micelles and liposomes, have hollow centres that are referred to as nano capsules. These nanoparticles are sensitive to electromagnetic radiation, including heat and light (Ealias & Saravanakumar, 2017).

2.3.1. Dendrimers: “Dendrimers” are synthetic nanoparticles having radially symmetric molecules and a well-defined covalent macromolecule structure with tree like branches. The periphery, the interior, and the core are the three separate zones that make up a normal dendrimer (Gitsov & Lin, 2005). Dendrimers are first discovered by Donald Tomalia et al. in early 1980s. Dendrimers with hydrophobic end groups are soluble in non-polar solvents while dendrimers with hydrophilic end groups are dissolved in polar solvents (Klajnert & Bryszewska, 2001). Two main synthetic approaches can be used to produce dendrimers.

a. The divergent approach which multiplies the number of peripheral groups by attaching branching unit to the core molecule
b. In convergent approach entire dendrimer is produced starting from outside towards center or core of the molecule (Vögtle et al., 2000)

Dendrimers can be easily changed to function as highly specific binders of various biological substances due to their special features that allow them to react to changes in solvent conditions. Dendrimers can be customized or altered to create bio-compatible molecules with favourable cyto-toxicity and bio permeability. Additionally, dendrimers are produced with few defects in structure and great purity, making them simple to analyze using methods viz. mass spectrometry, infrared spectroscopy and NMR spectroscopy (Boas & Heegaard, 2004).

2.3.2. Micelles: Micelles are a different class of nanoparticle, made from amphiphilic molecules which will form a monolayer with a hydrophobic core made up of the lipophilic tails and a hydrophilic surface made up of the hydrophilic heads exposed to the aqueous environment. These nanoparticles might be spherical, rod-shaped, or elliptical in shape. The concentration of the amphiphilic molecules must be greater than the critical micelle concentration (CMC), above which the micelles will begin to form.

2.4. Composite-based nano materials

The term "composite nanoparticles" refers to nano materials with composite structures made up of two or more nanoscale components with unique physical and chemical properties ("Encycl. Microfluid. Nanofluidics", 2013). Due to their significance in both science and technology, composite nano particles are a class of sophisticated materials that have attracted more attention recently. They have a wide range of uses including highly active and selective catalyst, metal semiconductor junctions, optical sensors and as packaging film modifiers for polymeric films (Calandra et al., 2013). In nano composites, one of the parts either has nanoscale dimensions (less than 100nm) or the composite structure shows nanoscale phase separation of the distinct constituents.

Composite nano particles are utilized in biomedical applications and in catalysis to shield particles from oxidation. Cu/Zn bimetallic nano particles i.e., have an antibacterial impact by altering the permeability of bacterial membranes due to zinc ions and oxidizing them due to copper ions. Similarly, Fe/Ag particles form a galvanic pair that contributes to the dissolution of nano particles, the generation of ions, and improved anti-cancer characteristics (Nomoev et al., 2019).

3. Properties of nanoparticles

3.1 Mechanical properties

Nano particles have unique properties, different from the microscopic and bulk particles. Nano particles have magnificent mechanical properties due to its large surface to volume ratio and quantum effects. Mechanical properties refer to the mechanical features of materials under different environments. Different materials exhibit different mechanical properties and different mechanical properties of nano particles compelled researchers to search novel applications in the fields such as surface engineering, nano-fabrication, tribology and nano-manufacturing. Metals have numerous mechanical parameters such as brittleness, strength, plasticity, hardness, toughness, fatigue strength, elastic modulus, adhesion, friction, ductility, malleability, rigidity, and stress & strain. The technique of nano-indentation is used to measure the hardness of a small volume non-metals which are usually brittle, devoid of properties i.e. plasticity, toughness, elasticity, ductility etc. Some of the organic materials are flexible and do not possess brittleness and rigidity (Wu et al., 2020). Additionally, surface coating, lubrication and coagulation are the mechanical properties of nano particles (Guo et al., 2014).

3.2 Optical and Electronic Properties

The optical and electronic properties of nanoparticles generally show interdependent on each other. Optical properties i.e., absorption will take place when electron transition occurs between the valence band and conduction band. Metal nanoparticles and semiconductors show large change in the optical properties depending on their size and show a strong absorption UV–visible band that is not present in the spectrum of the macroscopic metal eg. colour of gold colloid changes from yellow to red with the decrease in the particle size which is due to Surface Plasma Resonance effect. At constant light photon frequency, an absorption band appears with the collective transitions of the outer electrons referred as the localized surface plasma resonance (LSPR). The outer electrons vibrate at certain wavelength and absorb light with immense molar excitation coefficient resonance. LSPR effect enhances the electric fields near the particle's surface and optical absorption has the maximum value at the plasmon resonant frequency. The wavelength of the peaks in resonance spectrum depends on the dielectric properties, shape, and size and on the internuclear spacing between the particles (Eustis & El-Sayed, 2006). As the particle size decreases, oxide-polymer nanocomposites and some semiconducting nanomaterials exhibit fluorescence and there is decrease in the wavelength i.e., show blue shift (Zou et al., 2011).

3.3 Magnetic Properties

The unique magnetic properties of nanoparticles arise due to the interaction between the negatively charged electron and the magnetic spin of the building blocks. It was reported that the nanoparticles with dimensions ranging between 10-20 nm perform well (Reiss & Hütten, 2005). The magnetic properties of nanoparticles dominated effectively. These are cheap and may be used in several applications. Magnetic properties include bioprocessing, heterogenous and homogenous catalysis, magnetic fluids, magnetic resonance imaging (MRI), biomedicine, refrigeration as well as data storage media. The unequal magnetic coupling between the building blocks and the neighbouring atoms due to large surface area to volume ratio in nanoparticles leads to different magnetic properties (Bhagyaraj et al., 2018). These properties are dependent on various synthetic methods such as co-precipitation, solvo-thermal, sputtering, thermal decomposition, flame spray and micro-emulsion (Wu et al., 2008). Iron oxide nanoparticles are widely used as magnetic nanoparticles due to their good biocompatibility, high chemical stability and low cost (Wu et al., 2019).

4. Synthesis of Nanoparticles

Synthesis methods play an important role to control the size and surface area of nanoparticles. The nanoparticles are synthesized using different approaches categorized as bottom-up or top-down approaches as depicted in Table 1.2 and Fig. 1.1 (Ealias & Saravana kumar, 2017).

Table 1.2 Nanoparticles synthesis by different methods

CATEGORY	METHODS
TOP-DOWN	Mechanical milling Nanolithography Laser ablation Sputtering Thermal decomposition
BOTTOM-UP	Biosynthesis Sol-gel Hydro-thermal Spinning Chemical Vapour Deposition (CVD) Pyrolysis

4.1. Top-Down approach

Top-down or destructive approach starts with the breaking of a solid mass into stable nanometric sized particles by applying any mechanical method. It is difficult to have control over the surface chemistry, size and structure of the nanoparticles in order to synthesize nanoparticles of desired size and shape (Bhagyaraj et al., 2018). The commonly used methods for the synthesis of nanoparticles are mechanical milling, nanolithography, laser ablation, sputtering and thermal decomposition (Ealias & Saravanakumar, 2017).

4.1.1 Mechanical milling: Mechanical milling is the most substantial top-down method used to produce various nanoparticles. It is the simplest physical method for the synthesis of nanoparticles in the form of powder. The mechanical milling is used for milling and post annealing of nanoparticles during synthesis (Yadav et al., 2012). The consequence of mechanical milling is plastic contortion that changes the shape of the particles where, cracking leads to decrease in particle size and contact welding leads to increase in particle size (Ealias & Saravanakumar, 2017).

4.1.2 Nanolithography: Nanolithography is the study of manufacturing nano-sized scale structures with at least one of the dimensions ranging between 1 to 100 nm. There are various nanolithography processes for instance optical, electron-beam, multiphoton, nanoimprint and scanning probe lithography (Pimpin & Srituravanich, 2012). Generally, lithography is the process of printing a required shape or structure on a light sensitive material and selectively removes a portion of material to create the desired shape and structure. The main advantage of nanolithography is to produce cluster from a single nano particle of desired shape and size. The disadvantages are the requirement of complex equipment and often expensive (Hulteen et al., 1999).

4.1.3 Laser ablation: In laser ablation method, nano particles are generated by irradiating high laser flux on a target lying in a gaseous or a liquid environment. The source material vaporizes during the process and nano particles are collected in the form of nano powder or a colloidal solution. The irradiation of a metal by high laser beam converts it to plasma that produces nanoparticles (Amendola & Meneghetti, 2009). Single Wall Carbon Nanotubes (SWNTs) are mostly synthesized by this method. It is a physical method that provides an alternative means for the synthesis of metal-based nanoparticles. This method is easy, operative at low temperature and rate of synthesis is faster as compared to other methods. It produces several types of nanoparticles from metals, semiconductors and polymers. Laser ablation is a green synthesis method where, non-toxic and non- hazardous precursors are used which are environment friendly (Ozay et al., 2009).

4.1.4 Sputtering: Sputtering is the removal of atoms from the surface of the target by bombarding high-energy particles. It is a widely used deposition thin film technique, used to obtain stoichiometric thin films from target materials followed by annealing (Shah & Gavrin, 2006). Sputtered atoms are deposited on the surface to form a desired layer on striking a substrate (Okazaki et al., 2008). The shape and size of the nanoparticles depends on the thickness of the layer, substrate, temperature and duration of annealing (Lugscheider et al., 1998). The main advantage of this method is that nano particles with high purity and selective size can be synthesized, this technique do not require any substrate and other chemicals. The main drawback of this method is that rate of sputtering is low and it is often expensive (Gan & Li, 2012).

4.1.5 Thermal decomposition: Thermal decomposition is a process where, the chemical decomposition by heat breaks the chemical bonds in the compound and splits into the smaller ones (Salavati-Niasari et al., 2008). A particular temperature at which an element is chemically decomposed is called the decomposition temperature. The decomposition of metal at specific temperature undergoing a chemical reaction produces nano particles and secondary products (Ealias & Saravana Kumar, 2017).

4.2 Bottom-Up approach

Bottom-up or constructive method is the fusion of material from atom to clusters and then to nano particles. The aim of this method is to gain control over the shape and size of the produced nano particles (Bhagyaraj et al., 2018).

4.2.1 Biosynthesis

Biosynthesis is a green and environment friendly approach for the synthesis of nano particles. The resultant nano particles are non-toxic and biodegradable (Kuppusamy et al., 2016). Biosynthesis uses microbes like bacteria, fungi and plant extracts etc. along with the precursors to produce nano particles. The biological methods for the synthesis of nano particles are simple, easy and have unique and enhanced properties and have biomedical applications (Saba, 2014).

4.2.1.1 Synthesis of nano materials from plants: Plants contain secondary metabolites which help in the reduction of metal ions into metal nano particles. The various functional groups are present in plants which act as capping agents in the synthesis of nano particles. Synthesis of nano particles from this process involves:

a) Collection of plant material including root, leaf, stems, bark, seed and fruit.
b) Preparation of plant extract from different parts of plants viz root, leaf, stem bark, seed, and fruit using different methods from different parts of plant.

Plant extract from leaves/ seeds: It involves the washing of plant material (leaves and seeds) with de-ionised water followed its drying in oven for few hours. Dried material will be grinded to powdered form. Specific volume of water will be added to the desired amount of powder and the mixture will be boiled for a limited time and filtered to get plant extract.

Plant extract from bark: The bark will be collected and washed with de-ionised water and chopped into small pieces and water will be added to the dried and the chopped pieces. The mixture will be boiled up to 1/3 volume and filtered to get the extract. Similarly, the extract can be prepared from other parts of the plant.

Plant extract from fruit: The fruits will be washed properly and chopped into small pieces. The seeds are remove and fruit pieces are blended by adding desired amount of water, filtered with Whatman filter paper and the extract is kept it in refrigerator for further use (Masum et al., 2019).

In this method, secondary metabolites act as reducing or stabilizing agents. The mechanism involves the reduction of metal ions to metal atoms from plant by reducing agent which after nucleation formed the stable nano particles (Keat et al., 2015). The plant extract obtained is thus used to prepare the nano particles for various applications.

4.2.1.2 Synthesis of nanomaterials from microbes: The synthesis of nano particles from microbes involves fungi, bacteria, algae, etc. The groups present in the microbes act as reducing agents which help in the formation of nano particles. Jain et al. (2020) synthesised ZnO nano particles from bacterial strains *Serratia nematodiphila*, *Xanthomonas oryzae* and from fungal strain *Alternaria alternata*. They determined the antimicrobial and photocatalytic activities of synthesised nano particles. This method is considered as green method as no toxic reducing agent is used (Jain et al., 2020).

4.2.2 Sol gel method: This method is used for the synthesis of different nano particles and nanocomposites like metal oxide nano particles. The metal alkoxide, as precursor, is dissolved in solvent like water or alcohol which forms gels by heating and stirring (Ealias & Saravana Kumar, 2017). The so obtained gel is wet in nature which is dried by using different methods and the obtained powder is calcined. This method produces homogeneous materials with good purity (Fig. 1.2). In this method, nano materials and nanocomposites can be prepared at low temperature (> 35^{o} C) whereas, this is not possible in conventional methods. Meenakshi et al. (2018) synthesised ZnO thin films using sol gel method. The solution of zinc acetate dihydrate and water was stirred for half an hour at 60^{o}C to obtain homogeneous solution. Simultaneously, solution of potassium hydroxide and ethanol is prepared and both the solutions are mixed and stirred for 2 hours at 60^{o}C to obtain the

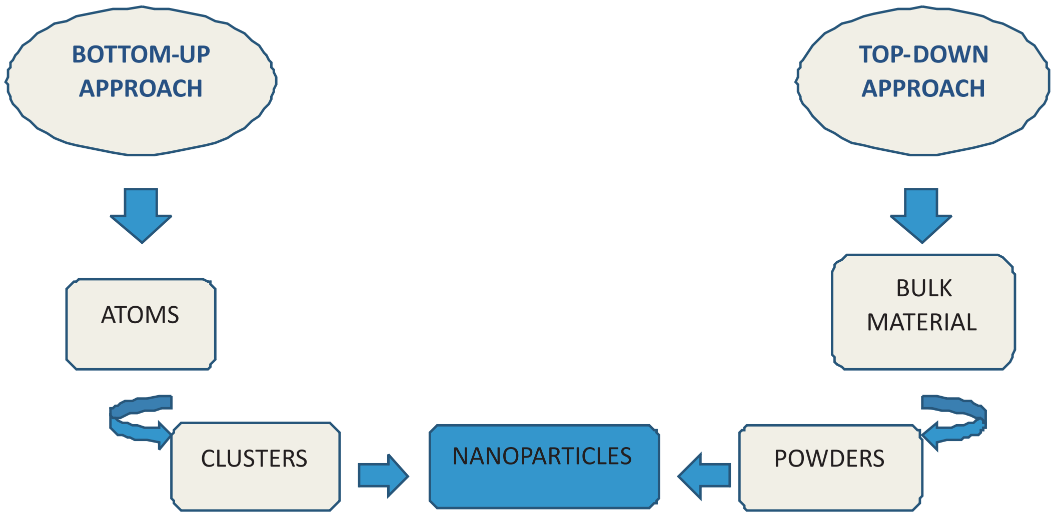


Fig. 1.1 Synthesis Process

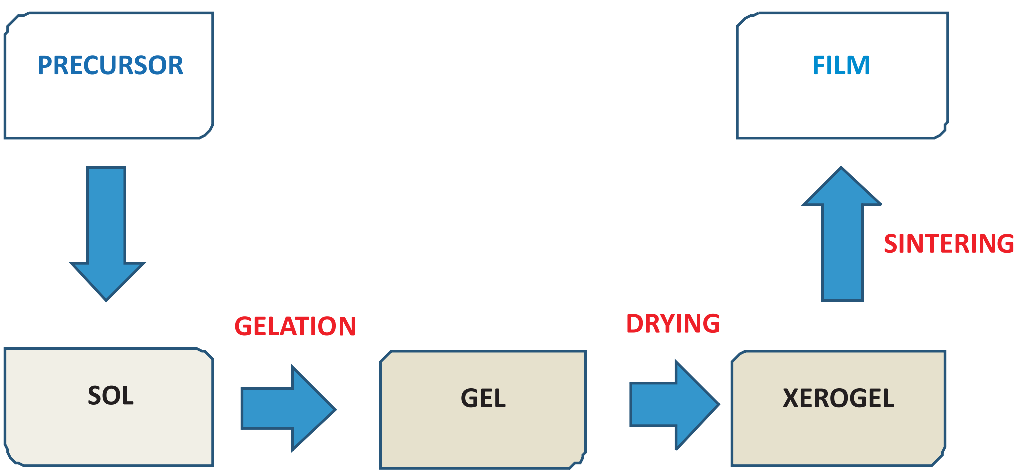


Fig. 1.2 Sol-gel methods for Nanoparticle Synthesis

homogeneous solution. This solution was kept for 24 hours and used for dip coating (Meenakshi et al., 2018).

4.2.3 Co-precipitation method: Co-precipitation method is the most convenient method for the synthesis of metal oxide nano particles in the presence of base under inert atmosphere at room temperature (Dembski et al., 2018). The base acts as the precipitating agent that helps in precipitation and for maintaining the pH of the solution. The formed nano particles are generally insoluble under high super saturation condition. The key step of this synthesis is nucleation which results into large number of nano particles. The physical properties of the resulting products are highly affected by some secondary processes which are Ostwald ripening as well as aggregation. Super saturation is the main condition for the induction of precipitation (Aacharya and Chhipa, 2020).The co-precipitation method is simple, high yielding, rapid production oriented, highly pure and involves low cost. The properties of the nano particles i.e., shape, size and composition are mainly dependent on various parameters viz. temperature, ionic strength, and pH and on the nature of basic solution. Moreover, iron oxide nano particles obtained through this method are not highly stable hence, to overcome this drawback surfactants and functionalized polymers with low molecular weight are usually used (Nawaz et al., 2018).

4.2.4 Hydro-thermal method: Hydrothermal refers to the synthesis of nano particles by chemical reactions of the substances in a sealed heated solution which are subjected to high pressure and temperature (Rane et al., 2018). The hydrothermal process has been used for the preparation of solids, such as microporous crystals, superionic conductors, chemical sensing oxides, electronically conducting solids, complex oxide ceramic and fluorides, magnetic materials and luminescence phosphorus (Rane et al., 2018). The main advantage of this method is the preparation of good quality crystals with controlled composition (Zhang et al., 2015). The temperature, pressure, pH, stability, time, concentration of reactants and size, morphology and surface chemistry will depend on the form of the nano particle to be synthesized (Zhang et al., 2015). This is an effective method for the synthesis of the least size nano particles without post annealing at relatively lower temperature which can be applied in the biological field. The hydrothermal reaction follows the mechanism of a liquid nucleation model. Highly homogeneous nano particles, single crystals, zeolites (Xia et al., 2019), oxides (Wang et al., 2019), many doped metals (Kolahalam et al., 2019), selenides and sulphides can be synthesised using this technique.

4.2.4 Spinning: Spinning is the process for the synthesis of nano particles, carried out by a spinning disc reactor (SDR). Inside the reactor a rotating disc controls the physical parameters like temperature. Nitrogen or other inert gases are filled inside the reactor to avoid any chemical reactions (Tai et al., 2007) and the disc is rotated with varying speed where, the precursor i.e., liquid and water are pumped in.

Spinning causes the atoms or molecules to combine together and their precipitation, collection and drying (Mohammadi et al., 2014). The characteristic nanoparticles synthesized from spinning disc reactor (SDR) is determined by a number of operating criteria such as the liquid flow rate, disc rotation speed, liquid/precursor ratio, location of feed, disc surface, etc. (Ealias & Saravanakumar, 2017).

4.2.5 Chemical vapour deposition (CVD): Chemical vapour deposition (CVD) is the process where, gaseous thin film reactants are deposited on the surface of substrate. The gaseous molecules are combined in a reaction chamber where the deposition is carried out at ambient temperature. These combined gases come in contact with the heated substrate and a chemical reaction takes place (Bhaviripudi et al., 2007). A thin film of product is produced on the surface of the substrate and it is collected and used. The dominating factor in CVD is the substrate temperature. The major advantages of CVD include synthesis of highly pure, uniform, hard and strong nano particles. The drawbacks of CVD are the requirement of special equipments and production highly toxic gaseous by-products (Adachi et al., 2003).

4.2.6 Pyrolysis: The most commonly used process in industries for the large-scale production of nano particles is pyrolysis. The precursor, either liquid or vapour, is burned with flame that is added through a small hole into the furnace at high pressure (Pratsinis et al., 2000). The combustion or by-product gas is then air classified to recover the nano particles. In some of the furnaces, laser and plasma is used instead of flame, to produce high temperature for easy evaporation. The advantages of pyrolysis are simple, efficient, cost effective and continuous process with high yield (D'Amato et al., 2013).

5. Characterization Techniques for Nano particles

The various characterization techniques have been depicted in Fig 1.3

5.1. SEM (Scanning electron microscopy): The SEM (Scanning electron microscopy) was developed in 1937 by Manfred Von Ardenne. SEM can reveal details about the surface topography, crystalline structure, chemical composition and electrical behaviour (*Microscopy: An Introduction*, 2000). Regular SEM works under vacuum conditions to prevent interaction of electrons with gas molecules. The SEM instrument is based on the principle that the primary electrons are ejected first from source, provide energy to the atomic electrons of the sample which can then be released as the secondary electrons (SEs). An image can be formed by accumulating these secondary electrons from each location of the specimen.

In addition, heating or supplying high energy in the range of 1-40 KeV accelerates the primary electrons generated and released from the electron gun. By using magnetic field lenses and metal slits, the released electrons are concentrated and constrained as a monochromatic beam and by using scanning coils primary electrons scan sample surface in raster scan pattern. On interaction of primary electron beam with sample surface several signals are generated. Scattering may be both elastical and inelastical depending on the sample. The atomic number, concentration of atoms, angle of incidence and incoming electrons all affect the scattering of electrons and interaction volume in the sample. Various signals produced on interaction are secondary electrons (SEs), backscattered electrons (BSE), photons (X-rays for elemental composition analysis) and visible light (cathodoluminescence). Detectors, *i.e.* electron collectors capture the signals, which the computer then manages to produce the desired image. Relevant information about the sample may be observed based on the detected signals. Secondary electrons are most significant electrons revealing sample morphology and topography whereas, backscattered electrons are used to indicate the differences in the composition of multiphase samples. For identification of elemental composition, X-rays are used by a technique called EDS (Energy dispersive spectrometer) (Akhtar et al., 2018).

Analysis of result: SEM and EDS results are shown in Fig. 1.5. Here hexagonal shape ZnO NPs were synthesised as shown in Fig. 1.4 (a). The elemental composition shows the preparation of pure ZnO NPs (Jaryal et al., 2022).

5.2. AFM (Atomic force microscopy).

IBM researchers developed the AFM in 1985. Gerd Binning and Heinrich Rohrer created the Scanning Tunnelling Microscope (STM), the forerunner to the atomic force microscopy (AFM) in 1980's and they were awarded the 1986 Nobel Prize in Physics for this work. AFM examines the sample surface and characterization of the sample is done by monitoring extremely weak interatomic interactions between the sample surface and the probe tip. The working principle is to fix one end of a micro-cantilever while the other end is brought close to the sample. This cantilever is very sensitive to weak forces therefore is effective in this technique (Fig. 1.6 a,b). Once the cantilever tip touches the sample, a very weak force which may be either attracting or repulsive exists between the probe's tip atoms and the atoms on the surface of the sample. The micro-cantilever's deformation and its state of motion are both affected by the strength of this force. The user can receive surface structure information with nanoscale resolution by scanning the sample, which uses sensors to detect these changes and gather force distribution data. AFM show three major imaging modes i.e contact mode (AFM probe maintains a steady force while maintaining a slight touch with the sample surface), non-contact mode (by detecting the atomic attraction between the probe and the sample, the surface morphology of the sample is generated) and tapping mode (intermittent contact between the probe and the sample) (Deng et al., 2018).

Analysis of sample: AFM was used to study the size and shape of silver nano particles. AFM image analysis (Fig. 1.7a) of silver nano particles with sizes ranging about 10-50nm and roughly spherical forms are displayed. The 3D perspective of the silver nanoparticles is depicted in the AFM image in Fig. 1.7b.

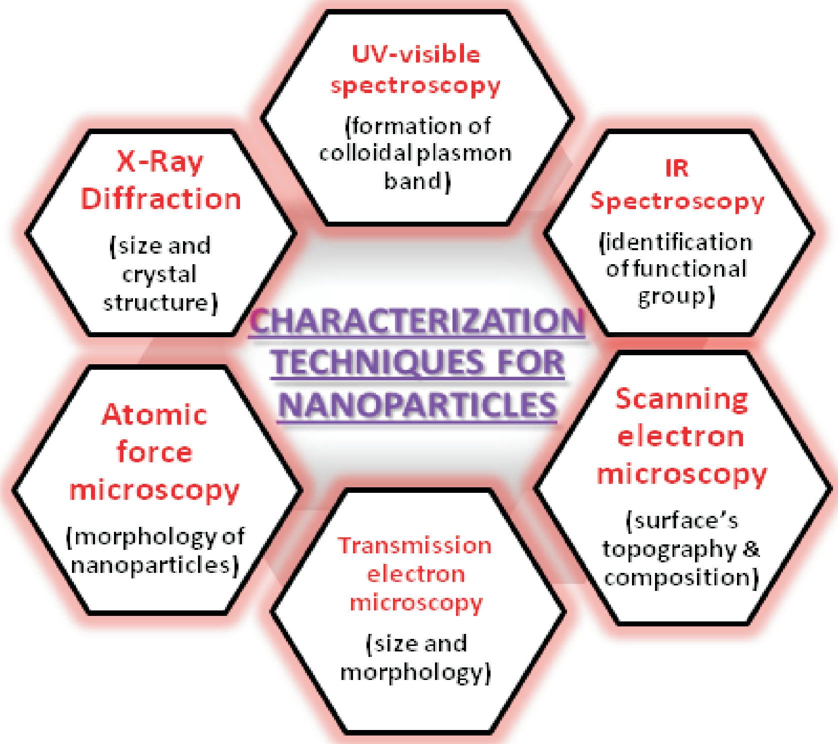


Fig. 1.3 Characterization techniques for nanoparticles

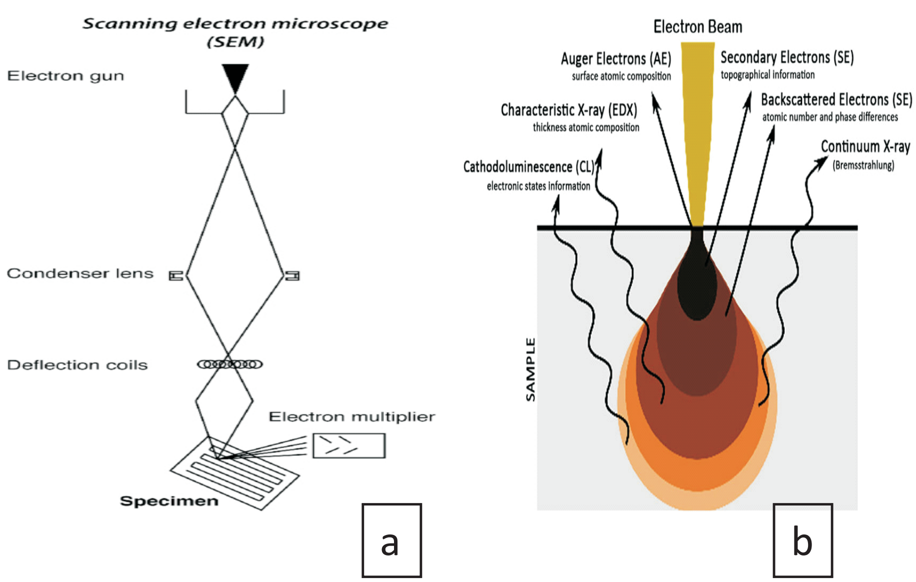


Fig. 1.4 (a) Working principle of SEM, (b) Various signals generated in SEM

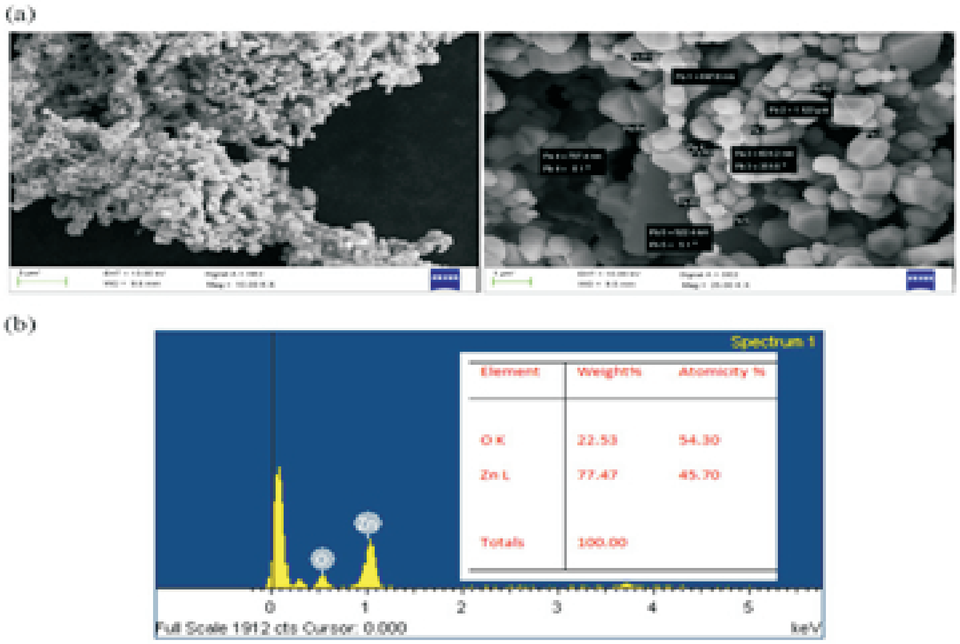


Fig. 1.5 (a) SEM images (b) EDX spectra of ZnO Nps

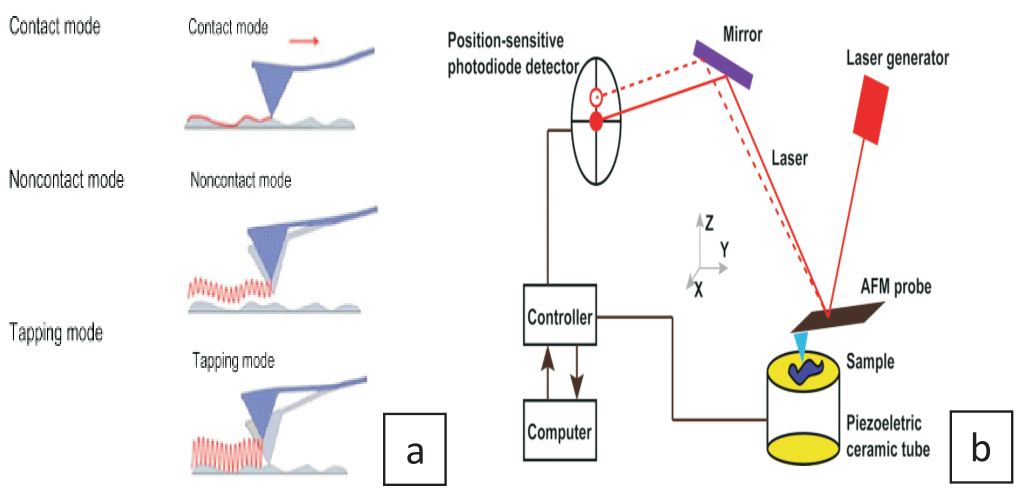


Fig. 1.6 (a) Working modes of AFM (b) Working principle of AFM

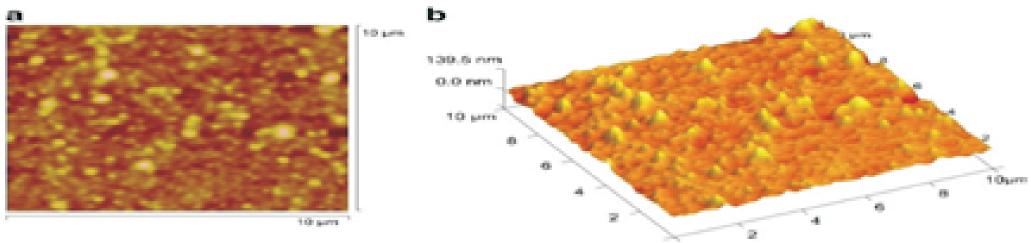


Fig. 1.7 (a,b) AFM images of silver nanoparticles

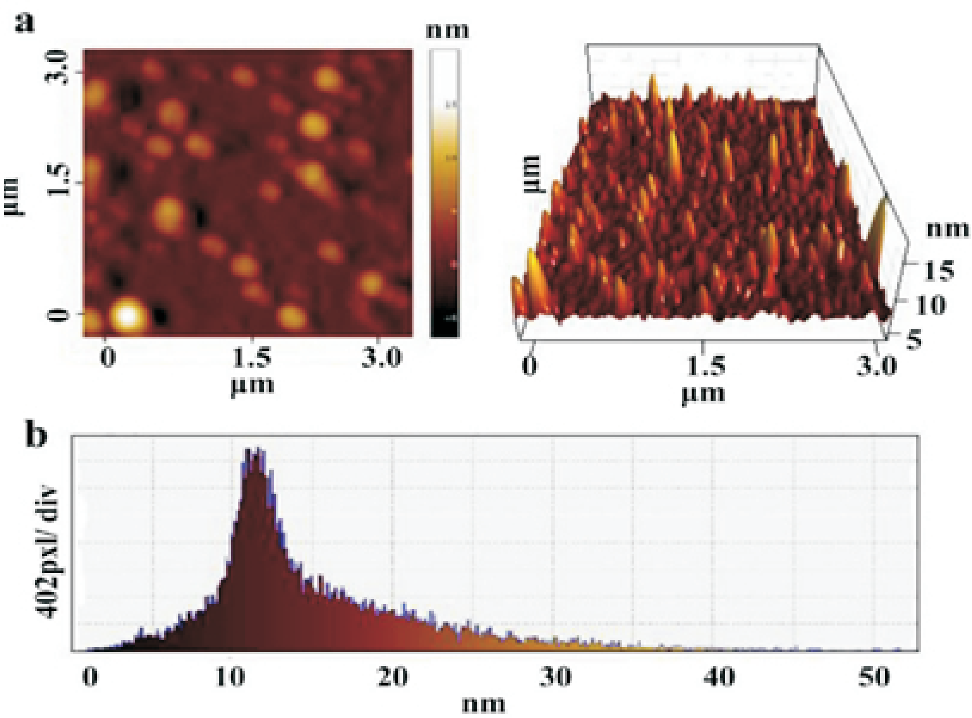


Fig. 1.8 AFM analysis image of silver nanoparticles prepared from *Sesbaniagrandiflora* extract.

