Nanoparticles: Properties, synthesis and characterization

Mrs.S.Mahalakshmi[1], Dr. K.P.Jaiganesh[2]

[1]Assistant Professor, Department of Humanities and Sciences, Roever Engineering College,
Perambalur, TamilNadu, India
E. mail id.: mahasuriyaa06@gmail.com

[2]Associate Professor, Division of Pharmacognosy and Phytochemistry, Nehru College of Pharmacy,
Pampady, Thrissur, Kerala, India.
E. mail id.: kpjaiyaganesh@gmail.com

ABSTRACT

Nanotechnology is a science, engineering and technology conducted at the nanoscale, which is about 1 to 100 nm where nano denotes the scale range of 10^{-9} and nanotechnology refers the properties of atoms and molecules measuring thoroughly 0.1 to 1000 nm. Nanotechnology is highly interdisciplinary as a field, and it requires knowledge drawn from a variety of scientific and engineering areas. Nanotechnology has become an all-embracing term, which means different things to different people. Nanotechnology is interface technologies that are include many different science and applications area. Nanotechnology falls into this category and offers fundamentally new capabilities to architect a board array of the novel materials, composites and structure on a molecular scale. Today the products made using nanomaterials having general as well as special applications like treating cancer, phosgene detection, energy harvesting for self powered nanosystems, chip fabrication, batteries, aerospace materials etc. The research in the area of carbon nanotubes, nano-polymers, nano-vectors, nanocomposites, nano-crystals, nanoparticles, nanofibers, nanoclays, nanotubes, nanofilters, nanohorn, nanowires, nanosprings, nanorods etc. have been reported.

Keywords: *Nanocomposites, Nanocrystals, nanocatylists, nanofibers, nanorods, nanofilters, nanocontainers.*

INTRODUCTION

Nanotechnology is a modern field of science which plays a dominant role in day to day life aspects. Nanotechnology deals with production, manipulation and use of material ranging in nanometres [1]. Nanotechnology is the science of material featuring between 10 −9 and 10 −7 of a meter [2] or in another words it's the science of materials and devices whose structures and constituents demonstrate novel and considerably altered physical, chemical and biological phenomenon due to their nanoscale size.

Thus nanotechnology is defined as the manipulation of matter on an atomic, molecular, and supramolecular scale involving the design, production, characterization and application of different nanoscale materials in different potential areas providing novel technological advances mainly in the field of medicine.

In the future, "nanotechnology" will likely to include building machines and mechanisms with nanoscale dimensions, referred to these days as Molecular Nanotechnology (MNT). Molecular manufacturing basically emphasizes the use of precisely engineered, computer-controlled nanoscale tools to construct vast numbers of improved tools as well as products with vast numbers of precisely engineered nanoscale features. Recently, the Foresight Institute has suggested an alternate term to represent the original meaning of nanotechnology: Zettatechnology. At the most basic technical level, MNT is building, with intent and design, molecule by molecule, these two things:

- Incredibly advanced and extremely capable nano-scale and micro-scale machines and computers,
- Ordinary size objects, using other incredibly small machines called assemblers or fabricators (found inside nanofactories).

The term, "nanotechnology," was proposed by K. Eric Drexler. Technically speaking, Nanotechnology refers to a field of applied science and technology whose theme is the control of matter on the atomic and molecular scale, generally 100 nanometers or smaller, and the fabrication of devices or materials that lie within that size range.

The history of Nano materials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like sea shells, skeletons etc. One of the first scientific report is the colloidal gold particles synthesized by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements [3].

NANO STRUCTURED MATERIALS

A material in which one of its dimension is below 100 nm (nanometre) is defined as Nano material or Nano-structured materials. Materials with structure at the Nanoscale often have unique optical, electronic, or mechanical properties (Size 10 & Normal).

Natural Nanomaterials

Biological systems often feature natural, functional nanomaterial. The structure of foraminifera (mainly chalk) and viruses (protein, capsid), the wax crystals covering a lotus or nasturtium leaf, spider and spider-mite silk, the blue hue of tarantulas, the "spatula" on the bottom of gecko feet, some butterfly wing scales, natural colloids (milk, blood), horny materials (skin, claws, beaks, feathers, horns, hair), paper, cotton, nacre, corals, and even our own bone matrix are all natural organic nanomaterial.

