

# Chapter 2

## Physical and Chemical Nature of Nanoparticles

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**Abstract** Nanoparticles have some specific features, including physical properties, chemical properties, merits, and demerits, which have drawn much attention for their application in nanobiotechnology. This chapter explains the state of the art of different properties of nanoparticles and their potential beneficial roles. In addition, this chapter discusses on the research on nanoparticles essentiality for plants and describes the current knowledge concerning the key nanoparticles with important studies for their future applications.

**Keywords** Nanoparticles · Physiochemical nature · Merits and demerits

### 2.1 Introduction

Nanoparticles in general refer to particles having internal structural measurement or external dimensions within the size range of a few nanometers, preferable up to 100 nm size. According to the European Committee for Standardization, nanomaterials are defined as the materials with any external dimension at the nanoscale, or that possess nanoscale internal or surface structures. Nanoscale describes the size range from approximately 1–100 nm (ISO/TS 27687: 2008) (Lövestam et al. 2010). It is most frequently used as a specific size description (usually <100 nm, though sometimes <50 nm), and this book chapter will use the term nanoparticle to refer to particles of <100 nm.

Nanoparticles have been developed for use in the area of agriculture (Nair et al. 2010; Campos et al. 2014), where they can increase the efficiency and productivity of crops. To properly assign the mechanisms for the application of nanoscale materials in plants, their synthesis and characterization must be well understood. Scientists have many methods to synthesize NPs of different size, shape, and

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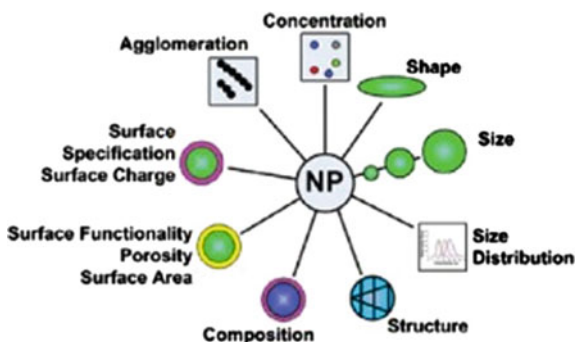
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surface properties. The major synthesis routes are liquid phase, gas-phase, and biological methods (Klaus et al. 1999; Konishi et al. 2007; Raliya and Tarafdar 2012; Mittal et al. 2013). The main liquid phase syntheses of inorganic NPs are coprecipitation, solgel processing, micro-emulsions, hydrothermal or solvothermal methods, template synthesis, and biometric synthesis (Cushing et al. 2004). The biological method can be approached for synthesis of NPs, which is rapid and cost-effective. (Gilaki 2010; Raliya and Tarafdar 2012). Besides these synthesis methods, the gas-phase synthesis methods are of interest because they allow elegant way to control process parameter in order to be able to produce size-, shape-, and chemical composition-controlled nanostructures, and also can be used to prepare the large quantity of NPs (Jiang et al. 2007; Thimsen et al. 2008).

Nanoparticles are of two types: non-engineered and engineered NPs. Non-engineered NPs present in the environment are derived from natural events such as terrestrial dust storms, erosion, volcanic eruption, and forest fires (Nowack and Bucheli 2007). Engineered NPs (ENPs) are intentionally produced by man using many different materials, such as metals (including Au, Ag, Zn, Ni, Fe, and Cu) (Fedlheim and Foss 2001), metal oxides ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_4$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ , and  $\text{Al}_2\text{O}_3$ ) (Fernández-García and Rodríguez 2011), nonmetals (silica and quantum dots) (Ehrman et al. 1999), carbon (graphene and fullerene) (Endo et al. 2013), polymers (alginate, chitosan, hydroxyethylcellulose, polyhydroxyalkanoates and polyhydroxyalkanoates, and poly-E-caprolactone) (Paques et al. 2014) (Rao and Geckeler 2011), and lipids (soybean lecithin and stearic acid) (Ekambaram et al. 2012).

Engineered NPs are able to enter into plants cells and leaves and also can transport DNA and chemicals into plant cells (Galbraith 2007; Tripathi et al. 2011; Raliya et al. 2015). The unique physical and chemical properties of nanoparticles could boost plant metabolism (Nair et al. 2011; Brew and Strano 2014). Here, we describe the physical and chemical nature of the NPs and compare their merits and demerits during application. Figure 2.1 shows the different physical and chemical nature of NPs.