Das et al. (2013) reported green synthesis approach to manufacture silver nano particles using *Sesbania grandiflora* extract. The produced silver nano particles were examined using a variety of experimental techniques. Surface morphology of silver nano particles was obtained by using AFM technique. The size of silver nano particles in the image (Fig. 1.8a) was directly observed to be in the range of 10-25nm and appears to have spherical shape. The most of the silver nano particles fell in the average range of 10-20nm, according to the size distribution of the silver nano particles shown in Fig. 1.8b.

5.3. TEM (Transmission electron microscopy).

The first TEM device was created by German physicist Ernst Ruska and electrical engineer Max Knoll (Das et al., 2013). Transmission electron microscopy (TEM) is capable of 0.1nm resolution of ultrafine sample and in the images of sample's interior structure is analysed due to the passage of electron beam through it (Rajabi et al., 2020). In TEM, a tungsten filament (cathode) is heated electrically to create a high voltage electron beam, which is attracted toward an anode (magnetic lens) and passes through the aperture, an electro-magnetic condenser, an objective lens, an intermediate lens, and finally a projector lens. A very thin specimen was passed through by the focused electron beam. The portion of the beam that was absorbed, scattered and transmitted through the objective aperture was projected by the projector lens on the fluorescent screen after being adjusted by intermediate lens. The image can be examined with the aid of an optical binocular attached to its viewing glass. Images created by transmission electron microscopes are two dimensional and monochromatic (Fig. 1.9).

Analysis of sample: TEM analysis of S-doped $TiSe_2$ nano particles was examined. S-$TiSe_2$ result is hexagonal nanoplates with an edge length of roughly 150nm, according to the TEM image (Fig.1.10b) of the material. Single crystalline plate of S-$TiSe_2$ was examined using a high-resolution TEM (Fig. 1.10c). The planes of $TiSe_2$ can be used to address the reported lattice fringes with interplanar distances of 0.17nm. The side view of the TEM image (Fig. 10d) indicated that nanoplates showed thickness of around of 15nm. The Ti, Se and S elements are uniformly distributed across the nanoplate, as was seen by the scanning TEM image and energy dispersive X-Ray spectroscopy (EDX) elemental mapping images (Subramanian et al., 2013).

5.4. UV-Visible spectroscopy.

UV spectrophotometer uses deuterium lamp (for ultraviolet region wavelength) or tungsten lamp (for visible region wavelength), sample and reference beams, detector and a monochromator. Cuvettes are used to hold samples and are exposed to UV light which produces UV spectrum. Cuvettes can be made of glass, plastic, quartz or silica cells (Fig. 1.11).

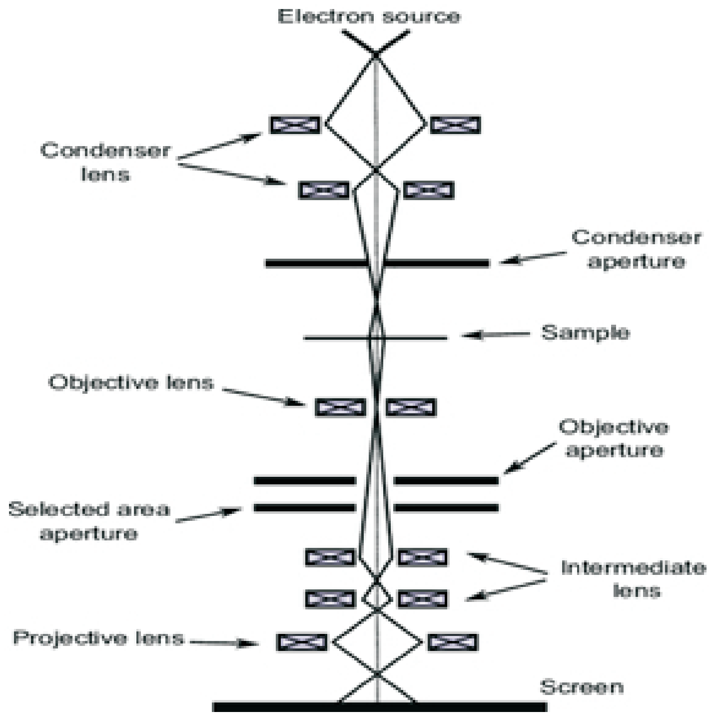


Fig. 1.9 Working principle of TEM

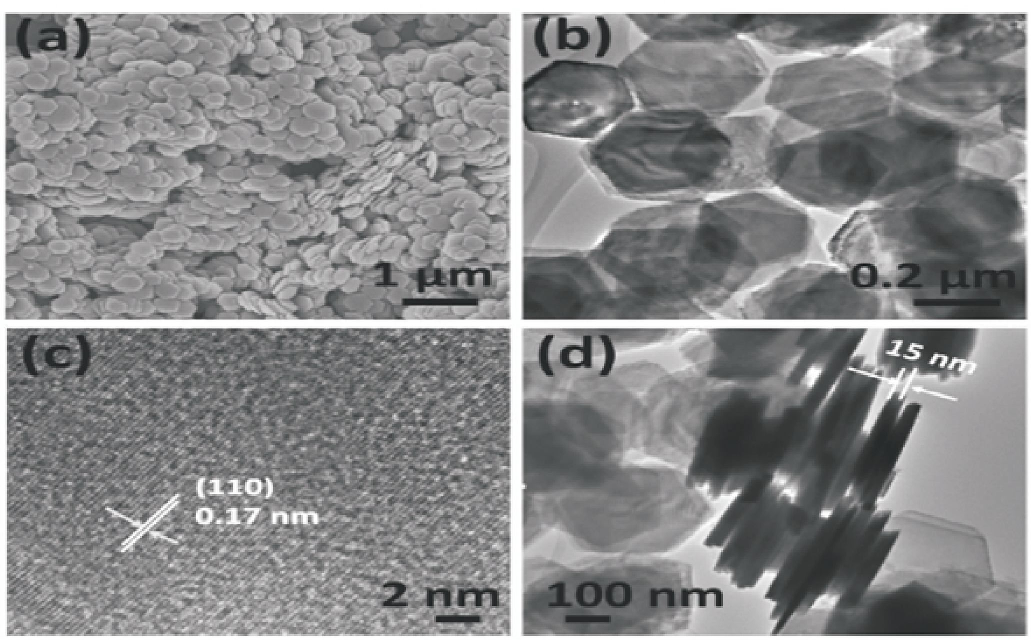


Fig. 1.10 (a) SEM image of S-$TiSe_2$ (b) TEM image of S-$TiSe_2$ (c) HRTEM image of S-$TiSe_2$ (d) Sectional TEM image of S-$TiSe_2$

The reference beam doesn't interact with the sample as it travels from the light source to the detector. The sample beam interacts with the sample, exposing it continuously to varying wavelengths of the UV light. When the radiated wavelength matches the energy level that elevates an electron to a higher chemical orbital, energy is absorbed. The detector keeps track of the contrast between the sample and reference beam intensities. A portion of the light may be absorbed when it passes through the solution but the remaining light will be transmitted through it. Transmittance is the measure of the quantity/intensity of light, at a specific wavelength enters and leaves a sample. The term "absorbance" refers to the transmittance's negative logarithm.

Beer-lambert's law: When a monochromatic beam of radiation is passed through a sample at a specific/ given wavelength then the sample's absorbance (A), is directly related to the concentration (C) of the absorbing substance as well as path length (l); $A = \mathcal{E}Cl$, where $\mathcal{E}$ = absorptivity (Yang et al., 2017).

<u>Analysis of sample:</u> The UV-visible spectrum of gold nano particle (AuNPs) synthesis is given in fig. 1.12. AuNPs are formed by the heating aqueous solution of $HAuCl_4$ with zein protein in the presence of SDS. This spectrum shows the formation of AuNPs with time and it clearly depicts that after some time all the gold salt has been converted into AuNPs with the maximum lambda value at 550nm (Titus et al., 2019).

5.5. XRD (X-Ray Diffraction).

Laue, Friedrich and Knipping's work on X-Ray diffraction (XRD) by crystals in 1912 opened up new avenues for the study of crystalline materials (Titus et al., 2019).

Working principle: A typical method for figuring out a sample's composition or crystalline structure is X-Ray diffraction. It can be used to ascertain the atomic structure of bigger crystals; including macromolecules and inorganic substances. It can determine sample composition, crystallinity and phase purity if the crystal is too tiny. In this method, X-ray beams are passed through sample and after passing the sample, the X-rays "bounce" off the atoms in the structure and alter the path of the beam at an angle, theta ($\mathcal{E}$), from the initial beam. This is known as angle of diffraction. This angle of diffraction may be used to calculate the difference between the atomic planes using the Bragg's law

$2d \sin\Theta = n\lambda$

Where; λ= wavelength, Θ=angle of diffraction and d=separation between atomic planes (Fig. 1.13). The composition or crystalline structure can thus be calculated from the spacing between atomic planes (Epp, 2016).

<u>Analysis of sample:</u> The diffractogram (Fig.1.14) of graphitic sulphur functionalized carbon nano-sheets lacks a distinct horizontal base line which demonstrates that the sample is largely amorphous in nature. A few diffraction peaks do, however appear from the baseline, indicating the existence of some crystalline

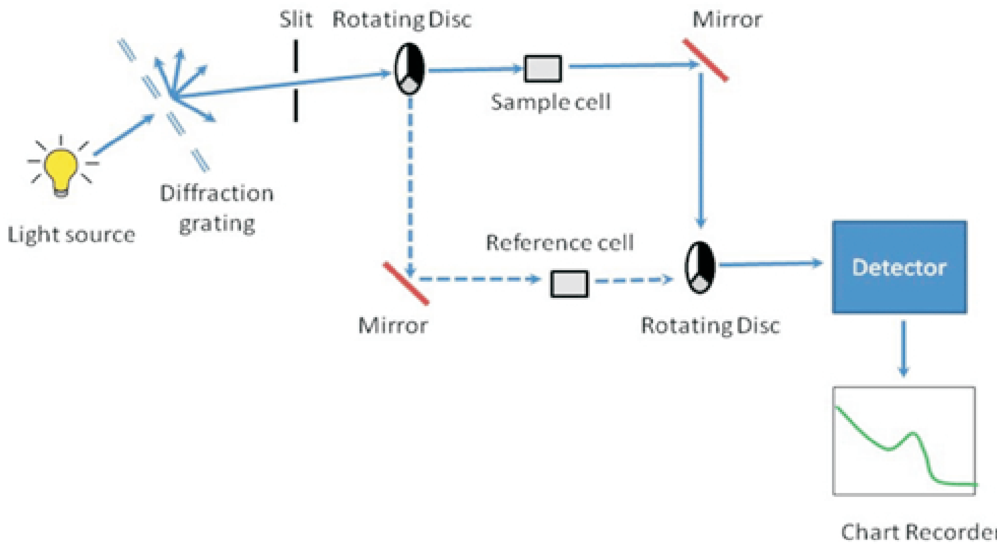


Fig. 1.11 Working principle of UV-Visible spectrometer

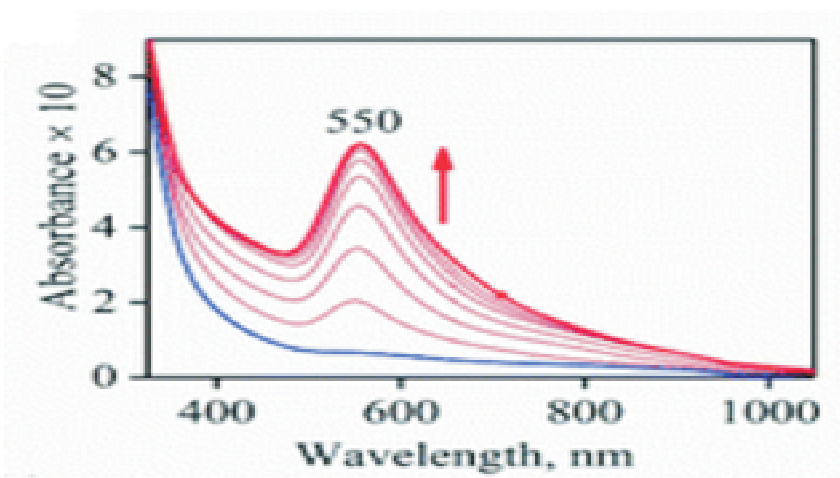


Fig. 1.12 UV-Visible spectrum of AuNPs

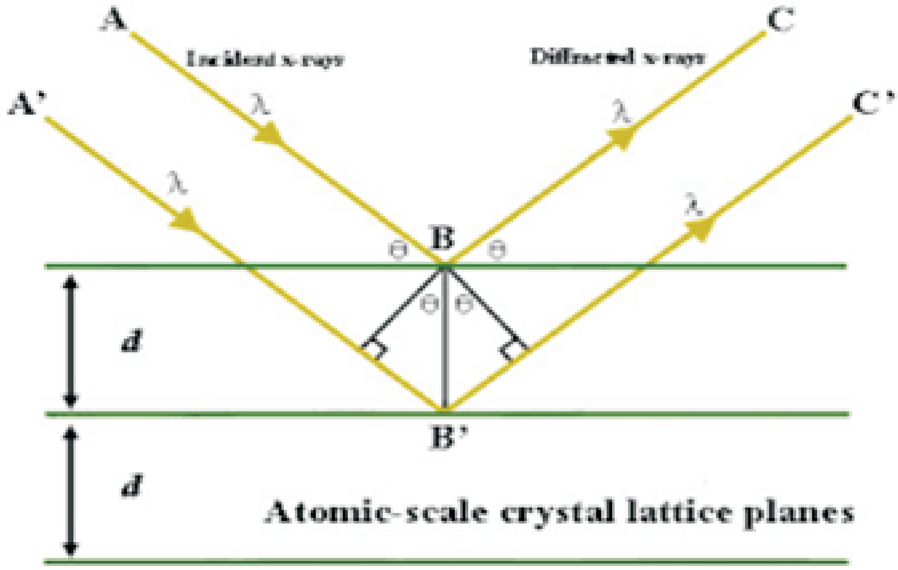


Fig. 1.13 Representation of Bragg's Law

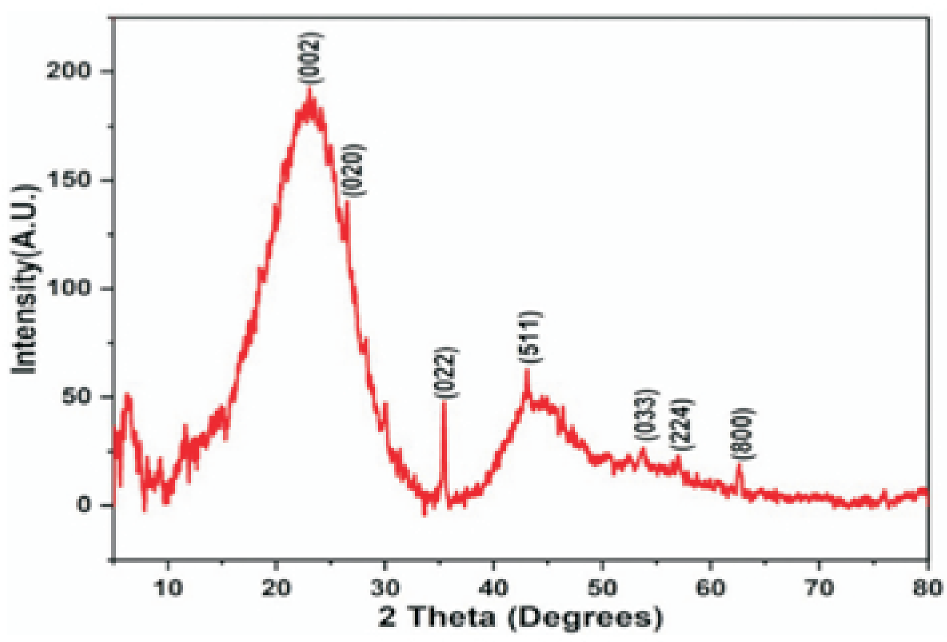


Fig. 1.14 XRD analysis of graphitic functionalized carbon nanosheets

materials. This was consistent with the crystallinity data which showed 45.54% crystallinity with amorphous percentage of 54.46%. The (002), (020), (131), (033) and (800) planes correspond to the 2Ɛ diffraction peaks, respectively seen at 22.91, 26.51, 35.11, 43.11, 53.71 and 67.71 respectively. The inorganic crystal structure database (ICSD) revealed a monoclinic crystalline lattice and these diffraction peaks matched it well (Jaryal et al., 2022).

To calculate the size crystallites from the XRD data; Scherrer equation is used,

$$D= K\lambda/\beta\cos Ɛ$$

Where; D= crystallites size (nm); k= 0.9 (Scherrer constant); λ= 0.15406nm (wavelength of the X-Ray sources); β= FWHM (full width at half maximum) and Ɛ = peak position (radians).

5.6. Infrared (IR) spectroscopy

IR spectroscopy is well established method for identifying and analysing the structural composition of a chemical compound. The absorption of electromagnetic radiations in the infrared portion of the spectrum leads to the transitions from electronic ground level between various rotational and vibrational levels. The peaks formed in the IR spectrum are due to various transitions into various distinct vibrational modes and correspond to the different chemical bonds and functional groups that molecule contain. A compound's IR spectrum can be thought of as its “fingerprint” and is one of its most distinctive physical characteristics. For any molecule, to exhibit IR absorptions the dipole moment must show change (Ismail et al., 1997).

Analysis of sample: Absorption band at 3393cm^{-1} is due to free O-H stretching. The symmetric and asymmetric stretching of C-H bonds in the methyl or methylene groups leads to strong absorption at 2896cm^{-1} and 2971cm^{-1}, respectively. A weak intensity peak at 2528cm^{-1} is due to S-H stretching which is indicative of the existence of sulphur in graphitic functionalized carbon nano-sheets. N-H bending in the main amine was represented by a weaker peak at 1550cm^{-1}, whereas O-H in-plane bending was represented by a stronger peak at 1260cm^{-1}. The aromatic C-H in plane bending and aromatic C-H stretching, give strong peaks of weak intensity at around 1226cm^{-1} and 862cm^{-1},respectively. A very strong and narrow band at about 1069cm^{-1} is due to C-O stretching in the materials. FTIR spectrum is shown in Fig. 1.15 (Jaryal et al., 2022).

6. Applications of Nano materials

Nano technology is an outstanding example of technological advancement is, which offers designed nano materials with the ability to produce products with considerably better functionalities. Nano materials and based composites find applications in almost all fields viz. as catalyst, as sensors and biosensor in medicine (diagnosis and drug delivery), fuel cell applications, electronic devices, water treatment application, agriculture, construction industry etc.

At present time, nano materials become important constituents in various products viz. scratch-resistant paints, surface coatings, electronics, cosmetics, environmental treatment processes, sports items, sensors, energy storage devices, power magnets, long-lasting medical implants etc. (Fig. 1.15) (Baig et al., 2021). Different applications are briefly described here Gajanan & Tijare, 2018; Kolahalam et al., 2019; Sharifi et al., 2012).

6.1. Medicine: Nano materials have long been used in the field of medicine and medical applications of nano technology date back to 1965 (Baig et al., 2021). Composite nanosystems are extensively used for internal diagnostics and treatment. A carrier platform, a payload for imaging, sensing, or therapy, and optional targeting ligands are common components of these systems (Lehner et al., 2013). Nano materials are employed in diverse medical applications like as nanocarriers, in targeted drug delivery, tissue engineering, biosensors, wound healing, antibacterial agents & diagnosis (Salem et al., 2023).

6.1.1. Targeted drug delivery: Pharmaceuticals must endure numerous transport barriers right from their introduction site to their point of chemical action. Hence, these need some sort of drug delivery system to reach the specific location safely. Different barriers encountered in the path comprise filtration in the kidney, bloodstream, plasma membrane, nuclear membrane etc. Hence, a formulation or a technology should control drug release at the site of action to give prolonged release of drugs. These methods are helpful to overcome the drawbacks of many pharmaceuticals eg. their poor solubility and inadequate absorption due to degradation in the path, non-targeted delivery, and harmful concerns from unsustained release (Bruschi, 2015). Biopolymer-based nano composites are generally used as drug delivery systems due to their bio-degradability, bio-compatibility, low immunogenicity, and antibacterial activity. These have applications in wound healing, as drug carriers, scaffolds for bone, cartilage, cardiac, skin, and tissue engineering etc. (Jacob et al., 2018). By using a colloid-electron spinning process, Li et al. (2017) invented silk fibroin nanofibers that were dual drug loaded. Curcumin and the anticancer medicine doxorubicin (DOX) were put into nanofibers that showed sustained and dual drug release. The resulting drug delivery system may be employed as a multi-drug delivery system to treat various disorders. Bettini et al. (2015) exemplified the use of nanocomposites in drug delivery by utilising the magnetic properties of iron oxide nano particles controlled by an external magnetic field. Hydrogels based on collagen were used to create iron oxide scaffolds, which were loaded with fluorescein sodium salt (a pharmaceutical agent). An external magnetic field was used to initiate the compound's release, followed by its precise tracking analysis using fluorescence spectroscopy. Therefore, collagen paramagnetic matrices can be used in tissue engineering and drug delivery.

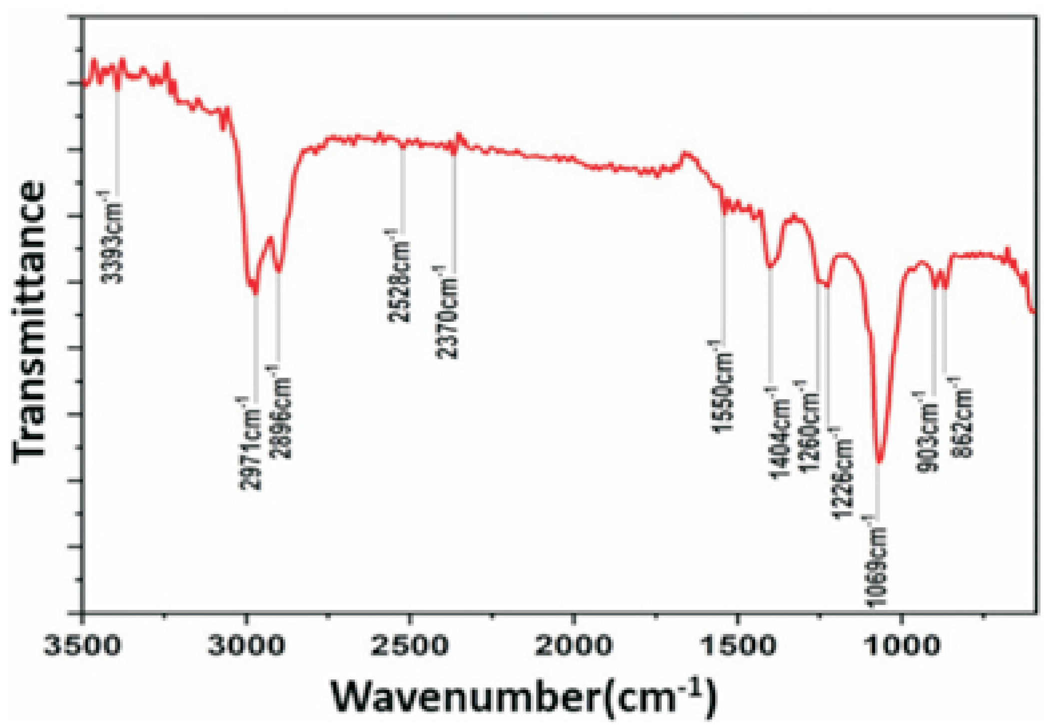


Fig. 1.15 FTIR spectrum of graphitic functionalised carbon nanosheets

6.1.2. Biosensors: A sensor is a device used to quantitatively detect the test substance (analyte) in a sample. Such a system should operate continuously, reversible, and should not destroy and contaminate the sample. A detection system that uses at least one nano constituent is referred to as a "nanosensor." In case one part in the sensor is a biological element (DNA strand, an antibody, an enzyme, nucleotide, antigen, amino acid, whole cell etc.) it is known as "Nano Biosensor" (Crespilho, 2013; Huang et al., 2021). Use of nano materials in the sensors increase and improve the detecting abilities of the sensors. Magnetic nano particles (MNPs), carbon nanotubes (CNTs), nanorods (NRs), quantum dots (QDs), nanowires (NWs), etc are the common and effective nano materials used in sensors. Utilizing nano-biosensors in the food sector may result in significant advancements in quality assurance, food safety and accountability. The nano-biosensors can be useful in many processes involved in manufacturing of food materials in the food industry eg, preparation of raw components, during food processing, supervising of storage environments besides etc. The nanosensors are also used for detection of different analytes viz. nutrients in food material, pathogens, carbohydrates in blood, pesticides, micro-organism etc. (Pérez-López & Merkoçi, 2011). Vinayaka et al. (2009) created a biosensor using cadmium telluride quantum dot nanoparticles (CdTe QD). It was useful to detect 2,4-dichlorophenoxyacetic acid (2,4-D), by utilizing a competitive fluoro immune assay. The fluoro immuneassay was synthesized by utilising an immune-reactor which acted as column and immobilising material constituted by anti-2,4- dichloro-phenoxy-acetic antibodies. It is pertinent to screen, detect and quantify herbicide in ultra small concentration for food analysis as it can affect and cause health problems even in ultra small concentrations. The synthesized biosensor can detect 2,4-D up to 250 pg/mL in 50 mM phosphate buffer solution (Vinayaka et al., 2009).

6.1.3. Wound Healing: The ideal wound healing system should moisten the wound, speed up wound closure, decrease scarring, minimize infection, and promote the body's natural healing processes. These requirements of a perfect wound healing system are not met by conventional ones whereas; introduction of nano materials for wound healing reduces and/or overcomes some of the shortcomings of conventional methods. It is done by:

1. Nano materials with antimicrobial abilities were embedded within the polymer matrix.
2. Nano-carriers were used for encapsulation which helps in the transport and delivery of the active agent (Barroso et al., 2020).

Horue et al. (2020) synthesized a nanocomposite comprising bacterial cellulose (BC) and montmorillonite (MMT) which was modified with silver (BC-MMT-Ag)to develop a potential scaffold for wound healing. Montmorillonite was immersed in a silver nitrate solution for ion exchange to integrate silver into the matrix. The derivative silver clay suspension was employed by using an ex situ approach to change the properties of bacterial cellulose membrane and synthesised nanocomposites had sufficient antimicrobial activity.

6.1.4. Diagnosis and therapy: The failure to correctly diagnose and treat infectious diseases result in large number of fatalities. The WHO recommends that diagnostic devices must be accessible to the needy, sensitive, precise, user-friendly, quick, and robust. Point of Care (PoC) diagnostics may be transported to remote sites, and have significant potential for detecting and monitoring infectious diseases in situations with limited resources. On-chip PoC diagnosis and real-time monitoring of infectious diseases may be possible using nanotechnology, eg, nanofluidic (Lee et al., 2010).

Cancer therapy is confronted with obstacles viz. the inability to transport therapeutic agents to the targeted tumour site without causing harm to healthy cells and the detection of cancer at an advanced level. Proteomics, genomics and nanotechnology advancements have made it possible to demonstrate the validity of the ideas of diagnostic and targeted delivery. Cancer-specific biomarkers may be formulated by combining novel approaches with biological agents. Numerous nanoprobes with associated ligands and chemotherapy medicines have been designed to interact with biomolecules with in living systems, allowing for the high-efficiency detection and monitoring of biochemical changes and the delivery of therapy (Singh, 2019, Štambuk et al., 2019) and is represented in Fig 1.16.

6.2. Catalyst: The heterogeneous catalysts increase selectivity and yield hence, are attracting interest. Research efforts needs to be undertaken to boost the effectiveness of catalystsfor the higher and product yields and the purity. Nanostructured catalysts, having improved physiochemical characteristics, are receiving more attention at present. The high surface energy and specific surface area of these nano - catalysts contribute immensely to their strong catalytic activity. Nano-catalyst enhances the selectivity of the reactions by enabling reactions to proceed at lower temperatures, minimising the incidence of unwanted side reactions, increasing recycling rates, and recovering energy usage. Hence, these are frequently utilised in green chemistry, environmental cleanup, effective biomass conversion, etc. Catalytic nano particles can be of three major types (Sharma et al., 2015).

