Chapter 1 Nanomaterials and Plant Potential: An Overview



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1.1 Introduction

During the last few decades, development of nanotechnology and use of nanomaterials (NMs) have been extensively on the rise. NMs are characterized by having at least one dimension in nanometre (nm) range. A nanometre is one billionth of a metre, i.e. 10^{-9} m, which denotes a length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line. Several terms, including nanoparticles (NPs), nanoscale particles, nanosized particles, nanoscale materials, nanosized materials, nanoobjects and/or nanostructured materials, are used to describe the NMs. They possess some exclusive physico-chemical properties, viz. high reactivity and surface area, tunable pore size and particle morphology. These materials are in great demand for their fascinating properties and diverse technological applications. They find potential applications in areas of disease management, biomedical sciences, electronics, nanosensors, biomarkers, display devices, pollution trace detection, environmental remediation, agriculture (quality improvement, growth and nutritional value enhancement, gene preservation, etc.), automotive, information and communication technology, energy, textile, construction and so on; the list of uses is expanding fast (Husen and Siddiqi 2014a, b; Siddiqi and Husen 2016a, b, c, d; Siddiqi et al. 2018a, **b**, **c**).

NMs are formed naturally or from anthropogenic sources and can therefore be divided into (i) natural and (ii) engineered NMs (Lidén 2011). Nanosized particles are present in the nature where they are automatically synthesized due to the natural processes like biomineralization and biodegradation (Uddin et al. 2013). NPs in

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vivo are produced by several natural processes such as volcanic eruption, erosion, friction, forest fires, marine wave strokes, chemical and physical weathering of rocks and so on. However, in our daily life, incidental NPs are produced by many anthropogenic processes/sources such as fossils fuel combustion, industrial effluents, automobile exhaust and welding fumes.

During the ancient times, NPs were used in some form by the Damascans to create swords with very sharp edges and by the Romans to craft iridescent glassware. For instance, Romans in the fourth century AD used the Lycurgus Cups (Fig. 1.1), made of a glass that changes colour when light strikes upon them. These contain silver-gold alloy NPs distributed in such a way that they look green in reflected light and brilliant red in transmitted light (Leonhardt 2007; Freestone et al. 2007). Richard Feynman, the Nobel Prize winner in Physics, presented an idea of atom-byatom construction of molecules in a scientific manner (Feynman 1960). In his lecture 'There is Plenty of Room at the Bottom' delivered in 1959, he predicted that the entire encyclopaedia would one day fit on the head of a pin, a library with all the world books would be adjusted in 3 square yards, and microcomputers and nanomedicines would float in veins. However, the scientific community did not take much notice of these comments at that point of time. The term 'nanotechnology' was first coined and defined in the year 1974 by Prof. Norio Taniguchi of the Tokyo Science University, Japan, who asserted that 'nanotechnology mainly consists of processing, separation, consolidation and deformation of materials by one atom or one molecule'. Ekimov and Onuschchenko (1981) reported three-dimensional quantum confinements of NPs in 1981. However, publication of the book 'Engines of Creation: The Coming Era of Nanotechnology' by Eric Drexler (1987) is considered to be the beginning of the present-day nanotechnology revolution. Eric Drexler proposed that the molecular nanotechnology is a branch of science and technology



Fig. 1.1 The Lycurgus Cup of glass that appears red (right) in transmitted light and green (left) in reflected light. © Trustees of the British Museum

that would allow manufacturers to fabricate products from the bottom-up with enhanced molecular control. This technology would allow every molecule to be inserted into its specific place so that the manufacturing systems using this process would be clean, efficient and highly productive. Around the same time, development of scanning probe microscopy by IBM scientists made it possible to fulfil the Feynman's vision of atom-by-atom construction of molecules. Furthermore, the discovery of two allotropes of carbon in nanosize form, i.e. fullerene by Smalley in 1986 (O'Brien et al. 1988) and carbon nanotubes by Iijima (1991), gave a new boost to nanotechnology research.

In recent years, nanosized particles, mostly of metals, metal oxides, carbon or fullerene, have been engineered to meet the specific objectives. Numerous methods including chemical methods (Sotiriou and Pratsinis 2010; Sotiriou et al. 2011; Zhang et al. 2011; Roldán et al. 2013), physical methods (Tien et al. 2008; Abou El-Nour et al. 2010; Asanithi et al. 2012) and biological methods (Husen and Siddiqi 2014b, c; Husen 2017; Siddiqi et al. 2018a) are now available for NP synthesis. NPs are produced in two ways, viz. 'bottom-up' (buildup of material from the bottom: atom by atom, molecule by molecule or cluster by cluster) and 'top-down' (slicing or successive cutting of a bulk material to get the nanosized particle) (Fig. 1.2). The 'bottom-up' approach is usually a superior choice for NPs preparation, as it involves a homogeneous system wherein catalysts (reducing agents and enzymes) synthesize the nanostructures that are controlled by the catalyst itself (Iravani 2011; Husen and Siddiqi 2014b). The 'top-down' approach generally works with the material in its bulk form, and the size reduction to nanoscale is achieved by specialized ablations, for instance, thermal decomposition, mechanical grinding, etching, cutting and sputtering. The main demerit of this approach is the surface structural defects, which have a significant impact on physical features and surface chemistry of the NPs produced.

