Chapter 1

Nanotechnology and Nanomaterials

1.1 Introduction

Nanotechnology refers broadly to a field of applied science and technology whose primary concern is the study of matter of size near molecular level normally ranging between 1 and 100 nano-meters (Moore, 2006). Application of nanotechnology has gained prominence in numerous fields such as optics, synthetic biology, electronics, chemical industry, drug-gene delivery (Pissuwan et al., 2011), space technology, cellular transportation, catalysis (Hoffman et al., 1992, Schmid et al., 1992), energy science, optoelectronic devices (Colvin et al., 1994, Wang et al., 1991), mechanics, photo-electrochemical applications (Chen et al., 2006), bio-nanotechnology (Chen et al., 2006), soil-water bioremediation process(Durán, 2008) and water treatment(Xu et al., 2012). The metal nano-particles play a vital role and cater to numerous applications based on their size, shape, and morphology (Tiwari et al., 2008). The presence of large grain size and grain boundary volume fraction promoted the nano-materials to acquire excellent mechanical properties in addition to physical properties (Nalwa, 2000). During the past decade, numerous novel synthesis techniques for nano-materials (such as metal nanoparticles, quantum dots, carbon nano-tubes, graphene and their composites) have been used (Hoffmann et al., 1995, Huang et al., 2006, Kim et al., 2007, Laurent et al., 2010, Livage et al., 1988, O'Neal et al., 2004, Oskam, 2006, Sastry et al., 2003 , Su et al., 2014). The large surface area to volume ratio and extremely small size, lead to sea-change in physical, chemical, mechanical, thermal, optical, biological, magnetic and catalytic properties compared to the bulk counterparts(Daniel and Astruc, 2004 (Bogunia-Kubik and Sugisaka, 2002, Zharov et al., 2005).

Nanoparticles are usually classified on the basis of their dimension, morphology, structure, composition and uniformity & agglomeration as illustrated in Figure 1.1 (Chokkareddy and Redhi, 2018). Based on their dimension, nano-particles are classified into four types - zero, one, two and three-dimensional nanoparticles. Zero dimensional nanoparticles include quantum dots, one-dimensional nanoparticles include thin films used in sensor devices and electronics, two-dimensional nanoparticles constitute nanotubes (e. g. carbon nano-tubes) which have quite high adsorption ability and stability (Baughman et al., 2002) and three-dimensional nanoparticles comprise dendrimers, nano-rods, etc. (Pal et al., 2011). Nanoparticles may also be classified as flat, spherical and rod like structures. On the basis of composition, they can be present in mixed form e. g. nano-composite form or single constituent form. Based on uniformity & agglomeration, nano-particles can be classified as dispersed and agglomerates. Figure 1.1 shows classification of nano-particles on various bases.