**Fig. 2.1** Physical and chemical nature of nanoparticles



## 2.2 Physical Properties of Nanoparticles

Physical properties of NPs include shape, size, specific surface area, agglomeration/aggregation, state of size distribution, surface morphology/topography, and structure including crystallinity, defect structure, and solubility (Cadden 1987; Rao and Biswas 2009). The size, shape, surface area, and size distribution of NPs are important deciding factors controlling their uptake by plants as it is highly dependent on cell wall pores and size of stomata (Eichert et al. 2008; Schreck et al. 2012; Wang et al. 2013). The following section will describe the basics of each physical property of NPs.

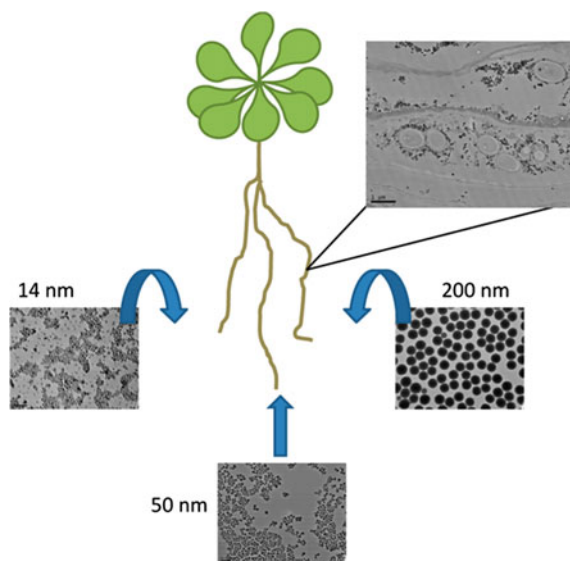
### 2.2.1 Size and Shape

The size and shape can be identified as the most important parameter to define the nanomaterial in general. Jolivet et al. (2004) and Jolivet et al. (2004) postulated that NPs below 20–30 nm in size are characterized by an excess of energy at the surface and are thermodynamically unstable because of the interfacial tension, acting as a driving force, which leads to a spontaneous reduction of the surface area. However, most types of particles have a critical size of about 30 nm below which NPs exhibit their typical “nano” properties from their bulk material. When the size of a nanoparticle decreases, the amount of molecules present at the particle’s surface increases in an exponential trend. Slomberg and Schoenfisch (2012) studied the size-dependent effects of silica particles on *Arabidopsis* (*Arabidopsis thaliana*) plants. The studies showed reduced development of plants for treatment with 50 and 200 nm silica NPs. Figure 2.2 shows the effect of different size of silica NPs on growth of *Arabidopsis* plant.

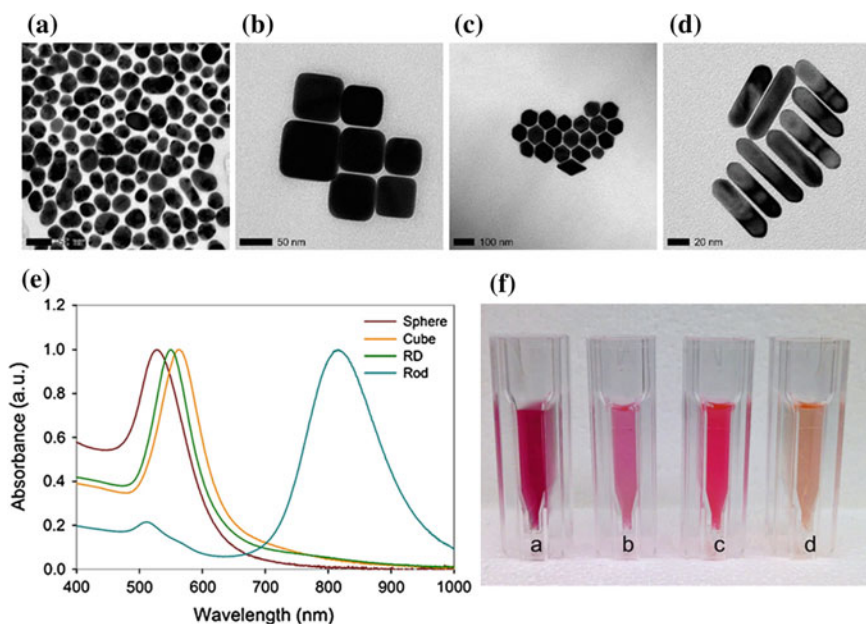
The design of NPs has gained a lot of attention, resulting in particles with various shapes such as spheres, rods, tubes, fibers, and disks, and more extraordinary geometries such as worms, squares, urchins, and ellipsoids. The optical properties of NPs also depend on its size and shape. Figure 2.3 exemplifies the difference in the optical properties of gold NPs for different shapes (synthesis and characterization done in Nano Research Facility, Washington University, in Saint Louis using the article (Wu et al. 2010).