The physical methods for NP synthesis normally include laser ablation and evaporation-condensation techniques (Jung et al. 2006), while the chemical methods employ chemical reductants (NaBH₄, ethanol, ethylene glycol, etc.), aerosol technique, electrochemical or sonochemical deposition, photochemical reduction and laser irradiation technique (Sotiriou and Pratsinis 2010; Liu et al. 2011; Sotiriou

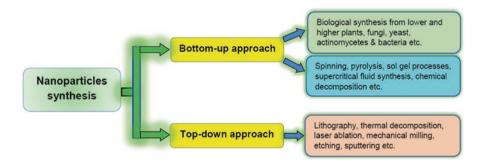


Fig. 1.2 The bottom-up and top-down approaches for NPs synthesis

et al. 2011; Zhang et al. 2011; Roldán et al. 2013). Physical methodologies are known to be costly due to high and continuous energy consumption to maintain the high pressure and temperature employed in NPs synthesis and require a highly sophisticated instrumentation. On the other side, chemical approach for NPs synthesis releases hazardous by-products and leads to environmental contamination. Moreover, certain chemicals are too costly and some of these may give rise to noxious chemical species tangled on the surface of NPs (Husen and Siddiqi 2014b). Biological methods involving the use of plants and/or microorganisms have several advantages over the chemical and physical methods. These are simple, cost-effective and eco-friendly and can be easily scaled up for high yields/production (Husen and Siddiqi 2014b; Husen 2017) (Fig. 1.3). Given this, biosynthesis of NPs, using the biological agents, viz. bacteria, fungi, yeast, plant and algal extracts, has rapidly gained the ground (Siddiqi and Husen 2016a, b, d, 2017a; Siddiqi et al. 2018a).

In recent years, the term 'green synthesis' has been used for the plant-based synthesis of NPs. Owing to rich biodiversity, several higher and lower plants and their parts (leaves, stems, roots, shoots, flowers, barks and seeds) and a big range of metabolic products or compounds (alkaloids, flavonoids, saponins, steroids, tannins, nutritional compounds) have been identified to possess a tremendous potential for this purpose and are being used successfully for an efficient and rapid green

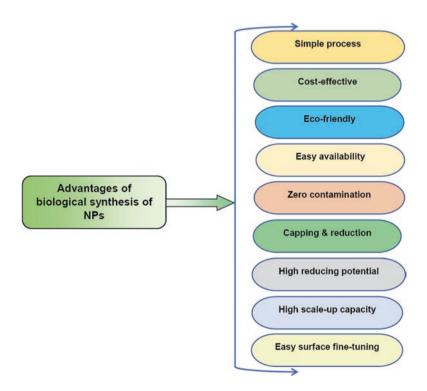


Fig. 1.3 Advantages of biological synthesis of nanoparticles

synthesis of NPs in nonhazardous ways (Fig. 1.4). Several factors determine the quality of synthesized NPs for their potential applications. The shape and size of NPs achieved in the plant-mediated synthesis depend on the protocol used, plantextract concentration, nature of reducing agents, pH of reaction mixture, incubation time, temperature and light intensity, etc. (Fig. 1.5). For instance, Tippayawat et al. (2016) have fabricated silver NPs from *Aloe vera* plant extract. The reaction time as well as the temperature of reaction mixture markedly influenced the process. Their size (70.70–192.02 nm) changed with reaction time and temperature of reaction mixture used during the fabrication. Chapters 3 and 5 of this book discuss these aspects in detail. Green synthesis has been used mainly for producing silver and gold NPs, possibly because of their wider applications, but the technique is also being applied for obtaining NPs of many other metal and metal oxides (e.g. Fe, Pd, Pt, Se, Ru, PbS, CdS, CuO, CeO₂, TiO₂, ZnO, Fe₂O₃, Fe₃O₄, Al₂O₃, NiO, MoS₃ and SiO₂). Fabrication of NMs is followed by their characterization so as to determine the size distribution, aggregation, surface area and porosity, solubility, hydrated surface analysis, zeta potential, wettability, adsorption potential, shape and size of

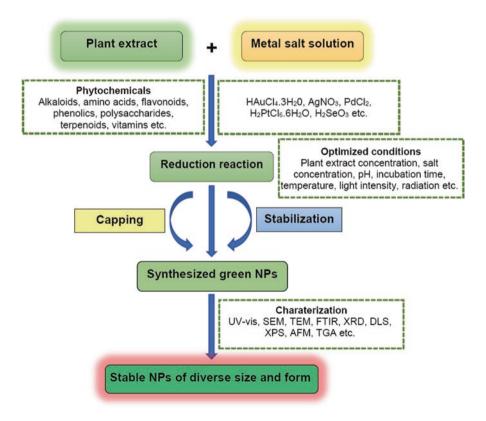


Fig. 1.4 Detailed scheme of plant-mediated (green) synthesis of NPs, optimization, stabilization and characterization techniques

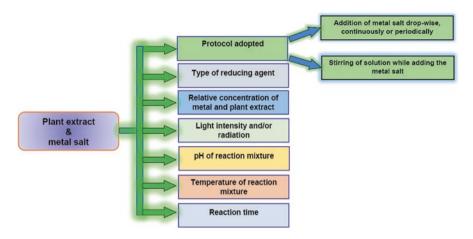


Fig. 1.5 A schematic illustration of optimization and the growth factors that affect plant-mediated synthesis of NPs

interactive surface, crystallinity, fractal dimensions, orientation, intercalation and dispersion of NPs and nanotubes. The whole procedure of green synthesis of NPs is summarized in Fig. 1.4.