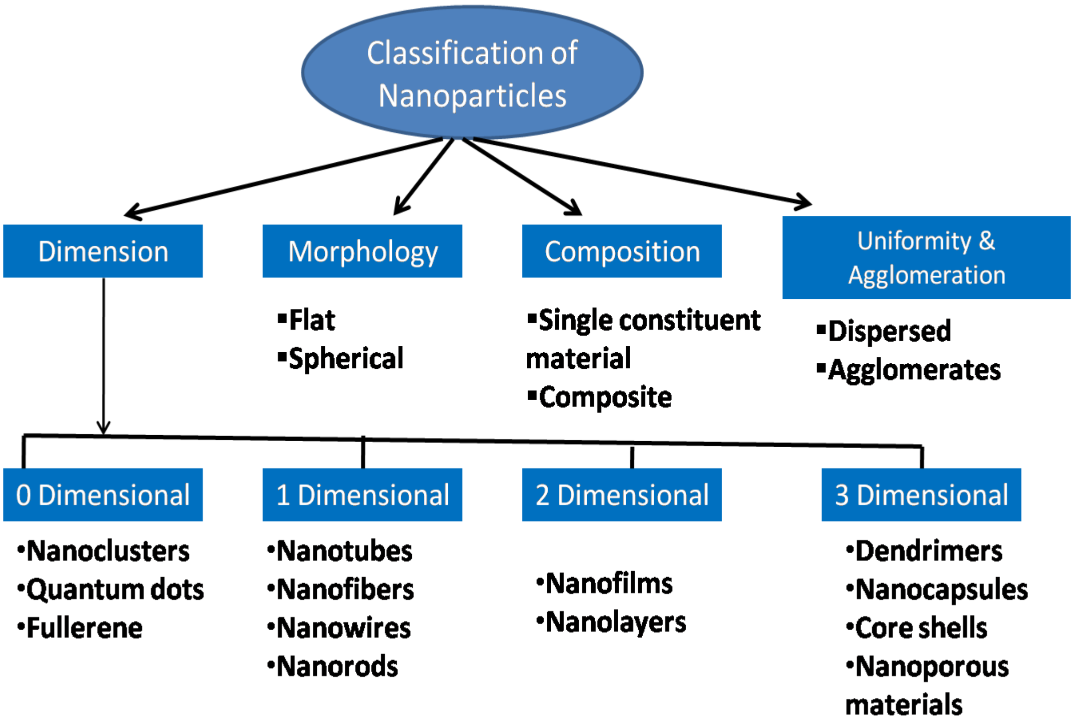

Figure 1.1 Classification of nano-particles

1.2 Synthesis of Metallic Nano-particles

Generally, for the synthesis of metallic nano-particles can be carried out using broad two methods, either “Top-down” approach or “Bottom-up” approach(Iqbal et al., 2012), as shown in Figure 1.2.

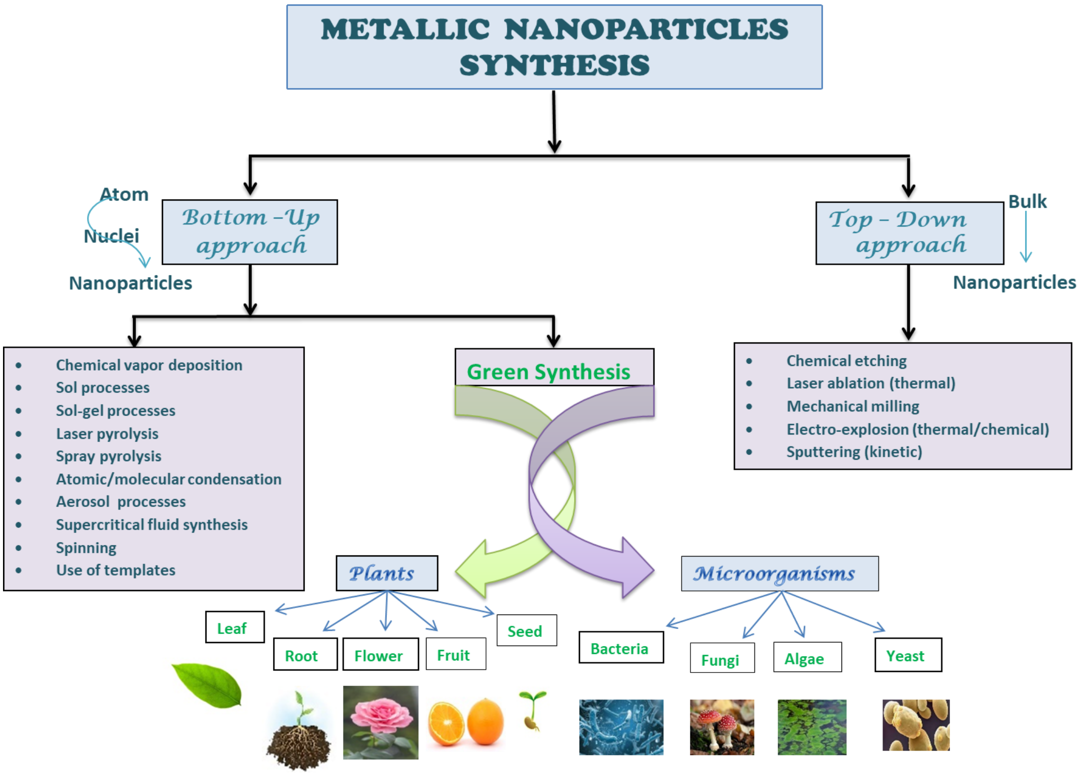

Figure 1.2 Bottom-up and top-down approaches for synthesizing nano-particles

In the case of top-down approach, size reduction plays an important role and is achieved by various physicochemical means, while in the case of bottom-up approach, small-sized particles like atoms or molecules undergo the oxidation or reduction to produce the nanoparticles (Verma et al., 2009).