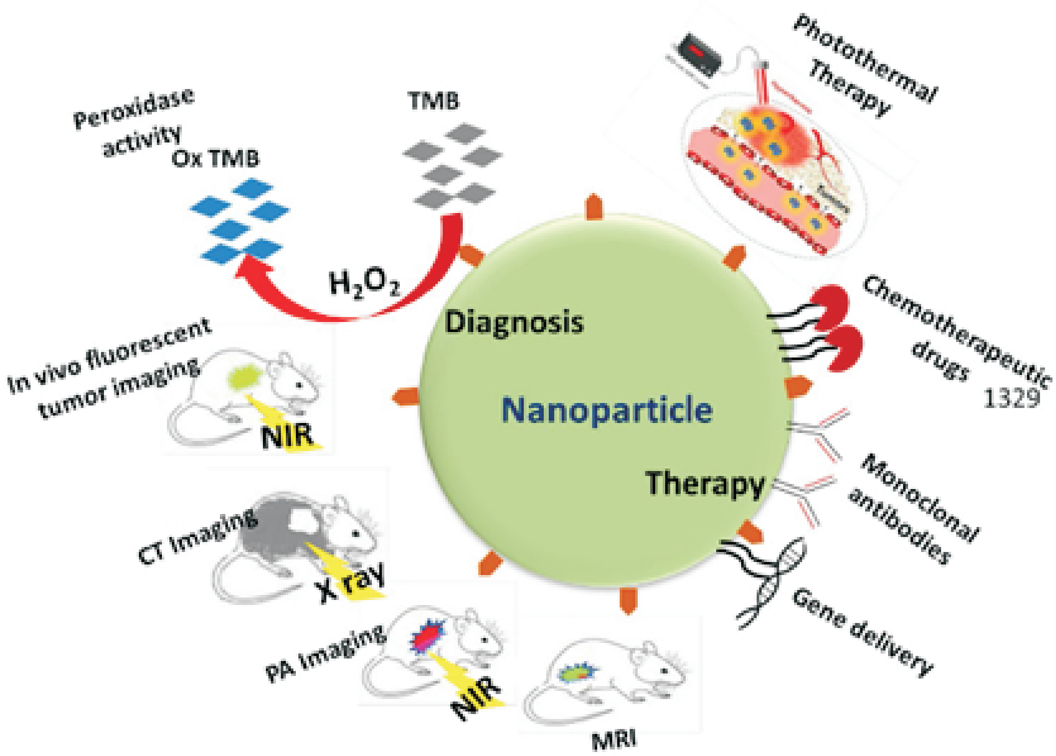
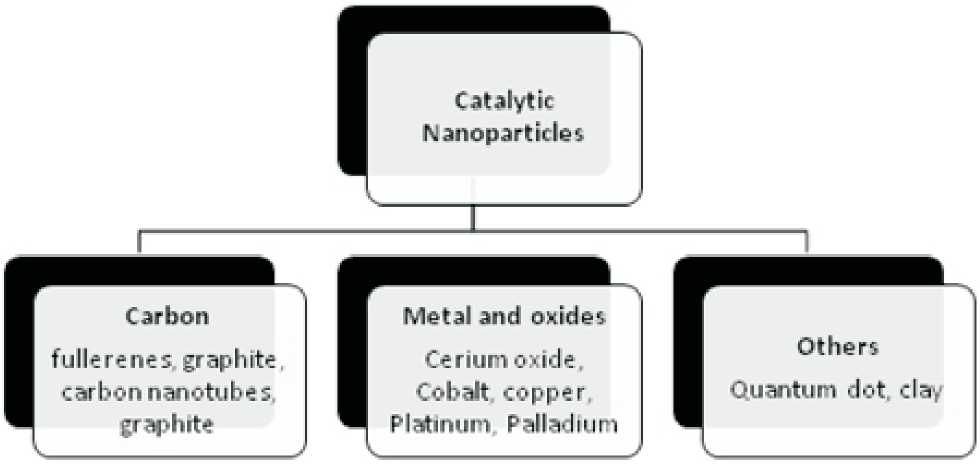


Fig. 1.16 Schematic showing various applications of nanoparticles in diagnosis and therapy of cancer



A nano-magnetic catalyst KF/CaO-Fe_3O4 with magnetic characteristics was created by Hu et al. (2011) and it was employed in the production of biodiesel. Under optimized reaction conditions in target fatty acid methyl esters yield of >95% was achieved using a manufactured catalyst (Tang et al., 2018). Nano-nickel catalysts have been synthesized using methyl cyclohexane, water, n-octanol, and AEO9, to reduce the viscosity of Liaohe extra-heavy oil by aqua-thermolysis (Li et al., 2007). The worm-like Pd nano catalyst was constituted and used to create azo compounds from nitro-aromatics under moderate reaction parameters. The conventional methods used for the same reaction resulted in catalysts made of environmentally harmful transition metals i.e. lead. With regard to the highly dispersible nano-Pd catalyst exhibited significant activity for the synthesis of various asymmetric and symmetric aromatic azo compounds. The shape of the nano catalyst also affects its efficiency and the worm like shape of nano-catalyst is highly effective (Hu et al., 2011). Fan and Gao (2006) described the utilization of several metal nano particle i.e. Au, Pt, Pd, Rh, and Co and supported catalysts for good yield and selectivity.

6.3. Water Treatment: Numerous nano materials and nano-composites have been reported which may be employed for the treatment or waste and polluted water individually or in combination with other agents. Use of nano-adsorbents is a significant method for it. Nanoscale particles made of organic or inorganic materials viz. nanoadsorbents have a strong propensity to adsorb substances. Nano-adsorbents' with high porosity, tiny size, and active surface enable them to rapidly absorb input materials without releasing harmful payload and may sequester pollutants with a range of molecular sizes, hydro-phobicities, and speciation behavior. Santhosh et al. (2016) reported that different types of nano materials are synthesized and employed for water treatment including carbon based (carbon nanotubes, graphene, graphite) and metal oxide based (nano metal oxide). These materials help in water treatment as adsorbent, antibacterial agent, and as catalyst. The use of TiO_2 TiO_2/graphene nano-hybrid materials nano particle-based treatment of waste water for the removal of toxic metal arsenic, other metals, dyes, pharmaceutical waste, and for disinfection of water against different microbes (Guan et al., 2012; Kusiak-Nejman & Morawski, 2019). Zeolite supported nano-metallic catalyst was applied in textile effluent treatment. The synthesized materials were used for the removal of synthetic CI acid orange 52 (AO52) azo dye in textile effluent (Rashid et al., 2020).Traditional treatment technologies are expensive for eliminating pollutants at low concentrations whereas, nano technology has shown great potential for environmental cleanup and water filtration (Adeleye et al., 2016).

6.4. Construction materials: Materials, scaled down to the nano size, exhibit exceptional chemical and physical capabilities for applications including improving structural strength, conserving energy, and creating self cleaning surfaces. Hence, the building sector has begun to switch to advanced-produced nano materials (MNMs). MNMs can enhance crucial features of building materials including strength, durability, and lightness that impart useful capabilities i.e., heat-insulating, self-cleaning, and antifogging and serve as important sensing components to monitor building safety and structural health (Lee et al., 2010). Bonding of concrete mixtures i.e., cementitious agents, concrete aggregates, carbon nanotubes (CNTs), a stand-in for polymeric chemical admixtures, can significantly improve mechanical durability and stop fracture propagation (Ding et al., 2006). Metal oxide of SiO_2 and Fe_2O_3 is used as a filling agent to pack the pores developed due to de-icer (chloride of calcium and magnesium) in the concrete. Additionally, due to antifouling property of TiO_2 these are used in the coating of pavement, walls, and roofs to keep the surfaces dirt-free, and bacterial-free (Lee et al., 2010). SiO_2 and TiO_2 NPs can be included or coated to add extra functionality to surfaces like window glass, pavement, walls, and roofs. Windows can be made fire-proof by sandwiching nano silica layers between two glass panes. Silica nano particles on windows act as an anti-reflection coating to restrict exterior light thus, assisting in energy (air conditioning) conservation. TiO_2 is photo-activated with UV wavelengths in artificial or natural light to produce reactive oxygen species (ROS), which allow the efficient removal of grime and bacterial films stuck to windows (Elsamanoudi, 2014; Rana et al., 2009; Shah & Belozerova, 2009). $CaCl_2$ and $MgCl_2$ reacts with components of concrete and thus can enter the small pores generated concrete as a result of cement hydration. SiO_2 and Fe_2O_3 nano particles (NPs) can be employed as packing agents to plug the pores and strengthen concrete to avoid this. The complex mechanical qualities of concrete can also be improved by incorporating them with fly ash in place of cement (Garboczi, 2009; Li, 2004).

6.5. **Agriculture:** Treatment of seed prior to sowing, germination, plant growth and development agents, pest control substances, pesticide delivery vehicles, fertilizer delivery systems, genetic material delivery devices, toxic agro-chemicals detection processes, pathogen detection systems, etc. are some of the main agricultural applications for nano materials, nanocomposites, and nanotechnologies. The nano-carrier i.e., smart nano-based formulations for agro-chemicals (pesticides, fertilizers etc.) administration, nano bio-sensors to detect pesticide residues, nano coating for seed treatment, metal-based pesticide and such other techniques are currently being developed (Nuruzzaman et al., 2016).

Nanoformulations of various agrochemicals (pesticide, fertilizer), nanosensors for identifying diseases and agrochemical residue, nano-techniques for animal health and breeding, post harvest management and storage of crops are some prominent applications of nanotechnology which have helped to increase agricultural production (Chhipa & Joshi, 2016). Nano materials and nanocomposites are used in the following different agricultural areas:

a) Plant germination and growth
b) Plant protection and production
c) Pesticide residue detection (Nasr et al., 2016)

6.5.1. Plant germination and growth: Pre-sowing seed treatment with various nano-materials resulted in improved germination abilities and additional effects in the plants (Das et al., 2019; Hassanisaadi et al., 2022; Khodakovskaya et al., 2009; Maity et al., 2018; Shah & Belozerova, 2009; Zheng et al., 2005). Zheng et al. (2005) reported that treatment of naturally aged spinach seeds with nano-TiO_2 (rutile) @ 0.25–4% resulted in increased germination rates, activity indexes, and growth rates. The dry weight of the plant increased during the growth stage due to increase in photosynthetic activity and the production of chlorophyll. The optimal concentration of nano-TiO_2 was 2.5% whereas; non-nano TiO2 has no discernible effects. It was discovered that carbon nanotubes (CNTs) can penetrate tomato seeds and affect the germination and growth kinetics. Khodakovskaya et al. (2009) reported that rate of germination of seeds grown on a CNTs containing medium was significantly greater. CNTs were shown to penetrate thick seed coats and support water uptake inside seeds leading to increased biomass output and faster germination rates of plants exposed to carbon nanotubes. Shah and Belozerova (2009) reported that treatment of lettuce with silica, palladium, gold, and copper nano materials resulted in better shoot/root ratio after 15 days of incubation. The plant growth was strongly influenced by Pd and Au nano particles at low concentrations, and at higher concentrations in case of Si and Cu a combination of Au and Cu nano particles. Maity et al. (2018) investigated the effects of zinc oxide (ZnO), titanium oxide (TiO_2), copper oxide (CuO), and silver (Ag) nano particles (NPs) on seed germination, vigour, seedling appearance speed, number of tillers, and yield in green fodder crops viz. oat, and berseem in the lab and in the field. Zinc oxide (ZnO), and silver (Ag) improved germination at lower dosages however, higher concentration levels resulted in reduced root and shoot length. Ag improved germination of berseem at the lowest dose whereas. TiO_2 resulted in higher seed production in all crops at the highest dose. Field experiments showed no discernible impact of nanoparticles on soil microbial population (Maity et al., 2018).

Efforts have been made on the application of nano materials and nano-based devices for the controlled delivery of the active plant growth stimulators, fertilizers etc. leading to improvement of plant growth and production. More efficient methods to enhance agricultural operations are highly required due to the demand for increased agricultural yields from a continually expanding worldwide population and scarcity of critical resources viz. phosphorus and potassium warrant more efficient techniques to enhance production. Hence, use of nanotechnology and nano materials is growing. Macronutrient fertilisers contain bulk zinc oxide however; the solubility of the Zn source in the soil plays a major role in determining the supply of Zn from the fertilisers to plants in a Zn deficient environment (Gogos et al., 2012). Aacharya and Chhipa (2019) reported that Nano carbons, diffused or dispersed in water were taken up by plant roots and carried through the xylem vessel channel. The size of the nanocarbon materials then type and functionalization, solubility in water, and the response of the plant to the nanocarbons are some variables affect the uptake and movement of nanocarbon in plants.

6.5.2. Plant protection and production: Various pesticides *viz*. insecticides, herbicides, fungicides, nematicides, bactericides, acaricides, larvicides, and rodenticides are used. In addition to it, multiple active ingredients and a variety of chemical additives, such as solvents, surfactants, anti-freeze agents, pigments, emulsifying agents, and thickening agents, etc., are frequently used in pesticide formulations to boost the efficacy and facilitate application and storage (Singh et al., 2022). The long-term effects of pesticides have proven to be too severe and deleterious in terms of acute and persistent poisoning of human beings and animals, contamination of the land, water, and food. Additionally, commercial formulations having inert chemicals and compounds with unknown composition are sold along with herbicides like glyphosate. The hazardous impact of the active ingredient glyphosate in *C. elegans* was exacerbated due to inclusion of inert substances rather than to active ingredient hence, such additives need to be avoided (Jacques et al., 2019). Similarly, issues related to the use of pesticides i.e., non targeted delivery, leaching to the environment due to persistent and long-time use needs to be considered. The nanoscale particles with novel properties i.e., enormous surface area, stiffness, permeability, thermal stability, and biodegradability, are proved to be ideal and smart candidates for use in the agricultural industry (Kah & Hofmann, 2014). Over the existing pesticide formulation (burst release of active ingredient), nano-based agrochemical formulation or nano-carrier is designed in a way that effective concentrations of chemicals reach the target site in controlled manner in response to an external stimulus such as pH, temperature, enzymes, light, and other factors. Various nano materials eg. polymer, solid-lipid, inorganic porous, etc. have already been used to target selective pesticides to the plants (Kumar et al., 2019). Xu et al. (2017) reported an excellent NIR-light and temperature-sensitive nano-carrier of poly(N-isopropyl acrylamide) (PNIPAm)-capped polydopamine (PDA) to encapsulate imidacloprid which releases the active ingredient in controlled and target selective manner. Nano-carrier, the emerging application of nanomaterial as an active ingredient for crop protection also gained attention. The antifungal, antibacterial, and antimicrobial properties promote the use of metal and metal oxide as eco-friendly pesticides (Kanmani & Lim, 2013). Among the different inorganic nanomaterials, non-toxic silver and zinc nanoparticles show antimicrobial activity against various pathogens, and copper nano-particles show insecticidal and herbicidal activity. Kanhed et al. (2014) reported the antifungal efficacy of chemical synthesized copper nanoparticles by reduction of Cu^{2+} in the presence of Cetyl Trimethyl Ammonium Bromide and isopropyl alcohol against plant pathogenic fungi, i.e., *Curvularia lunata*, *Phoma destructive*, and *Alternaria alternata.*

6.5.3. Pesticide residue detection: Smart agriculture can be benefitted from the use of nanosensors to quickly and locally detect pests and weeds in real situations and thus apply remediation instantly with target specificity (like use of pesticides against pest). They help to forecast the occurrence of pests, weeds, hazardous metals, and contaminants in the environment. Different categories of nano-materials, including nano-particles, nano-composites, and nanotubes are used to electro-chemically determine the remaining pesticidal particles (Sharma et al., 2021). Du et al. (2008) created a sensitive electro-chemical stripping voltammetric approach based on solid-phase extraction (SPE) at an electrode modified with zirconia (ZrO2) nano particles which was used to analyse organo-phosphate (OP) chemicals. It was demonstrated that ZrO_2 nano particles are a novel sorbent for SPE of OP pesticides. Nitro-aromatic OPs can firmly connect to the ZrO_2 nano-particle surface as the ZrO_2 has high affinity for the phosphoric group. Using methyl parathion (MP) as a model, SPE and square-wave voltammetry (SWV) provided a quick, sensitive and picky electro-chemical technique for nitro-aromatic OP compounds (Du et al., 2008). Qu et al. (2008) created an Au-TiO_2/Chit modified electrode using a combination of Au-TiO_2 nanocomposite and chitosan. The responses of the Au-TiO_2/Chit modified electrode were found to be linear with parathion concentrations ranging from 1.0 - 7.0 ng/ml with a detection limit of 0.5 ng/ml by differential pulse voltammetry (DPV) measurement. Nano-composite demonstrated a precise, quick, and user-friendly method for the quick determination of even less number of pesticides.

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2. Nano-enabled strategies for crop protection

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Abstract: Food safety and environmental protection are two parallel pillars of sustainable agriculture and to meet the increased food demands of the world's ever-increasing population along with maintaining environmental sustainability, agriculture needs to innovate and modernise. In this context, concerns about the reliability of nanotechnology in agriculture has emerged as a potential discipline due to its associated positive health and environmental effects by delivering site-specific and controlled active ingredient releases, lowering runoff and residual contamination. However, but for the numerous advantages of nanoparticles over traditional chemicals, caution must be taken to avoid any unforeseen problems. Therefore, more research is required to identify and reduce the risks associated with nano-agrochemicals before they are commercialized.

Introduction

Agriculture is the primary source of income for most of the Indians. Conventional agriculture uses agro-chemicals i.e. chemical fertilizers, insecticides, and other industrial items to increase crop yield. These practices have negative consequences on ecosystems, soil fertility, and biodiversity (Agrawal et al., 2022). In addition to the traditional agricultural methods, nanotechnology has attracted interest in the agricultural sector (Fig. 2.1).

There are numerous advantages of using nanotechnology. The most important advantage is the significant reduction in active chemicals that actually enter the agricultural system. Numerous applied fertilizers and pesticides don't reach their intended sites and rather harm the environment. Nanoparticles are preferred over conventional methods because of their small size, ease of handling, long shelf life, and high efficiency. Nanotechnology can benefit agriculture and minimize environmental issues by using nano-pesticides to control plant diseases and insect pests (Hazarika et al., 2022). This can be accomplished by using ecologically safe nano particles to increase the effectiveness of chemicals at lower dosages. Nano materials (1-100 nm in size) have larger surface area, higher penetration capacity and more effectiveness, which prevent them from building up as residues in the environment. Consequently, nanopesticides act as a cutting-edge and alternative strategy to overcome the shortcomings of currently used standard pesticide formulations (Okey-Onyesolu et al., 2021). Nano-scale particles with pesticide features or nano-sized particles with active ingredients can be used to produce nano-pesticides. They have the power to enhance the wettability and dispersion of many agricultural formulations hence, lowering pesticide movement and organic solvent runoff. To avoid the negative effects of chemical pesticides on the environment, nano-pesticides must be used judiciously for successful insect control. Nano-pesticide formulations behave similarly to traditional pesticides, but these expose the active ingredient more gradually and selectively while also improving the apparent solubility of a poorly soluble active ingredient, these can prevent pre-mature degradation. Hence, the development of nano-pesticides to manage plant pests in agricultural production has become a promising and very successful area of nanoscience research.

1. Categories of nano-materials

Based on their chemical makeup, engineered nano materials are divided primarily into four different categories (Agrawal et al., 2022):

1. Composites made of carbon-based NMs such as single- and multi-walled carbon nanotubes (SWCNTs, MWCNTs), fullerenes, etc
2. Dendrimers that incorporate nano particles with other nanoparticles or bulk-like substances
3. Nanoscale polymer networks comprised of branching units that can be modified to carry out particular chemical tasks
4. Cadmium sulphide, cadmium selenide, metal oxides (such as ZnO, TiO_2, Al_2O_3, CeO_2, Fe_3O_4, etc.), and metal-based inorganic NPs (Au, Ag, Al, and zero-valent iron)

On the basis of their dimensionality, NMs are additionally categorised into three types

One-dimensional: NMs, which are needle- or rod-like materials with lengths ranging from 10 to 100 nm, include nanowires, nanorods, and nanotubes.

Two-dimensional: Nanolayers, nanofilms, and nano coatings are examples of the second category of nano material, which is two dimensional (2D) and has a plate-like form.

Three-dimensional: Multi-nanolayer nanowire bundles, multi-nanolayer nanocrystalline frame works, etc.

2. Nano-based systems for crop protection

Chemical pesticides are often used to get rid of pests and diseases. However, most pesticides are lost in the air through runoff or spray drift, which results in off-target deposition. The target is only reached by less than 0.1% of the pesticides used; the remainder are photo-degraded or damage the environment. A cutting-edge solution to overcome the aforementioned limitations is to use nano materials. Fig. 2.2 provides a thorough representation of various nano-based crop protection techniques. Reducing the amount of agrochemicals used for pest control, delivering biocides to specific targets, managing the release of active ingredients, nano-formulation of insoluble chemicals to make them more soluble, and increasing the

Fig. 2.1 Applications of nanotechnology in crop development and protection (Adapted from Agrawal et al., 2022)

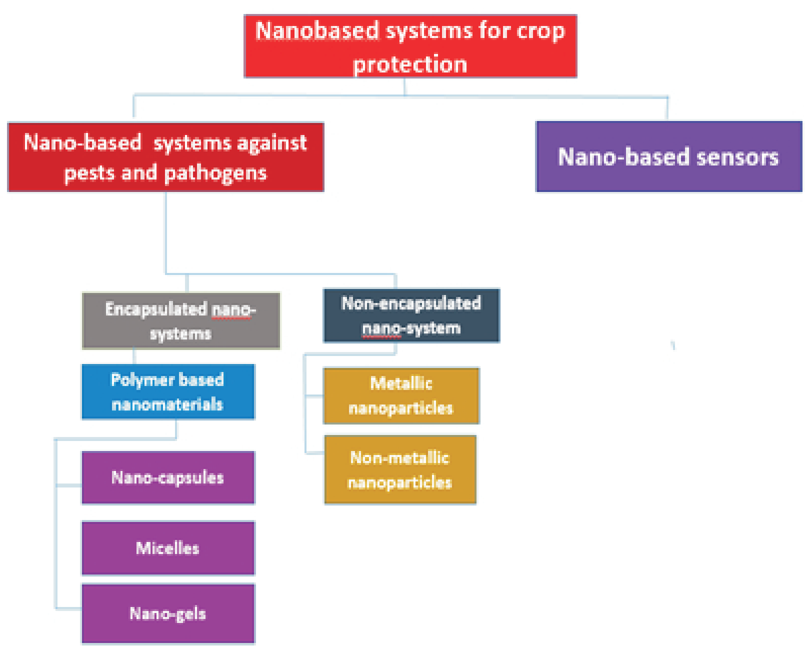

Fig. 2.2 Different nano-based systems for crop protection

stability of pesticides by shielding them from leaching, evaporation, photo-degradation, hydrolysis and microbial degradation are some of the benefits of using nano materials in agriculture (Ojha et al., 2018).

2.1. Encapsulated Nano-systems

2.1.1. Biopolymers: Plants, bacteria, animals, and agricultural waste serve as sources of biopolymers. This group of bio-polymers includes substances including cellulose, starch, chitin, chitosan, proteins, and peptides. In contrast to synthetic polymers, which lack the underlying structure of sequential repetition of monomer units, bio-polymers are structurally well defined. They are easily accessible and can be constituted in great numbers. They are a reliable source of reasonably priced, eco-friendly, biodegradable, non-toxic polymeric materials. Both synthetic and natural polymers are used to encapsulate the active ingredients for pesticide delivery. These encapsulating chemicals produce a variety of forms, such as nano-capsules, micelles and nanogels for the delivery of active compounds.

2.1.2. Nano-capsules: Nano-capsules consist of a solid or liquid internal core containing active chemicals or insecticides and a polymeric exterior protecting shell. They include an active ingredient in molecular dispersion, a polymeric matrix coated in a polymeric membrane, or a liquid core surrounded by a polymeric membrane. A few methods for producing nanocapsules include layer-by-layer procedures, polymer coating, double emulsification, emulsification-diffusion, emulsification-coacervation, and nano-precipitation. Other modified procedures include melt dispersion, emulsion polymerization, interfacial polymerization, interfacial deposition technique etc. (Esmaeili et al., 2013). The most popular of these techniques is inter-facial deposition. This approach involves mixing the drug/chemical in a water-miscible solvent, either with or without a surfactant, and then adding similar solvent-miscible oil, thereafter, the mixture is distributed in an aqueous phase that contains a hydrophilic surfactant. On agitation of this, nanocapsules are produced.

2.1.3. Micelle: Water insoluble agrochemicals, are delivered using micelles. In an aqueous solution, amphiphillic block copolymers self-assemble to produce micelles. Two techniques can be used to form micelles in the case of water-soluble copolymers such polyethylene glycol (PEG) and poly vinyl pyrrolidone. Prior to adding the pesticides that make up the micelle's core, copolymers are first dissolved in an aqueous media above the critical concentration for micelles. Second, copolymers and pesticide dissolved in a volatile solvent are cast to form a thin film and then, warm water is added while continuously stirring to produce a micelle that is loaded with pesticides (Ojha et al., 2018).

2.1.4. Nanogels: Nanogels are aqueous dispersions of hydrogel particles produced by nanoscale-sized, physically or chemically cross-linked polymer networks

(Nuruzzaman et al., 2016). In a drug delivery system, nanogels have shown their potential as carriers of the active compounds because of their high loading capacity, high stability, and responsiveness to environmental factors such as ionic strength, pH and temperature. The common methods for preparing nanogels are:

i. physical assembly of interactive polymers
ii. homogeneous phase or micro- or nanoscale heterogeneous environment polymerization of monomers
iii. cross-linking of preformed polymers and
iv. nano-fabrication of nanogel particles with the use of templates

Nanogels are formed through the controlled aggregation of interactive polymers due to their self-assembly properties in aqueous media. Employing nanogels as a medium to deliver pesticide is a very recent phenomenon. Nanogels synthesized from natural polymers, is an eco-friendly approach to pest control using nanotechnology.

3. Non-encapsulated nano-materials

A non-polymeric system of pesticide delivery includes use of metallic, nonmetallic NPs and their combination as hybrids against plant pests and pathogens.

3.1. Metallic nano-particles: Metallic nano particles (NPs) with antibacterial capabilities include copper oxide, silver, gold, zinc, titanium, and silver oxide (Vimbela et al., 2017). These NPs are evaluated for their capacity to kill bacteria, insects, and fungi when used alone or in conjunction with other metallic NPs to kill phytopathogens. Metal NPs inhibit or delay the growth of many pathogen species because of their diverse mode of inhibition (Ojha et al., 2018). Therefore, these NPs can be used as new antimicrobial agents and as an alternative to synthetic fungicides.

There are two main methods for synthesising metallic NPs: top-down and bottom-up methods (Fig 2.3). A bulk metal is broken down into NPs using mechanical or chemical methods in the top-down approach. NPs are produced by the bottom-up method from atoms, molecules, or clusters and have a homogeneous chemical composition (Abed et al., 2022).

The mechanical, chemical, and biological systems can all be used to carry out the bottom-up strategy. The biological approach which synthesises NPs using biological components is the most affordable, environmental friendly and energy-efficient technique. Bottom-up technique is known as "green synthesis," for the synthesis of metallic nano particles and it makes use of phyto-constituents (phenolics, flavonoids, tannins, etc.), enzymes, proteins, sugars, and polysaccharides (Singh et al., 2016). It has been explained in Fig 2.4.

In this technique, nano particles are produced by joining together incredibly tiny atoms. One can change the physical properties by adjusting reaction conditions such chemical concentrations, reaction time, temperature, and pH, of nano particles and can develop their own nano material. The biological generation of nano particles is preferred to the alternative methods since it is efficient and cost-effective (Kumar

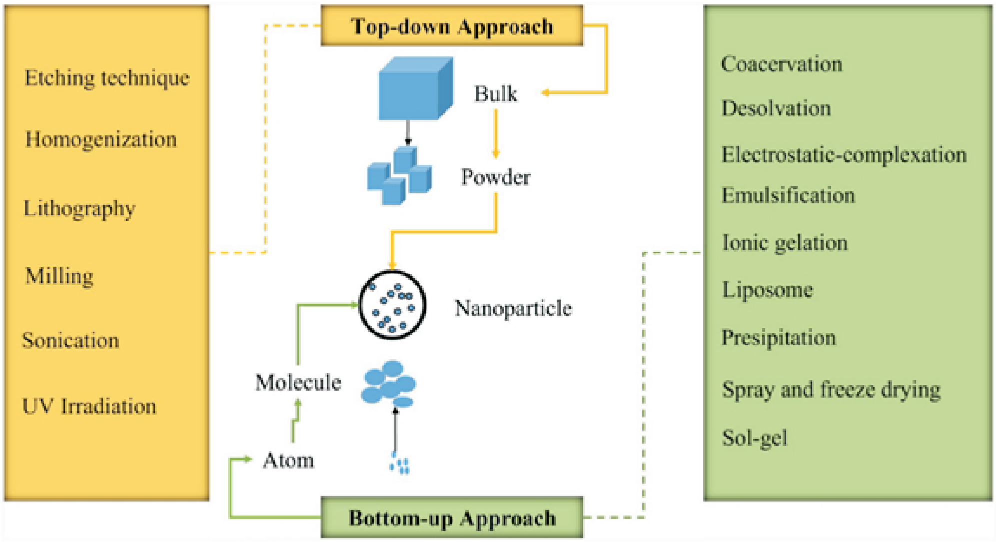

Fig. 2.3 Top-down and bottom-up synthesis techniques for nanostructures. (Adapted from Indiarto et al., 2021)

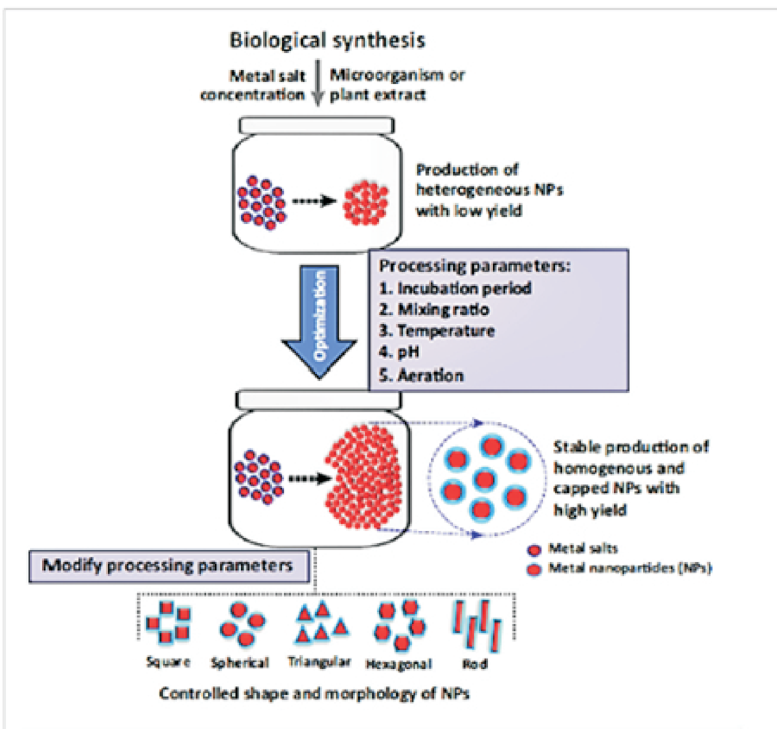

Fig. 2.4 Biological synthesis of nanoparticles (Adapted from Singh et al., 2016).

and Yadav, 2009). Among various metal nano particles, copper (Cu), silver (Ag), and zinc (Zn) nano particles are the most common antibacterial agents. Cu is more affordable and comparatively more inexpensive. Copper nano particles (CuNPs) are frequently employed in agriculture for many applications due to their cost-effectiveness (Hazarika et al., 2022).

3.2. Non-metallic nano-particles

Solid silica nano particles (SiNPs) and mesoporous silica nano particles (MSNs) have been widely examined and characterised for use in many of applications over the past few decades. Sol-gel synthesis and the water-in-oil micro-emulsion approach are two prominent synthesis methods among many that have been suggested so far for producing customizable particle diameters and morphologies in silica nano particles (Chen et al., 2013). Essentially, the choice of synthetic method depends on the requirement of the desired application. Silica NPs have been reported to induce a plant defense mechanism by activating systemic acquired resistance (SAR).

High levels of antibacterial capabilities are present in carbon nanostructures. Carbon-based nano materials include fullerenes, graphene oxide, and carbon nanotubes (Iijima, 1991). While metallic nano particles (NPs) are harmful to soil bacteria, fullerenes and their derivatives are less hazardous. Carbon nanotubes treated plants have been found to display complete resistance against viral infection by activating plant defense-related phytohormones- abscisic acid and salicylic acid and inhibiting viral replication (Rajni et al., 2022).

4.3. Characterization of nanoparticles

Several procedures should be followed in order to characterise the produced nano materials' size, shape, crystal structure, atomic composition, surface charge, and other physical, chemical, and biological characteristics (Mourdikoudis, 2018). Modern microscopy techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray fluorescence microscopy (XFM), and scanning transmission X-ray microscopy, are used to determine the size and morphology of the nano particles (Figs. 2.5 and 2.6). By using the dynamic light scattering (DLS) technique, it is possible to determine the Brownian mobility of nano particles in a colloidal suspension. Surface charge, a factor in the electrostatic interaction of nano particles with bioactive compounds, can be quantified by the zeta potential value. Another essential tool for analysing nano particles is the X-ray diffraction (XRD) technique. XRD can be used to determine the nano particles' crystalline structures. Nuclear magnetic resonance (NMR) is used to identify different structural characteristics. UV-visible spectroscopy can be used to observe the optical properties of nano particles, or how much light they reflect. Additionally, it evaluates the stability of the nano particles in the colloidal suspension. These techniques have been discussed in detail in chapter 1. It is common practise to characterise materials using these and other novel ways.