Another aspect of nanomaterial-plant interaction relates to the use of NMs for enhanced production, growth and protection of plants. Increase in food production with the minimum and efficient use of fertilizer and pesticides without polluting the environment is now the main cynosure of agriculture scientists. According to an FAO estimate, productivity of food crops needs to be increased by 70% for an extra 2.3 billion individuals by the year 2050 (FAO 2009). On the other hand, increasing abiotic stresses in the environment are consistently inhibiting the growth and yield of food crops (Husen et al. 2014, 2016, 2017, 2018, 2019; Getnet et al. 2015; Yousuf et al. 2015; Embiale et al. 2016; Hussein et al. 2017; Umar et al. 2018). In addition, infections caused by bacteria, viruses, fungi and pests to crop plants are another major cause for agricultural losses. Recent studies have pointed out the beneficial effects of NMs on plants exposed to biotic and abiotic stresses (de Oliveira et al. 2014; Hossain et al. 2015; Iavicoli et al. 2017; Mishra et al. 2017; Rastogi et al. 2017; Siddigi and Husen 2017b). Only few techniques involving the use of NMs could be successfully translated to real-world applications by now, and many questions concerning the risk of the use of these NMs in plant system remain unanswered (Siddiqi and Husen 2016c, 2017b). Although collation of information on the toxicity of engineered NMs to terrestrial and plant system is in progress, most of it is based on short-term laboratory experiments. Therefore, the information available on the inherent role of NM hazards is inadequate. We present here an account of efforts hitherto made to generate, characterize and utilize the plant-mediated NMs and assess their impact on plants and environment.

1.2 Type of Engineered NMs

Based on their morphology, size (physical) and chemical properties, the engineered NMs are categorized as carbon NPs, metal NPs, ceramics NPs, semiconductor NPs, polymeric NPs and lipid-based NPs. Carbon-based NPs represent two major classes, i.e. carbon nanotubes (CNTs) and fullerenes. CNTs are elongated, tubular structure and 1–2 nm in diameter (Ibrahim 2013).

According to Aqel et al. (2012), CNTs are reliant on their diameter telicity and look like a graphite sheet rolling upon itself. They are called single-walled, double-walled or multi-walled CNTs, depending on the number of walls they have. Fullerenes contain NMs made of globular hollow cage, i.e. allotropic form of carbon. They are commercially important due to their high strength, structure, electrical conductivity, electron affinity and versatility (Astefanei et al. 2015).

Metal NPs are made of metals [gold (Au), silver (Ag), palladium (Pd), platinum (Pt), selenium (Se), copper (Cu), iron (Fe), etc.] and/or metal oxides [titanium dioxide (TiO₂), zinc oxide (ZnO), copper oxide (CuO), cuprous oxide (CuO), indium oxide (In₂O₃), etc.] showing specific opto-electrical properties due to their localized surface plasmon resonance (SPR) features (SPR is a phenomenon occurring at metal surfaces, typically gold or silver, when an incident light beam strikes the surface at a particular angle. Depending on the thickness of a molecular layer at the metal surface, SPR makes a graded reduction in intensity of the reflected light. Many standard tools for measuring adsorption of material onto planar metal surface or the surface of metal NPs are based on it).

Ceramics materials are the inorganic non-metallic solid materials synthesized through successive heating and cooling and are found in amorphous, polycrystalline, dense, porous or hollow forms (Sigmund et al. 2006). These particles are used in catalysis, photocatalysis, photodegradation of dyes and imaging applications (Thomas et al. 2015). Semiconductor NPs carry properties intermediate of metals and non-metals and are therefore useful in photocatalysis, photo-optics, electronic devices, etc.

Polymeric NPs are solid colloidal particles containing macromolecular materials that attach, adsorb, dissolve and encapsulate drugs or therapeutic compounds. These particles are identified as nanospheres or nano-capsules. The former are matrix particles whose overall mass is generally solid and the other molecules are adsorbed at the outer boundary of their spherical surface. However, in nano-capsules, the solid mass is encapsulated within the particle completely (Rao and Geckeler 2011). They protect active compounds and facilitate easy delivery and permeability of drugs into the target cells with higher efficacy and efficiency.

Lipid-based NPs are in general spherical with their diameter ranging from 10 to 1000 nm. Like polymeric NPs, lipid NPs contain a solid core made of lipid and a matrix that comprises of soluble lipophilic molecules. Surfactants or emulsifiers stabilize the external core of these NPs (Rawat et al. 2011). These days, lipid nano-technology is recognized as a special area of science, which mainly focuses on designing and synthesis of lipid NPs that are used as drug carriers for delivery and

RNA release, for instance, in cancer treatment (Puri et al. 2009; Gujrati et al. 2014). These particles have the advantage of better reproducibility using multiple strategies and larger scale-up feasibility.

1.3 Characterization Techniques

Currently, several techniques such as UV-visible spectroscopy (UV-vis), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fouriertransform infrared spectroscopy (FTIR), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), energydispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS), zeta potential, surface-enhanced Raman spectroscopy (SERS), nuclear magnetic resonance spectroscopy (NMR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), dual polarization interferometry and many others are available for NPs characterization (Fig. 1.6).

Out of these, some techniques (spectroscopy and microscopy) that include UV-vis, DLS, AFM, TEM, SEM, XRD and FTIR, are used more frequently. The AFM, SEM and TEM are regarded as the direct techniques to obtain data from

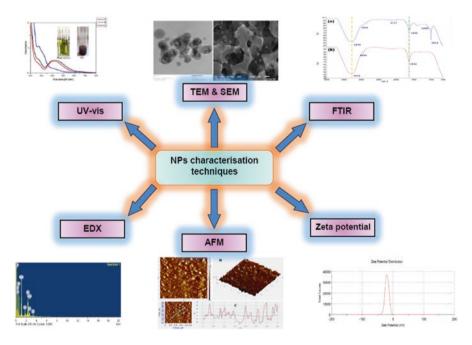


Fig. 1.6 Frequently used techniques for NPs characterization

images at various resolutions. Moreover, SEM and TEM have been widely used to determine the shape and size of NPs, as shown in Fig. 1.7.