Typical examples of top-down approach are chemical etching (Hu et al., 2012), laser ablation(Ayyub et al., 2001), mechanical milling (Indris et al., 2005), electro-explosion(Siwach and Sen, 2008) and sputtering(Ayyub et al., 2001). But these methods are costly, require large labour, take a lot of time to manufacture and are not eco-friendly. High temperature conditions are required hence not suitable for large-scale production.

In the bottom-up approach materials are aggregated from molecular level to nano-particle level. It is further categorized into two types i) physico-chemical approach, and ii) green approach. The physico-chemical approach includes the methods such as chemical vapor deposition (Swihart, 2003), sol process, sol-gel process (Mackenzie and Bescher, 2007), laser pyrolysis(Figgemeier et al., 2007), spray pyrolysis (Mueller et al., 2003), atomic or molecular condensation, aerosol processes(Xia et al., 2001), supercritical fluid synthesis (Byrappa et al., 2008), spinning and use of templates. These approaches generally require high temperature, expensive instruments, high energy (Guzman et al., 2009) and involve the rigorous use of harsh and toxic chemicals (Singh et al., 2018). Considering the aforementioned limitations of the chemical approach and rapid growth in the demand for nano-materials in diverse fields, an alternative approach the 'Green synthesis' has evolved and has been the attraction of many researchers worldwide. It is an important and eco-friendly synthesis technique which comes under the bottom-up approach and requires either plants or microorganisms as one of the material for the synthesis of nanoparticle. It helps in prevention / minimization of waste, minimal use of non-toxic solvents(Singh et al., 2018) and reduction of pollution. Contrary to the chemically synthesized nanoparticles, the nano-particles from the green synthesis route pose lesser hazards to the environment and avoid the production of unwanted or harmful by-products through the build-up of stable, sustainable, and eco-friendly synthesis procedures.

Out of various sources under the green synthesis heading, plants and plant parts can be used for massive and substantial production of metallic nanoparticles due to their low cost of production (Anirudh et al., 2019). Plant components are more favoured due to the faster rate of synthesis than by microorganisms and the nanoparticles thus obtained are also of various shapes and sizes(Iravani, 2011) while the synthesis using microorganisms requires a very strict and careful control on cell structure, thus making it less favoured. Figure 1.3 briefly illustrates the advantages of green synthesis in general and highlights the differences between green synthesis using plants and the drawbacks of green synthesis using microorganisms.