### 2.2.2 Surface and Size Distribution of Nanoparticles

The surface morphology and surface area of NPs can be analyzed using scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET), respectively (Hayat 1974). To get a higher resolution of approximately 0.2 nm, atomic force microscopy (AFM) can be used. It provides real topographical images of sample



**Fig. 2.2** Effect of different sized (14, 50, and 200 nm) silica nanoparticles on growth of *Arabidopsis thaliana* plant (reprinted with permission from Slomberg and Schoenfish 2012 copyright of American Chemical Society)



**Fig. 2.3** Characterization of gold NPs. TEM images of gold nanostructure **a** spheres, **b** truncated cubes, **c** rhombic dodecahedra, and **d** rods **e** UV-visible absorption spectra showing characteristic absorption peak(s) for each nanostructure **f** Pictured from *left a* to *right d*: nanospheres, truncated cubes, rhombic dodecahedra, and rods as synthesized in aqueous suspension

surfaces. Dynamic light scattering (DLS) enables evaluation of the size distribution of NPs, and zetasizer can be used to determine the surface charge of NPs. The attachment of NPs to cell membrane seems to be most affected by the surface charge of the NPs (Honary and Zahir 2013). The plant cellular uptake is usually a prerequisite and is also governed by surface hydrophobicity and charge in addition to size. Compared to NPs having a neutral or negative charge, positively charged NPs are taken up at faster rate. The dispersion status of NPs in aqueous media principally depends on the surface charge of the given NPs. A number of in vitro studies with different NPs have been published in which the effect of the different parameters such as dispersion, surface properties, and agglomeration and de-agglomeration can be controlled using ultrasonication, ionic strength and pH of aqueous solutions, physiological buffers, and cell culture media (Orts-Gil et al. 2011; Barreto et al. 2015).

### ***2.2.3 Structural and Species Specifics of Nanoparticles***

Determinations of purity of NPs are important in biological application. X-ray diffraction (XRD) is the most essential tool used to characterize crystal structures (Warren 1969). The most commonly used database for the identification of crystal structures is the Joint Committee on Powder Diffraction Standards—International Center for Diffraction Data (JCPDS-ICDD) system. Detailed profile analysis of experimental XRD patterns provides information about a given material's space group and structural parameters. (Jain et al. 2009; Kumar and Yadav 2009). Syu et al. (2014) studied the effects of size and shape of silver NPs on growth and gene expression in Arabidopsis plants and found that the application could result in a complex physiological response in the treated tissues. The literature reported the species specificity of NPs in which their effects vary with the type of NPs and type and nature of biological systems that got treated with NPs (Zhang et al. 2013; Song et al. 2014).

## **2.3 Chemical Properties of Nanoparticles**

Chemical properties include the elemental composition of nanomaterials and its surface chemistry such as zeta potential and photocatalytic properties (Cadden 1987; Rao and Biswas 2009). The chemical properties of a material are determined by the type of motion of its electrons. There is a wide range of NPs contributing to many different chemical properties (Schmid 2011). Here, we describe the chemical characteristics separately with different kinds of NPs.

### 2.3.1 *Metallic Nanoparticles*

Compared with other nanostructures, metallic NPs have been proven to be the most flexible nanostructures owing to the synthetic control of their size, shape, composition, structure, assembly, and encapsulation, as well as the resulting tunability of their optical properties. Compared with other metallic nanostructures, colloidal gold and silver NPs are especially promising in nanobiotechnology because of their simple and fast preparation and bioconjugation. The attraction of surface plasmon excitations for the applications typically arises from the large electromagnetic field enhancement near the metal surface and the dependence of the resonance wavelength on the size, shape, and local dielectric properties of NPs. Such nanoparticles work as platform materials for biomolecular ultrasensitive detection, hyperthermal treatment for cancer, cell and protein labeling, and targeted delivery of therapeutic agents within the cells. Whereas silver NPs have a comparatively high cytotoxicity (Greulich et al. 2009), gold NPs are biologically almost inert (Mahl et al. 2011) and have a remarkable role on seed germination and antioxidant systems in Arabidopsis and altered levels of micro-RNAs expression that regulates various morphological, physiological, and metabolic processes in plants (Kumar et al. 2013).