Inorganic Nanomaterials

In the field of Modern material science Inorganic nanoparticle has been developed and the role based upon their unique physical properties and particularly in biotechnology. Based upon these two factors of inorganic nanoparticles they should have certain physical properties that mainly include size dependent optical, magnetic, electronic, and catalytic properties. Bio related applications are involved for the preparation of these interesting nanoparticles like iron oxides, gold, silver, silica, quantum dots. Novel physical properties mainly related because of their size approaches nanometer scale dimension [4], [5].

Classification of nanoparticles

There are various approaches for classification of nanomaterials. Nanoparticles are classified based on one, two and three dimensions [6].

One dimension nanoparticles

One dimensional system, such as thin film or manufactured surfaces, has been used for decades in electronics, chemistry and engineering. Production of thin films (1-100 nm) or monolayer is now common place in the field of solar cells or catalysis. This thin films are using in different technological applications, including information storage systems, chemical and biological sensors, fibre-optic systems, magneto-optic and optical device [7].

Nanotubes

Nanotube is a nanometer scale tube likestructure. Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon called graphene. These sheets are rolled at specific and discrete ("*chiral*") angles and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes.

Two dimension nanoparticles

Carbon nanotubes (CNTs)

Carbon nanotubes are hexagonal network of carbon atoms, 1 nm in diameter and 100 nm in length, as a layer of graphite rolled up into cylinder. CNTs are of two types, single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), the small dimensions of carbon nanotubes, combined with their remarkable physical, mechanical and electrical properties, make them unique materials [8].

Three dimension nanoparticles

Fullerenes (Carbon 60)

Fullerenes are spherical cages containing from 28 to more than 100 carbon atoms, contain C60. This is a hollow ball composed of interconnected carbon pentagons and hexagons, resembling a soccer ball. Fullerenes are class of materials displaying unique physical properties. They can be subjected to extreme pressure and regain their original shape when the pressure is released. These molecules do not combine with each other, thus giving them major potential for application as lubricants.

They have interesting electrical properties and it has been suggested to use them in the electronic field, ranging from data storage to production of solar cells. Fullerenes are offering potential application in the rich area of nanoelectronics. Since fullerenes are empty structures with dimensions similar to several biological active molecules, they can be filled with different substances and find potential medical applications [9].

Dendrimers

Dendrimers represents a new class of controlled-structure polymers with nanometric dimensions. Dendrimers arise from two Greek words: *Dendron* meaning *tree* and *Meros* meaning *part*. Dendrimers used in drug delivery and imaging are usually 10 to 100 nm in diameter with multiple functional groups on their surface, rendering them ideal carriers for targeted drug delivery [9]. The structure and function of dendrimers has been well studied.

Contemporary dendrimers can be highly specialized, encapsulating functional molecules (i.e., therapeutic or diagnostic agents) inside their core [10]. They are considered to be basic elements for large-scale synthesis of organic and inorganic nanostructures with dimensions of 1 to 100 nm [11].

Nanocrystals

A nanocrystal is a type of nanomaterial having particle size at least one dimension smaller than 100 nanometres and mainly composed of atoms in either a single or poly-crystalline arrangement [12]. Nanocrystals are aggregates of around hundreds or thousands of molecules that combined in a crystalline form, composed of pure drug with only a thin coating comprised of surfactant or combination of surfactants.

Nanovectors

It is a hollow solid structure, with diameter between 1-1000 nanometer range, which can be filled with anticancer drugs and detection agents. Targeting moieties can also be attached to the surface. Nanovectors can be used for targeted gene therapy. Liposome is a type of nanovector made up of lipids surrounding a water core [13].

Nanocantilever arrays

They are among the leading approaches under development for the early detection of precancerous and malignant leisons from biological fluids. These and other nanodevices can provide essential breakthroughs in the fight against cancer [13].