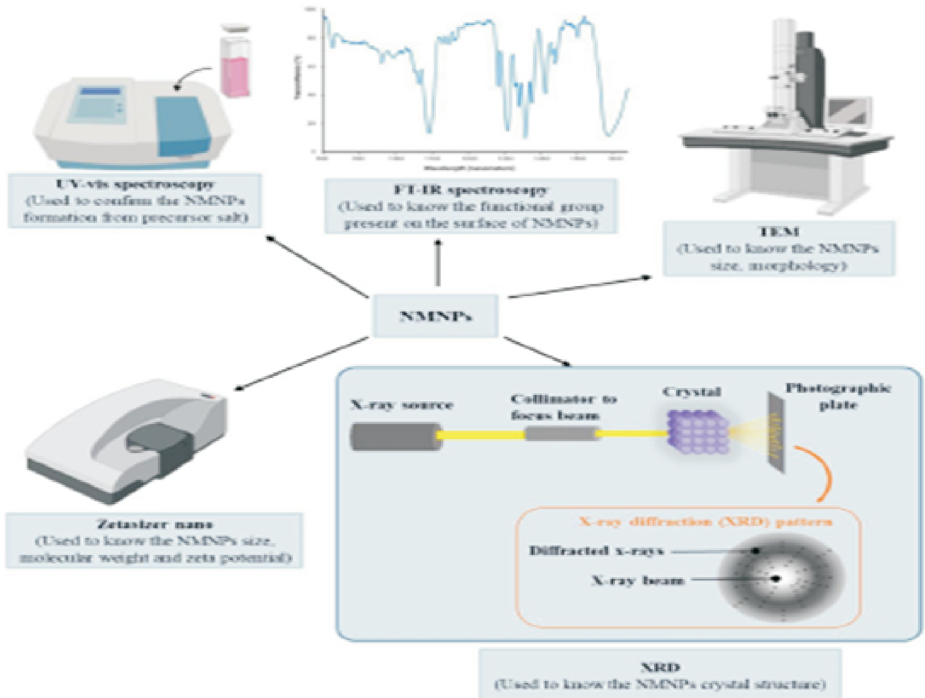

Fig. 2.5 Different types of characterization techniques of noble metallic nanoparticles (Adapted from Dam et al., 2022)

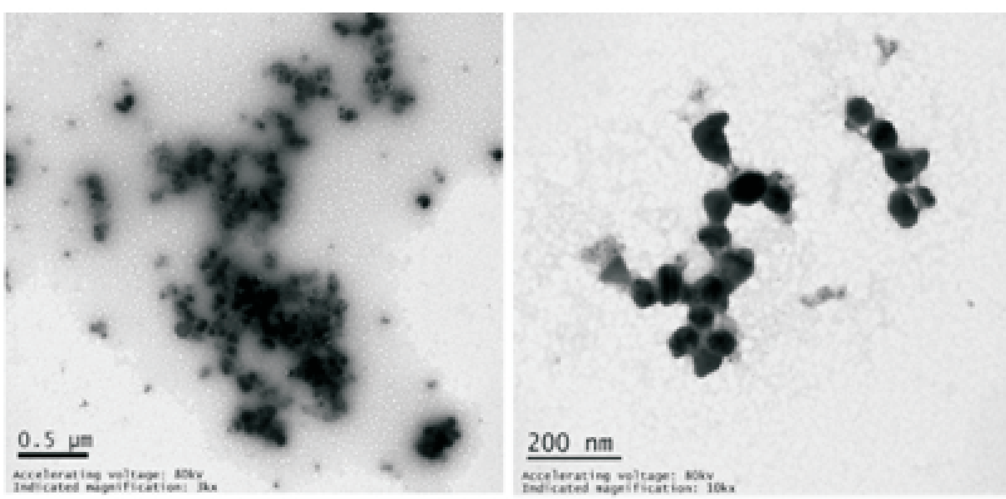

Fig. 2.6 TEM images of silver nanoparticles synthesized from aqueous leaf extract of *Ocimum gratissimum* (Adapted from Sharma et al., 2019)

Nanotechnology is gaining popularity and piqueing the interest of researchers in other scientific fields (Dam et al., 2022). Hence, it is essential to devise fresh, creative, affordable, and straightforward means for its effective utilization in various scientific fields including agriculture.

3.4. Mechanism of antibacterial activity of metal nano particles

Despite the fact that the precise mechanisms underlying the biocidal activity of metallic nano particles are yet unknown, three conjectural pathways are among the most well-known and commonly mentioned in the literature (Brandelli et al., 2017) and are given below and depicted in Fig. 2.7.

1. The movement and internalisation of metal ions into the cells, which causes the intracellular ATP to degrade and DNA replication to be interrupted
2. Cellular structural damage brought on by the production of reactive oxygen species (ROS) by metal nano particles
3. Nano particle buildup and cause dissolution in bacterial membranes affect membrane permeability, causing a slow release of internal components such membrane proteins and lipopolysaccharides (Okeke et al., 2022). This dissipates the proton motive force (PMF)

3.5. Activation of plant defense mechanism using NPs

Nano particles activate the production of plant secondary metabolites, plant hormones such as jasmonic acid (JA), salicylic acid (SA), ethylene, reactive oxygen species (ROS), and expression of pathogenesis-related genes (PRs). ROS levels increase in plants during stress conditions which can disturb pathogen integrity (Rajani et al., 2022). The mechanism is depicted in Fig. 2.8.

4. Nano-biosensors for plant health monitoring

A key advancement in nanotechnology has been the creation of nano-sensors, which support monitoring, data management, and management of plant health. The tracking, detecting, and control of plant diseases with the help of nano-biomaterials used in the development of biosensors are important. Numerous fertilisers, herbicides, pesticides, insecticides, diseases, moisture, and pH levels canbe accurately detected using nano-biosensors. Furthermore, the judicious and controlled use of nano-biosensors can promote sustainable agriculture and boost crop yields as the nano-biosensors provide real-time information on disease diagnosis, potential environmental forecasts, field conditions, and the crop monitoring (Sarkar et al., 2022). This information would help to protect the crop from diseases, pests and viruses. These sensing techniques transform the traditional agricultural system to a precise farming method.

5. Adverse effects of nanomaterial on plants

Although nano materials have numerous beneficial uses but prolonged exposure to nano particles may pose harmful effects on the environment. The

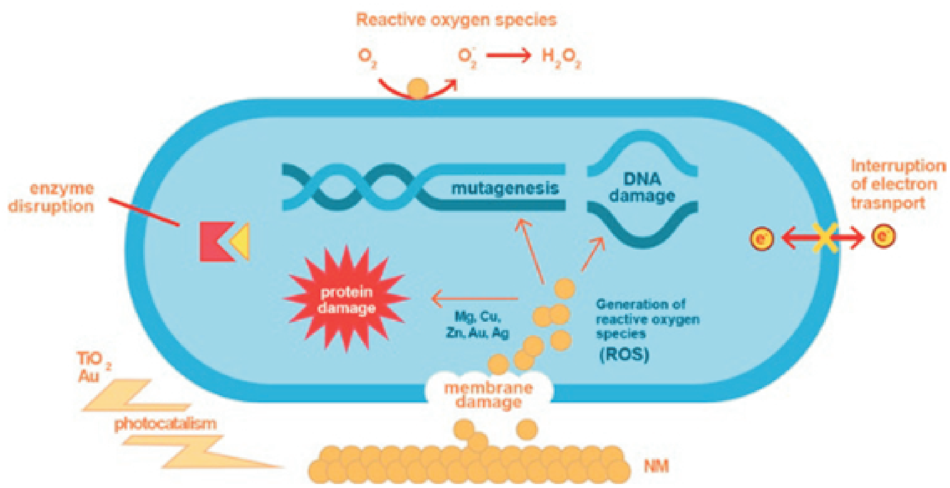

Fig. 2.7 Antibacterial effects of metal nanoparticles (Adapted from Brandelli et al., 2017).

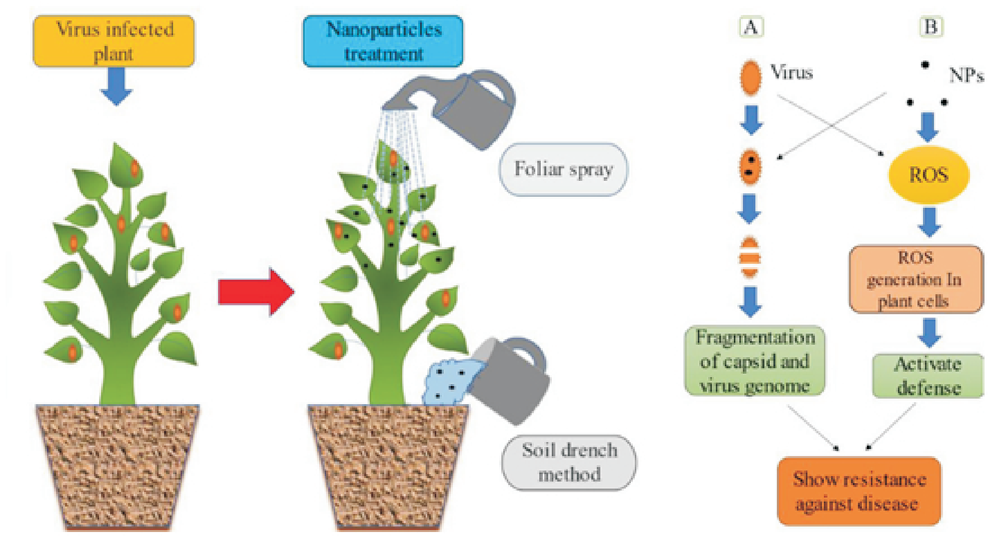

Fig. 2.8 (A) NPs directly affect the virus (B) NPs activate the defense mechanism of the plant and indirectly protect the plant (Adapted from Rajani et al., 2022)

beneficial and detrimental effects of NPs have been reported on plant growth and development depending on their size, concentration, physical and chemical characteristics of NPs and the type of plant, (Giorgetti, 2019). NPs interact with plants by direct contact, dissolution, and co-transport with other molecules. These interactions are harmful to seed germination, plant viability, root development, photosynthesis, and plant growth along with other aspects of plant development. NPs accumulate in soil and plants and eventually these enter the food chain and pose a serious hazard to both human and animal health (Rajani et al., 2022).

6. Health implications of nano-enabled agrochemicals

In agriculture, nano-enabled agrochemicals can be used for production, protection, processing and packaging, conservation and preservation, and the development of functional foods however, there is anticipated exposure of consumers by their direct application (i.e., applied at various stages of food production) due to the inert particle in foods (Fig. 2.9), occupational exposures, or generally the consumption of agro-products containing residues of the nano particles (Okeke et al., 2022). Nano particles as a result of direct use might be found in the food chain. The properties of NPs, such as toxico-kinetic and toxico-dynamic behaviour interfere with their capacities for absorption, biotransformation (metabolism), distribution, and elimination (excretion), as well as the substance's interaction with target sites and the subsequent reactions that lead to harmful effects, determine the extent to which NPs are toxic.

The structural diversity of nano particles affects their toxico-kinetic and toxico-dynamic characteristics. The effects of nano agrochemicals on human health are poorly understood and there is a lack of toxicological data. Compared to bigger molecules of the same chemical, nano particles can penetrate the cell wall and bio-accumulate because of their size and physico-chemical characteristics (Gupta et al., 2012). The usage of NP has a number of negative effects, eg. on male reproductive toxicity, negative effects on the proliferation and expression of cytokines by PMBCs, and mitochondrial dysfunction as a result of reported changes in cell permeability for the two important ions i.e. Na+ and K+. This type of toxicity is seen in those who come into touch with the substance directly during the creation of the nano particle (occupational exposures), when it is applied, or even by ingestion. Because of the fact that the toxic effects of nano-enabled agrochemicals and materials depend on their physico-chemical characteristics (such as shape, solubility, and coating), dose, administration method/route, exposure duration, etc., it is necessary to critically assess how these characteristics of nano material are linked to their detrimental effects on human health (Okeke et al., 2022). To enable biological and therapeutic uses for nano materials, a deeper understanding of the mechanisms underlying their interactions with biomolecules would be required. Extensive toxicity studies are required to identify and evaluate the potential risks associated with the use of nano-enabled agrochemicals.

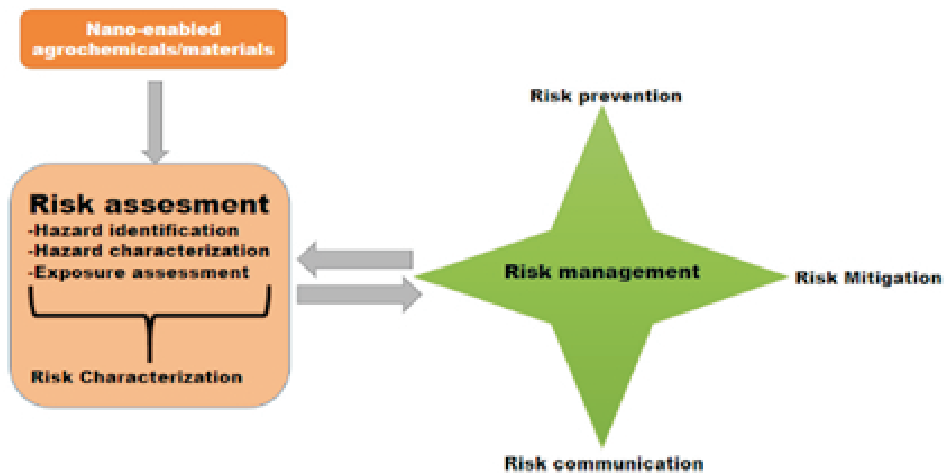

Fig. 2.9 Schematic presentation of the toxicological risk assessment of nanomaterials on humans and the management strategies (Adapted from Okeke et al., 2022)

7. Conclusions

Food safety and environmental protection have become more important and essential components of sustainable agriculture. To fulfil the increased food demands of the world's growing population, agriculture must develop and modernise, but not at the cost of environment sustainability. The main component of sustainable agriculture is the use of the least agrochemicals, leading to reduced production costs and higher yields. Due to the associated health and environmental implications of nanotechnology in agriculture, researchers and experts have feared its reliability. Nano-agrochemicals can reduce runoff and residual contamination by delivering site-specific and controlled active component releases. Nano-chemicals have a lot of benefits over conventional chemicals, but they must be used cautiously to avoid any issues. In order to detect and reduce the risks related to nano-agrochemicals before they are commercialized, extensive and systematic research is required.

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3. Systematic study to unravel the potential of nano-technological approaches for insect pest management

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Abstract: The word 'nano' is generally used for materials having size ranging between 1 to 100nm. However, these materials should display characteristic features distinct from properties of bulk materials because of their size. This chapter deals with the traditional strategies used for insect pest management and potential of nano materials' as modern approach of nano-science and nano-technology in insect pest management. Nano-pesticide products may show numerous benefits including amplified efficacy, durability, and a reduction in the quantity of active ingredients required to be used for effective management of insect pests. Several nano formulations viz. nano-emulsions, nano-capsules and products containing immaculate engineered nano particles like metals, metal oxides and nano-clays have been recommended. Nano-technological deliverables like nano materials, encapsulated nanoscale plant production and protection inputs such as fertilizers, pesticides, herbicides, plant growth regulators and other formulations using surfactants, polymers, dendrimers, surface ionic attachments and other related mechanisms can be utilized in controlled release of agricultural and horticultural inputs. Nano-particles present the possibilities for well-organized and effective control of pests in crops and transformation of green revolution to ever green revolution.

Introduction

In horticultural and agriculture production system, insect pests are the major challenges in increasing productivity, and require regular application of insecticides for their management. Irregular, excessive and non judicious application of pesticides result in development of 3Rs *viz.,* resistance, resurgence and residue besides the environmental hazards. The challenge of balance between crop production and protection can be achieved by adopting nanotechnology. Nano particles often exhibit novel features like extra-ordinary strength, chemical reactivity and high electrical conductivity. The outcome of nanotechnology may play imperative role in decreasing the non-targeted toxicity and enhance the efficiency on targeted organisms with less quantity of selective ingredient. Therefore, nanotechnology would provide efficient, eco-friendly and safe alternatives for crop protection (Kannan et al., 2020a and b). Nanotechnology has made enormously quick and intrusive growth in agriculture and horticulture in the last decade and has resulted in development of novel input materials with wide applications to resolve the unsolved pest problems.

Importance of Nanotechnology

The term 'nanotechnology' means 'dwarf' in Greek and more precisely, the word 'nano' means 10^{-9} of a metre (Bhattacharyya et al., 2010). Nanotechnology is usually represented by two different approaches, 'top-down' and 'bottom-up'. 'Top-down' refers to making nanoscale structures from smallest structures by machining, templating and lithographic techniques, for example photonics applications in nano-electronics and nano-engineering. The 'bottom-up' refers to atom by atom or molecule by molecule, often by self-assembly or self-organization which are applicable in several biological processes. Due to these properties, nanotechnology is being visualized as a rapidly evolving field that has the potential to revolutionize agriculture, horticulture and food technology (Salata, 2004).

Principles of nanotechnology

Nano materials offer the advantages of effective delivery of agrochemical due to their small size, large surface area and easy attachment (Ghormade et al., 2011). Nano particles release agro-chemicals to plant system using controlled delivery systems compared to conventional pesticide formulation where, more than 90% of pesticides run off into the environment and residue in agricultural products in the process of application. The control delivery systems facilitate the sustained release of the active ingredient at the target site for a required quantity of release and extended period of time. Thus, targeted delivery increases the efficiency of pesticide into action targets such as plants, insects and pathogens; increasing solubility; dispersion for fat-soluble chemicals in aqueous solution; reducing pesticide application; treatment frequency by extended lasting validity period and enhancing the bio-efficacy; reducing the chemical input to plants; solving the problem of non-target toxicity and improving chemical stability for light-sensitive compounds by restricting photo-degradation (Jha et al., 2011). The sustained release of pesticide protects bio-diversity in ecosystem. Nano materials such as carbon, titanium dioxide, zeolites, silver, silica, copper and alumina have the potential for the use in controlling varied insect pests. Nano materials are synthesized using various methods from solid doped particles (often non persistent) to polymer, oil–water based structures, besides as additives (mostly for controlled release) and active constituents. Nano materials in plant protection products modify the functionality or threat profile of active ingredients (nano-enabled pesticides) and promise benefits of efficient formulation, easier application, better targeting of pest species, increased effectiveness, lower application rates, and better environmental safety (Walker et al., 2017).

Nano materials and pest management in agricultural and horticultural crops

Nano materials such as carbon, titanium dioxide, zeolites, silver, silica, copper and alumina have the potential for use in controlling a range of insect pests (Roy, 2009)

Clay minerals: Clays are fine grained materials belonging to the wider group of minerals. The hydrophilic properties of the clay minerals' surface can be attained through hydration of exchangeable cations and the presence of Si-OH clay mineral groups. In the absence of water, the clay minerals have higher affinity to the hydrophobic compounds. Hence, clay enables to absorb both hydrophilic and hydrophobic compounds from the insect body and cause desiccation followed by death. The flat surfaces of the insect facilitate the adherence of more particles to the surface of their bodies. Now a days, nanosilica is widely used in the field of medicine, drug development, packaging, coating, filtration and has also gained importance as a novel nano-biopesticide (Barik et al., 2008). Application of diatomaceous earth @ 1.5g/kg after 7 days of exposure caused mortality in both adults and larvae of *Tribolium confusum* (flour beetle), adults of rice weevil (*Sitophilus oryzae)* and silica nano particles @ 200 mg/kg in *Tribolium castaneum* and *Rhyzopertha dominica* (Debnath et al., 2011,2012).

Nanoscale silver: Silver nano particles, having high surface area and high fraction of surface atoms, exhibit high antimicrobial effect as compared to the bulk silver. Double capsulized nano silver was prepared by chemical reaction of silver ion involving physical method, reducing agents and stabilizers. They were highly stable and very well dispersive in aqueous solution. It eliminates unwanted microorganisms in planting soils and hydroponic systems. It is being used as foliar spray. Moreover, silver is an excellent plant-growth stimulator. Metal-based nano particles can be combined with pesticides which enable the reduction in application dose. Rouhani et al. (2012) confirmed that silver nano particles showed higher insecticidal activity to oleander aphid (*Aphis nerii)* in several ornamental plants. Sahayaraj et al.(2016) reported that Ag^+ aqueous solution and pungam oil-based gold nano particles caused more mortality, while aqueous solutions of Ag^+ - AuNPs treatment drastically enhanced the food consumption, assimilation but reduced the conversion hence, affected the growth in *Pericallia ricini*. Plant-synthesized (*Sargassum muticum*) silver nanoparticles exhibited promising activity @ 30 ppm as ovicides and adulticides against *Anopheles stephensi*, *A. aegypti*, and *C. quinquefasciatus* (Madhiyazhagan et al., 2015). Sankar et al. (2015) prepared silver and lead nanoparticles from *Avicennia marina* plant extracts. The results of their insecticidal effect against *S. oryzae* showed higher mortality on third day after treatment with Pb NP and fourth day after treatment in case of Ag NP. Biologically synthesised silver nanoparticles from curry leaves (*Murraya koenigii*) were used against pulse beetle (*Callosobruchus chinensis*) on soybean seeds. Ag NPs at 35 ppm showed >93% mortality on the 14^{th}day after treatment whereas, 100% mortality was observed at 70 ppm on the same day (Yerragopu et al., 2019).

Nanoscale alumino-silicates: Nanoscale pesticides are efficiently formulated by chemical companies. Alumino-silicate nanotubes sprayed on plant surfaces are easily picked up in insect hairs where these are actively groomed and pesticide-filled nanotubes are consumed by insects. Nanotubes are biologically more active and relatively more environmentally-safe pesticides. The insecticidal activity of nanotubes demonstrated against two stored grain insect pests *viz. S. oryzae* and *R. dominica*. Nanotubes caused mortality after 3 days of continuous exposure, and were projected as the potential cheaper and reliable alternative for the control of such insect pests (Stadler et al., 2010). Stadler et al. (2012) compared insecticidal efficiency of nanostructured alumina (NSA) and DE dust on *S. oryzae* and *R. dominica* at different humidity levels and reported that NSA was capable of causing more mortality in *S. oryzae* and *R. dominica* than DE dust (Protect-It®). Both the treatments suppressed the progeny generation. NSA may be used as a counterpart of the commercial DE based dusts. Belhamel et al. (2020) reported that NSA could act as seed protectant against *Oryzaephilus surinamensis, Stegobium paniceum* and *C. confusum*. The mortality of insects was the highest in *S. paniceum* (100%) followed by *O. surinamensis* (80.64%) and *T. confusum* (79.41%) at the highest dose of 400 mg/kg. However, NSA had no significant effect on germination of treated seeds.

Silica nano particles: Silica nano particle is a unique nano material, prepared from silica resources and used as nano-pesticide. Nanosilica gets absorbed into the cuticular lipids by physiosorption and causes death of insects purely by physical means when applied on leaves, stem surface and could be successfully used to manage a range of agricultural insect pests and animal ecto-parasites of veterinary importance as well. Nanosilica caused abrasion and injury on the external surface and can effectively replace the chemical insecticides in the management of stored pests (Zahran and Sayed, 2021). The mesoporus silica nano particles also enable to deliver DNA and chemicals into plants thus, may emerge as a powerful new tool for targeted delivery into plant cells and help in pest control (Barik et al., 2008). Silica nano particles were highly effective against *S. oryzae, R. dominica*, *Callosobruchus maculatus* and *Lasioderma serricorne* @ 2.5, 1.5 1.0 and 0.5 g/kg of seeds, respectively (Borie et al., 2015 and Ravikumar et al., 2017). Silica nano particles could be efficiently used in stored grain integrated pest management. Arumugam *et al.* (2016) reported the use of nanosilica as a stored pulse protector against bruchid (*C. maculatus)*. It resulted in significant decrease in egg laying, adult development and seed damage potential and among various treatments, *C. cajan* treated seeds showed complete retardation of bruchid growth. Biologically derived nano-silica from wild sugarcane (*Erianthus arundinaceus*) had proved insecticidal activity against larvae of diamond backmoth, *Plutella xylostella* with LC_{50} value of 30.03 µg/ml (Kannan et al., 2017). The nano silica used @ 500 ppm/kg showed 100% mortality over nano clay and nano alumina. In addition to adult mortality, silica nano particles also inhibited oviposition (Padmasri et al., 2018). Ibrahim and Salem (2019) reported that nano zeolite showed toxicity on storage pests *T. confusum* and *C. maculatus* with 96.66% mortality on *T. confusum* adults after 14 days of exposure on wheat kernels at the highest dose of 800 ppm. *C. maculatus* on cowpea seeds, treated with 500 ppm of nano zeolite, showed 100% mortality within 72 hours. Nano zeolite could be efficient substitute for the chemicals in stored pest management.

Zinc oxide: Zinc oxide has wide applications because its nanostructure displays high catalytic and strong adsorption ability. Malaikozhundan and Vinodhini (2017) studied the insecticidal efficacy of *Pongamia pinnata* leaf extract coated zinc oxide nano particles against pulse beetle, *C. maculatus*.The synthesised nano particles reduced the activity of enzymes viz. midgut α-amylase, cysteine protease, α-glucosidase, β-glucosidase, glutathione S-transferase (GST) and lipase in *C. maculatus.* ZnO nano particles applied at 25 µg mL^{-1} resulted in 100% mortality and delay in the developmental period of beetle thus, ultimately leading to mortality. ZnO nano particles from spinach leaves applied @ 1500 ppm showed insecticidal effect on the adults of *C. analis* in the form of higher mortality, reduced fecundity and less seed damage (Wazid et al., 2018). Toxicity bioassays from biologically synthesised ZnO nano particles from leaf powder of *R. communis*, *Jatropha curcas* and *Citrus paradise* were conducted against *T. castaneum* and *Trogoderma granarium* and revealed 66.32 and 49.51% mortality against *T. castaneum* and *T. granarium,* respectively (Abbas et al., 2020). Haroun et al. (2020) reported that ZnO and hydrophilic SiO_2 NPs had a significant lethal effect on *S. oryzae* and *C. maculatus* whereas, *T. castaneum* showed maximum resistance against nano particles.

Titanium dioxide: Titanium dioxide (TiO_2) is a non-toxic, white pigment widely used as a very strong disinfectant as compared to chlorine and ozone. Since TiO_2 is harmless it is approved for use in food products up to 1% of the final weight of the product. TiO_2 photo catalyst technique has great potential in various agricultural applications, including plant protection since it does not form toxic and dangerous compounds and possesses great pathogen disinfection efficiency (Yao et al., 2009). TiO_2 nano particles expressed its insecticidal property in leaf worm, *Spodoptera littoralis* with LC_{50} value of 125 µg/mL (Shaker et al., 2017), diamondback moth (*P. xylostella*) with LC_{50} of 37.57 µg/mL in cauliflower (Preetha et al., 2018), human head parasite (*Pediculosis humanus capitis*) with LC_{50} of 68.7 and 34.1 µg/mL in nymph and adult, respectively, mosquitoes vectors (*Anopheles stephensi*) with LC_{50} of 14.3 µg/mL and *Culex quinquefasciatus* with LC_{50} of 20.8 µg/mL, affected the biological parameters of the insect.

Carbon nano materials: Carbon based nano materials viz. single walled carbon nanotubes, multi walled carbon, bucky balls, graphene, etc. occupy a prominent position in various nano-biotechnolgy applications. The advantage of using carbon-based nano materials, functionalized with magnetic nano particles, is that the internal space allows filling of suitable plant protecting chemicals and the functionalized magnetic nano particles allow external control for the movement of nano carriers inside the plant system. CNT materials can be utilized for detection of hidden insects by nano-sensor based monitoring through electronic devices for sensing the toxic gases released by the insects (Lee et al., 2014).

Magnetic nano particles: Magnetic-based nano materials could be utilized for site-targeted delivery of systemic plant protection chemicals which affect only specific regions of plants. The movement of internalized magnetic nano materials could be tracked externally using high power external magnets. It is well known that insects possess ferro-magnetic resonance which is temperature dependent and that magnetic nano particle in social insects act as geomagnetic sensors (Esquivel, 2007).

Polymer nano particles: Polymer nano particles are eco-friendly, readily bio-degradable, and do not generate toxic degradation by-products and are cost effective. The uses of several biopolymers, i.e. polymers produced by natural sources have good physical and chemical properties for mild biodegradation to avoid environmental contamination. The commonly used synthetic and natural polymers in CRFs for insecticide application are listed in Table 3.1.

Types of nano-based pesticide formulations for controlled release (CRFS)

Nanotechnology created innovative nano-based pesticide formulations i.e., nanopesticides. Nanopesticides can be prepared using emulsion, polymer, lipid, ceramics, proteins and metals. The common methods for preparation of nanopesticides are by using oil in water emulsion system (micro-emulsion and nano-emulsion) and the conversion of emulsion to organic nano particles by milling, solvent evaporation, co-acervation and precipitation techniques (Ragaei and Sabry, 2014; Nuruzzaman et al., 2017). Nano-pesticides can also be developed by directly processing into nano particles (nanosized pesticides) or by loading pesticides with nano-carriers in delivery systems. In nano-carrier systems, pesticides are loaded by encapsulation inside the nanoparticulate polymeric shell, absorption onto the nano particle surface, attachment on the nano particle core via ligands or entrapment within the polymeric matrix. Various nanoformulations have been developed which include nanoemulsions, nanocapsules, nanosphere, nanosuspensions, solid lipid nano particles, mesoporus nano particles, electrospun nanofiber, polymer nano particles, magnetic nano particles, nanogels and dendrimers (Zhao et al., 2017).

Nanoencapsulation for smart delivery of pesticides

Nano-encapsulation is another component of nanotechnology that offer variety of desirable features including reduction in human exposure to active ingredients, controlled release, longer residual concentrations, elimination of organic solvents and increased efficacy (Hack et al., 2012). Encapsulation of formulations have revolutionized the application of pesticides due to the development of nanotechnology in insect pest management as it reduces the doses compared to the conventional pesticides to have maximum effect with more target-oriented action of the pesticides. In this method, the core material (pesticide) is coated i.e encapsulated by capsulation material or shell and the size of the pesticide reduces up to the nano

Table 3.1 List of polymers often used in the nanoparticle production

Polymer	Active compound	Nano Material	References
Lignin-polyethylene glycol-ethyl cellulose	Imidacloprid	Capsule	Flores-Cespedes et al. (2012)
Polyethylene glycol	B-Cyfluthrin	Capsule	Loha et al. (2012)
Chitosan	Etofenprox	Capsule	Hwang et al. (2011)
Polyethylene	Piperonyl Butoxide & Deltamethrin	Capsule	Frandsen et al. (2010)
Polyethylene glycol	Garlic Essential Oil	Capsule	Yang et al. (2009)
Poly (acrylic acid)-bpoly (butyl acrylate) Polyvinyl alcohol Poly vinyl pyrrolidone	Bifenthrin	Capsule	Liu et al. (2008)
Alginate-glutar aldehyde	Neem Seed Oil	Capsule	Kulkarni et al. (1999)
Alginate-bentonite	Imidacloprid	Clay	Fernandez-Perez et al. (2011)
Polyamide	Pheromones	Fiber	Hellmann et al. (2011)
Methyl methacrylate and methacrylic acid with and without 2-hydroxy ethyl meth-acrylate cross linkage	Cypermethrin	Gel	Rudzinski et al.(2003)
Lignin	Imidacloprid or Cyromazine	Granules	Fernandez-Perez et al.(2011)
N-(octadecanol-1-glycidyl ether)-O-sulfate chito sanoctad ecanol glycidyl ether	Rotenone	Micelle	Lao et al. (2010)
Poly ethylene glycol dimethyl Esters	Carbofuran	Micelle	Shakil et al. (2010)
Carboxy methyl chitosanric inoleic acid	Azadirachtin	Particle	Feng and Peng (2012)
Chitosan-poly (lactide)	Imidacloprid	Particle	Li et al. (2011)
Poly vinyl chloride	Chlorpyrifos	Particle	Liu et al. (2002)
Vinyl ethylene and Vinyl acetate	Pheromones	Resin	Wright (1997)
Poly (methyl metha-crylate)-Poly (ethylene glycol) Poly vinyl pyrrolidone	Carbofuran	Suspension	Chin et al. (2011)
Anionic surfactants (Sodium linear alkyl Benzene sulfonate, naphthalene sulfonate condensate sodium salt and sodium dodecyl sulfate)	Novaluron	Powder	Elek et al. (2010)

size.