With the help of TEM, small particles can be observed and the crystallographic structure of a sample can be imaged at an atomic scale. The arrangement of atoms and their local microstructures such as lattice fringe, glide plane, lattice vacancies and defects, screw axes and the surface atomic arrangement of crystalline NPs can be analysed using HRTEM (Brice-Profeta et al. 2005). With the help of SEM, normally data for selected areas of the surface of NM are collected, and a twodimensional image with spatial variations is displayed. AFM can be used in either liquid or gas medium. This technique facilitates the study of morphology of NPs and biomolecules. Unlike TEM and SEM, it produces three-dimensional images so that the particle volume and height can be assessed (Vesenka et al. 1993; Mucalo et al. 2002). This technique is proficient of ultra-high resolution for particle size measurement and is based on the physical scanning of samples at the submicron level using a probe tip (Zur Mühlen et al. 1996). Using AFM, quantitative ideas regarding individual NPs and groups of particles, viz. size (length, width and height), morphology and surface texture, can be evaluated with the help of softwarebased image processing.

The UV-vis, DLS, XRD, EDS, FTIR and Raman spectroscopy techniques are the indirect procedures for observing the details related to structure, composition,

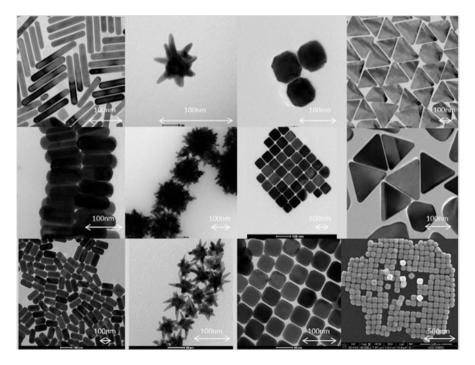


Fig. 1.7 TEM and SEM micrographs depicting various morphologically different types of NPs. (Adopted from: www.ucd.ie/cbni/newsevents/cbni-in-the-news/name,196987,en.html)

crystal phase and properties of NPs. It is known that UV-vis spectroscopy covers the UV range between 190 and 380 nm, while the visible range extends between 380 and 800 nm. Both the radiations interact with matter and promote electronic transitions from the ground state to higher energy states. Poinern (2014) has mentioned that the wavelengths between 300 and 800 nm are commonly used for characterization of metallic NPs ranging in size from 2 to about 100 nm. Absorption measurements are detected by the presence of peaks usually between 500 and 550 nm for gold NPs (Siddiqi and Husen 2017a; Husen 2017) and between 400 and 450 nm for silver NPs (Siddiqi and Husen 2016b; Siddiqi et al. 2018a).

DLS spectroscopy can be used to determine the pattern of size distribution and surface charge quantification of NPs suspended in a liquid (Jiang et al. 2009; Siddiqi and Husen 2017a). This technique is extensively used to record the size of Brownian NPs in colloidal suspensions (De Jaeger et al. 1991). Once a monochromatic beam of light (laser) is directed onto a solution of spherical particles in Brownian motion, a Doppler shift occurs when the light hits the moving particles, thereby changing the wavelength of the incoming beam of light by a value related to the particle size. Consequently, DLS allows computation of size distribution and NP motion in the medium and can be computed by recording the diffusion coefficient of the particle.

The XPS technique is used to investigate the mechanism of reaction that occurs on the surface of magnetic NPs, to measure the bonding features of different elements involved and to approve the structure of elements present in the magnetic NPs (Faraji et al. 2010). NPs elemental composition is determined via EDS mapping. XRD analysis exhibits a diffraction pattern that is subsequently compared with data contained in a standard crystallographic database to determine the structural details. XRD analysis of the data identifies the crystallite size, structure, preferred crystal orientation and phases present in the samples (Klug and Alexander 1974; Barrett et al. 1986).

TGA technique is practiced to confirm the composition of coatings, such as surfactants or polymers, and to estimate the binding efficiency on the surface of magnetic NPs. Raman spectroscopy is suitable for detecting the molecules in vibrational modes. This technique is used to identify the vibrational signals of a variety of chemical species that are attached to the surface of NPs during the synthesis (Poinern 2014). Moreover, using SERS it was possible to determine the single molecular attachments on silver NPs (Kneipp et al. 1997).

The FTIR techniques are used to determine the surface chemistry and identify surface residues, viz. functional groups like carbonyls and hydroxyls moieties, that adhere to the surface of the product during NP synthesis. Availability of functional groups in the NMs can be easily examined by the size of peaks of the spectrum (Faraji et al. 2010; Chauhan et al. 2012). Further details of NPs characterization techniques are given in Table 1.1.