Nanocomposites [14]

Generally polymer based with nanosized fillers. Nanoceramics are available commercially in the form of dry powders or liquid dispersions. The most commercially important nanoceramic materials are simple metal oxides, silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), iron oxide (Fe_3O_4, Fe_2O_3), zinc oxide (ZnO), ceria (CeO_2) and zircona (ZrO_2). Silica and iron oxide nanoparticles have a commercial history spanning half a century or more of increasing importance are the mixed oxides and titanates

- Indium-tin oxide (In_2O_3-SnO_2 or ITO)
- Antimony-tin oxide (ATO),
- Barium titanate ($BaTiO_3$).

Nanocrystalline titania, zinc oxide, ceria, ITO, and other oxides have more recently entered the marketplace.

SYNTHESIS OF NANO MATERIALS

The goal of any synthetic method for Nanomaterials is to yield a material that exhibits properties that are a result of their characteristic length scale being in the Nano meter range (~1 –100nm). Accordingly, the synthetic method should exhibit control of size in this range so that one property or another can be attained. Often the methods are divided into two main types "Bottom Up" and "Top Down." In bottom-up approach the clusters of atoms are adhere together to make a Nano material. While in top-down approach the bulk material is divided till it became a Nano structure material.

A. Bottom Up [15]

Bottom up methods involve the assembly of atoms or molecules into nanostructured arrays. In these methods the raw material sources can be in the form of gases, liquids or solids. The latter requiring some sort of disassembly prior to their incorporation onto a nanostructure. Bottom methods generally fall into two categories: chaotic and controlled. Bottom-up approach uses the techniques of molecular synthesis, colloid chemistry, polymer science, and related areas to make structures with nanometre dimensions.

B. Top Down

Knowledge of processes for bottom-up assembly of structures remains in their infancy in comparison to traditional manufacturing techniques. As a result, the most mature products of nanotechnology (such as modern CPUs) rely heavily on top-down processes to define structures. The traditional example of a top-down technique for fabrication is lithography in which instruments (such as a modern stepper) are used to scale a macroscopic plan to the Nano scale.

NANOPARTICLE SYNTHESIS

Physical and chemical methods

Sol-gel technique

In Sol-gel technique discrete particles are integrated network precursor involved in chemical solution that mainly used for the fabrication of metal oxides hence it is a chemical technique. The precursor sol can be either deposited on the substrate to form a film or used to synthesize powders [16].

Solvothermal synthesis

In Solovothermal [17] synthesis process the polar solvents are involved in different condition like at temperatures above their boiling points and in the condition of under pressure at versatile low temperature. Hence the reaction does not involve in lower temperature because the solubility of reaction get significantly increases in Solovothermal condition.

Hydrothermal synthesis

Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction in aqueous solution. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation.

Hydrothermal synthesis is widely used for the preparation of TiO_2 nanoparticles which can easily be obtained through hydrothermal treatment of peptized precipitates of a titanium precursor with water [18]. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase and surface chemistry through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time [19].

Laser ablation

The laser ablation laser beam is a technique [20], that is used for removing materials from a solid surface. Absorption of laser energy and evaporation mainly involves when the material is heated at low laser flux. The material is converted to plasma in case of higher flux. For example Carbon nanotubes can be produced by this method.

Chemical Vapor Deposition (CVD)

Chemical vapor deposition process is often used in the semiconductor industry to produce high-purity, high-performance thin films. In a typical CVD process, the substrate is exposed to volatile precursors, which react and/or decompose on the substrate surface to produce the desired film. Frequently, volatile by products that are produced are removed by gas flow through the reaction chamber. Sn_4 +-doped TiO_2 nanoparticles [21] and M (Cr, V, Fe, Co)-doped TiO_2 by CVD [22].

Thermal Decomposition

Pure and doped metal nanomaterials can be synthesized via decomposing metal alkoxides and salts by applying high energy using heat or electricity. However, the properties of the produced nanomaterials strongly depend on the precursor concentrations, the flow rate of the precursors and the environment. Kim *et. al.,* 2003, were synthesized TiO_2 nanoparticles with a diameter less than 30nm by thermal decomposition of titanium alkoxide or $TiCl_4$ at 1200°C [23]. Liang, *et. al.,* 2004, were produced TiO_2 nanoparticles with a diameter ranging from 3 to 8 nm by pulsed laser ablation of a titanium target immersed in an aqueous solution of surfactant or deionized water [24].