In nano-encapsulation, insecticide is slowly and efficiently released for insect pest control. In this process, individual particles or droplets of solid or liquid core material are surrounded or covered with a continuous film of polymeric material and pesticide is released only in the targeted environment i.e. in specific pH (e.g., in the stomach or inside a cell), specific temperature, moisture, external ultrasound frequency or in the occurrence of explicit compounds. Some encapsulation is done in such a way that it gets absorbed in the surface of the plant and facilitates protract release which lasts for longer time compared to conventional pesticides.

Polymers based nanoformulations for insect control

Commonly used biodegradable polymers incorporated with nano-pesticides include Alignate, Carboxyl methyl cellulose, Pecktin, Chitosan and Guar gum. Amphiphilic copolymers, synthesized from poly ethylene glycols and various aliphatic diacids, which self-assemble into nano-micellar aggregates in aqueous media, were used to develop controlled release formulations (CRFs) of imidacloprid [1-(6 chloro-3-pyridinyl methyl)-N-nitro imidazolidin-2-ylideneamine] using encapsulation technique (Adak et al., 2012). The time taken for the release of 50% of imidacloprid ranged from 2.32 to 9.31 days for the CR formulations. The developed CR formulations can be used for efficient pest management. The use of many biopolymers, i.e. polymers produced by natural sources having good physical and chemical properties but present mild biodegradation conditions, are an interesting approach to avoid the use of petrochemical derivatives that might be another source of environmental contamination. Release mechanisms can be controlled by diffusion and/or dissolution (erosion), depending on the polymer properties i.e. the way the active ingredient is distributed, loaded and its solubility. Polymer matrix, subjected to swelling and dissolution (i.e., hydrophilic polymers) and the thickness of the gel-layer formed will influence the diffusion pathways and hence, alter the release behaviour (Kaunisto et al., 2013). The processes leading to polymer degradation are expected to greatly influence the release profiles. Sometimes the remaining active ingredient is released as a result of severe degradation of the polymer matrix. In addition, in case the active ingredients are not homogeneously distributed within the polymer matrixes, rapid desorption and diffusion from the surface may result in a burst of release of the active ingredients. This undesirable effect has been reported for a number of nanopesticides and has motivated the subsequent development of alternatives like nanogels or nanofibers.

Nano-encapsulation process of insecticides

Nanopesticides consist of organic elements like polymers and /or inorganic elements like metal oxides in various forms (eg. particles and micelles).The nano-formulations are used with the aim to increase the apparent solubility of poorly soluble active ingredient, and to release the active ingredient in a slow/targeted manner and/or protecting the active ingredient against premature degradation. Formulated pesticides in the market are a blend of active ingredients, solvents, surface active ingredients, stabilizers etc. Among them, the active ingredients alone are responsible for killing target pests and other materials like organic solvents, surface active ingredients (stickers or spreaders) and stabilizers help to maintain their solubility, stability and pesticide activity. Persistence of insecticides in the initial stage of crop growth helps to bring down the pest population below economic thresh hold level and to have an effective control for a longer period. In order to protect the active ingredient from environmental conditions and promote the pre-existence, a nano-technological approach i.e. micro-encapsulation can be used to improve the insecticidal value. Nano-encapsulation techniques propose the use of nano particle to formulate insecticide formulations wherein, the active molecules are held and are reoriented for their slow release. Nano-encapsulated products facilitate proper absorption of the active ingredients into the plants and protect them from abiotic degradation (Scrinis and Lyons, 2007). Nano encapsulates release the micro-encapsulation comprising nanosized particles of the active ingredients being sealed by a thin walled sacor shell (Protective coating). Micro-capsules generally measures 50 - 500 microns in size. Nano encapsulation with nano particles in form of pesticides allows proper absorption of the chemical into the plants unlike the case of larger particles present in the conventional insecticide formulations. The process involved in encapsulation of pesticides is given in Fig. 3.1.

Advantages of nano-encapsulation of pesticides

- Long lasting biological activity
- Improved safety by removing flammable solvents
- Less effect on other species
- Reduction in damage to crops
- Prevents degradation
- Less pesticide loss by evaporation
- Improved handling properties of a sticky material
- Isolating a reactive core from chemical attack.

Characteristics of Nano-encapsulated sphere

Nanosphere can be designed to release under different conditions i.e.

a. Quick and specific release
b. Slow release
c. Moisture release
d. Heat release
e. pH release
f. Ultrasound release

Release mechanism of active ingredient from controlled release nano-formulations

An efficient controlled release formulation must remain inactive until the active compound is released. The way how an inert material i.e. the nanopolymers, controls the amount and rate of chemical release depends basically on the chemical nature of the formulation. In most of the systems, broadly two main release mechanisms are associated with controlled releases; (i) model-independent and (ii) model dependent (curve fitting) approach which are governed by various thermos-dynamic factors. In the former case, the data are represented by sample times, similarity factor, or a dissimilarity factor. The later approach is prescribed in the situations when plenty of data points are available or in a "data rich" scenario, where a mathematical function can be applied for in vitro release data. In the beginning, the release rate is usually believed to be controlled by diffusion while during the final stage of the release period it is degradation/erosion (Singh et al., 2020).

There are four possible release mechanisms:

- Diffusion of pesticide through water-occupied pores
- Solvent release of pesticide due to osmotic pressure
- Stimuli of pesticide
- Degradation controlled pesticide release due to polymer degradation

Mostly, diffusion is the main release mechanism that occurs through water occupied pores and relies on the porous structure of the matrix having a polymeric coating. Pores in the matrix must be consecutively extending from the pesticide molecule to the external surface, and large enough for the pesticide molecules to pass through. Water seeps through the coating layer forming a reservoir of active ingredient (AI). As represented in Fig. 3.2, the active component shifts towards the surface through the pores filled with water, and this process takes some time resulting in a sustained release. The outflow of the AI is again governed by a few factors like thickness of the membrane, solubility of AI in water and the surrounding environment.

Nano-encapsulated pesticides used for crop pests management

Nano-encapsulation is a process through which a chemical is slowly but efficiently released to the particular host for the insect pest control. Nano-technologically derived materials improve the bio-availability of active molecules, reduce toxicity, extent of the release time, solubility, stability, protect the early degradation and reduce the required dose to kill the target organism (Smith et al., 2008). Nano-encapsulated formulations allow the release of active ingredients in a controlled manner, resulting in the retention of pest control efficacy over extended time than the commercial pesticides. Various controlled release formulations have been synthesized using wide nano encapsulation techniques, materials and their improved characters have been well documented.

Micro-encapsulation has been used as a versatile tool for hydrophobic pesticides, enhancing their dispersion in aqueous media and allowing a controlled

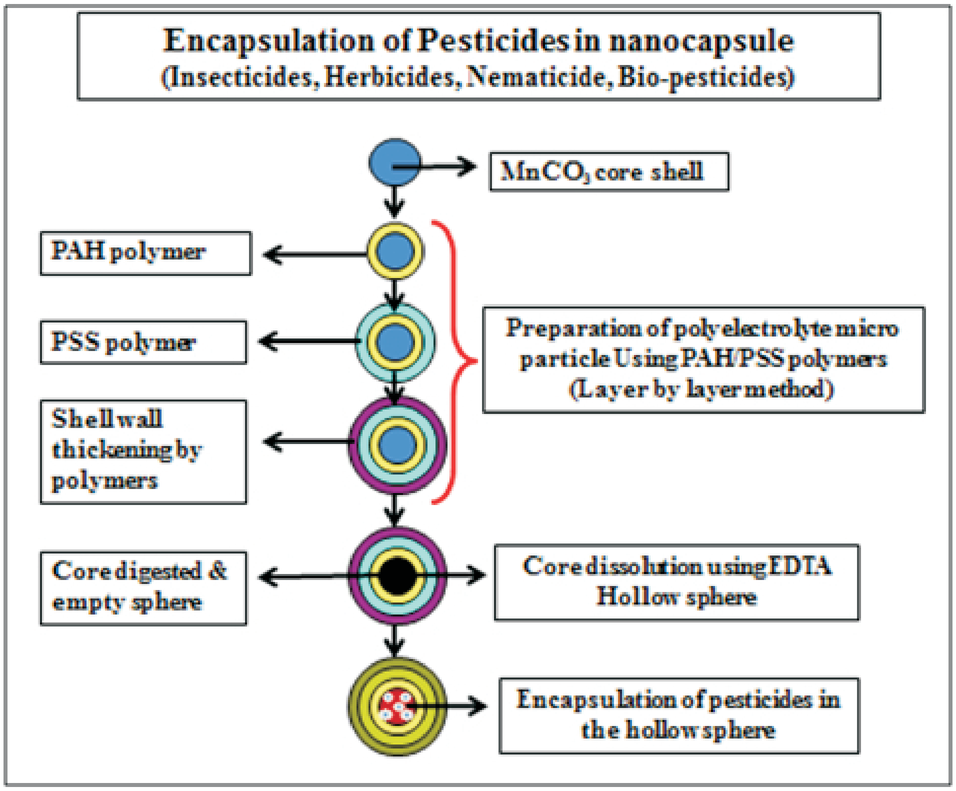

Fig. 3.1 Process involved in encapsulation of pesticides for their controlled release

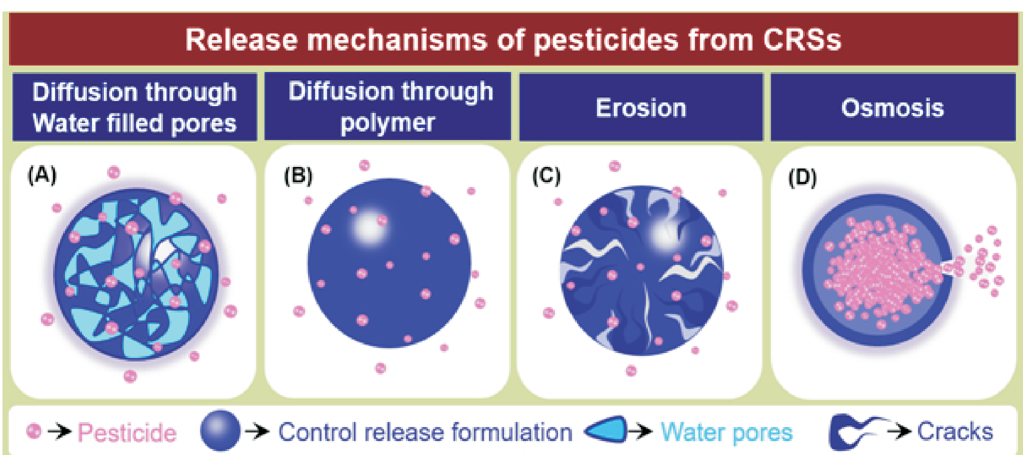

Fig. 3.2 Schematic illustration of release mechanisms of pesticides from CRSs. (a) Diffusion of pesticide through water-filled pores, (b) Pesticide movement due to osmotic pressure, (c) Direct diffusion through the polymer, (d) Pesticide release due to polymer degradation (Cited from Singh et al., 2019)

release of the active compound. It reduces the problems associated with drifting and leaching due to its solid nature and leads to more effective interaction with the target insect. There is no need for repeated applications, leading to decrease in cost and the environmental damage.

Nanoencapsulated CRFs pesticides and biopesticides are very effective in controlling stored grain pests (Table 3.2). Loha et al. (2012) assessed the effect of nano encapsulated CRFs of β-cyfluthrin with PEG which showed higher mortality of *C. maculatus* than the commercial formulation. The EC_{50} of commercial and nano CRFs with PEG β-cyfluthrin on the 7^{th} day were 43.24 mg L^{-1} and 1.89 mg L^{-1}, respectively, Similarly, the CRFs of carbofuran against the root-knot nematode (*M. incognita*) infecting tomato plant and utility of encapsulated insecticide pyrifluquinazon with polymeric chitosan on *Myzus persicae* (green peach aphid) were explained by Kang et al. (2012). Adak et al. (2012) synthesized nanoencapsulated CRFs of imidacloprid using polyethylene glycol, 1 aliphatic diacids and tested these against *Melanagromyza sojae* (stem fly) and *Bemisia tabaci* (whitefly) in soybean. It was revealed that CRFs were better than commercial formulations at lower dose without any residues in crops and soil. Particle size dependent efficiency of spinosad was experienced in *Spodoptera litura*. of the Nano suspension comprising particle size of 404 nm resulted in the LC_{50} value of 15 mg L^{-1}, which further decreased to 11, 7.6 and 4 mg L^{-1} for particle size of 372, 332 and 163nm, respectively and the smaller sizes resulted in higher efficacy of commercial pesticide (Hwang et al., 2011).

Nano formulations of botanical bio-pesticides in insect control

Bio-pesticides and plant-based botanicals are considered as an eco-friendly and cost-effective alternative to synthetic chemical insecticides. Nano-particles are being used as an effective strategy at Tamil Nadu Agricultural University, Coimbatore. A neem-based formulation (198 nm) has been developed and was observed to be effective in controlling sucking pests such as thrips, aphids and mites. Yang et al. (2009) reported the insecticidal activity of garlic essential oil encapsulated with polyethylene glycol against adults of *T. castaneum* showing 80% mortality. Likewise, nano particles containing essential oils of geranium or bergamot also showed contact toxicity against *T. castaneum* and *R. dominica* (Gonzalez et al., 2014). Forim et al. (2013) reported 100% mortality of *P. xyllostella* for the nano particles encapsulated with neem extract. Nano-emulsions of the essential oils from three local plants *Ageratum conyzoides, Achillea fragrantissima* and *Tagetes minuta* showed ovicidal, adulticidal and residual activities against the cowpea beetle, *C. maculatus*. Nano-emulsion of Eucalyptus oil exhibited higher insecticidal and biological activity against newly-hatched larvae of *Pectinophora gossypiella* and *Earias insulana.* Nano-formulation of the botanical biopesticide based on sweet flag (*Acorus calamus)* has been evaluated for comparative toxicity to the red flour beetle, *T. castaneum* and indicated that the lower doses (below 1%) of nano formulation was sufficient for 100% mortality (Prabakaran et al., 2017). Similar studies by

Kalyanakumar et al. (2017) with the same two products have shown comparable results on ovicidal efficacy on eggs of the rice moth *Corcyra cephalonica*. Among the nano particles, silver nano particles are widely used accounting for more than 30% of nano-based commercial products in the world (Table 3.2).

Nano materials for controlled release of semio-chemicals

The pheromones are naturally occurring volatile semio-chemicals and are considered as eco-friendly biological control agents. They induce impaired sexual communication and mating disruptions among pests**.** One of the ready to adopt immediate possibilities is using nanoscience in pest control is through pheromones. Pheromones are highly volatile compounds and their release pattern can be regulated through nano-formulations.

Nano material based formulations of semio-chemicals facilitates controlled release of volatile molecules for insect attraction and repellent action. Dharanivasan et al.(2017) explored the scope of metal oxide nano particles (SiO_2, TiO_2, and ZnO) for controlled release of methyl eugenol (ME) from plywood lure dispensers. Among the nano materials, ME loaded with TiO_2 nano particles exhibited a higher number of fruit fly catches than the commercial traps under field condition. The scope for combining both cue lure and methyl eugenol parapheromones in enhancing the attractiveness to *Bactrocera cucurbitae* has been well documented in India (Kanan et al., 2022). Pradhan et al. (2013) suggested that slow release of pheromone for 7 weeks was observed in nano zeolite formulation followed by rubber septa for 4 weeks in rice yellow stem borer, *Scirpophaga incertulas*. Similarly, Kannan and Soundararajan (2017) loaded the male attracting female sex pheromone of rice yellow stem borer, *S. incertulas* in a polymer-based electro spun fiber matrix for extended release and enhanced moth caches.

Table 3.2 Use of nanoparticles in insect pest management

Application	Nano particles	References
Pesticide delivery		
Avermectin	Porous hollow silica (15 nm)	Li et al. (2007)
Ethiprole / phenylpyrozole	Poly-caprolacetone (135 nm)	Boehm et al. (2003)
Gamma cyhalothrin	Solid lipid (300 nm)	Frederiksen et al. (2003)
Tebucanazole/ chlorothanil	Polyvinylpyridine and polyvinyl-pyridine co-styrene (100 nm)	Liu et al. (2001)
Biopesticide		
Plant origin nano silica for control of *Artemisia arborescens*	Nanosilica (3-5 nm)	Barik et al. (2008)
Essential oil encapsulation	Solid lipid (200-294 nm)	Lai et al. (2006)
Microorganisms *Lagenidium gigantum* cells in emulsion	Silica (7-14 nm)	Vandergheynst et al. (2007)
Pesticide sensor		
Carbofuran/triazhophos	Gold (40 nm)	Torney et al. (2007)
Dimethoate	Iron oxide (30 nm)	Gan et al. (2010)
Organophosphate	Zirconium oxide 50 nm	Wang et al. (2009)
Pyrethroid	Iron oxide (22 nm)	Kaushik et al. (2009)
Pesticide degradation		
Imidachloprid	Titanium oxide (30 nm)	Gaun et al. (2008)

(Cited from Manjunatha et al., 2016)

This fortification process assisted in regulated release of pheromone upto to 63 days for the moth catches while conventional rubber septa attracted the moth up to 24 days only. In other approaches, sex pheromone of European grapevine moth *Lobesia botrana* (E, Z0-7, 9-dodecadien-l-yl acetate (DA) was immobilised in an electro spun fibre matrix made of oligo lactide (OLA). The synthetic pheromone delivery for the red palm weevil at the Central Plantation Crops Research Institute (CPCRI), Kasaragod, Kerala revealed that nano-matrix pheromone trap set @ one trap/ha significantly attracted more number of red palm weevils of both the sexes with the longest period than the commercially available Chemtica® and PCI® pheromone lures. Nanogels were prepared from a pheromone, methyl eugenol using a low molecular mass gelator (ME). Nanogels are thermos reversible, which can be re-activated by adding the pheromone material by changing the temperature of the gels. These are mostly used for control of fruit flies (*Batocera dorsalis*) attacking the fruit crops like mango, banana, apple, orange, peach etc., can be controlled by the use of nanogel pheromone traps. Advantages of using nanogels include low cost, green chemical (less toxic to animals and human beings), long lasting residual activity and higher efficacy. Similarly, Bhagat et al. (2013) has developed a pheromone-based nano-gel to regulate the release of methyl eugenol against fruit fly (*B. dorsalis*) in guava. The nano-gel has been developed using supramolecular principles and nanotechnological approaches that are chemically, mechanically and thermally stable and offered extended release of eugenol up to 30 weeks under field conditions whereas, the normal eugenol release existed within three weeks. There is good scope to develop nano material-based formulations of semio-chemicals of rhinoceros beetle *Oryctus rhinoceros*, banana stem weevil (*Odoiporus longicollis),* sweet potato weevil (*Cylas formicarius)*, cashew stem borer, citrus leaf miner and oil palm psychid (*Metesia plana).*

Use of nanosensors to deduct the pest incidence and pesticide residues

Early detection of pest incidence is of utmost importance to protect the crops. Biosensors can be used to detect the pest incidence in crops. Magnetic nano-particles are known to be omnipresent, and their distribution pattern could be used for the detection of pest incidence in crops. Nano-sensors for pesticide residue detection offer highly sensitive, low detection limits, super selectivity, fast responses and small sizes (Liu et al*.,* 2008). Nano-sensors have been aimed to detect the pesticide residues such as methyl parathion, parathion, fenitrothion and dichlorvos. Some of the biosensors C, Au, hybrid Titanium (Ti), Au-Platinum (Pt), and nanostructured lead dioxide (PbO_2)/TiO_2/Ti are used to immobilize the enzymes on sensor substrate and to increase the sensor sensitivity. Enzyme based biosensors for organochlorines, organophosphates and carbamates residue detection are also effective. Nano materials, in addition to its use for pesticide detection, have also been applied for pesticide degradation. The potential of using nano-TiO_2 film in photocatalytic degradation of organochlorine pesticides is also reported. Enzyme based biosensors for organochlorines, organophosphates, and carbamates residue detection are also effective.

Safety of Nano insecticides

Nano materials need to be evaluated, so that this novel technology does not meet the same apprehensions and bottle-necks as has been faced by genetically modified crops. Potential human health concerns presented in the EPA Pesticide Program Dialogue Committee (PPDC) meeting held on April 2010, are:

1. Dermal absorption (NPs are so small that these may pass through cell membranes)
2. Inhalation (These may be inhaled deep into lungs, and translocated to the brain i.e, could cross the blood brain barrier)
3. Potential Environmental Concerns - High durability or reactivity of some nano materials raises the issues on their fate in environment
4. Lack of information to assess environmental exposure to engineered nano materials. The current state of knowledge does not seems to be sufficient to make a reliable assessment for the benefits and risks associated with nano-pesticides.

Human safety

Many of the nano particles have a fairly short life span because of their tendency to agglomerate or dissolve in water. Moreover, the human body is endowed with various mechanisms for filtering out or removing such particles. Nevertheless, the effects of exposure to engineered nano particles may differ from the effects caused by naturally occurring nano particles. Engineered nano particles may be able to evade the body's defences because of their size or protective coatings and may pose health and environmental risks due to the exposure to engineered nano particles. Therefore, extensive studies are required to understand the mechanism for nano materials' toxicity and their impact on natural environment. Walker et al. (2017) pointed out various issues for regulators, including as to how does the ecological risk assessment of nano-enabled pesticide products differ from that of conventional plant protection products.

Safety of beneficial insects in agricultural eco-system

In the recent past, many nano materials and nano-formulations have been exploited for the management of insect pest of crops. The knowledge on the interaction of nano materials on growth, development, parasitism or predatory efficiency and emergence capacity as well as to safeguard beneficial insects is studied and experimented completely. However, Kannan et al. (2020b) studied the effects of chemically engineered silica nanomaterials against predators (green lace wing) and parasitoids (*Trichogramma*) and indicated that nano materials are not causing deleterious effects to the natural enemies. Little harmfulness was observed at 500-fold (20,000 ppm) increased LC_{50} dose of host insect pests. Compared to nano materials, the synthetic chemical insecticides caused toxicity and impaired the development of natural enemies from host insects even at very low doses. Further, the potential environmental impacts of exposure to nano materials are less understood than the human health effects. Nano-emulsion of hexanal is reckoned as more owing to its extremely small droplet size of <100 nm and uniform surface coverage, high kinetic stability, low viscosity and optical transparency hence, it is emerging as a very attractive alternative product for the input delivery. It has also been targeted for assessing its eco-safety to beneficial biodiversity in the target ecosystem. It has been amply demonstrated that this product is safe to the natural enemies of insects like *Trichogramma* besides, being benign to honey bee workers (Kitherian, 2017).

Ecological risk assessment

The perspective and the key elements in the ecological risk assessment are presented in the form of the following questions-

i. What is the agronomic context for the use of the nano-enabled pesticide formulationƐ
ii. What is the nature and purpose of the nano material in the formulationƐ and
iii. What are the ecological protection priorities that need to be considered in the risk assessment of the nano-enabled pesticide formulationƐ

The collection of relevant information from various stakeholder groups, the formulation phase was undertaken focusing on another set of key questions, i.e.

i. How does the environmental behaviour of the nano-enabled pesticide differ from conventional formulations of the same a.i.Ɛ
ii. How does the nano material release the a.i. in the environmentƐ
iii. What information is necessary to characterize the novel properties of the nano-enabled pesticide formulationƐ and
iv. What risk reduction measures can be used to manage any environmental risks that are considered possible from the intended use of the nano-enabled pesticide productƐ

The answers for the above questions may explain the safety of nano insecticides to beneficial and other non- targeted organisms in the agricultural ecosystem.

Conclusion

Nanotechnology has the potential to revolutionize the existing conventional technologies in insect pest management in agriculture. The application of nano materials in crop protection remains unexplored. But nano based pesticides have the potential to play a key role in the management of pests. Nano-encapsulated pesticides formulation contains slow-releasing properties with increased high stability, high permeability, high solubility and high specificity. The development of eco-friendly nano-formulations with efficient delivery system and small quantities of nano-pesticides will be in great demand in future. The controlled release properties of nano-encapsulation materials to release the AIs to the target area using autosensing power needs further investigation. Although complete features (e.g., synthesis, efficacy and their fate) related to these nanomaterials are rarely found and their safety to human, beneficial insects in the agro-ecosystem, environmental hazards and ecological risk assessment process need to be investigated further in details.

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4. Nanotechnological approaches for plant disease management with special reference to Silver and Zinc nanoparticles

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Abstract: Nanotechnology finds its applications in numerous fields including agriculture where it has the potential to improve the farm productivity. It can minimise the cost of resources to mitigate biotic and abiotic stress with significantly reduced damage to the environment as compared to the conventional pesticides. Silver and zinc are amongst the most widely studied nanoparticles known for their disinfectant properties against many harmful microbes. The antimicrobial activity of Ag is due to the formation of insoluble compounds by inactivation of sulfhydryl groups in the fungal cell wall and disruption of membrane bound enzymes and lipids which cause cell lysis. Ag NP treated fungi lose their ability to replicate the DNA. These compounds exhibit higher toxicity to microorganism in a broad range of biological processes including cell membrane structure and functions with lower toxicity to mammalian cells. Thus, these may be employed for controlling various plant pathogens in a relatively safer way as compared to synthetic fungicides.

Introduction

Nanotechnology is an art and science of the design, characterization, production and application of structures, devices and systems by controlling shape and size on the nanoscale. It deals with the creation of useful materials, devices and systems using the particles of nanometer length scale and exploitation of novel properties (physical, chemical, biological) at that scale of length. In recent years, nanotechnology is emerging as a cutting- edge technology interdisciplinary with physics, chemistry, biology, material science and medicine.

Now-a-days, engineered nanoparticles become most important index in the area of nanotechnology which has entered into all aspects of human life and their various applications may be quickly expanded as compared to bulk materials due to their new and unique characteristics. There are many reports stating that biological processes have been improved by using engineered nanoparticles (Husen and Siddiqui, 2014).

Nanotechnology has also been used in agriculture for controlling the plant pathogens. Pesticides generally cause environmental hazard due to which the researcher developed a new technology, named as "nanotechnology" to manage pathogens (Jo et al., 2009). Nanotechnology has a potential to improve the farm productivity and it can minimise the cost of resources and environment related to agricultural sectors (Dutta, 2012). Nanomaterials can be used in different areas of agriculture. It can be useful for crop improvement, management of water and weeds, seed and food technology etc.

Antimicrobial activity of nano particles

Antimicrobial activity of silver nano particles: Among various nano particles, silver has been widely studied as disinfectant against many harmful microbes (Aghamoosa and Sabokbar, 2014). Silver exhibits higher toxicity to microorganism in a broad range of biological processes including cell membrane structure and functions with lower toxicity to mammalian cells (Yehia and Ahmed, 2013). It may be used for controlling various plant pathogens in a relatively safer way compared to synthetic fungicides (Martinez et al., 2008). Silver nano particle is required in lesser quantity and 1g of silver nano particles (Ag NPs) is capable of imparting antimicrobial properties to hundreds of square meters of substrate material (Li et al., 2010).

Antifungal activity of silver nano particles: Pawar et al. (2019) worked on antifungal activity of Ag NPs against *Phomopsis* sp. of soybean and it was revealed that with the increase in concentration of Ag NPs there was reduction in colony formation of the fungus. Ouda (2014) studied the inhibitory properties of silver nano particles against *Alternaria alternata* and *Botrytis cinerea* at various concentrations and observed the highest inhibitory growth at 15 mg L^{-1}. Jo et al., (2009) reported that antifungal activity of silver ions and nano particles against *Magnaporthe grisea* and *Bipolaris sorokiniana* where *in vitro* assays showed their significant effect on colony formation. Das and Dutta (2021) evaluated silver nano particles against *Rhizoctonia solani* causing sheath blight of rice at 1, 5, 10, 50, 100 and 200 ppm along with chemical check and found that at 200 ppm the NPs caused the highest inhibition (73.39%) in the radial growth of *R. solani* and at 200 and 100 ppm caused complete inhibition of sclerotial germination. Pot experiment showed that application of Ag NP at 200 ppm increased the plant growth parameters as compared to control, and reduced per cent disease incidence (20.00%) as compared to inoculated control *R. solani* (88.00%). Application of Ag NP also increased the concentration of vital secondary metabolites like phenols, flavonoids, terpenoids and total soluble sugars also, Elamawi and Al-Harbi (2014) reported that application of biosynthesized Ag NP from *T. longibrachiatum* reduced the per cent incidence of seed rot of faba bean, tomato and barley caused by *Fusarium oxysporum*.

Microscopic observations showed that silver nano particles damaged the fungal hyphae and conidia whereas, AgNPs also reduced the effect of sugar and protein of the fungal pathogens studied till date. Jung et al. (2010) reported that nanosilver liquid inhibited the soil borne plant pathogen, *Sclerotium cepivorum,* causing white rot of green onion, by more than 90% at 7 ppm whereas, *in vivo* studies revealed that nanosilver liquid helped in the plant growth through increase in the biomass and dry weights and by decreasing the pathogen population in the soil.

The antimicrobial activity of Ag is manifested due to the formation of insoluble compounds by the inactivation of sulfhydryl groups in the fungal cell wall and disruption of membrane bound enzymes and lipids resulting in cell lysis (Alananbeh et al., 2017). On treatment of fungi with Ag NP, there is loss of ability to replicate the

DNA resulting in inactivated expression of ribosomal subunit proteins (George et al., 2014). Ag NP also inhibits the expression of proteins associated with ATP production (Wang et al., 2012). Ag NP may affect the function of membrane-bound enzymes viz. those involved in the respiratory chain (Raja et al., 2019). Qi et al. (2004) suggested that Ag NP disrupt the cell membrane structure and destroy the membrane integrity there by inhibiting the normal budding.

The scanning electron microscopy studies revealed that in Ag NPs treated fungi hyphae is severely damaged resulting in its shrinkage, reduced sporulation rate and distortion of conidia. Silver ions produce reactive oxygen species via their reaction with oxygen, which is detrimental to cells, causing damage to proteins, lipids and nucleic acids (Maroufi et al., 2011). Ouda (2014) reported that AgNP treated fungi revealed reduction in total protein content of culture filtrate, total protein and N-acetylglucosamine (NAG) of cell wall but there is increase in total lipid content of both culture filtrate and the cell wall.

Mode of action of AgNP on *R. solani* was studied using Scanning Electron Microscopy (SEM) revealed accumulation of AgNP within the fungal cell of *R. solani* (Das and Dutta, 2022) and swelling and break down of the treated fungal cells resulted in plasmolysis and death of the cells. Balashanmugam et al. (2016) reported similar observation of accumulation of AgNP within fungal cell of *Aspergillus niger*, *A. fumigatus*, *A. flavus*, *Penicillium* sp., *Candida albicans* and the plant pathogens such as *R. solani*, *Fusarium oxysporum* and *Curvularia* sp. and damage of the cell wall, thereby releasing its components leading to further growth of the pathogen. Min et al. (2009) reported that upon treatment with AgNP, it caused plasmolysis of sclerotium forming fungal hyphae of *R. solani, Sclerotinia sclerotiorum* and *S. minor*. Das and Dutta (2022) reported the complete inhibition of *R. solani* germination at 200 and 100 ppm of AgNP but on decreasing the concentration from 50 to 1 ppm, the sclerotial germination (%) increased from 10-100 (%). No sclerotial germination (%) was recorded at 100 and 200 ppm concentration. Similarly, Reis et al. (2006) studied the antifungal activity of chemically synthesized AgNP against *R. solani* and observed that AgNP at 50 ppm effectively suppressed the mycelial growth and sclerotial germination at 50 ppm by 92 and 85%, respectively. Prazak et al. (2020) reported that ingenically synthesized AgNP from *T. harzianum,* the product at concentration of 0.31×10^{12} NPs/mL could inhibit the mycelial growth to some extent but completely inhibited the formation of new sclerotia of *S. sclerotiorum*.