Type of studies	Characterization techniques and their uses			
NPs formation	<i>UV-vis</i> : Offers information on the size, structure, stabilization and aggregation of NPs			
NPs shape and size determination	<i>TEM</i> : Examines the shape, size (10^{-10} m) , morphology and allographic structure of NPs <i>HTEM</i> : Examines the arrangement of the atoms and their local microstructures, viz. lattice fringe, glide plane, lattice vacancies and defects, screw axes and surface atomic arrangement of crystalline NPs <i>SEM</i> : Examines the morphology by direct visualization <i>AFM</i> : Examines the size and form, i.e. length, width and height, and other physical properties, viz. morphology and surface texture <i>DLS</i> : Displays the particle size distribution			
Surface charge	<i>FTIR</i> : Describes NPs to understand their functional groups and determine the emission, absorption, photoconductivity or Raman scattering of a solid, liquid or gas <i>XPS</i> : Examines the mechanism of reaction that occurs on the surface of magnetic NPs and the characteristics of bonding of different elements involved, in addition to confirming the structure and speciation of elements present in the chemical composition of the magnetic NPs <i>TGA</i> : Approves the formation of coatings, viz. surfactants or polymers, to estimate the binding efficiency on the surface of magnetic NPs <i>Zeta potential</i> : Determines the stability and surface charge of colloidal NPs as well as the nature of materials encapsulated inside the NPs or coated on their surface			
Crystallinity	<i>XRD</i> : Identifies and quantifies the various crystalline forms or elemental compositions of NPs			
Magnetic properties	<i>Vibrating sample magnetometry</i> : Estimates the magnetization of magnetic NPs <i>Superconducting quantum interference device magnetometry</i> : Examines the magnetic properties of magnetic NPs			
Other techniques	Chromatography and related techniques: Separate NPs on the basis of their affinity towards the mobile phase EDX: Identifies the elemental composition of NPs Field flow flotation: Separates different NPs based on their magnetic susceptibility Filtration and centrifugation technique: Fractionates the preparative size of NPs Laser-induced breakdown detection: Examines the concentration and size of colloids Mass spectrometry: Examines the fluorescent labelled NPs Small angle X-ray scattering: Performs the structural characterization of solid and fluid materials in the nanometre range X-ray fluorescence spectroscopy: Recognizes and examines the concentrations of elements present in solid, powdered or liquid samples Hyperspectral imaging: Identifies the type of NPs, studies the fate and transformation of these particles in water samples and characterizes the unique surface chemistry and functional groups added to the NM			

 Table 1.1
 Characterization techniques used during NPs synthesis

1.4 Physical and Chemical Characters of NMs

The large surface area, shape, composition, mechanical strength, optically dynamic and chemically reactive physico-chemical characters of NMs make them suitable for use in different disciplines of science and technology. The surface area of NMs plays a critical role in their toxic manifestations (Holgate 2010). With a decrease in the particle size, the surface area increases, leading to a concentration-dependent enhancement in oxidation and DNA-damaging capabilities (Risom et al. 2005). Additionally, other characteristics, like surface roughness, hydrophobicity and charge of NPs, affect their cellular uptake (Nel et al. 2009). Plant responses (absorption, translocation, accumulation and overall interaction) to NMs also depend on particle size (Husen and Siddiqi 2014a, b; Siddiqi and Husen 2017a). Lin and Xing (2007) found no sign of toxicity in radish, rape, ryegrass, lettuce and cucumber after the application of Al₂O₃ NPs of 60 nm size, although root elongation in maize was reduced by 35%. Doshi et al. (2008) reported that the treatment of 100 nm Al_2O_3 NPs had no adverse effect on plant growth in Phaseolus vulgaris and Lolium perenne, while Arabidopsis thaliana did not show any phytotoxicity with 150 nm NPs (Lee et al. 2010). Sadiq et al. (2011) reported the negative effect of below 50 nm Al₂O₃ NPs on the development of some microalgae. Chen et al. (2006) used zebrafish to examine the in vivo toxicity of different gold and silver NPs in the size range of 3, 10, 50 and 100 nm. Silver NPs caused a size-dependent mortality, while the impact of gold NPs was independent of size. On the whole, the size and surface area are important factors in determining the impact of NPs on plants as well as animals. The chemical nature of the constituents also has a role to play. Both the electronic and optical characters of NPs are interdependent to a large extent. For example, size-dependent optical characters are observed in metal NPs. They exhibit a strong UV-vis excitation band, which is not seen in the spectrum of the bulk metal. This band appears when the incident photon frequency is persistent through the collective excitation of the conduction electrons and is termed as the localized SPR. The wavelength peak of the localized SPR spectrum depends on the shape, size, dielectric features and interparticle spacing of NPs along with the conditions of solvents, substrate and adsorbates (Eustis and El-Sayed 2006).

The magnetic property of NPs, a result of uneven electronic distribution pattern, which in turn is dependent on the types of fabrication process such as the solvothermal, co-precipitation, microemulsion and thermal decomposition techniques, decides their suitability for several applications (Wu et al. 2015; Qi et al. 2016). Various mechanical features such as hardness, stress and strain, elastic modulus, adhesion and friction are examined to understand the exact mechanical nature of NMs. These characters facilitate their application in tribology, surface engineering, nanofabrication and nanomanufacturing. Additional features like surface coating, coagulation and lubrication also help in defining their mechanical characters (Guo et al. 2014). Solid metallic NPs exhibit higher thermal conductivities in comparison to fluid ones. For instance, thermal conductivity of copper at room temperature is ~700 times higher in comparison to water and ~3000 times higher in comparison to

the engine oil. Hence, fluids containing the suspended solid materials or particles are supposed to have a higher thermal conductivity than the conventional heat transfer fluids. For instance, Cao (2002) reported that the nanofluids containing CuO or Al_2O_3 NPs in water or ethylene show a higher thermal conductivity.