Templating

The synthesis of nanostructure materials using the template method has become extremely popular during the last decade. In order to construct materials with a similar morphology of known characterized materials (templates); this method utilizes the morphological properties with reactive deposition or dissolution. A variety of templates have been studied for synthesizing titania nanomaterials [25], [26]. This method has some disadvantages including the complicated synthetic procedures and, in most cases, templates need to be removed, normally by calcinations, leading to an increase in the cost of the materials and the possibility of contamination [27].

Combustion

Combustion synthesis leads to highly crystalline particles with large surface areas [28], [29]. The process involves a rapid heating of a solution containing redox groups. During combustion, the temperature reaches approximately 650°C for one or two minutes making the material crystalline. Since the time is so short, the transition from anatase to rutile is inhibited.

Gas Phase Method

Physical vapour deposition (PVD) is a thin film deposition technique. Films are formed from the gas phase but without a chemical transition from precursor to product. For TiO2 thin films, a focused beam of electrons heats the titanium dioxide material. The electrons are produced from a tungsten wire heated by a current. This is known as Electron beam (E-beam) evaporation. Titanium dioxide films deposited with E-beam evaporation have superior characteristics over

CVD grown films such as, smoothness, conductivity, presence of contaminations and crystallinity. Reduced TiO_2 powder (heated at 900°C in a hydrogen atmosphere) is necessary for the required conductance needed to focus an electron beam on the TiO_2 [30].

Solvent evaporation technique

Solvent evaporation technique was fully developed in 1979 [31], [32]. This technique is based on the evaporation of the internal phase of an emulsion by agitation. Generally, the polymeric coat material is dissolved in a volatile organic solvent. The drug core is then dissolved or dispersed in the above polymer solution to form a suspension, an emulsion or a solution. Then the organic phase is emulsified under agitation in a dispersing phase consisting of a non solvent of the polymer, which is immiscible with the organic solvent, which contains an appropriate emulsifying agent. Once the emulsion is stabilized, agitation is maintained and the solvent evaporates after diffusing through the continuous phase resulting in solid microspheres. The microspheres are recovered by filtration or centrifugation and are washed and dried [33]. Several researchers have prepared microspheres of various bioactive materials using this technique and its variants.

Nanoprecipitation method [34]

Nanoprecipitation is a facile, mild, and low energy input process to carry out polymeric nanoparticles synthesis which is also termed as solvent displacement method. The process of preparing involves preformed polymer of organic solution (acetone, ethanol, or methanol) and then in the presence or absence of surfactant he organic solvent is allowed to diffuse generally using polymer Poly-Lactic Acid (PLA).

The polymer PLA of intermediate polarity is allowed to dissolved in a water-miscible solvent, resulting in formation of nanospheres and the solution is injected into an aqueous solution containing stabilizer as a surfactant as to result the formation of nanoparticles due to interaction between the water and the organic solvent. The nanoparticles synthesised through the process are of submicron size (<210 nm) with of low polydispersity (35], [36]. Biodegradable nanocarriers such as lipid or polymer based nanoparticles that were designed to enhance the efficacy of nanoparticles and reduce the toxic effects of drugs that results from therapeutic delivery of drugs for treatment of diseases. The Nanoprecipitation, without using surfactant of hydrophobic compounds in a non-solvent solutions leads to scattering of nanoparticles with effect of nanosized particles and such process is termed as “Ouzo” effect.

Emulsification Diffusion

Emulsification or solvent diffusion (ESD) technique is the modification of solvent evaporation method which utilizes water miscible solvent [37] and a small amount of water immiscible organic solvent due to the spontaneous diffusion of immiscible solvents that generate turbulence between the two phases results the formation of nanosized particles. The formation of nanoparticles depends only on the diffusion of the solvent of the dispersed phase and the formation of nanospheres or nanocapsules, according to the oil-to-polymer ratio in which an aqueous solution containing stabilizer successfully leads to solvent diffusion to the external phase of the solution for nanoparticle formation.