Antibacterial activity of silver nanoparticles: Silver NPs have antibacterial activity on *E. coli.* Kaviya et al., (2011) reported that room temperature biosynthesized AgNPs, at room temperature (25°C), *Citrus sinensis* peel extract had antibacterial activity against *E. coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus.*

Silver NPs also possess strong antibacterial property which can penetrate through the cell membrane and make them rough, loose and hollow leading to the leaking of the cellular content and subsequently death of the bacteria (Raja et al., 2019). AgNP also causes the release of free radicals in the form of reactive oxygen species which react with the proteins, DNA and other biomolecules there by killing the bacteria. Based on the Scanning Tunneling Electron Microscopy (STEM) and the X-ray Energy Dispersive Spectrometer, Min et al. (2009) reported that silver nano particles were present on the surface of cell membrane and inside the bacteria. Mahakham et al., (2016) reported that AgNPs resulted in inhibiting the growth rate of the bacteria and loosening the chromosomal DNA and thus, disrupted its integrity. There was reduction in reductase activity and P_{hag}-GFP expression levels, indicating decrease in protein expression and an enriched ROS response, which caused loss of membrane integrity and cell viability. Maroufi et al. (2011) showed that AgNPs can also cause discrepancy in peptide chain by changing the position of α-helix and discharge of muramic acid that lead to cell wall distraction and disruption of glycan strands and inhibition of enzymes involved in respiration as it interacts with thiol group which is found in respiratory enzymes of bacteria and thus alter DNA synthesis.

Ag NPs have antibacterial activity on *E. coli.* AgNPs can harm the bacterial structure and slow down the activity of some membranous enzyme (Li et al., 2010).

Antimicrobial activity of gold nanoparticles: Gold (Au) in its bulk form is a very precious metal and used for making jewellery and it is chemically unreactive whereas, gold nano particles (AuNps), known as colloidal gold, is a suspension of gold nano particle in fluid and is highly reactive. AuNPs are widely used in the field of diagnostics and therapeutics. It is also used in genomics, immunoassays and clinical chemistry. In the field of medical science, it is used to identify the pathogen and the disease, photo thermolysis of microorganisms and cancer cells and site specific delivery of peptides or DNA (Grabouska et al., 2020). Au salts are used for treating rheumatoid arthritis, psoriatic arthritis and bronchial asthma and it possesses anti-inflammatory property. AuNPs possess various properties like surface plasmon resonance (SPR), and ability to quench fluorescence. They are also biocompatible with human cells and can be easily conjugated with different biomolecules such as DNA, RNA, antibodies, polyethylene glycol etc (Shah et al., 2021). AuNPs can help in reducing air pollution by converting the harmful air pollutants into harmless molecules. Au NP in plants increase seed germination, number of leaves, leaf area, plant height, chlorophyll content, and sugar content which ultimately leads to better crop yield (Shukla et al., 2019). Several methods like turkevich, brust, seeded growth, digestive ripening and biological methods are used for the synthesis of Au NPs (Shah et al, 2021).

Gold NP possesses antimicrobial (Turos et al., 2007), antibacterial and antifungal property of AuNP is size and shape dependent. Smaller the size of AuNP, more will be its ability to penetrate the bacteria and cause damage (Bai et. al., 2007). The more sharper and pointed the shape of AuNPs, more will be its ability to pierce the bacterial cells and impair it. Therefore, triangular AuNPs show better antibacterial activity than the round shaped AuNPs (Jung et al, 2010).

Antifungal activity of gold nanoparticles: Gold NP causes intracellular acidification due to inhibition of H^{+-}ATPase activity ultimately leading to its death (Boas, 2001). When the proton pump is disturbed, the fungal cells are incapable of taking up nutrients from the surroundings which retard their growth and finally the fungus dies. In addition to it, AuNPs can cause disorder in the enzymes and lipids of the fungi or inactivation of the sulphide groups in its cell wall leading to the formation of insoluble compounds which ultimately leads to death (Itroutwar et al., 2020). The AuNP can cause damage in the hydrogen bond of DNA, thereby causing mutation in it and also disrupt the membrane permeability and respiratory chain enzyme complex (Emmami and Chehrazi, 2011).

Antibaterial activity of gold nano particles: AuNP possesses great antimicrobial property. It attaches itself to the membrane of the bacteria and the integrity of the cell is disturbed (Mao et al., 2013), alters the membrane potential by deterring the activity of the ATPase enzyme resulting in lower concentration of ATP inside the cell, and also disrupts the translation process by preventing the binding of tRNA to the ribosomal subunits (Qi et al., 2004). AuNP can cause outflow of the contents of the cell and subsequently increase the permeability of the cell wall due to creation of holes in it and ultimately death of the bacteria. It also prevents transcription to occur by binding with the DNA (Raja et al., 2019). Intracellular reactive oxygen species (ROS) are produced on reaction of AuNP with the bacterial cells affecting the metabolites present in the cell and ultimately it results in death of the bacteria (Xie et al., 2016). According to Mohamed et al. (2017), interaction of AuNP with the bacterial cells causes formation of vacuoles inside the cells due to the generation of ROS. Zawrah and El-Moez (2011) reported that integration of AuNPs with antibiotics, result in complete damage to the bacterial cell by loosening the cell wall and separating it from the membrane hence, totally destroying the flagella which were present when the bacteria was treated alone with antibiotic drug. Valadkhan et al., (2015) reported that AuNPs do not allow the formation of bacterial biofilm which is essential for its pathogenicity and directed the stimulation of immune response-related genes.

Antimicrobial activity of zinc oxide nanoparticles

ZnO NPs are gaining more popularity for being cheaper and easy to prepare. ZnO is an inorganic material and possess superior durability, greater selectivity, and heat resistance (Padmavathy and Vijayaraghavan, 2008) as compared to organic materials. Moreover, ZnO serves as a daily supplement for zinc which is an essential element to human health. ZnO NPs have good biocompatibility with human cells (Padmavathy and Vijayaraghavan, 2008). In agriculture, Zn based compound may have stronger fungicidal activity.

Antifungal activity of zinc oxide nano particles: Some studies reported that the surface of the fungal cell wall is negatively charged (Lee, 2004) at biological pH due to the presence of carboxyl and phosphate groups. There is a physical interaction between the charged ZnO NPs and fungal cells by direct electrostatic adsorption. It results into damage to fungal cell membrane (Espitia et al., 2012) promoting cellular internalization of ZnONPs (Xie et al., 2016). Hence, it induced the generation of reactive oxygen species which cause oxidative stress inside the fungal cell.

Excessive generation of ROS damages the cell but most cell types can tolerate small amount of ROS (Soenen, 2011). However, when ROS defense system gets weakened or inactivated, then the same amount of ZnONPs exhibit higher toxicity to the fungal cells (Xie et al., 2016). Exposure to ZnONPs decreases the content of non-enzymatic glutathione (GSH) concentration inside the cells (Soltani et al., 2017). GSH protect cells against the devastating effects of oxidative stress caused by ROS which has also been reported to modulate cellular processes like stabilization of cell membrane (Meister, 1983), regulation of gene expression and apoptosis (Grosicka, 2005). Thus, decrease in GSH level disturbs the normal cellular processes thereby, making the fungal cells more vulnerable to oxidative damage. Dimkpa et al., (2013) studied the potential of ZnO nano particles and biocontrol bacteria against the growth of *F. graminearum*. It was found that ZnONPs was significantly more inhibitory to fungal growth than micro-sized particles of ZnO, although both types of particles released similar levels of soluble Zn, indicating the size-dependent toxicity of the particles. Yehia et al., (2013) investigated the antifungal activity of Zinc oxide nanoparticles (ZnONPs) against pathogenic fungal species, *F. oxysporum* and *P. expansum* and antifungal activity of ZnONPs was found to be concentration dependent. Maximum inhibition of mycelial growth of 77 and 100% was found for *F. oxysporum* and *P. expansum*, respectively at 12 mg/ L.

Karimiyan et al. (2015) studied *in vitro* the antifungal effects of ZnONPs in *Candida albicans* and compared with amphotericin B. Minimum inhibitory concentration (MIC) and minimum fungicidal concentration (MFC) of acetic acid solution nano-particles were evaluated. It was observed that that MIC and MFC of nano-ZnO was recorded 200 and 400 µg/mL, respectively whereas, MIC and MFC of amphotericin B was 0.5 and 2 µg/mL, respectively. It was concluded that, ZnO have anti *C. albicans* properties and may be used in treatment of infections caused by this fungus and should be investigated *in vivo*.

Antibacterial activity of zinc oxide nano particles: There is only one cytoplasmic membrane in gram positive bacteria with multiple layers of peptidoglycan polymers (Roozbeh et al., 2017), and thickness of cell wall varies from 20–80 nm. Gram-negative bacteria have two cell membranes i.e., an outer and plasma membrane with a thin layer of peptidoglycan (Roozbeh et al., 2017) and thickness of cell wall is 7–8 nm. NPs size within such ranges can easily pass through the peptidoglycan. ZnONPs are positively charge in a water suspension and bacteria being negatively charged make a strong bond with ZnONPs through electrostatic force of attraction. Uptake of metal ions into the cell system leads to depletion in intra-cellular ATP production and disruption of DNA replication. Generation of ROS from metal oxide nano particles and ions is regarded as the main mechanism responsible for antibacterial activity of ZnONPs (Jalal et al., 2010). These include superoxide anion (O_2), hydrogen peroxide (H_2O_2), and hydroxide (OH^-) and these species cause destruction of cellular components like lipids, DNA, and proteins due to their internalization into the cellular system of bacteria. The superoxides and hydroxyl radicals contain negative charge due to which they cannot penetrate into the cell membrane (Xie et al., 2016) hence, are found only on the outer surface of the bacteria whereas, H_2O_2 molecules can pass through the bacterial cell wall, thereby causing injuries and destruction, and finally trigger cell death.

Emami- Karvani et al. (2011) reported the antimicrobial activity of Zinc Oxide nano particles (ZnONP) against gram-positive and gram-negative bacteria. Bacterial species *E. coli* and S. *aureus* were used to test against ZnO by disc and well diffusion agar method and it was observed that gram-negative bacteria were more resistant to ZnO than gram-positive bacteria. The main advantages of using Zn nano particles is their excellent stability or long shelf life with organic antimicrobial agents. ZnNP are considered as an elite nano material and also been generally recognized as a safe material (GRAS) by Food and Drug Association which is non toxic, biosafe and biocompatible (Raghupathy et al.,2011). Kaushik and Dutta (2017) while testing the effect of ZnO nano particle at different dosage observed that ZnO nano particle at 200 ppm caused the highest inhibition of mycelial growth of *S. sclerotiorum* causing whilte mold of fench bean. Electron micrography study showed that upon exposure to ZnO nano particles mycelium of *S. sclerotiorum* showed swelling and plasmolysis of ZnO NPs exhibit antimicrobial properties, however, the properties of nano-particles (NPs) are depended upon on their size and shape, which make them specific for various applications (Hidayat Mohd Yusof et al., 2019). Das and Dutta (2022) reported that ZnO and Ag nano-particles can be an effective nano-priming agent for longer storage of chickpea seeds upto 9 months without any affect on seedling vigour index, yield and biochemical properties. Further, primed seeds were found to have more 80% more plant stand as compared to unprimed seeds against *Fusarium oxysporum* f. sp. *ciceri* infestation.

Nano particles in drug delivery system

Drug delivery using engineered nano particles is an emerging technology where, a particular therapeutic material/agents can be delivered to the targeted site in a controlled manner with the use of nano particles. The main aim of this technology involves minimizing the dose and frequency of a particular medicine and ultimately to minimize the probable side effects. In addition to it, the use of nano particle in medical sciences is increasing day by day because of their noble properties *viz*. high surface-area-to-volume ratio, chemical and geometric tunability, and their ability to interact with biomolecules to facilitate uptake across the cell membrane etc.

Due to the nobel property like large surface area to volume ratio the nano particles have high affinity for therapeutic agents or drugs and small molecules (ligands or antibodies) and this property helps for targeting and controlled release of these molecules and enhances their use efficiency. The nano particles are considered as building block elements and refer to a large family of both organic and inorganic materials. Each material has uniquely tunable properties and may be selectively designed for specific applications as per the desire of users. Different nanoparticles may be used for delivery of drugs as exemplified below:

a) Nano particles like polymeric nano particles are synthetic polymers with a size ranging from 10 to 100 nm and include polyacrylamide (Bai et al., 2007), polyacrylate (Jung et al., 2010) and chitosan (Mao et al, 2001). In polymeric nano particles, drug molecules can be incorporated either during or after polymerization. Based on the polymerization, the drug can be covalently bonded with the polymeric nanoparticles, encapsulated in a hydrophobic core, or conjugated electrostatically (Bai et al., 2007). Common synthetic strategies for polymeric nano particles include microfluidic approaches (Shim et al., 2012), electrodropping (Choi et al., 2013), high pressure homogenization, and emulsion-based interfacial polymerization (Song et al., 2014). For choosing any polymeric nano particles for the chemistry of drug delivery, polymer biodegradability is generally considered as an important aspect as nano-carriers composed of biodegradable polymers undergo hydrolysis in the body, producing biocompatible small molecules such as lactic acid and glycolic acid (Kumari et al., 2010).

b) Nano particles like dendrimers are unique hyper-branched synthetic polymers with mono-dispersed size, well-defined structure. Highly functionalized terminal surface is a good example of nano particles used in drug delivery purposes. Synthetic or natural amino acids, nucleic acids, and carbohydrates are the main constituents of dendrimer nano particles. Therapeutics agents can be loaded with relative ease onto the interior of the dendrimers or the terminal surface of the branches via electrostatic interaction, hydrophobic interactions, hydrogen bonds, chemical linkages, or covalent conjugation (Jung et al., 2010; Gillies et al., 2005; Svenson and Tomalia, 2005). Drug-dendrimer conjugation can elongate the half-life of drugs. However, it has been observed that, dendrimers used in biological systems passage toxicity and limited to synthesis and use in biological system (Jain et al., 2010; Pooja et al., 2018). Dendrimer are also confined within a narrow size range (<15 nm) and their current synthesis methods are subject to low yield. The surface groups will reach the dense packing limit at high generation level, which seals the interior from the bulk solution – this can be useful for encapsulation of hydrophobic and poorly soluble drug molecules. The seal can be tuned by intramolecular interactions between adjacent surface groups, which can be varied as per the condition of the solution, such as pH, polarity, and temperature, a property which can be utilized to tailor encapsulation and controlled release properties (Boas, 2001).

c) Besides, the inorganic nano particles have emerged as highly valuable functional building blocks for drug delivery systems due to their well-defined and highly tunable properties i.e. size, shape, and surface functionalization. Inorganic nano particles have been largely adopted in biological and medical applications ranging from imaging and diagnoses to drug delivery (Giner- Casares, 2016). Inorganic nanoparticles are usually composed of inert metals such as gold and titanium that form nanospheres, however, iron oxide nano particles have also become an option.

d) Inorganic semi-conductor or quantum dot (QD) nanocrystals have also emerged as valuable tools in the field of bio-nanotechnology because of their unique size-dependent optical properties and versatile surface chemistry. Their diameters (2-10 nm) are on the order of the exciton Bohr radius, resulting in quantum confinement effects analogous to the “particle-in-a-box” model. As a result, optical and electronic properties of quantum dots vary with their size: nanocrystals of larger sizes will emit lower energy light upon fluorescence excitation (Jung et al., 2010). Surface engineering of QDs is crucial for creating nano particle–biomolecule hybrids capable of participating in biological processes. Manipulation of nanocrystal core composition, size, and structure changes QD photo-physical properties. Design coating materials which encapsulate the QD core in an organic shell make nanocrystals biocompatible, and QDs can be further decorated with biomolecules to enable more specific interaction with biological targets. The design of inorganic nanocrystal core coupled with biologically compatible organic shell and surface ligands can combine useful properties of both materials, i.e. optical properties of the QDs and biological functions of ligands attached (Zhazeviskiy et al., 2018)

e) Organic nanocrystals, defined as carrier-free submicron colloidal drug delivery systems, with a mean particle size in the nanometer range that composed of pure drugs and surface-active agents required for stabilization. The primary importance of the formulation of drugs into nano crystals is the increase in particle surface area in contact with the dissolution medium, therefore, increasing their bio-availability.

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5. Nanotechnology in agriculture protection and sensing

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Abstract: The prevailing voids in agricultural technology at various stages like protection, production, preservation and sensing provides for multifaceted application of nanotechnology. The properties of multi facet graphene oxide (GO), bio-degradable polymers like jute grafted silica nano-ring and metal oxides have been carefully matched for many agricultural applications during the past decade. These careful designs and meticulous plannings have developed targeted pesticide composite (protection), triple smart fungicide composite (protection), targeted pheromone application for the pest control (protection), efficient plant gene tailoring (production), photosynthesis modulation (production), controlled fertilizer release (production), targeted preservative application (preservation) and latent crop diagnosis (sensing). Therefore, in near future, all the above applications will complement each other and bring a revolution in agriculture research to develop a pollution free environment with sustainable agricultural practices.

Introduction

Based on the C-C bond hybridization, carbon exists in 2 forms, i) sp3 (diamond like) and ii) sp2 (graphite like). Although all types of carbons are available in the nanoforms, however our research concentrated more in the sp3 form of carbon during the past 5-10 decades. Many allotropes of sp3 carbon are available, like carbon nanotubes, fullerene, graphene and graphene oxide (GO). However, special interest on graphene oxide is due to its metal free presence, inexpensive and simple synthesis. Classically, it is synthesized by the Hummer method, (Morcano et al., 2010), that uses the reactive oxidizing radials *insitu* generated from the mixture of $KMnO_4$ and H_2SO_4, that breaks the strong C-C bond and create oxygen groups in the form of –OH, -COO, C=O and C-O-C. These dangling bonds aid in the exfoliation of the graphene oxide sheet from bulk composite of piled up graphite.

Since graphene oxide is inert and hence, its toxicity is relatively less, and have exceptional functional qualities for various applications particularly shown smart cutting-edge functionality in the drug delivery and electronic applications (Shanmugam et al., 2014) various applications have been explained in the context of agriculture:

1. High absorption coefficient in the NIR that is more effectual than the gold nano particles and qualifies them for the photothermal property (Robinson et al., 2011) which in-turn qualifies for the targeted pesticide application to the diurnal pests.
2. The 2D sheet like structure of the GO make it possible to bind with the leaf and resist the drift for the pesticide application, otherwise there could be a significant pesticide loss.

3 Abundant functional groups (–OH, -COO, C=O and C-O-C), which are not available in any other material without special effort to augment them through surface functionalization, is of great advantage. This density can be tuned with the degree of oxidation during synthesis, eg. the oxygen element percent in GO can reach upto 40 % of the total number of elements *i.e.*, 40: 60 O:C, which qualifies the material for the huge preservative loading and fruit packing.
4. The size reduction of the GO introduces a band gap in the material which begins to function as semi-conductor material and produce photo induced electrons for the enhanced modulation of photosynthesis. Additionally, the ability to express functional groups with different redox potential also aids in the transport of the synthesized electron for the potential enhancement in the photosynthesis.
5. Sharp edges of the graphite made it eligible for the plant gene delivery and transformation applications.
6. Lastly, GO qualifies to hold pheromone in the inter-layers and release it in the controlled fashion for the extended pest control owing to its ability to stake while drying.

Recently, special attention was given for the development of coated urea fertilizers to enhance its nutrient use efficiency and crop productivity by using farm waste bio-degradable polymers. In this context, unique properties of porous silica contributed for sustained and controlled release of fertilizers. For the first time, at INST, Mohali research explored the jute grafted silica nano-ring supported with egg white, as bio-degradable and hydrophobic coating for slow release of urea and its efficiency for crop productivity. Beside this, after noticing the need of sensors for efficient future farm management through IoT, gas sensor for sensing plant volatiles released during the latent stage of plant infection were developed to get maximum signal at minimum concentration. It is a pioneer effort that; volatile with multiple oxidation sites *i.e.,* ionone has been attempted for sensing purpose. Thus, in the present chapter these successful and technology-oriented applications will be discussed which have been developed with the aim for sustainable agriculture (Fig. 5.1).

Targeted pesticide application (Sharma et al., 2017)

Non-targeted accumulation and poor target efficiency of pesticides are two primary issues confronted by farmers until now. Pesticide drift is one of the main reasons due to which more than 90% of applied pesticides miss their intended target. In this context, nano-formulations proved to be a boon to farmers. Various nano-formulations of polymeric nano particles (Loha et al., 2011; Sarkar et al., 2012) TiO_2 based composite (~15 μ) (Guan et al., 2011) for slow, targeted release and pesticide degradation, respectively have been widely explored but they have either not been examined directly on pests or tested on stored pests only (Yang et al., 2009). Nowadays, graphene oxide (GO) has been highlighted for pesticide adsorption and their release (Maliyekkal et al., 2013). Decoration of GO with metal nano particles (gold) or chalcogenide like copper selenide ($Cu_{2-x}Se$) can enhance the sensitivity of GO for photothermal property (Lim et al., 2013; Hessel et al., 2011).

These findings encouraged us to synthesize $Cu_{2-x}Se$ nano particles of 15±8 nm size decorated on reduced GO by arrested precipitation (rGO-$Cu_{2-x}Se$) approach. The chlorpyrifos (CPF) loading in it was accomplished by using solvent evaporation method through hydrophobic interaction for its targeted release against white butter fly pest in cauliflower. This composite was further transferred to aqueous phase through evaporation assisted wrapping with amphiphilic poly (styrene-maelic acid) (PSMA) polymer (Fig. 5.2). The findings of this investigation suggested 3.2 times greater CPF loading in the rGO-$Cu_{2-x}Se$ composite and an increase in anti-drift adhesion from 34 to 57% as a result of its hydrophobic nature. These findings doubled the efficiency of controlling white butterfly pest. Moreover, release of pesticide was accompanied by alkaline gut pH of larva in targeted fashion. The photothermal property of GO, which is further enhanced by $Cu_{2-x}Se$ nano particles led to photo stimuli-based release of pesticide in diurnal pests. The composite's photocatalytic property led to 50% photo degradation of remaining pesticides within 48h from the field which help to reduce environmental pollution. Considering 5h as the active sunshine hours, the pesticide will last for 10 days and after that it will be significantly degraded, thus avoiding the non-target effects.

Targeted fungicide application (Kaur et al., 2021)

Current agricultural formulations are primarily concerned for non-target accumulation of leached pesticide that leads to soil/ground water pollution. Engineered nano materials like CuO, Cu_2O and CuS have shown potential for disease control at lower concentration. The carbon nano materials with polymers exhibit a novel physical property likely to hold the drug from non-targeted release. In this context, GO can be a potential drift resistant reservoir for a variety of guest like fungicide by laying with the long axis in plane with the leaf surface and owe to plant protection. Therefore, the 2D lamellar Cu adorned rGO was employed for the pesticide application in the aforementioned application and has been modified with polymer having different surface charge along with fungicide which has been examined for the following triple smart behaviour:

1. Hold the fungicide from leaching by adhering to the leaf surface,
2. Perform targeted release function in response to incidence of the fungus and
3. Hold the fungicide from leaching to the ground water from the minimum particles that drifted to the soil (Fig. 5.3).

The polymer with different charge viz., cationic chitosan, anionic poly styrene maleic acid and non-ionic f-127 were employed to wrap the fungicide with the GO copper selenide composite. The nano-composite rGO- $Cu_{2-x}Se$ coated with cationic polymer exhibited 30 % more binding of rGO on leaf surface than control. The composite exhibited 45% reduction in soil leaching compared to the control.

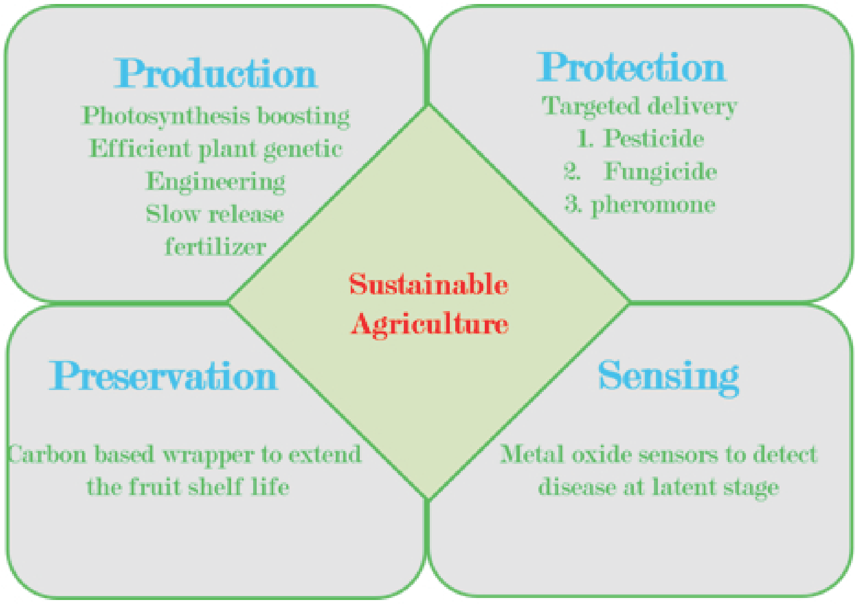

Fig. 5.1 Schematic showing the sustainable agriculture with the application of carbon nanomaterials, polymers and metal oxides (Black and white in book)

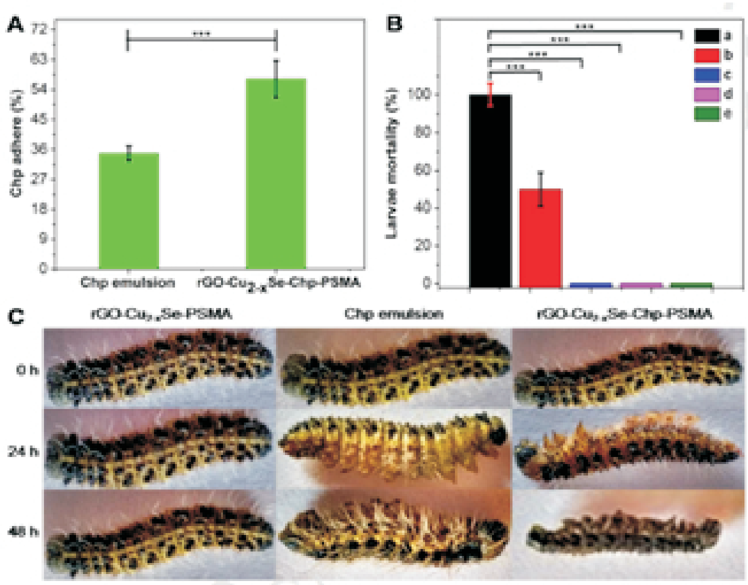

Fig. 5.2 Runoff resistance and pest mortality (A) Percent chlorpyrifos adhered on leaf (B) Mortality percent of the pest with different treatments after 72 h (a) rGO-Cu2-xSe-chp- PSMA, (b) chlorpyrifos emulsion, (c) rGO-Cu2-xSe-PSMA, (d) Cu2-xSe, (e) GO (C) *P. rapae* larvae image before and after (24 and 48 h) feeding the respective treatment. [Image is used from Sharma et al. (2017), with publisher's permission]ref 2

Targeted pheromone application (Vijaykumar et al., 2010)

Tuta absoluta is the primary devastating pest of solanaceae family as it actively feeds on different tissues of plant such as stem, leaf and fruits. Additionally, because of its high reproductive rate (10-12 generations per year), it results in the overall decrease of 40-100 % in yield. The primary strategy for mitigating the leaf miner led to huge use of insecticides or pesticides however, the unavoidable persistence of pesticides in the ecosystem is a major global concern. A semio-chemical lure, pheromone can be an eco-friendly next generation alternative for mass trapping of insect pest without hampering the environment. The sex pheromones of *T. absoluta* has been identified as 9:1 ratio of (E, Z, Z) 3,8,11 Tetradeca-trienyl acetate and (E, Z)-3,8 Tetra decadienyl acetate. Polyethylene sachets, polyethylene tubes, cotton balls, PVC resins, and rubber septa are the most widely used pheromone platform to control the pest. These delivery systems cause the burst release, which limits its field efficacy in short span.

Hence, the potential of GO for the controlled release application of pheromone and pest management was foreseen and two types of GO were synthesized in the form of

1. Prepared GO and
2. Amine conjugated GO. In this, a 4-5 layered GO sheet and amine functionalized GO (AGO) was synthesized by improved Hummer's method and amine conjugation by the nucleophilic EDA attack on the electrophilic epoxide ring of GO, respectively. GO has been found to be an effective scaffold to hold pheromone and control the burst release by forming maze like structure in contrast to amine modified GO. The electro-physiological response of pheromone with GO matrix by electro-antennogram study exhibited that insects' response was the same as commercial lure. Later on, the field efficacy of this nano matrix was demonstrated by hanging the composite in the middle of plastic sticky sheet. On the other hand, commercial septa containing 3 mg of pheromone was attached to plastic sticky traps and hung similarly for comparison purpose. The number of insects were monitored at weekly intervals. It was found that the nanocomposite (GO @ *T. absoluta*) with a reduced pheromone load (i.e 1 mg) was able to trap a greater number of insects/traps (10-15) in contrast to the commercially used septa containing 3 mg of pheromone providing a means of sustainable agriculture practice. This technology offers a green and ecofriendly approach for controlled pheromone release and pest management.

Efficient plant genetic engineering (Sharma et al., 2018)

In plant gene transfection two modules i.e. bio-transfection and material assisted transfection are broadly followed. The host is infected with the virus or the bacteria to tailor the gene of interest to the host gene in bio-transfection while in material assisted transfection, the host was incorporated with lipids, polymeric capsules, carbohydrate dendrimers and polypeptide. As a standard protocol, the biolistic gun assisted plant gene transfection has been believed as the last salvage strategy when all the other methods fail. In this case, gold micro particles having large particles size and heavy weight were used along with high pressure that will largely damage the tissue. Although this has good transfection efficiency, the regeneration efficiency is very poor.

Hence, in this context a nanocomposite was developed with the gold nano particles embedded in the low dense light weight carbon matric (Fig. 5.4). The composite has been synthesized simply by burning the fungal biomass that produced gold nano particles intracellularly in nitrogen or argon inert environment at >600 °C. The synthesized carbon composite was then grinded with the pestle and mortar to give some micro size sharp carbon composite. TEM imaging of prepared composite showed dense gold nano particles embedded in the graphitic carbon composite with high sp^2 carbon formation which was confirmed with the Raman spectroscopy.

After successful synthesis, this composite has been loaded with the gene of interest to be transfected with the plant and coated with the spermidine and PEG in sequence followed by a brief incubation in calcium. This gene and the nanocomposites have been tested for the nucleotide binding by using gel electrophoresis, which showed the composite was stable with the gene. Whereas, a drift in the nucleotide was observed in the composite without coating. It was followed by loading the composite on the rupture disk, with the x-plant placed vertically at the bottom for the bombardment. Helium pressure in the pressure chamber was increased in such a way that the rupture dick cracked and introduced the composite on the x-plant. The material vs GUS foci count were calculated to check the efficiency of this composite with the market gold standard, *viz*., micron size gold particles. The GUS is the quick assay taken to count the transfection efficiency visually. Here, GUS foci shown by composite with four times less gold were equivalent to GUS foci shown by the micron size gold. This composite was having good regeneration efficiency compared to the micron size gold. The less regeneration by the gold micron particles is attributed to the physical impairment caused by the larger particles due to the more damage to the x-plant while the regeneration is more in composite due to sharp edge that cause less damage to the x-plant tissue. Further, the inherent black color of the material aids in the wound recovery. It is well known in the classical method that after the bombardment, the tissue is kept in the dark for maximum recovery. The less damage in the embryo was confirmed with SEM imaging.