### 2.3.2 *Metal Oxide Nanoparticles*

Metal oxide NPs can exhibit unique chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence important groups of basic properties in any material. The properties such as structural characteristics, namely the lattice symmetry, cell parameters, and effect of size, are related to the electronic properties of the oxide, and structural and electronic properties obviously drive the chemical properties of the solid and also by size in a simple classification (Ayyub et al. 1995). Metal oxide particles serve many functions in the various field of plant technology (Picó and Blasco 2012; Raliya and Tarafdar 2013; Tarafdar et al. 2013). For example, nanosized silicon dioxide ( $\text{SiO}_2$ ) treatments in proper concentration increased the percentage germination (Siddiqui and Al-Whaibi 2014). It was also reported that alumina NPs increased the root growth of plants (Lin and Xing 2007). Magnetic NPs exhibit a wide variety of attributions, which make them highly promising connection with biological system and bioapplications usually exists or can be prepared in the form of either single domain or superparamagnetic magnetite ( $\text{Fe}_2\text{O}_3$ ) or greigite ( $\text{Fe}_3\text{S}_4$ ). Due to their favorable beneficial effects, magnetic NPs approved for clinical use by Food and Drug Administration.

### 2.3.3 *Quantum Dots*

The size effects in metal oxide chemistry have frequently two interrelated faces, structural/electronic quantum-size and size-defect or non-stoichiometry effects. Structurally quantum dots (QDs) consist of a variety of metal complexes such as semiconductors, metals, and magnetic transition metals. The bioactivity of QDs can be improved by suitable surface coating with biocompatible material and/or modification with desired functional groups.

Depending on their size, it fluoresces with different colors and QD's composed of cadmium selenide core wrapped in zinc sulfide shell is such of a kind (Chan and Nie 1998; Kloepper et al. 2003). To make them biologically compatible/active, newly synthesized QDs are functionalized or given secondary coatings, which improves water solubility. Studies also reported the effects of QDs on plant system showing both positive and negative effects (Nair et al. 2011).

### 2.3.4 *Carbon Nanoparticles*

The fullerene provided an exciting insight into carbon nanostructure and how architectures built from  $sp^2$  carbon units based on simple geometrical principles can change the physical and chemical properties. Carbon nanotubes (CNTs) represent the more evident example. About decade after discovery, the knowledge available increased the interest in biological and biomedical applications of carbon nanotubes (Liu et al. 2007; Prato et al. 2007). There is a certain duality in the nanotubes. On the one hand, single-walled nanotubes consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. Multiwalled nanotubes comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk. Several of the enabling technology required for nanotube application are under development, for example, the ability to disperse individual multiwalled nanotubes uniformly into a polymer matrix and controlling its alignment within a composite material (Qian et al. 2000; Andrews et al. 2002). Recently, several works have been reported with the use of CNTs as smart delivery system for the delivery of desired molecules/chemicals to animal and plant cells. Another carbon modification from the NPs group are graphene oxide (GO) and their best known representative precursor for chemical preparation of graphene (Zhang et al. 2011). Recently, graphene/GOs have been extensively explored as imaging agents, drugs carriers, and tissue engineering materials. The main advantage of these material is biodistribution and pharmacokinetics properties that can be turned by controlling the size, the surface chemistry, and the targeting ligand and highest Young's modulus among any known materials and the ability to increase the tensile strength of other materials. The combination of these advantages makes graphene an ideal platform for multimodal application in the biotechnological fields. Apart from these advantages, the important challenge and current limitations in this area are still the