CHARACTERIZATION OF NANO PARTICLES

UV-visible absorption spectroscopy

Absorbance spectroscopy is used to determine the optical properties of a solution. A Light is send through the sample solution and the amount of absorbed light is measured. When the wavelength is varied and the absorbance is measured at each wavelength. The absorbance can be used to measure the concentration of a solution by using Beer-Lamberts Law. The optical measurement of UV-visible spectrophotometer has different absorbance peak like 400nm – 800nm [38].

X-ray diffraction (XRD) analysis

X-ray diffraction is a conventional technique for determination of crystallographic structure and morphology. There is increase or decrease in intensity with the amount of constituent. This Technique is used to establish the metallic nature of particles gives information on translational symmetry size and shape of the unit cell from peak positions and information on electron density inside the unit cell, namely where the atoms are located from peak intensities. X ray diffraction analysis with various nanoparticles has been studied by various research workers to find the high crystallinity of the prepared sample [39].

Fourier Transform Infrared [FTIR] spectroscopy

Measures infrared intensity *vs.* wavelength of light, it is used to determine the nature of associated functional groups and structural features of biological extracts with nanoparticles. The calculated spectra clearly reflect the well-known dependence of nanoparticle optical properties. The green synthesized silver nanoparticle by employing various leaf extract was analysed using Fourier Transform Infrared [FTIR] Spectroscopy showed characteristic peaks [40].

Table 1. Various characterization tools and methods for nanoparticles [41]

Parameter	Characterization method
Carrier-drug interaction	Diffential scanning calorimetry
Charge determination	Laser Doppler Anemometry
Chemical analysis of surface Static secondary ion	Zeta potentiometer Mass spectrometry Sorptometer
Drug stability	Bioassay of drug extacted from Nanoparticles Chemical analysis of drug
Nanoparticle dispersion stability	Critical flocculation temperature (CFT) Atomic force microscopy
Particle size and distribution	Laser defractometry Photon correlation spectroscopy (PCS) Scanning electron microscopy Transmission electron microscopy
Release profile	In vitro release characteristics under physiologic and sink conditions
Surface hydrophobicity	Rose Bengal(dye) binding Water contact angle measurement X-ray photoelectron spectroscopy

Microscopic techniques

These techniques namely SEM and TEM Mainly used for morphological studies of nanoparticles. Many researchers used these techniques to show that the synthesized nanoparticles were more or less uniform in size and shape [42].

Transmission electron microscopy (TEM)

Transmission electron microscopy is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through [43]. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEM is useful in cancer research, virology, materials science as well as pollution, nanotechnology and semi-conductor research.

Scanning electron microscope

The characterization of Scanning electron microscope analysis is employed to determine the size, shape & morphologies of formed nanoparticle SEM gives high resolution images of the surface of a sample is desired. The scanning electron microscope works as same principle as an optical microscope, but it measures the electrons scattered from the sample rather than photon. Because electrons can be accelerated by an electric potential, the wavelength can be made shorter than the one of photons. This makes the SEM capable of magnifying images up to 200.000 times. SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM photo micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample. Measures the particle size and characterization, Conductive or sputter coated sample involved and the sensitivity down to 1nm [44].

CONCLUSION

This paper has reviewed recent knowledge and built a data base of nanoparticles. This review provides an overview of nanoparticle based upon the characterization methods, types, protocols based upon Strategies used to synthesize nanoparticles and wide range of applications. Our study concludes that nanoparticle has a tremendous growth in recent years. A wide range of opportunities or upcoming projects are available some of the nanoparticles get synthesized are cost effectiveness. For example nanoparticle synthesis using plant sources is largely adopted due to its eco-friendly nature and cost effectiveness etc., Nano structured materials will be our future materials.

REFERENCES

1. Kavitha, K.S., Syed Baker., Rakshith, D., Kavitha, H.U., Yashwantha Rao, H.C., Harini, B., Pand Satish, S. (2013), “Plants as green source towards synthesis of nanoparticles”, *Int. Res. J. Biol. Sci.,* 2 (6), 66 - 76.