1.5 Application and Impact of NMs

The statement 'There's plenty of room at the bottom' made by Richard Feynman in 1959 regarding the nonotechnology (Feynman 1960) still holds good. This technology has started influencing our lifestyle with a lot of promise and is expected to boom further in the near future through its tremendous impact on material science, electronics, medicine, pharmacology and agriculture sectors. By now, the NMs of carbon, fullerene, Au, Ag, Cu, Zn, Pt, Pd, Se, Fe, ZnO, TiO₂, Fe₂O₃, Fe₃O₄, Al₂O₃, NiO, CeO_2 , MoS_3 , SiO_2 , CdSe, TiO_2 and nanoclay have found significant applications in the areas of agri-food, agrochemicals, biosensors, cosmetics, catalysts, lubricants, fuel additives, paints and coatings, food packaging, nanomedicine and nanocarriers, among others (Fig. 1.8 and Table 1.2). Many research institutions and commercial organizations have taken up the nanotechnology-based R&D programmes all over the globe. The number of nanotechnology-based products available in the market now runs into thousands. The global market for nanocomposites totalled US \$ 2.0 billion in 2017 and is estimated to reach US \$ 7.3 billion by 2022, growing at a compound annual growth rate (CAGR) of 29.5% for the period of 2017–2022 (McWilliams 2018).

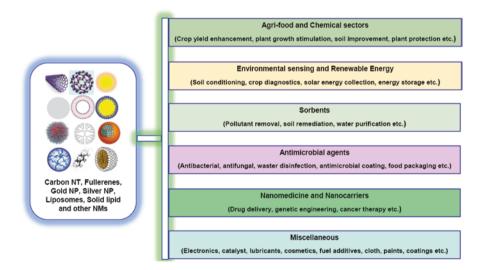


Fig. 1.8 Various applications of nanomaterials

I Z C		Fabrication	0 10 1	
Key references	NMs	process	Specific role	
	Modulation of plant gr			
Arora et al. (2012)	Gold	Chemical	Increased germination rate	
Barrena et al. (2009)	Gold	Chemical	Increased germination rate	
Jasim et al. (2016)	Silver	Chemical	Increased plant growth	
Khodakovskaya et al. (2009)	MWCT	Chemical	Increased seed germination and growth rate	
Laware and Raskar (2014)	Zinc oxide	Chemical	Increased flowering and seed productivity	
Ngo et al. (2014)	Iron, cobalt, copper	Chemical	Increased germination rate	
Nhan et al. (2015)		Chemical	Destruction of vascular bundles	
Qian et al. (2013)	Silver	Chemical	Root growth inhibition	
Soares et al. (2016)	Nickle oxide	Chemical	Decrease in leaf surface area, chlorophyll and carotenoids	
Song et al. (2016)	Copper oxide	Chemical	Inhibition of plant growth	
Syu et al. (2014)	Silver	Chemical	ROS generation, root growth promotion, activation of gene expression of indoleacetic acid protein 8, 9-cis-epoxycarotenoid dioxygenase and dehydration- responsive RD22	
Vinković et al. (2017)	Silver	Chemical	Dose-dependent decrease in plan growth	
	Seed treatment			
Anand and Kulothungan (2014)	Silver	Biological	Seed dressing	
Morsy et al. (2014)	Silver	Biological	Surface sterilizer	
	Plant protection			
El-Rahman and Mohammad (2013)		Biological	Bactericidal	
Hafez et al. (2014)	Zinc oxide	Chemical	Bactericidal	
Kanhed et al. (2014)	Copper	Chemical	Fungicidal	
Khadri et al. (2013)	Silver	Biological	Fungicidal	
Ouda (2014)	Copper and silver Nano-formulation	Chemical	Fungicidal	
Ali et al. (2015)	Silver	Biological	Pesticidal	

 Table 1.2
 Role of NMs in plant system

(continued)

		Fabrication	
Key references	NMs	process	Specific role
Grillo et al. (2014)	Chitosan	Chemical	Herbicidal
Pereira et al. (2014)	Polyepsiloncaprolactone	Chemical	Herbicidal
Yu et al. (2015)	Carboxymethyl chitosan	Chemical	Herbicidal
	Biosensing		
Boro et al. (2011)	Gold	Chemical	Herbicide detection
Dubas and Pimpan (2008)	Silver	Chemical	Herbicide detection
Kang et al. (2010)	Gold	Chemical	Organophosphates detection
Luo et al. (2014)	Carbon	Chemical	Herbicide detection
Zhao et al. (2011)	Graphene	Chemical	Herbicide detection

Table 1.2 (continued)

By tradition, silver and gold acquire elite properties and have numerous applications. In general, silver NMs have gained more attraction due to their intrinsic antimicrobial activity and are already used in a wide range of commercially available medical and other consumer stuffs (Salata 2004; Sondi and Salopek-Sondi 2004; Asha-Rani et al. 2009; Husen and Siddigi 2014b; Siddigi et al. 2018a). These are also effective in crop protection and disease management (Khot et al. 2012; Ocsoy et al. 2013; Siddiqi and Husen 2016a) and can be used to control many types of plant pathogen in a benign way, compared to the conventional fungicides (Park et al. 2006). They have also shown activity against various cancer cell lines and plasmodial pathogens (Sukirtha et al. 2012; Husen and Siddiqi 2014b; Murugan et al. 2015). Over 320 tons of silver NMs were being manufactured annually during the last decade and used in nanomedical imaging, biosensing and food products (Chen and Schluesener 2008; Ahamed et al. 2010). Silver-based NMs are also used in wound dressings, catheters and various home care products due to their antimicrobial activity (Asha-Rani et al. 2009). Their applications are discussed in detail in Chap. 5 of this book.