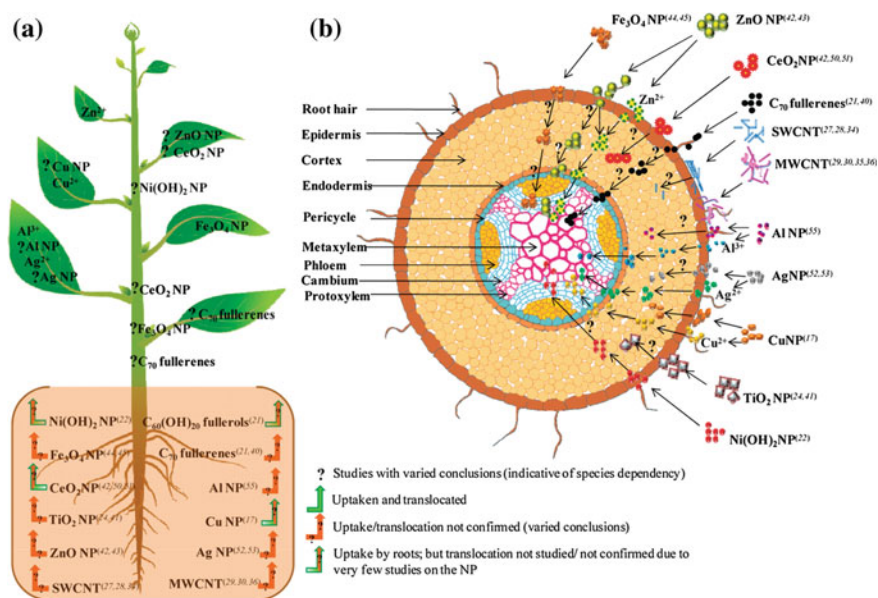


potential long-term toxicity. It was reported that fullerene and carbon nanotubes increased the water-retaining capacity, biomass, and fruit yield in plants up to 118 % which is highly remarkable (Husen and Siddiqi 2014).

### 2.3.5 Polymeric Nanoparticles

Polymer NPs have attracted the interest of many plant research groups. The term polymer nanoparticle is given for any type of polymer NPs but specifically for nanospheres and nanocapsules. These are obtained from synthetic such as from synthetic polymers, such as polycaprolactone (Bilensoy et al. 2009), polyacrylamide (Bilensoy et al. 2009), and polyacrylate (Turos et al. 2007), or natural polymers, albumin, DNA and chitosan (Martínez et al. 2011), gelatin, and poly (L-lactide) (PLA) (Mainardes et al. 2010; Saraogi et al. 2010). The various polymer NPs had been used to improve the pharmacokinetics and pharmacodynamics properties of various drugs, for example, chitosan polymer used as a carrier of plant extract (Bhatia et al. 2011).

Figure 2.4 shows the selective uptake, translocation, and biotransformation pathway of different NPs in plant organs. According to the scientist, data about NPs uptake by plants are still not conclusive (Rico et al. 2011).



**Fig. 2.4** Selective uptake, translocation, and biotransformation pathway of different NPs in plant organs (reprinted with permission from Cyrén and Hermansson 2012, copyright of American Chemical Society)



## 2.4 Merits and Demerits of Nanoparticles

Due to instability of the NPs, retaining the size and shape of NPs is highly challenging. As the kinetics associated with NPs is rapid and is highly reactive, they inherently interact with impurities. In addition, encapsulation of NPs becomes necessary when they are synthesized in a solution. Synthesis of pure NPs becomes highly difficult. Hence, retaining high purity in NPs can become a challenge hard to overcome. It is noticeable that most experimental studies with NPs have been carried out with aggregates/agglomerates of NPs. This has significantly repercussions on the biokinetics of the material. Several questions can be raised: What is the size distribution of the aggregates/agglomerates and what is the portion of the particles present as a monodispersed material?

Current research work revealed that the uptake, translocation, and accumulation of NPs depend on the species of plant and the size, chemical composition, functionalization, and stability of the NPs (Kole et al. 2013; Raliya et al. 2015). Among the carbon-based NPs, only the fullerene C<sub>70</sub> and fullerols were shown to get readily accumulated in plants (Rico et al. 2011; Nair et al. 2012). Most of the data corresponding to the germination stage and cell culture, because the protocols for quantification of NPs within tissues, are not well defined yet.

The discussion of the current research is more oriented to the effect of the NPs on plants. A very few of the NPs to the next generation of plants exposed to NPs is unknown.

## 2.5 Conclusion

The major physical and chemical properties and comparative merits and demerits of NPs are discussed. NPs are capable of penetrating living plant tissues and migrating to different organs of the plant, although detailed study of their nature is very important. These studies allow us to constitute an important step forward in elucidating the mechanisms of interaction between plant cells and NPs and thus in designing strategies for using NPs for targeted delivery of substances. Although there are many exciting potential applications of NPs, considerable challenges and issues remain to be resolved. For example, nanomaterial remains a major problem, and it is hard to precisely control the number of functional molecules on the surface of NPs. Researchers need to develop better strategies for producing NPs that have precise composition, uniform surface modification, and reproducible functionalization. For applications, the purity, dispersity, and stability of the NPs in a physiological environment are highly important. Therefore, it is necessary to further study and explore physical and chemical properties for creating successful nanobiotechnology. Also, more studies are needed to explore the mode of action of NPs and their interaction and status in plant biomass.

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