2. Martin, C.R. (2006), "Welcome to Nanomedicine", *Nanomedicine*, 1(1), 5.
3. Praveen Kumar Kanti., Karthika, U.P. (2016), A review paper on role of nano-structured materials in mechanical engineering applications, *National Conference on Advances in Mechanical Engineering Science (NCAMES-2016),* http://www.ijettjournal.org, 414-418.
4. Ladj, R., Bitar, A., Eissa, M., Mugnier, Y., Le Dantec, R., Fessi, H., Elaissari, A. (2013), "Individual inorganic nanoparticles: preparation, functionalization and *in vitro* biomedical diagnostic applications", *J. Mater. Chem. B.,* 1, 1381-1396.
5. Mark Asta., Susan M. Kauzlarich., Kai Liu., Alexandra Navrotsky., Frank, E. Osterloh. (2007), "Inorganic nanoparticles unique properties and novel applications", *Materials and Matters.,* 2(1), 1-5.
6. Hett A. Nanotechnology: Small Matters, Many Unknown, 2004.
7. Kuldeep Purohit., Pooja Khitoliya., Rajesh Purohit. (2012), "Recent Advances in Nanotechnology", *Int. J. Sci. & Eng. Res.,* 3(11), 1-11.
8. Sovan Lal Pal., Utpal Jana., Manna, P.K., Mohanta, G.P., Manavalan, R. (2011), "Nanoparticle: An overview of preparation and characterization", *J. App. Pharmaceut. Sci.,* 1(6), 228-234.
9. Tomalia, D.A. (2004), "Birth of a new macromolecular architecture: Dendrimers as quantized building blocks for nanoscale synthetic organic chemistry", *Aldrichimica Acta.,* 37(2), 39-57.
10. Li Y., Cheng Y., Xu T. (2007), "Design, synthesis and potent pharmaceutical applications of glycodendrimers: a mini review", *Curr. Drug Discov. Tech.,* 4, 246-254.
11. Wiener, E.C., Brechbiel, M.W., Brothers, H., Magin, R.L., Gansow, O.A., Tomalia, D.A. (1994), "Dendrimer-based metal chelates: a new class of magnetic resonance imaging contrast agents", *Magn. Reson. Med.,* 31, 1-8.
12. Jens-Uwe, A., Junghanns, H., Rainer H. Müller. (2008), "Nanocrystal technology, drug delivery and clinical applications", *Int. J. Nanomed.,* 3(3), 295- 310.
13. Ferrari, M. (2005), "Cancer Nanotechnology: Opportunities and Challenges", *Nature Rev. Cancer*, 5, 161-171.
14. Vijaykumar, G., Tile, H.S., Suraj, B.M., Uday, Sahana, S.G. (2016), "Recent trends in nanotechnology and its future scope-a review", *Int. J. Emerging Technol.,* 7(2), 377-385.
15. Prathna, T.C., Lazar Mathew, N., Chandrasekaran, Ashok M. Raichur., Amitava Mukherjee. (2010), "Biomimetic Synthesis of Nanoparticles: Science, Technology & Applicability", In: Amitava Mukherjee (Ed.), Biomimetics, learning from nature, Published by InTech Open.
16. Ramesh, R. (2013), "Sol-Gel Synthesis and Characterization of $Ag_{3\ (2+x)}\ Al_{\ x}\ Ti_{4-\ x}\ O_{11+\ \delta}$ + ($0.0 \leq x \leq 1.0$) Nanoparticles", *J. Nanosci.,* ID 929321, 1-10.
17. Jianlin Lia., Qingliu Wub., Ji Wuc. (2015), "Synthesis of nanoparticles via solvothermal and hydrothermal methods", Handbook of Nanoparticles, DOI 10.1007/978-3-319-13188-7-17-1 #, Springer International Publishing, Switzerland, 1-28.
18. Yang, J., Mei, S., Ferreira, J.M.F. (2001), "Hydrothermal synthesis of TiO_2 nanopowers from tetra alkyl ammonium hydroxide peptized sols", *Mat. Sci. Eng. C.,* 15(1-2), 183–185.
19. Carp, O., Huisman, C.L., Reller, A. (2004), "Photoinduced reactivity of titanium dioxide:, *Prog.in Solid State Chem.*, 32(1-2), 133-177.
20. Semaltianos, N.G. (2010), "Nanoparticles by Laser Ablation, *Critical Rev. Solid State Mat. Sci.*, 35(2), 105–124,
21. Cao, Y., Yang, W., Zhang, W., Liub, G., Yue, P. (2004), "Improved photocatalytic activity of Sn4þ doped TiO_2 nanoparticulate films prepared by plasma-enhanced chemical vapor deposition", *New. J. Chem.,* 2(8), 218 – 222.
22. Gracia, F., Holgado, J.P., Caballero, A., Gonzalez-Elipe, A.R. (2004), "Structural, optical, and photoelectrochemical properties of Mn+-TiO_2 model thin film photocatalysts", *J. Phys. Chem. B.,* 108(45), 17466-17476.
23. Kim, C., Nakaso, K., Xia B., Okuyama, K., Shimada, M. (2005), "A new observation on the phase transformation of TiO_2 nanoparticles produced by a CVD method", *Aerosol Sci. & Tech.,* 39(2), 104-112.
24. Liang, C., Shimizu, Y., Sasaki, T., Koshizaki, N. (2004), "Synthesis, characterization, and phase stability of ultrafine TiO_2 nanoparticles by pulsed laser ablation in liquid media", *J. Mater. Res.,* 19(5), 551-1557.
25. Jinsoo, K., Jae Won, L., Tai Gyu, L., Suk Woo, N., Jonghee, H. (2005), "Nanostructured titania membranes with improved thermal stability", *J. Mat. Sci.,* 40(7), 1797-1799.