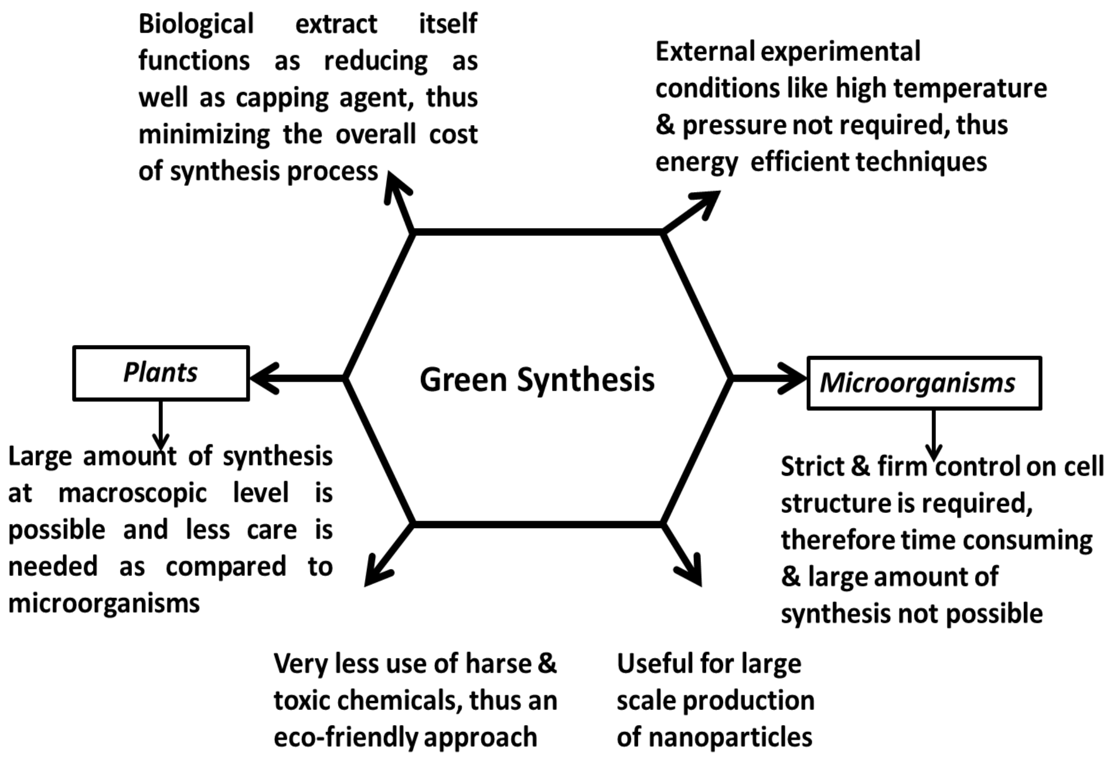

Figure 1.3 Advantages of green synthesis using plant components over microorganisms

Constituents of plant extract act both as reducing and capping agents in nanoparticle synthesis (Iravani, 2011). The plant extracts contain a variety of naturally occurring phytomolecules such as alkaloids, water-soluble flavonoids, and several other phenolic compounds, which are widely classified as polyphenols (Komes et al., 2011, Quideau et al., 2011). These polyphenol based phytomolecules are associated with strong reducing properties and have a strong tendency to adsorb on the nano-particles surface and act as stabilizers. The antioxidant properties of phenolic phytomolecules are principally owing to their reducing abilities, which enable them to act as reductants and singlet oxygen quenchers (Rice-evans et al., 1995).

1.3 TiO_2Nano-particles

Titanium dioxide (TiO_2) is highly important due to its unique physicochemical properties and wide band gap i.e. 3.2 eV for anatase phase(Chen et al., 2006). Titanium dioxide (TiO_2) also known as titania has three crystal structures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic)(Behpour et al., 2012). Rutile phase forms above 600 °C while anatase forms at a lower temperature. At lower temperature, TiO_2 nano-particles acquire tetragonal structure (anatase phase) as the surface Gibbs free energy is lower than the rutile phase. The unique physicochemical properties, i.e., higher refractive index and absorption of ultraviolet (UV) light facilitates TiO_2 to work as a multifunction material. Several physical and chemical processes occur on the surface of the TiO_2 nanoparticles with high efficiency, so large surface to volume ratio is always favourable for its application.

Due to the inherent properties of TiO_2 nanoparticles like nontoxicity, photo induced super-hydrophobicity, antifogging effect(Borhani and Taghdisi, 2011) and low cost productivity, it has found applications in diversified fields like photo-catalytic degradation and splitting (Ahmed et al., 2013), electro-chromic devices(Tian et al., 2012), photovoltaic cells, sensing instruments, hydrogen storage and environmental remediation. Amongst numerous nano-photo-catalyst studied till date, TiO_2 has proved to be the most efficient photo-catalyst due to its appropriate electronic band structure, photo stability, chemical inertness and commercial availability (Gupta and Tripathi, 2012).Even though TiO_2 is an excellent photo-catalyst, its application in powder form poses many material handling difficulties which not only affect its catalytic ability but also hamper its reusability.

1.4 SiO_2Nano-particles

In nature, silica exists as sand, quartz, etc. Naturally occurring silica is crystalline, whereas synthetic silica is amorphous in nature. Silica nano-particles have received much interest for applications such as catalysis, pharmaceuticals, drug delivery and pigments (Stober et al., 1968). Amorphous SiO_2 nano-particles are used to make electronic substrates, thin film substrates, electrical insulators, thermal insulators and humidity sensors. The silica particles play a different role in each of these products. The quality of some of these products is highly dependent on the size and size distribution of the silica particles (Herber, 1994). It is essential to have silica particles of a narrow size distribution and a high purity, as high-tech industries dealing with biotechnology and photonics are putting tremendous demand for such materials (Vacassy et al., 2000). The optical properties of silica nano-particles can be attained with respect to surface defect related to large surface/volume ratio.