Nanobio-luminoelectrics in photosynthesis (Bindra et al., 2022)

Photosynthesis uses electrons harvested from the water splitting through photo reduction for the production of glucose from Co_2. It is the main energy source on earth. Here, photo-electron production and electron transfer are the two rate limiting processes. Hence, semiconducting particles were added to the chloroplast for the higher photo-electron production, ultimately improving photosynthesis efficiency.

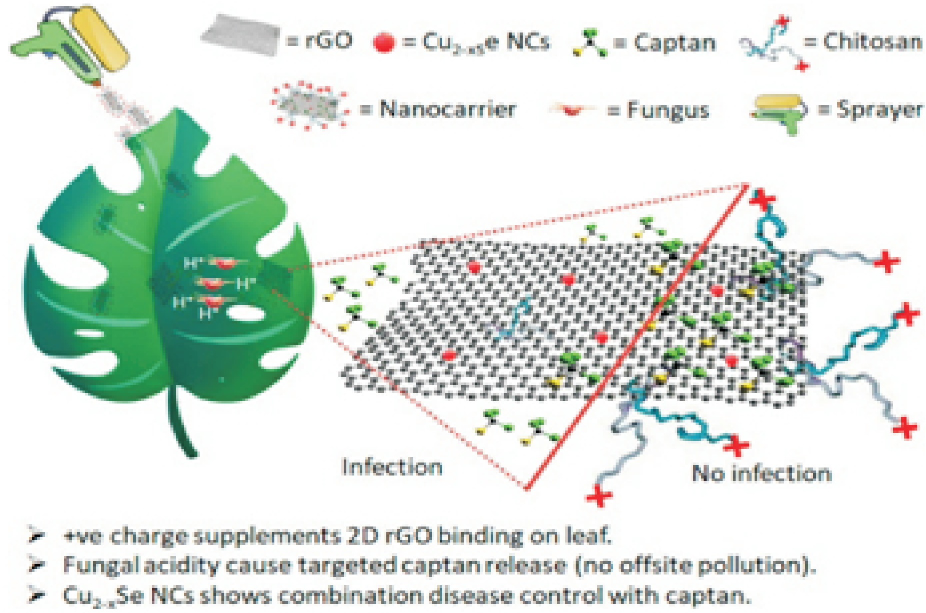

Fig. 5.3The schematic of the targeted fungicide application showing triple smart behavior. [Image is used from Sharma et al. (2021), with publisher's permission] ref 12

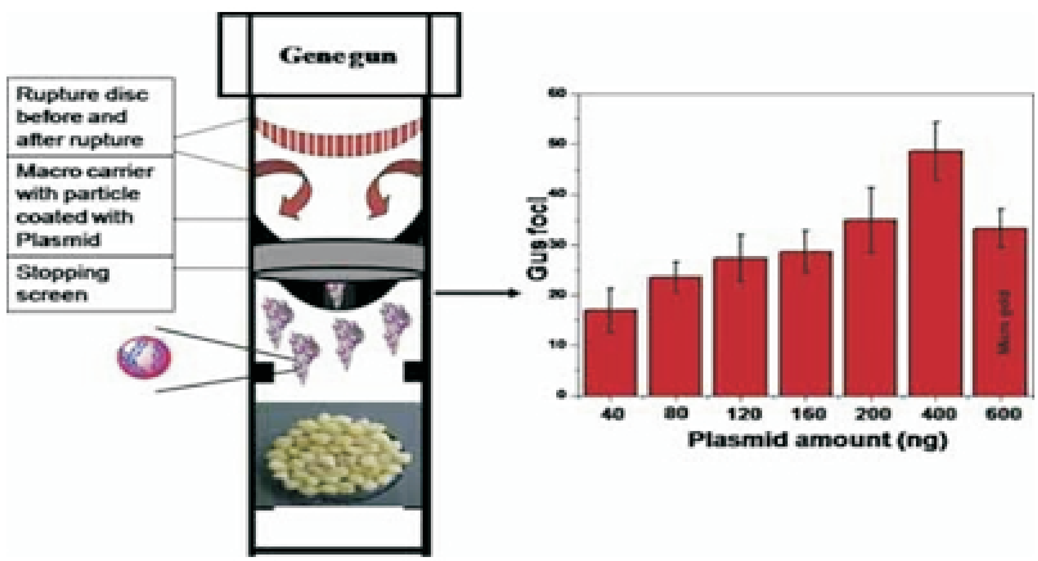

Fig. 5.4 showing the cartoon of the gene gun loaded with the carbon gold composite for the gene delivery application. [Image is used from Vijayakumar et al. (2010), with publisher's permission] ref 14.

In this line, GO was synthesized in the form of very small particles having semi-conducting property, and can be attuned to enter the chloroplast without damage. Since, the particles with cationic surface area show more uptake therefore, amine GO (AGO) have been constituted by conjugating electron donating diamine to easily cleavable epoxy containing GO. The formation of AGO has been confirmed with NMR spectroscopy.

Thus, GO and AGO were incubated with the chloroplast extracted from the spinach and the rate of photosynthesis was checked with the dichloro-phenol-indo-phenol (DCPIP) dye. Here, GO showed substantial improvement (1.3 times) in the photosynthesis efficiency. This increase in the photosynthesis rate may be due to the efficient transfer of electrons by GO particles having different redox functional groups and increasing the redox protein in the chloroplast. This was undertaken by being an inspiration from algae, which have both copper and iron based redox protein in the photosynthesis apparatus to transport electron more efficiently than the plant chloroplast (whose efficiency is < 15 %). On contrary, AGO showed reduction in the photosynthesis rate compared to the control, due to more uptake which will cause reactive production of radicals and catalase synthesis with the membrane damage (Fig. 5.5). The higher uptake by AGO was confirmed with UV vis, biolayer interferometry, and confocal quantification.

Targeted preservative application (Chandel et al., 2022)

According to Food and Agriculture Organization 2015 report, the loss of perishable vegetable and fruits scaled upto 50%. Therefore, the post-harvest farm productivity needs as much attention as in the pre-harvest period. As a result, food preservatives are used to control microbial infection, ripening rate and cold injury. However, the administration of the preservatives directly on the fruit leads to chronic toxicity via membrane disruption and energy drain to reinstate homeostasis. Hence, there is a dire need for the customized smart wrapper material with programmed preservative delivery, which can work in a contactless fashion in response to the fruit ripening stimuli. Due to the high surface area, GO can serve as an inert platform to accommodate maximum preservative that can be released from GO after getting specific stimuli.

Hence, GO composite with preservative has been synthesized with hydrazone linkage (SA_{hyd}-GO^{A}) after two-step activation with ethylene-diamine and 4-nitrophenyl chloroformate for maximum loading capacity. After its successful synthesis, the composite has been fabricated into stable membrane of wrapper through simple vacuum filtration with porous filter paper support (Fig. 5.6). The acid synthesized during pre-climacteric to post-climacteric transition may cause cleavage of acid-labile hydrazine. After incubation of 50 h, the release behaviour of SA from the composite (SA_{hyd}-GO^{A}) showed 80 and 15% release in acidic and neutral pH, respectively. The fermented banana juice, having pH of 3.2, collected from post-climacteric fruit exudation also showed 11.5% SA release after 5 h incubation. The fruit ripening and stress markers i.e., MDA (malon-dialdehyde), TPC (total phenol

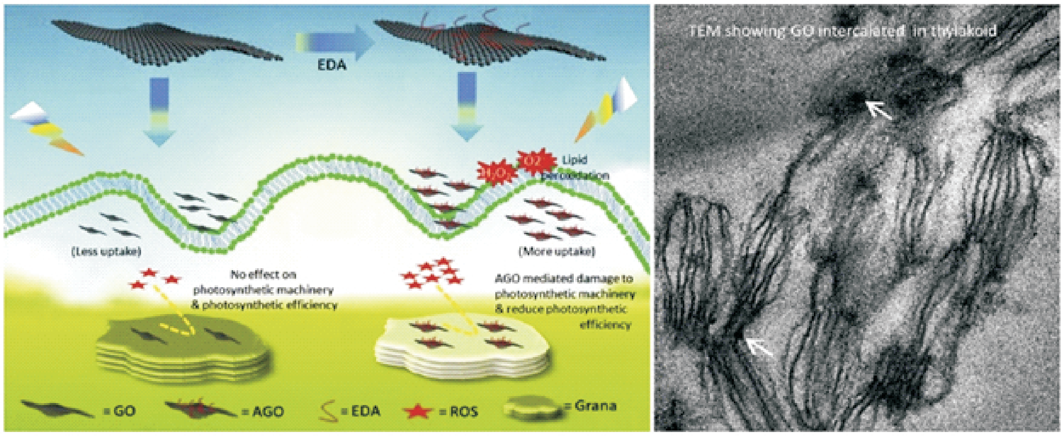

Fig. 5.5 showing the integration of the GO with the photosynthesis apparatus. [Image is used from Sharma et al. (2020), with publisher's permission] ref 15

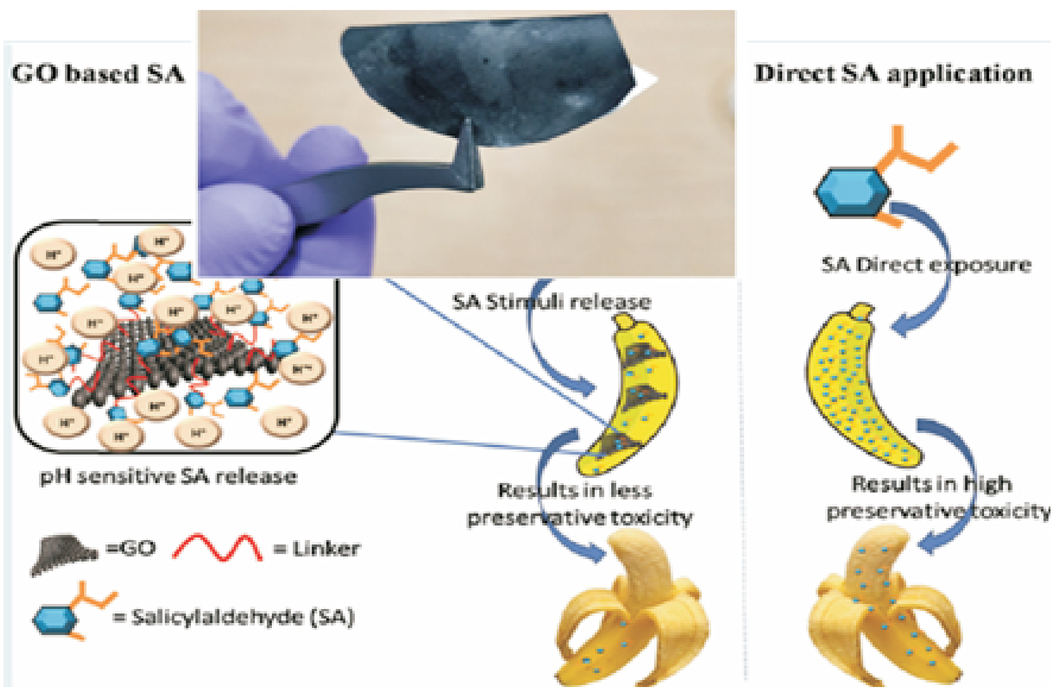

Fig. 5.6 showing the fruit wrapper containing GO composite with preservative. [Image is used from Sharma et al. (2018), with publisher's permission] ref 16

content) and proline content were observed to be maintained in composite (SA_{hyd}-GO^{A}) treated bunch as much as free SA treatments. This was due to the antioxidant property of SA, which tends to reduce membrane permeability. Thus, browning of the fruit flesh was prevented as lignin polymerization was reduced by the conversion enzyme which initially convert phenylalanine to phenol and then to quinone. The antibacterial activity of the composite (SA_{hyd}-GO^{A}) examined in common food contaminant *Escherichia coli* and bacterial plant pathogen species *Pseudomonas syringae* showed more control than that of the free SA due to the complementary action of SA with the antibacterial mechanism of GO. Therefore, GO-based smart wrapper with preservative can act as a boon for fruits with more freshness.

Slow-release fertilizer (Sharma et al., 2021)

Leaching and volatilization loss of urea is a siren to environmental and human health. There have been advances in the preparation of coated urea fertilizers; however, it has some disadvantages such as inescapable effects of petroleum-based polymers on environmental pollution. On the other hand, bio-polymers do not give desired control, due to its hydrophilic nature. Thus, a biodegradable hydrophobic enclosure can be a potential candidate to slower the fertilizer release as well as to enhance the nutrient use efficiency and crop productivity. In this context, engineered porous silica has drawn more attention for sustained and controlled release of fertilizers; however, the increased silica content for diffusion control leads the coating brittle.

Hence, this motivated us to synthesize for the first time, jute grafted silica fibre, as matrix for slow release of urea.

Plant infection sensing at latent stage

Plants face myriad of biotic and abiotic stresses during their life cycle leading to great loss and these crop diseases cause release of various volatiles. The detection of these volatiles proves to be significant for the early diagnosis of disease that will be beneficial for efficient farm management through IoT. The volatile viz., β-ionone a cyclic antimicrobial apocarotene compound, is released in multiple folds (upto 600 times) by carotenoid cleavage dioxygenase 1 (CCD1) expression, and non-enzymatic cleavage of carotene during the latent stage of some biotic stress like bacterial leaf spot disease caused by virulent strain of *Pseudomonas syringae*. Techniques used till now for detection of volatile organic compounds (VOCs) involve gas chromatography-mass spectroscopy (GC-MS), proton-transfer-reaction mass spectroscopy (PTR-MS), selected-ion-flow tube mass spectroscopy (SIFT-MS), and chem-illuminescence. Very recently, metal oxide based chemoresistive sensor (MOS) is found to substitute the above conventional methods. Metal oxide sensors are basically semiconductors which work on the principle of change in resistance of a sensitive metal oxide layer after the exposure and interaction of metal oxide surface with the ambient gases such as NO_x, H_2, SO_x, CO_2, O_2, and volatile organic compounds (VOCs) etc. by either donating or accepting the electrons from these reducing or oxidizing gases. They have good detection sensitivity, robustness and the ability to withstand high temperatures. MOS sensors may include the semiconductors such as ZnO, α-MoO_3, SnO_2, and ε-WO_3.

Here, SnO_2 based chemoresistive gas sensors for early diagnose of *P. syringae* infection has been attempted due to wide band gap (3.6 eV) of SnO_2 which is also versatile for the detection of isoprene, formaldehyde, acetone and benzene. The sensitivity of this gas sensor was increased by monitoring the particle size, morphology, composition, thickness, and doping of catalysts. Therefore, 0.5 mol% Pt doped SnO_2 nanoparticles prepared by solvothermal method were found to be optimum for sensing purpose which increased the sensitivity as compared to pristine SnO_2 and SnO_2 doped with Pd, Au. This was due to small particle size (< 7nm), space charge layer expansion by doping, catalytic behaviour of Pt and formation of platinum oxide island at the interface confirmed by XRD. DFT calculations and XPS analysis further revealed the mechanistic effect by oxygen vacancy formation and reactive oxygen assisted enhanced binding, respectively. The standardized nanoparticles fabricated over the electrode showed a cracking pattern via SEM which favours the gas molecules to percolate and interact with the sensor. The 0.5 mol % Pt doped SnO_2 sensor was found to give a maximum response at 216°C. Further, increase in temperature caused quick desorption of gaseous molecules.

The sensor was found to be stable up to 10 days with good reproducibility for 5 alternate on/off cycles at 50% relative humidity and 170 ppb exposure to ionone. It was able to detect a minimum 62 ppb of ionone concentration with 11.3 signal to noise ratio with response, recovery time of 32 and 35 sec respectively (Fig. 5.7). The sensor developed in this study was less sensitive to other volatiles released by plant during physical, temperature or pest stress such as α-phellandrene and myrcene at 1.5 ppm and 500 ppb concentrations, respectively, when ionone is maintained at a minimum of 170 ppb. The reason behind the selectivity and increased response of sensor towards ionone was optimum working temperature or catalytic selectivity of ionone and presence of multiple oxidation sites (four oxidation sites) on ionone which will avoid false alarming results. Further, sensor was able to detect ionone in real time plant experiment, which goes in flow with the results obtained by GC-MS.

Conclusion

Thus, in order to fill the gaps in agricultural technology in various stages i.e. protection, production, preservation and sensing, we have carefully matched the properties of multi facet GO, biodegradable polymers like jute grafted silica nano-ring and metal oxides for many agricultural applications during the past 10 years. These careful designs and meticulous planning have developed targeted pesticide composite (protection), triple smart fungicide composite (protection), targeted pheromone application for the pest control (protection), efficient plant gene tailoring (production), photosynthesis modulation (production), controlled fertilizer release (production), targeted preservative application (preservation) and latent crop

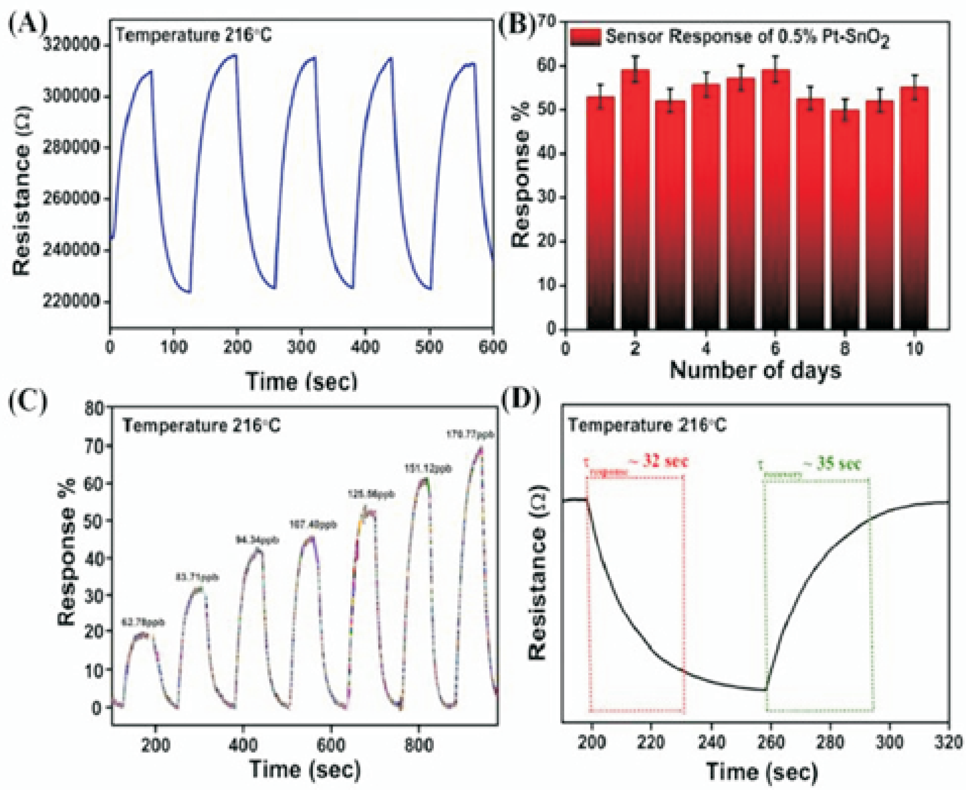

Fig. 5.7 is showing the sensor characterization. [Image is used from Chandel et al. (2022), with publisher's permission] ref 18

diagnosis (sensing). Therefore, in near future, in order to develop a pollution free environment with sustainable agricultural practices, all the above applications will complement each other and bring a revolution in agriculture research. In addition to this, our review article complies all of the research in this area.

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6. Bio-sysnthesis of nanoparticles and its applications in agriculture with special reference to plant disease management

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Abstract: Application of nanotechnology can modify agricultural science to a great extent. Biogenic synthesis of the nano particles using microorganisms viz., bacteria, fungi, plant extracts, is a relatively, simple, clean, sustainable and economical option. The resultant products are non-toxic and biodegradable and may be synthesized by bottom-up or top and bottom down approaches. In this case, capping occurs simultaneously with the formation of the nano particles with no additional step. Various nanotechnology approaches viz., bio nano material, nano bio-barcode assay, nanopore system, nano diagnostic kit and quantum dots. are used for the detection of plant diseases. Nano particles can be utilized in agriculture as nano farming, nano pesticide etc. and has an immense scope in the nano particle enabled smart delivery of agrochemicals. Nano fertilizers have an increased popularity due to the slow and consistent release activity of the nutrients. Nano materials help in seed germination and crop growth along with acceleration of plant adaptation to climate change.

Introduction

In the era of climate change, global agricultural systems face numerous, unprecedented challenges and to achieve food security, advanced nano-engineering is a handy tool for boosting crop production and assuring sustainability (Shang et al., 2019). Nanotechnology is a versatile discipline which embraces information from natural science, chemistry, physics and other fields. Crop production experiences depicted that approximately 20–30% of its total annual loss is due to plant diseases (Nezhad, 2014). Food sustainability has been identified as one of the biggest problems faced by humanity leading to conflicts in nations, societies, and administrations since time immoral. Plant pathogens result in decreased yields, economic loss and possible crop damage in the cash and food crops (Pan et al., 2010; Thind, 2012). There is consistent and fast increase in the global population and, the main challenge is to meet the needs of ever burgeoning population while reducing the stress on environment. This can be achieved by timely and eco-friendly management of diseases and this challenge can be fought more effectively with the advent of nanotechnology. Nanotechnology is described as the operation or assemblies of discrete atoms, molecule, or molecular collections into structures in order to generate novel or extremely diverse assets. The application of nanotechnology in agriculture can modify the agricultural science with advanced apparatuses for quick infection recognition, directed dealing, improved plant nutrient absorption, microbial infection and ecological stress resistance. Certainly, agronomic production will benefit from smart sensors and smart delivery systems to combat fungal, bacterial and viral diseases and boost the harvest.

Sustainable agriculture entails a minimum use of agrochemicals that can eventually protect the environment and conserve and save different species from extinction. Notably, nanomaterials enhance the productivity of crops by increasing the efficiency of agricultural inputs by facilitating site-targeted and controlled delivery of nutrients, thereby ensuring the minimal use of agri-inputs. The assistance of nanotechnology in plant protection products has exponentially increased, which may assure increased crop yield. Moreover, the major concern in agricultural production is to enable accelerated adaptation of plants to progressive climate change factors, such as extreme temperatures, water deficiency, salinity, alkalinity and environmental pollution with toxic metals without threatening existing sensitive ecosystems (Vermeulen et al., 2012)

Nano material engineering is the cutting-edge track of research that supports the development of high-tech agricultural fields by offering a wider specific surface area crucial for the sustainable development of agriculture systems (Panpatte et al., 2016; He et al., 2019). Therefore, nanotechnology can not only reduce the uncertainty, but also coordinate the management strategies of agricultural production as an alternative to conventional technologies.

1. Properties of nanoparticles (NP)

When material is reduced to nano size, it acts differently and expresses some new properties completely lacking in its macro scale form. The nanoparticles (NPs) have a high surface to volume ratio that increases their reactivity and possible biochemical activity (Dubchak et al., 2010) eg. when 1 g gold is converted into nano scale, the particles may cover an area of 100 km^2.

Properties of nanoparticles are as given below and are depicted in Fig. 1

- Nanoparticles consist of three layers i.e., the surface, shell and the core. The surface layer usually consists of a various molecules such as metal ion, surfactants, and polymers.
- Nanoparticles may contain a single material or a combination of several materials.
- Nanoparticles are of different shapes and sizes. The particle size is smaller than a virus particle eg. influenza virus (80-120 nm diameter) and tomato mosaic virus (300 nm length and 10-18 nm diameter).
- Nanoparticles may be spherical, polyhedral rod shaped, etc.
- The nanoparticle cannot be imaged by the optical microscopes and can exist as suspensions, colloids or dispersed aerosols depending on their chemical and electro-magnetic properties.
- The properties of nanoparticles are dependent on their size eg. copper nanoparticles smaller than 50 nm are super hard materials and do not exhibit the properties of malleability or ductility of bulk copper.

- Absorption of solar radiation in photovoltaic cells is much higher in nanoparticles than in thin films of continuous sheets of bulk material as nanoparticles are smaller and can absorb greater amounts of solar radiation.

Nanoparticles can melt at lower temperature and are more reactive than their larger bulk equivalent (Elmer and White, 2018).

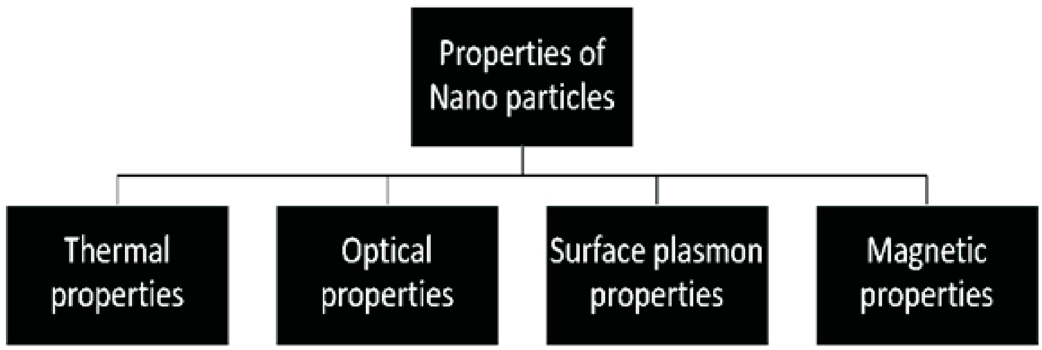

Fig. 1 Properties of Nano-particles

Nanoparticles, employing biomolecules derived from the organisms are used in the synthesis hence, no additional steps are required (Chowdhury et al., 2014). Biomolecules derived from the reducing organism have higher capacities for binding to metals, with proteins and amino acid residues binding to the nanoparticle surfaces form cappings that confer stability and prevent particle agglomeration and aggregation (Basavaraja et al., 2008).

According to Gurunathan et al. (2009), the stability of silver nanoparticles is also attributed to nucleophilic OH- ions that are adsorbed on the surfaces, preventing aggregation and contributing to the synthesis of smaller nanoparticles by providing electrons for the reduction of silver ions. In addition to conferring stability to the nanoparticles, the protein capping resulting from biogenic synthesis can act in the anchoring of drugs and genetic material for subsequent transport into cells (Hu et al., 2011).

Chowdhary et al. (2014) used scanning electron microscopy to detect the presence of cappings on biogenic silver nanoparticles. The nanoparticles were spherical, poly-dispersed, and were not in direct contact, even within aggregates, indicating good stability. The SDS-Page protein electrophoresis technique was employed to characterize the extracellular fungal proteins associated with the nanoparticles. Molecular weight bands between 50-116 kDa were attributed to proteins responsible for synthesis and stabilization of the nanoparticles. Both the filtrate and the capping removed from nanoparticles showed a band at 85 kDa, which corresponded to a protein that was suggested to be responsible for the stability of the nanoparticles.

2 Effect of nanoparticles on the pathogens/microorganisms

It has been confirmed scientifically that the chemical and physical properties of nanoform materials actually shift between their macroform and nanoform. All these transformations ultimately end up with useful real-world applications in plant defense and plant protection. Nanoparticles have the advantages of both small size and more surface area hence, they influence plant pathogens precisely (Alghuthaymi et al., 2015; Balakumaran et al., 2015). Larger macroscopic entities are less likely to interact with microorganisms as these are farther away from them.

2.1 Effect of nanoparticles on bacteria: Nanoparticles have antibacterial properties, which may be the result of broken cell wall of the bacteria or high levels of reactive oxygen species (ROS) being produced (Wiesner et al., 2006; Azmath et al., 2016). Bacterial infection is a major factor of contamination and mortality due to the prolonged presence of pathogens. Antibiotics, being cheap and highly effective, have been selected for the treatment of bacterial contamination. The mode of action of nanoparticles is directly linked with the bacterial cell wall, which enables the nanoparticles to control super-resistant bacteria. Though it is most likely that bacteria may become resistant to the antibacterial activity of these NP in case of continued use in the future.

2.2 Nanotechnology for plant viral diseases and insect pests: Nanoparticles were investigated for the control of *Sitophilus oryzae* and baculovirus *Bombyx mori* nuclear polyhedrosis virus (BmNPV) in silkworm (*B. mori*) disease caused by *S. oryzae* and BmNPV, respectively (Goswami et al., 2010). Bioassay involved in preparation of solid and liquid formulations of nanoparticles; and their applications to rice and storing in a plastic box with 20 adult *S. oryzae* for seven days. It was observed that hydrophilic silver nanoparticles were most effective and >90% of mortality was recorded on the day 2. Silver and aluminium nanoparticles were the primary source. It was observed that 73 and 100% insect died after seven days of exposure to lipophilic silver nanoparticles and aluminium nanoparticle, respectively.

3. Nanotechnology approaches for the detection of plant diseases

3.1 Bio-nano materials: There are some bio-nano materials which are categorized through X-ray diffraction (XRD) technique, X-ray photo-electron spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDS), UV visible spectroscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTlR), Coupled plasma spectrometry (ICP), Transmission electron microscope (TEM) and atomic force microscopy (AFM) techniques. These bio-nano materials played an important role in field of agriculture, medicine and biology. Bio-synthesis of bio-nanomaterials may also be achieved by using plant extracts (Sahayaraj et al., 2015; Khandelwal and Joshi, 2018; Molnar et al., 2018) and microbial cultures or their enzymes and proteins.

3.2 Nano bio-barcode assay: The technology of biological barcodes is increasingly used in nanotechnology and incorporating new advancements in nanotechnology to help in the identification of non- enzyme-containing ultra-sensitive proteins and DNAs. Instead of using an orthodox ELISA, a protein barcode assay could be employed, which is more complicated, more sensitive and profound. The nanoparticle-based bio-barcode assay being dependent on nanoparticles is more sensitive to identify pathogens than traditional techniques like ELISA, Real-time PCR, etc. and can also help in early and better detection of plant diseases. The bio-barcode technique consists of two probes.

1. Magnetic micro beads (MMB): MMB target recognition and carry an antibody or DNA as a biological probe.
2. Gold nanoparticles (Au-NP): It has a polyclonal antibody or an oligonucleotide (Bio-barcode). Bio-barcode is a developing technique with the help of advancements in nanotechnology. It is an enzyme and PCR free technique and highly sensitive for protein and DNA detection.

DNA barcoding has been suggested for fungal identification (Xu, 2016) as a reliable and rapid method of detection. A DNA barcode should be standardized and scalable. Similar techniques can be developed for speedy and onsite detection of plant pathogens especially viruses to mitigate crops losses.

3.3 Nanopore system: Nano-pore systems can be used to examine genetic information at a low cost. It has low sample preparation requirements and is quick (Branton et al., 2006). Nanopore is a nano-sized pore through which nanoparticle ions flow. Nanopore-based systems determine nucleotides through conductivity changes, which enable them to identify nucleotides because of their lipid membrane. Newly, nanopore based sequencing (Nano-SBS) distinguished four DNA bases through discovering four different sized tags released from 5'-phosphate-modified nucleotides at the particular molecule level for sequence determination (Kumar et al., 2012). An UK-based nanopore technology, a portable DNA sequencing machine (MinION) has been released. It enables researchers to sequence a 10 kb sample of single-stranded and double stranded DNA, making next generation sequencing easily approachable (Hayden, 2015). This technique enables to detect and track the spread of an epidemic, differentiation between various bacteria, fungi, viruses, complex genomic components, and difference between two different gene sequences located on the same chromosome.

3.4 Nanodiagnostic kit: Nanodiagnostic kit, also called "lab in a box", is used as a small box for measuring important tasks in plants which can be performed in small space. A smart kit helps to detect the plant pathogens and can help the farmers in prevention of wide spread diseases (Pimentel, 2009). Nanodiagnostic kit contained four myco-sensors which can detect the ZEA, T-2/HT-2, DON and FB1/FB2 myco-toxins on one strip only. It is used for cash crops like wheat, barley and corn (Edmundson and Capeness, 2015). This method is fast, convenient and less expensive for finding out if crops have a fungal infection. For antigen and antibodies, for the nucleotide sequence nano kit can be used and all have multiple additional purposes. Moreover, it can also detect particular gene target and isolate and purify specific genes.

3.5 Quantum dot (QDs): This is another level of nanocrystals that release specific wavelengths of light i.e. Quantum Dots (QDs). These are three-dimensional nanoparticles having a broad excitation spectrum.