Likewise, advancement in synthesis and surface functionalization of NMs, i.e. their effective manipulation, has increased the scope of gold NMs application. Facile tuneable size and functionality make them a valuable scaffold for efficient recognition and delivery of biomolecules, and they can also deliver large molecule drugs with ease. Because of their size and exclusive optical and chemical properties, they have the capacity to gather inactively around tumours and can therefore be used in thermal treatment procedures (Hirsch et al. 2003; Zheng and Sache 2009). They also find use in diagnostics, biological imaging, biosensors, therapeutic agent delivery, photodynamic therapy, electronics, textile, energy harvesting, water disinfection and environmental monitoring/cleanup and possess catalytic, antioxidant and antimicrobial activities (Salata 2004; Chen et al. 2008; Holzinger et al. 2014; Shaalan et al. 2016; Yu et al. 2016; Husen 2017; Siddiqi and Husen 2017a). Applications of gold NMs are discussed in details in Chaps. 3 and 4 of this book.

Silver and gold NMs exhibit both beneficial and adverse effects on growth and yield of plants (Husen and Siddiqi 2014b; Jasim et al. 2017; Rui et al. 2018; Siddiqi and Husen 2016a, 2017a; Kim et al. 2018). It needs to be identified which trace elements are useful for the given plant species so that the same NPs may be used.

Platinum NMs have proved to be excellent therapeutic agents for use in chemotherapy, especially in the treatment of cancer cells (Hou et al. 2013; Wang et al. 2013; Min et al. 2014; Pandey et al. 2014). In combination with ion irradiation, they enhance the efficiency of cancer therapy (Periasamy and Alshatwi 2013). Further, these are used in water electrolysis (Soundarrajan et al. 2012).

Palladium NMs synthesized from *Hippophae rhamnoides* leaf extract have been examined for their heterogeneous catalytic activity in Suzuki-Miyaura coupling reaction (Nasrollahzadeh et al. 2015). Selenium NMs have shown growth inhibition of *Staphylococcus aureus* and can be used as a medicine against the *S. aureus* infection (Tran and Webster 2011). They also act as photovoltaic and semiconductor, antioxidant and chemoprotective agents (Chen et al. 2008).

Alumina-, titania- and carbon-based NMs are frequently used to get the desirable mechanical properties in coatings industries (Shao et al. 2012; Mallakpour and Sirous 2015; Kot et al. 2016). Coating enhances the mechanical strength, as it increases the toughness and wear resistance. Copper-based NMs have shown strong antimicrobial, antioxidant, anticancer as well as catalytic activity (Stoimenov et al. 2002; Akhavan and Ghaderi 2012; Hassan et al. 2012; Duman et al. 2016; Nagajyothi et al. 2017; Ojha et al. 2017). Titanium dioxide-based NMs are used in degrading the organic contamination and wastewater disinfection and in antiseptic and antibacterial compositions for their photocatalytic properties (Zhang and Chen 2009; Mahmoud et al. 2017). Moreover, these particles are used in UV-resistant material, printing ink, paper industry, self-cleaning ceramics and glass, coating and cosmetic products such as sunscreen creams, whitening creams, morning and night creams and skin milks (Wolf et al. 2003; Kaida et al. 2004; Wang et al. 2007; Weir et al. 2012; Husen and Siddiqi 2014b).

Iron oxide NMs (e.g. Fe_3O_4 or Fe_2O_3) have also gained ground in medical and some other sectors such as pesticide detection and removal of dyes (Ali et al. 2016; Siddiqi et al. 2016). Arokiyaraj et al. (2013) have reported the antibacterial activity of Argemone mexicana-mediated iron oxide NPs against Proteus mirabilis and Escherichia coli. Iron NPs synthesized from the Lawsonia inermis and Gardenia jasminoides leaves extract proved toxic to various bacterial strains (Naseem and Farrukh 2015). Iron oxide NMs are also used as a nano-fertilizer. For instance, a study on the effectiveness of Fe₂O₃ NPs as fertilizer for Arachis hypogaea has revealed that the Fe₂O₃ NPs and Fe₂O₃-EDTA effectively increased the root length and plant height and biomass by regulating the phytohormones and antioxidant enzymes' activity (Rui et al. 2016). The Fe₂O₃ NPs were adsorbed onto the soil, increasing easy availability of iron to peanut plants. Likewise, growth parameters of Solanum lycopersicum were improved under the influence of Fe₂O₃ NPs (Shankramma et al. 2016). In this study, NPs were dumped on root hairs and root tips, followed by the nodal and middle zones of the plant. The authors proposed that biomineralization of NPs occurred due to the presence of rich phytochemicals in

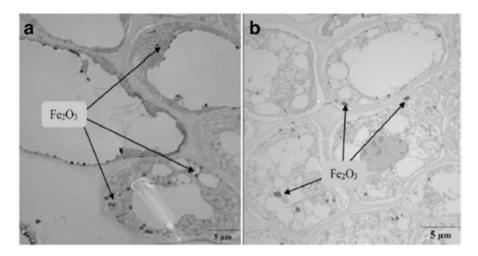


Fig. 1.9 TEM images of root sections of non-transgenic cotton (a) and Bt transgenic cotton (b) plants obtained after 10 days of treatment with Fe_2O_3 NPs. (Adopted from: Nhan et al. 2016)

plants. Further, exposure of Bt transgenic and non-transgenic cotton to Fe_2O_3 NPs (1000 mg L⁻¹) showed the presence of dark dots (particles) primarily localized in the endodermis and vascular cylinder (Fig. 1.9) (Nhan et al. 2016). Absorption of Fe_2O_3 NPs and their aggregation in roots were apparent; iron content in shoots and roots increased in a dose-dependent manner. It was speculated that the bioaccumulation of Fe_2O_3 NPs in these cotton might cause potential risk for environmental and human health.