While evaluating numerous chemical synthesis approaches, extraction of silica nanoparticles from biomass/biological resources is deemed to be one of the most economical production routes. The production of silica nano-particles is anticipated to be non-toxic and economic in nature. Silica is essential constituent of many plants (Ding et al., 2005). It is well known that certain plants, including grasses (Poaceae), rice (Oryzasativa), sugarbeet (Beta vulgaris), and horse-tail (Equisetum), contain high levels of biogenic silica (Sun & Gong, 2001). The chemical compositions of these biomasses are similar to that of other common biomasses, containing cellulose, lignin, hemicelluloses, etc., but silica is the primary component of their ash (Chandra., 2007, Hwang et al., 1989, Lin, 1975). Few precursors like tetraethoxysilane (TEOS) (Kim et al., 2002) and tetramethoxysilane (TMOS) (Niki et al., 2009) has been mainly used as the silica source to produce nanosilica. However, these are relatively expensive and exhibit high toxicity (Niki et al., 2009, Hiroshi., 1994).

Rice husk and bamboo leaves are rich sources of silica. Among them, rice husk has potential use as animal fodder and also has other applications. On the other hand, bamboo leaves are essentially waste after removed from the stem part which is used in rubber making and as construction material. Bamboo can be easily found in India and are one of the fastest growing plants on the earth (upto 1m/day) (Kumar et al., 2016). This fast growth results in bamboo being the richest natural source of silica accounting for about 70% of the inorganic content of the plant extract. Bamboo leaves on pyrolysis or carbonization at a higher temperature (>873K) can yield good amount of amorphous silica (Kandula and Jeevanandam, 2015, Shin and Banerjee, 2015, Wan et al., 2016, Xu et al., 2015). High purity amorphous silica was prepared from the bamboo leaves by alkali and acid treatment. Here the yield percentage was more than 50% (Kow et al., 2016, Vaibhava et al., 2014). Roselló et al., 2015 used the silica-rich ashes from the bamboo leaves in the preparation of inorganic binder. Also silica synthesized from bamboo leaf ash was used in the hydrothermal synthesis of zeolite A (Ng et al., 2017). Synthesized silica particle from the bamboo leaves ash by sol-gel technique used for removal of heavy metals in the aqueous solution as an adsorbent (Durairaj et al., 2019). If recovered and processed properly bamboo leaves can serve as a good source of nano-silica.

1.5 Utilization of Nano-TiO_2 and Nano-SiO_2

Anatase TiO_2 Powder was used for the degradation of azo dye and catalytic performance achieved up to 64.84% at 3 h visible light irradiation (Jun et al., 2007). Anatase and rutile nanocrystalline TiO_2 for the degradation of acetophenone, nitrobenzene, methylene blue and malachite green present in aqueous solutions. The photocatalytic performance of anatase TiO_2 particle was better than the rutile TiO_2 particle for dyes and organic contaminants present in the water (Tayade et al., 2007). Synthetic wastewater composed of organic carbon was treated with different combination of UV light, titanium dioxide, and hydrogen peroxide. Total carbon (TC) removal in case of UV/TiO_2 and UV/H_2O_2 process was achieved up to 58% and 56% respectively (Poulopoulos et al., 2019). TiO_2 in suspension or on support were used for the degradation of dye in presence of UV light. High photocatalytic activities were observed with supported TiO_2 (Guillard et al., 2003).

SiO_2 nanoparticle used as an efficient adsorbent for removal methyl orange and other anionic dyes from solutions (Liu et al., 2013). Saleh, 2015 applied a nanocomposite of carbon nanotubes and silica nanoparticles as adsorbent to remove the lead, Pb (II) from the aqueous solution. The adsorption performance was achieved up to 50% by the silica nanoparticles. Silica nanoparticle and its composite with graphite oxide were used to remove the heavy metals like nickel, zinc, lead, cadmium, and chromium from the aqueous solution (sheet et al., 2014). Fluoride was successfully adsorbed from the aqueous solution by taking SiO_2 nanoparticle as an adsorbent (Balarak et al., 2015). Sugar cane waste ash was used by Rovani et al., 2018 for the synthesis of silica nanoparticles. Also its performance was checked upon acid orange 8 dye. Silica nanoparticle based technology was used for the removal of dyes (Jadhav et al., 2019).