In the near future, quantum dots will be used in almost every form of diagnostics and medical testing eg. fluorescent QDs can be used for various molecular diagnostics and genotyping procedures. These studies may help to contribute in complex diagnosis. Combination with other therapies may be useful in cancer diagnosis applications. QD bio conjugates enable the visualization of living cancer cells in animals and the visual differentiation of cancer cells using fluorescence microscope.

4. Applications of Nanoparticles in Agriculture

4.1 Applications of silver nanoparticles (AgNPs): *Phanerochaete chrysosporium* white rot fungus is used to synthesize silver nanoparticles. The non-pathogenic character of this fungi allows abundant production of silver nanoparticles (Vigneshwaran et al., 2006). *Cladosporium cladosporioides* - mediated synthesis of silver nanoparticles have been used to control the size and shape of biogenic nanoparticles (Balaji et al., 2009).

Silver nanoparticles synthesized by using *Verticillium sp*. 'acidophilic fungus' isolated from *Taxus* plants in an intracellular method and have various applications. It is maintained in potato dextrose agar (Sastry et al., 2003). *Penicillium citrinum,* isolated from soil, has also been used to synthesize silver nanoparticles. The silver nanoparticles effect energy consumption and help in resolving the health problems due to the intake of the very effective drug. The fungal biomolecules are responsible for the capping and efficient stabilization of silver nanoparticles, according to the fourier transform infrared (FTIR) result (Barabadi et al., 2014).

Neurospora crassa extract has been used to synthesize silver nanoparticles of small size with narrow dispersion under various environmental conditions. It was responsible for stabilizing the nanostructures of nano particles (Quester et al., 2016).

Silver nanoparticles have been used for crop yield enhancement, protect plant from diseases and pests in the form of nano-packages to increase the shelf life of agricultural produce i.e. fruits and vegetables. Stored rice treated with AgNPs remains unifested with rice weevils even after 2 months of treatment. The AgNPs-PVP coating on green asparagus reduced the weight loss, ascorbic acid, total chlorophyll content and change in skin color, and increased tissue firmness. The growth of microorganism was also considerably low thereby, increasing its shelf life by about 10 days at 2°C (Kale et al., 2021).

4.2 Applications of gold nanoparticle (AuNPs): The non-pathogenic and agriculturally useful fungus *Trichoderma harzianum* has been used to mediate synthesis of gold nanoparticles. Gold nanoparticles, synthesized using a simple method involving *Aspergillus* sp., have been effectively employed in degradation of aromatic pollutants. This catalytic activity was analyzed using toxic refractory pollutants eg. nitro-aromatics and azo dyes (Qu et al., 2017). The myco-nano-technology interface between mycology and nanotechnology was employed for extracellular synthesis of gold nanoparticles, using the phosphate-solubilizing fungus *Bipolaris tetramera* isolated from soil rhizosphere. It has antibacterial efficacy against *Bacillus subtilis*, *B. cereus, Staphylococcus aureus, Escherichia coli*, and *Psedomonas aeruginosa*; and antifungal efficacy against *A. niger* and *Trichoderma sp.* and cytotoxic effects (Fatima et al., 2015).

A cell-free extract of *Candida parapsilosis* has also been used in biological synthesis of gold nanoparticles. The biosynthesized gold nanoparticles, with pH 12, make the particles mono-dispersity which has been identified by size-dependent catalytic activity for reduction of 4-nitrophenol (Krishnan et al., 2016). *Colletotrichum sp*. isolated from the surface of disinfected leaves of *Pelargonium graveolens* has been used for synthesis of gold nanoparticles. It is possible to produce secondary metabolites through symbiotic systems (Shankar et al., 2003). Gold nanoparticles have also been biosynthesized from *C. cladosporioides*, an endophytic fungus on the seaweed *Sargassum wightii*. Marine endophytes are the most untapped group of microorganisms. These nanoparticles had antimicrobial i.e. antibacterial activity, as shown by well-diffusion method. These nanoparticles were effective against *S. aureus* (MTCC 7443) but less effective against *B. subtilis* (MTCC 441) and also had antioxidant activity (Joshi et al., 2018).

4.3 Nano farming: Fabrication of nanomaterials of different sizes and shapes have resulted in wide array of applications in agriculture and food processing. Nanotechnology provides an excellent solutions against environmental challenges. The development of nanosensors have huge potential for the study of environmental stress and enhancing the combating potentials of plants against diseases (Afsharinejad et al., 2016; Kwak et al., 2017). Nano- carbon tube fertilizers are being used to increase seedling growth in various crops. The two types i.e., single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) affect physiology and biochemistry of the plant. SWCNTs especially affect root development of the plants. These have been shown to affect the expression of genes involved in stress responses in tomatoes, a trait controllable for controlled plant development. They also increase seedling growth of tomatoes, soybeans and corns whereas, both types of CNT increase the seed germination percentage (Celebi et al., 2021)

4.4 Nanoparticle-enabled smart delivery options: The delivery system of agrochemicals and organic molecules including transport of DNA molecules or oligonucleotides into the plant cells are important aspects of sustainable agricultural production and precision farming (Joga et al., 2016). In conventional methods, agrochemicals are generally applied to crops by spraying and/or broadcasting and very low number of agrochemicals reach the target sites of crops that too much below the minimum effective concentration which may not be sufficient for successful plant growth or pest control. The losses are attributed to leaching, degradation by photolysis, hydrolysis and microbial degradation (Nair et al., 2010, Yang et al., 2016). In fertilizer application, emphasis should be given to the bio-availability of nutrients due to the chelation in soil, degradation by microorganisms, evaporation, over-application, hydrolysis, and run-off problems (Gogos et al., 2012). In pesticide applications, the efficacy may be enhanced with spray drift management (Ghormade et al., 2011).

Nanoparticles help in effective delivery of agrochemical due to their large surface area, easy attachment and fast mass transfer. Hence, micronic or submicronic particles are incorporated into the agrochemicals through various mechanisms viz., capsulation, absorption, surface ionic or weak bond attachments and entrapment of active ingredients into the nano-matrix (Pandey et al., 2018). Nanomaterials improve stability of agrochemicals and protect them from degradation and subsequent release into the environment, thus eventually increase in the effectiveness and reduce in the quantities.

The convergence of nanotechnology with biotechnology has the opportunities as new tools of molecular transporter to modify genes and even produce new organisms (Lyons et al., 2010) eg. nano-biotechnologies implicate nanoparticles, nanocapsules and nanofibres to carry foreign DNA and the chemicals that facilitate to modify the target genes. Viral gene delivery vectors face numerous challenges during the delivery of genetic materials eg. limited host range, limited size of inserted genetic material, transportation across the cell membrane and the trafficking problem of the nucleus.

In genetic engineering, silicon dioxide nanoparticles have been devised to deliver DNA fragments/sequences to the target species eg. tobacco and corn plants without any undesirable side effects. In addition, NP-assisted delivery system is used to develop insect resistant novel crop varieties eg. DNA-coated NPs are used as bullets in gene-gun technology for bombardment of cells or tissues to transfer the desired genes to the target plants (Vijayakumar et al., 2010). The recent progress in chitosan NPs entrapped SiRNA delivery vehicle has provided a new plot of crop improvement allowing the target specific control of insect pests as chitosan has an efficient binding potential with RNA and penetration ability through the cell membranes (Zhang et al., 2010). Contemporary advances in nanomaterial-based specific delivery of CRISPR/Cas9 single guide RNA (sgRNA) has undertaken a new era in genetic engineering.

Nanomaterials could minimize the degree of off-target changes by improving the efficiency and specificity of CRISPR/Cas systems eg. cationic arginine gold nanoparticles (ArgNPs) assembled Cas9En (E-tag)-RNP (ribo-nucleo-proteins) delivery of sgRNA provides about 30% effective cytoplasmic/nuclear gene editing efficiency in cultured cell lines, which would greatly facilitate future research into crop development (Mout et al., 2017). Nanomaterials can help to overcome some challenges of CRISPR genome editing in plants by improving the cargo delivery, species independence, germline transformation and gene editing efficiency (Demirer et al., 2021).

4.5 Nano fertilizers: Approximately 40% of the world's agricultural land has been degraded, leading to a severe loss in soil fertility due to intensive farming practices (Zhang et al., 2014; Kale and Gawade, 2016). Very low amount of fertilizer and much below the minimum desired concentration, reaches the targeted site due to leaching, drift, runoff, hydrolysis, evaporation, photolytic or even microbial degradation (Sabir et al., 2014). Hence, the repeated and over use of fertilizers adversely affects the inherent nutrient equilibrium of the soil and water has been seriously contaminated due to leaching of toxic materials into rivers and water reservoirs (Solanki et al., 2015). In this context, engineered nanomaterials may overcome the uncertainty in crop sector in sustainable agriculture with limited available resources (Godfray et al., 2010). Nano-fertilizers may be the best alternatives to alleviate macro- and micro-nutrient deficiency through enhanced nutrient use efficiency and by overcoming the eutrophication (Shukla et al., 2019). Nano-fertilizers synthesized to regulate the release of nutrients based on the crop requirement while minimizing differential losses, have immense potential. Nitrogen fertilizers show 50–70% losses through leaching, evaporation, or degradation leading to their reduced efficiency and elevating the cost of production (Wang et al., 2011). However, nano-formulations synchronize the release of N fertilizer with the uptake demand by crops. Thus, prevent undesirable losses of nutrients *via* direct internalization by crops, and avoid interaction of nutrients with soil, water, air and microorganisms. Application of porous nanomaterials, such as zeolites, clay or chitosan significantly reduced the losses of nitrogen by regulating the demand-based release and by enhancing the plant uptake process (Abdel-Aziz et al., 2016). Ammonium charged zeolites increase the solubility of phosphate minerals and thus exhibit improved phosphorus availability and its uptake by crops. Nano fertilizers, based on their mode of action, are classified as control or slow-release fertilizers, control loss fertilizers, magnetic fertilizers or nano-composite fertilizers as combined nanodevice to supply wide range of macro- and micro-nutrients in desirable properties (Lateef et al., 2016). Nano fertilizers are mainly produced by the encapsulation of nutrients with nanomaterials. Initial nanomaterials are produced using physical (top-down) and chemical (bottom-up) approaches. The targeted nutrients are encapsulated inside nano porous materials or coated with thin polymer film or delivered as particles or emulsions of nanoscale dimensions for the cationic nutrients (NH_4^+, K^+, Ca^{2+}, Mg^{2+}) or after surface modification for anionic nutrients i.e., NO_3^-, PO_4^-, SO_4^- (Subramaniam et al., 2015).

Nanomaterials stimulate vital aspects of plant biology, as plant root and leaf surfaces the main nutrient gateway of plants are highly porous at the nanoscale (Rico et al., 2011). The, application of nano fertilizers may improve plant nutrients uptake through these pores, or the process may facilitate complexation with molecular transporters or root exudates through the creation of new pores, or by the exploitation of endocytosis or ion channels (Mastronardi et al., 2015).Application of nano zinc oxide at low doses positively influenced the growth and physiological responses i.e., shoot and root elongation, the fresh dry weight and photosynthesis in zinc deficient soil, compared to the control. Kale et al. (2016) reported that in zinc deficient soil application of zinc oxide nanoparticles with other fertilizers promoted nutrient use efficiency and increased barley productivity by 91% whereas, traditional $ZnSO_4$ increased productivity by 31% compared to the control.

Liu et al. (2016) demonstrated that NF decreased nitrogen runoff and leaching losses by 21.6 and 24.5%, respectively and augmented 9.8 and 5.5% increase of soil residual mineral nitrogen and grain production as compared to the traditional fertilizers. Nanofertilizers penetrate the aerial regions of the plant by entering the xylem vessels through the root epidermis and endodermis, and may be delivered to different areas of the plant through the phloem and leaf stomata (Kaningini et al., 2022).

Nanoparticles play an important role in environment clean up. Nanobioremediation avoids the process of usage of nanoparticles which increase the microbian activity for the clean-up of environment. Nanomaterials show some of the physiochemical properties e.g. low melting point, high surface reactivity, magnetization and relatively larger surface area which enhances the removal of heavy metals. Iron oxide nanoparticles have been utilized for heavy metal removal from contaminated water (Saravanan et al., 2020).

The species specific phytotoxic effect of nanoparticles have been reported which are dependent on species, dose, application method and type of NPs (composition, size, shape and surface properties). The transformation of nanoparticles on interaction with soil and plant compounds should be studied to examine the degree of toxicity (Zulfiqar et al., 2019). The mechanism of nanoparticles is flexible on both root entry and foliar entry and nano-assisted materials in nanofertilizers play a significant role against abiotic stresses like drought, salinity, metal stress and temperature effects etc. Organisations like Indian Farmers Fertilizers Cooperative Limited (IFFCO) are promoting nanotechnology-based fertilizers by manufacturing nano-fertilizers viz, nano urea, nano zinc, and nano copper which utilize the dynamics of shape, size, surface area and bio-assimilation. These have also been tested for bio-efficacy, bio safety-toxicity and environment suitability (Kumar et al., 2021). The nano-goods help in environmental protection, financial stability and biological sustainability. The fertilizers from biological resources may be beneficial over synthetic fertilizers in maximizing crop expansion with nutrient utilization efficiency and mitigation of climate change thus, nanofertilizers may be essential for the exploration of another green/grain revolution globally with a healthy ecosystem under climate change in the future (Verma et al., 2022).

4.6 Nanobiofertilizers: Nanobiofertilizers consist of biofertilizers encapsulated in nanoparticles which are cost-effective and more potent and more eco-friendly than nanoparticles or biofertilizers alone. Biofertilizers are the preparations of plant-based carriers having beneficial microbial cells, while nanoparticles are microscopic (1–100 nm) particles. Silicon, zinc, copper, iron, and silver are the commonly used nanoparticles for the formulation of nanobiofertilizer. The green synthesis of these nanoparticles enhances their performance and characteristics. Nano-biofertilizer gives better and more long-lasting results as compared to traditional chemical fertilizers in improving the structure and function of soil and the morphological, physiological, biochemical, and yield attributes of plants. Production and application of nano-biofertilizer is a practical step toward smart fertilizers that enhance growth and augment the yield of crops (Al-Mamun et al., 2021; Akhtar et al., 2022).

4.7 Nanomaterials in seed germination, crop growth and quality enrichment: Seed germination is largely affected by environmental factors, genetic trait, moisture availability and soil fertility (Manjaiah et al., 2019). Application of nanomaterials has positive effects on germination as well as plant growth and development eg. application of multiwalled carbon nanotubes (MWCNTs) positively influenced seed germination of different crop species including tomato, corn, soybean, barley, wheat, peanut, and garlic (Joshi et al., 2018). Similarly, nano SiO_2, TiO_2 and Zeolite application positively stimulate seed germination in crop plants.

Nanomaterials i.e. ZnO, TiO_2, MWCNTs, FeO, ZnFeCu-oxide, and hydroxy fullerenes increased crop growth and development with quality enhancement in crops like peanut, soybean, mung bean, wheat, onion, spinach, tomato, potato and mustard. Carbon nano materials fullerols, as OH-functionalized fullerenes had positive effects on plant growth. Ahluwalia et al. (2014) demonstrated that fullerenes enhanced hypocotyl growth in *Arabidopsis* due to stimulation of cell division. It has also been observed that seed dressings with Fullerol increased number and size of fruit, and final yield by 128% and it stimulated bioactive compounds i.e., cucurbitacin-B, lycopene, charantin and inulin in fruits of bitter melon (*Momordica charantia*). It may be to the ability of nanomaterials to absorb more nutrients and water which in turn helps to enhance the vigor of root systems with increased enzymatic activity.

El-Feky et al. (2013) showed that foliar application of nano Fe_3O_4 could significantly enhance total chlorophyll, total carbohydrate, levels of essential oil, iron content, plant height, branches/plant, leaves/plant, fresh weight, and dry weight of *Ocimum basilicum* plants compared to that of soil application.

4.8 Nanomaterials accelerate plant adaptation to progressive climate change factors: Progressive climate change refers the changes in the baseline of climate factors, eg. temperatures, water deficiency, cold, salinity, alkalinity, and environmental pollution with toxic metals over time spans. Therefore, the plant may be enable accelerated adaptation without threatening existing sensitive ecosystems to cope with environmental stresses. It requires a multi-pronged strategy of activation of plant enzymatic system, hormonal regulation, stress gene expression, regulation of toxic metal uptake and avoiding water deficit stress or flash flood through shortening plant life cycle. Nanomaterial engineering suggested that nano fertilizers can increase crop production in existing adverse environments. Salinity stress seriously limits crop production in 23% of the cultivated lands worldwide (Onaga et al., 2016). Application of nano-SiO_2 improves seed germination, increases plant fresh weight, dry weight and chlorophyll content with proline accumulation in tomato and squash plants under NaCl stress (Siddiqui et al., 2014). Torabian et al. (2017) reported that foliar spray of nano-particles, iron sulfate ($FeSO_4$), showed positive response to salinity stress tolerance in sunflower cultivars with increased leaf area, shoot dry weight, net carbon dioxide (CO_2) assimilation rate, sub-stomatal CO_2 concentration (Ci), chlorophyll content, maximum photochemical efficiency of photosystem II (Fv/Fm) and iron (Fe) content and also decreased significant amount of sodium (Na) content in leaves. Silicon nano-particles (SiNPs) could effectively alleviate UV-B induced stress in wheat (Tripathi et al., 2017)

Abdel-Aziz et al. (2016) reported that the life cycle of nanofertilizer-applied wheat plants was 23.5% shorter i.e. 130 days compared with 170 days for yield production from the date of sowing, compared to conventional fertilizer-applied plants. Such an acceleration of plant growth and productivity with the application of nanofertilizers demonstrated their potential as effective tools in agricultural practices, especially in drought-prone, or sudden flash flood-prone areas where, the early maturity of crops is important for sustainable crop production.

Wang et al. (2015) showed that the foliar application of nano-Si at 2.5 mM concentration significantly improves Cd stress tolerance in rice by regulating Cd accumulation. In another study, the same group showed that nano-Si is also effective against Pb, Cu, and Zn with Cd. It appears that nano-Si fertilizers may putatively have an advantage over traditional fertilizers in reducing heavy metal accumulation.

4.9 Nanomaterials as nano sensors: Nano-sensors help to measure and monitor crop growth and soil conditions, nutrient deficiency, toxicity, diseases and the entry of agrochemicals to the environment. These will be useful to assure soil and plant health, product quality, and overall safety for sustainable agriculture and environmental systems.

Integration of biology with nano-materials in sensors has widened the prospects to increase specificity, sensitivity and rapid responses to precisely sense the impairments. Nanosensor-based global positioning system (GPS) is used for real time monitoring of cultivated fields throughout the growing season. Such networks of wireless nano-sensors monitor the controlled release mechanism via nanoscale carriers employing wireless signals located throughout the cultivated fields. This can assure a real time and comprehensive monitoring of the crop growth and effective high-quality data for the timely and precise management practices by avoiding over dose of agricultural inputs.

Nano sensors estimate soil water tension in real-time coupled with autonomous irrigation control. A rapid and accurate detection of insects or pathogens would help in timely application of pesticides or fertilizers. Afsharinejad et al. (2016) developed wireless nano sensor to detect the insect attack which distinguishes volatile organics emitted in many host plant species by specific insects. Singh et al. (2010) demonstrated that nano-gold based immunosensor was effective to detect Karnal bunt disease in wheat.

Plants respond to stress through different physiological changes mediated by stress hormones i.e., jasmonic acid, methyl jasmonate, and salicylic acid. Wang et al. (2010) developed a modified gold electrode nanosensor with copper nanoparticles to detect the pathogenic fungus infestation by monitoring level of salicylic acid in oil seed. Multiwalled carbon nanotubes (MWCNTs) may study plant growth by hormones regulation i.e., auxins which may help to explore the acclimatization of plant roots in their environment, particularly to marginal soils (McLamore et al., 2010). Nanosensors may be used to determine microbe contaminants and pollutants in food (Joyner and Kumar, 2015). Fields detection of a pesticide residue and chemotaxonomy, wood and paper production, management, and protecting the forest health. Use of nanosensors in living plants may help in communication as infrared devices and sensing items in the plant's environment. Hence, nanotechnology may be most affectly applied in precision farming (Prakash et al., 2022). Various advantages of nanosensors over conventional sensors are smaller detection limits, rapid response times and high surface-to-volume ratios. Hence, studies have indicated that detection limits for atrazine, acetamiprid, and glyphosate, in parts per trillion, nanomoles to micromoles and nanograms, respectively. The nanosensors have been used to measure soil and water parameters in the field , and may play an important role in intelligent agricultural system (Beegum and Das, 2022).

The intelligent plant-diagnostic biosensors, as inspired by the internet of nano-things, has recently been upscaled by the integration of nano-biosensors with artificial intelligence, cloud computing, drones, and 5G connectivity. These potential uses of current plant-pathogen biosensors have the potential to develop 5th generation agriculture methods (Chaudhary, 2022).

4.10 Encapsulation of pesticides by nano particles: In conventional crop protection practices >90% of fungicides, herbicides and insecticides are either lost in the environment and/or are unable to reach the target sites in effective quantity for pest control, leading to enhanced expenses of crop production and environment deterioration. The nano-formulation/encapsulation of pesticides help to make available the active ingredients in minimum effective concentration at the target sites for better protection of plants from pests. Nano-formulation of pesticides have small number of particles, acting as active ingredients of pesticides, whereas, other engineered nano-structures have useful pesticidal properties. The nano-encapsulation is the coating of active ingredients of pesticides with another material of nano-range size. Encapsulated materials are referred to as internal phase of the pesticides and capsulation materials as external phase, i.e., the coating nano materials.

Nano-formulations or encapsulations facilitate the persistence or controlled release of active ingredients in the root zones or inside plants without compromising effectiveness whereas, conventional formulations of pesticides limit water solubility and injure other organisms, leading to increased resistance to target organisms. Petosa et al. (2017) showed that nano-formulations of pesticides boost crop yields by increasing pesticide efficacy by regulated transport potential of pesticide. Nano-formulations combining polymeric nano-capsules and the pyrethroid bifenthrin (nCAP4-BIF) showed increased elution with time and enhanced transport potential even with the addition of fertilizer in loamy sand soil saturated with artificial porewater containing Ca^{2+} and Mg^{2+} cations. It was inferred that nCAP4 could be a promising de livery vehicle of pesticides like pyrethroid.

Nano materials in pesticides have some useful properties viz. increased stiffness, permeability, thermal stability, solubility, crystallinity, biodegradability and sustainable agro-environmental system. The timely and controlled releases of active ingredients reduce the total amount of pesticides. It is an important feature of integrated pest management (IPM).

Bhangale et al. (2019) explored that nanofiber formulation of *Grapholita molesta* (Lepidoptera: Tortricidae) (Busck) pheromone have no effects on mortality over time, suggesting a controlled release of AI and long-term attract-and-kill effect of the pheromone and insecticide. Nanoformulations of pesticides facilitate the widening of plant-based systemic acquired resistance (SAR) against pests eg. silica nanosphere formulations can increase ability of pesticides to penetrate through the plant and reach the cell sap, thereby exerting systemic effect to control chewing or sucking type insects like aphids (Li et al., 2007). Such hollow formulations also protect pesticides from photo-degradation due to direct exposure to sun rays and nanoformulations alter non-systemic behavior of pesticides (Husseiny et al., 2015; Hou et al., 2016).

Inorganic NPs, such as ZnO, Cu, SiO_2, TiO_2, CaO, MgO, MnO and AgNPs played important roles in management of fungal and bacterial diseases (Patil et al, 2016). ZnO nanoparticles provided effective growth control of *Fusarium graminearum, Penicillium expansum, Alternaria alternata, F. oxysporum, Rhizopus stolonifer, Mucor plumbeus and A. flavus* as well as pathogenic bacteria *Pseudomonas aeruginosa*. Nano-Cu was more effective against *Phytophthora infestans* compared to the non-nano Cu formulations in tomato (Giannousi et al., 2013; Golami et al., 2014; Gudikandula et al., 2017).

TiO_2 suppressed crop diseases directly, through antimicrobial activity. MoNPs inhibited the development of fungal conidia and conidiophores resulting in death of hyphae. Application of engineered herbicidal nano materials provided eco-friendly management of weeds. Sharifi-Rad et al. (2016) demonstrated that germination, root and shoot lengths, fresh and dry weights, and photosynthetic pigments with total protein significantly decreased in weeds exposed to SiO_2 nano particles. Kumar et al. (2017) showed that methyl loaded pectin (polysaccharide) nano particles metsulfuron was more cytotoxic to *Chenopodium album* plants both *in vitro* under - field conditions. In contrast to commercial herbicides, nanoherbicides affect the below-ground parts like rhizomes or tubers and prevent the regrowth of weeds.

4.11 Nanotechnology based detection of plant diseases: Metallic nano particles of silver, silica, gold, zinc, and copper are frequently used antimicrobial agents. Silver nano particles have antimicrobial property both in ionic and nano forms that are capable to kill plant pathogens (Sharon et al., 2010) with strong antifungal and antimicrobial mode of action against bacterial and fungal pathogens.

Silica NPs have been reported to assist in the acquisition of resistance to diseases the activation of plant physiological mechanisms (Brecht et al., 2004). Iron NPs come into direct contact with fungal cell membranes and disturb its permeability, leading to reduction in the cell growth and ultimately causing death through the development of oxidative stress. Zinc NPs release hydroxyl and superoxide radicals which destroy fungal cell walls, hyphae, and prevent conidiogenesis leading to cellular death. The gold NPs had greater toxic effects on *Salmonella.* In some plant diseases, nano-silver was found to be highly effective. Nano-sized mesoporous silica particles have a regular pattern of pores with increased surface area and improved delivery, efficiency, and effectiveness for site-specific chemicals. AgNPs show color change from yellow to brown between dispersed and aggregated forms. The intensity of color change can be correlated with the concentration of the analyte. DNA-directed silver nanoparticles produced on graphene oxide was examined for its antibacterial efficacy on *Xanthomonas perforans*, the cause of tomato bacterial spot (Polash et al.,2017). Future crop development research would be considerably aided by the use of cationic arginine gold nanoparticles (ArgNPs), that are constructed Cas9En (Etag)- RNP (ribonucleoproteins), to deliver sgRNA with about 30% effective cytoplasmic/nuclear gene editing efficiency in cultivated cell lines (Elamawi et al., 2018). Engineered nanoparticles (NPs) have been added in traditional molecular assays or laboratory sequence technologies, resulting in a significant improvement in selectivity and sensitivity. They are helpful for managing plant diseases and monitoring plant health (Kumar et al., 2022).

4.12 Fungicides (Nano fungicides): Polymeric nano fungicide formulations are delivered slowly enhance solubility, thus increasing their bioavailability (Kah and Hoffmann, 2014; Khan and Rizvi, 2014). Nano emulsions (NEs) with smaller size, lower viscosity, and higher stability should be opted. The active ingredient is placed within a core surrounded by a membrane in a nano capsule. Polymers and inorganic compounds have been tested for their possible use in nano pesticide formulations which should be potent and stable while still meeting the safety criteria of the systems to the environment and human beings. Chitosan demonstrated a strong ability to increase plant resistance to *Harpophora maydis* at both the nano and conventional scales (Qidwai et al., 2018; Hassan et al., 2022). The effectiveness of plant-based natural products and nano particles has been shown effective in controlling rice blast disease (Silva et al., 2017; El-Beltagi et al., 2022). The efficacy of gold nano particles was been investigated for their toxicity to six plant pathogens, viz. *Dematophora necatrix, Fusarium oxysporum, Alternaria aternata, A. mali, Sclerotium rolfsii* and *Colletotrichum capsici*, at doses of 0, 20, 40, 60, and 80 ppm. The growth of *S. rolfsii, A. alernata and F. oxysporum* was significantly inhibited at 80 ppm. Inhibition of *A.* was observed at 60 and 80 ppm and there was significant alteration in the shape of the mycelium (Thakur & Prasad, 2022).

5 Toxicity or biosafety of nano particles in plant disease management

There is an urgent need to assess the possible inhalation of nano pesticides by the agricultural workers during applications. Wan-Jun et al.(2010) reported that toxicity of nano formulation of chlorfenapyr on mice was 4.84-19.36mg/kg and it was less toxic than the common formulation indicating its decreased effect on environmental and humans. Formulation stability is important in biosafety of nano materials and Li et al. (2018) formulated a stable nanopesticide (bifenthrin) using polymer stabilizers viz. poly (acrylicacid)-b-poly (butylacrylate) (PAA-b-PBA), Poly Vinyl Pyrrolidone (PVP) and polyvinyl alcohol (PVOH). Flash nano-precipitation technique was used to prepare 60-200 nm bifenthrin particle. The polymers should be stable over an extended period of time. Anjali et al. (2010) reported formulation of artificial polymer-free nano permethrin as an effective larvicide which was stabilized by plant extracted natural surfactants. The health of living things and ecosystems is a growing concern in the use of artificial nano materials in many industrial sectors. However, little is known about the toxicity of these materials, particularly in complex soil systems. Soil factors such as soil density, soil organisms are being affected by nano materials. They are also toxic to terrestrial plants, animals, and microbes. Membrane damage, metal ion release, oxidative stress, and metabolic problems are examples of toxicological effects seen in humans (Worrall et al., 2018; Xu et al., 2022).

5.1 Environmental and human risk of nano particles: The ultra-small sizes of nanoparticles cause several adverse effects on environment, animals, human beings andplants:

- The air borne nano pesticides, nano fertilizers etc. may deposit on leaves and floral parts of plants. It may plug stomata and create a fine physical and toxic barrier layer on stigma, preventing the pollen germination and tube penetration in to stigma. The NPs may enter the vascular tissue and impair translocation of water, minerals and photosynthates.
- The nano particles may get inhaled by the human beings and animals deep

into lungs, enter the bloodstream and accumulate in lungs and kidneys, Bowman's capsule of nephron and may result into various ill effects and disorders.

- The entry of NPs into lungs and blood stream may cause pro-inflammatory effects depending on the nature of NPs, leading to inflammation, protein fibrillation, induction of genotoxicity etc.
- Use of nano pesticides may create new contamination in soil and water bodies due to enhanced transport, longer persistence and higher reactivity of the particles.

Some organizations concerning health, as given below, have issued warnings about novel risks posed by nano particles, nano materials, and nano-devices.

1. Organization for Economic Co-operation and Development (OECD) evaluates risk assessment approaches for manufactured nanomaterials, it is done by information exchange and identification of opportunities to strengthen and enhance risk assessment capacity.
2. The US National Institute for Occupational Safety and Health (NIOSH) develops and implements commercial nanotechnology by conducting strategic planning and research to provide national and world leadership for incorporation of research findings on the implications and applications of nanotechnology into good occupational safety and health practice.
3. The EU Nano Safety Cluster works on projects addressing all aspects of nanosafety, including toxicology, eco-toxicology, exposure assessment, mechanisms of interaction, risk assessment, and standardization. Moreover, it conducts workshops and seminars to educate and enlighten people, particularly nanotechnology workers.

Conclusion

The emergence of engineered nano materials and their effects within the frame of sustainable agriculture have revolutionized world agriculture by novelty, fast growth and enormity to meet the ever-increasing global food demand. In sustainable agriculture, protection of environment from pollution is a crucial target for trade, and nano materials assure better management and conservation of inputs for plant production. The future research in the field of synthesis of nano particles from microorganisms especially fungi, plays an important role in field of chemistry, medicine, agriculture, and electronic related industries etc. Recent studies have shown that the biogenic synthesis of silver nano particles using fungi is highly beneficial and these materials have huge potential for many applications in the fields of health and agriculture. The nano particles possess cappings derived from the fungi, which confer stability. Depending on the fungus used, this capping may also exhibit biological activity, acting in synergy with the nano particle core. However, there are several disadvantages for successful use of fungi for biogenic synthesism, i.e. of information about the candidate fungus, its growth parameters, the necessity for sterile conditions, and time required for fungal growth and its synthesis. Use of nanotechnology has progressed and the applications of green chemistry have nanocarriers as per the requirement. The potential of nanomaterials encourages a new green revolution with reduced farming risks. However, there are still huge gaps in our knowledge regarding the uptake capacity, permissible limit and the ecotoxicity of different nanomaterials. Therefore, further research is urgently needed to unravel the behavior and fate of altered agriculture inputs and their interaction with bio-macromolecules present in living systems and environments.

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