Zinc oxide NMs also exhibit antimicrobial activity, photodegradation or photocatalytic property and show potential in drug delivery and anticancer therapy (Vimala et al. 2014; Bhuyan et al. 2015; Ali et al. 2016; Karnan and Selvakumar 2016; Thatoi et al. 2016; Nava et al. 2017; Siddiqi et al. 2018b). These particles carrying phycomolecule ligands acted as a novel growth promotor in cotton plants (Venkatachalam et al. 2016) and helped in increasing the plant productivity. Other studies have revealed the potential of zinc oxide NPs in stimulating seed germination and plant growth (Siddiqi and Husen 2017b).

Carbon nanotubes are able to penetrate the seed coat and plant cell wall, depending on their size, concentration and solubility. This penetration can bring changes in the metabolic functions of plants, leading to increase in plant biomass and the fruit/ grain yield. However, carbon NMs have shown toxicity in some plant species (Husen and Siddiqi 2014a). Details of plant response to carbon NMs are discussed in Chap. 22 of this book.

In general, plants may show both positive and negative responses to metal oxide NPs with respect to the developmental, physiological and biochemical processes (Siddiqi and Husen 2017b). These responses are summarized in Table 1.1 of Chap. 22 of this book. NPs are capable to infiltrate in living plant tissues and migrate to different regions of the plant system (Corredor et al. 2009). In the aqueous medium

or soil matrix, they move through the symplastic or apoplastic region to penetrate the epidermis of roots, pass through the cortex and finally translocate to the stem and leaves via the xylem and phloem (Corredor et al. 2009; Wang et al. 2012) and hence, often cause a widespread impact on the plant system. Their toxicity on plant system depends on their dose, shape and size (Husen and Siddigi 2014b; Siddigi and Husen 2016a, 2017b). Besides, the fate of these NPs in the ecosystem and food chain integrity is of great concern (Fig. 1.10). Application of NPs to some plant species has shown remarkable changes in the antioxidant enzyme activity and the upregulation of heat-shock proteins. Various plant species have evolved antioxidant defence mechanisms to prevent oxidative damage and enhance plant resistance to toxicity caused by the metal or metal oxide NMs; these mechanisms are yet to be fully explored and understood (Anjum et al. 2015). The NMs absorption and their translocation in different parts of the plant depend on their bioavailability, concentration, solubility and exposure time. Despite their useful applications, NMs may cause toxicities in the terrestrial as well as aquatic system. As the enhanced production, application and disposal of NMs will inexorably increase their release into the ecosystem, biodiversity is likely to be affected. Therefore, consequences of their

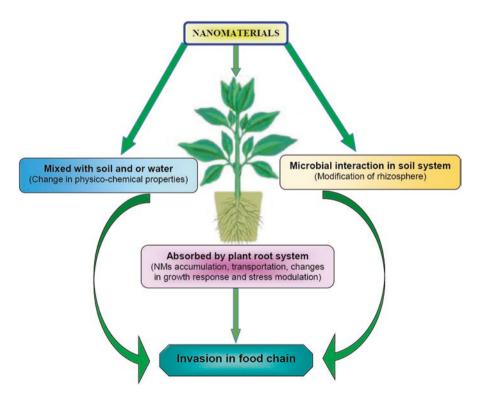


Fig. 1.10 Interaction of NMs with soil-plant system and their invasion in food chain or ecosystem

interaction with living beings (plants, animals and humans), direct or through the food chain, need to be fully investigated and understood.

1.6 Conclusion

Plant-mediated production of NMs is a green synthetic route, which is clean, safe, cost-effective and eco-friendly, giving conveniently utilizable NMs for application in various disciplines of science and technology. Plant-based green synthesis of NMs has a great promise for applications in cutting-edge technologies such as the fluorescent labelling, drug delivery, tumour destruction via heating and development of effective antimicrobial bandages. The amount of accumulation of NPs varies with the reduction potential of ions, and the reducing capacity of the plant depends on the presence of various types of metabolites in its tissues. Concentrations of plant extract and the substrate, temperature and pH of reaction mixture and exposure time largely determine the morphology, size and stability of NPs. Many issues concerning the required morphology, size and stability of NMs, reproducibility of synthesis process and the exact mechanisms involved still remain unresolved or partially resolved. Physico-chemical characters of NMs such as surface area, shape, composition, mechanical strength, optical dynamicity and chemical reactivity have a role in determining their toxicity to plant and animal systems. These materials can enable the antimicrobial compounds' delivery for use as pesticides in plant protection practices. Some of these may replace toxic chemicals and fertilizers or at least minimize their use in agriculture/horticulture in the near future. A variety of NMs have caused both beneficial and adverse effects in plants. The absorption, transportation and accumulation of NMs in plant system depend on the exposure time, shape and size of the NM and on the nature of plants species. In lower concentrations, NMs often have promotive role. At higher doses, they may cause toxicity, ultimately enhancing the generation of reactive oxygen species, which leads to disruption of the cellular metabolism and the consequent modulation of antioxidant defence system. By the way, almost all the NM vs plant studies have been carried out on plants in early developmental stages, maintained in laboratories. Long-term investigations based on field trials in natural environmental conditions are still required to develop a comprehensive and clear concept. Instead of making an arbitrary use of NMs, it is important to know which trace elements, and in what quantity, are useful for a given plant species so that a precise and effective treatment is applied. The overall cost involved should also be worked out to evaluate the economical feasibilities. The future research should also focus on the impact of NMs (1) on food chain and ultimately on the health of consumers (animals and humans) and (2) on the habitat environment as a whole.

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