Nano-particles being used as photo-catalyst in the suspension form pose the problem of removal after the reaction and demand a solid–liquid separation step that consumes both money and time. Also the loss of catalyst will be high (Li et al., 2008). The residual nano-particles may affect environment as well as human health (Singh et al., 2013). To overcome this problem support material having high surface areas such as porous SiO_2 particle can be used. Porous silicious materials (clays, zeolites, mesoporous materials) have some inherent properties like chemically inert, high surface area, transparent to UV radiation, and high physical stability for supporting nano-photo catalysts like TiO_2 and ZnO etc.(Kuwahara et al., 2011, Qian et al., 2014). The porous solid supports also have some drawback related to the photo-catalytic action as light cannot penetrate into the pore surface to access the nano-photo-catalyst dispersed inside the pore surface (Cho et al., 2003, Lee et al., 2004, Toyoda et al., 2003, Wang et al., 2007, Zhang et al., 2004, Zhou et al., 2006). It has been observed that the photo-catalyst particles deposited on the external surface of the porous support are effective in photo-catalytic decomposition of organic compounds. This is because the external surface is easily accessible to both light and contaminants to the active sites due to less mass transfer resistance. It is known that the photo-catalytic activity of a material combined with a support having higher surface area shows significant improvement (Fateh et al., 2013, Liu et al., 2013). The SiO_2 nano-particles are used to reduce the recombination of electron-hole pair generated by the photo-catalyst in the presence of light and to increase the surface area of the photo-catalyst which provides more active sites for the photo-catalytic degradation of dyes or organic molecules (Li et al., 2013, Li et al., 2008, Wilhelm et al., 2007).

To have the optimal use of the catalytic activity and to ensure the reuse of a photo-catalyst, nano-particles of the photo-catalyst may be embedded into a polymer matrix. The characteristic features of polymer support would control the leaching of catalyst as well as eliminate/reduce the loss of catalyst during recovery. Moreover, polymer support is expected not to affect the specific surface area and activity of photo-catalyst. Recently, many researchers have immobilized the photo catalyst within different polymer matrices. Nano-particles have been successfully dispersed in the polymers like polymethyl methacrylate (PMMA) (Meng at al., 2009, Zhang et al., 2011), polyvinyl alcohol (PVA) (Matsuzawa et al., 2008) and polydimethyl siloxane(PDMS)(Paul at al., 2010) etc. If the nano-particle is not chemically bonded with polymer substrate or matrix there may be a chance of leaching of nano-particles which affects the reusability of catalyst. Furthermore, higher concentration of nanoparticles into the polymer matrix makes the polymer solution more viscous affecting its film-making process. Hence choice of polymer as per application is an important factor. For example a hydrophobic polymer can be used to immobilize the nanoparticles when water is the media for photo-catalysis. Also the nano-composite film can be used as a membrane for the separation of organic-water mixture (Aminabhavi et al., 2005, Kittur et al., 2003, Kurkuri et al., 2004). Presence of nano-particles as fillers enhances the physicochemical stability and separation performance of the membrane (Chen et al., 2008, Guo et al., 2007, Liu et al., 2008, Panek et al., 2007, Peng et al., 2006, Yang et al., 2009, Zhao et al., 2009). Thus, photo catalytic advantages of TiO_2 nanoparticles combined with the high surface area of SiO_2 nanoparticles is a good combination for various applications. As many researchers had used several inorganic materials like carbon black, carbon nanotube, nano-silica, nano-iron, polyphosphazene nanotube, TiO_2 and zeolite as filler in the membrane to enhance the separation performance as well as physicochemical properties of the polymeric membrane (Sun et al., 2013).

In this work TiO_2 and SiO_2 nano-particles synthesised from novel bio-sources are used in combination to achieve the target. Also silica nanoparticle was used as filler in the polymeric membrane to check the separation performance. Details on background literature, work done and key findings are discussed in the chapters below.