26. Iwasaki, M., Davis, S.A., Mann, S. (2004), "Spongelike macroporous TiO_2 monoliths prepared from starch gel template", *J. Sol-Gel Sci. Techn.,* 32(1-3), 99-105.
27. Bavykin, D.V., Friedrich, J.M., Walsh, F.C. (2006), "Protonated titanates and TiO_2 nanostructured materials: synthesis, properties, and applications", *Advanced Materials.,* 18(21), 2807-2824.
28. Nagaveni, K., Hegde, M.S., Ravishankar, N., Subbanna, G.N., Madras, G. (2004), "Synthesis and structure of nanocrystalline TiO_2 with lower band gap showing high photocatalytic activity", *Langmuir.*, 20(7), 2900-2907.
29. Nagaveni, K., Sivalingam, G., Hegde, M.S., Madras, G. (2004), "Photocatalytic degradation of organic compounds over combustion-synthesized nano - TiO_2", *Environ. Sci. Technol.*, 38(5), 1600-1604.
30. Van de Krol, R., Goossens, A., Schoonman, J., Mott-Schottky. (1997), "Analysis of nanometer-scale thin-film anatase TiO_2", *J. Electro Chem. Soc.,* 144(5), 1723-1727.
31. Hickey, A.J., Tian, Y., Parasrampuria, D., Kanke, M. (1933), *Biopharmaceut. Drug Dispos.,* 14, 181-186.
32. Beck, L.R., Cowsar, D.R., Lewis, D.H., Cosgrove, R.J., Riddle, C.T., Lowry, S.L., Epperly, T. (1979), "A new long-acting injectable microcapsule system for the administration of progesterone", *Fertility and Sterility*., 31(5), 545-551.
33. Watts, P.J., Davies, M.C., Melia, C.D. (1990), "Microencapsulation using emulsification/solvent evaporation: an overview of techniques and applications", *Crit. Rev. Ther. Drug Carrier Syst.,* 7(3), 235-259.
34. Stephanie Hornig, Thomas Heinze, C., Remzi Becerbc., Ulrich S. Schubert. (2009), Synthetic polymeric nanoparticles by nanoprecopitation, *J. Mat. Chem.,* 19, 3838-3840.
35. Suprava Patel., Rachita Nanda., Sibasish Sahoo. (2015), "Nanotechnology in healthcare:applications and challenges", *Med. Chem.,* 5(12), 528-533.
36. The Royal Society and The Royal Academy of Engineering, Nanoscience and nanotechnologies - Opportunities and uncertainities, The Royal Society, London, UK, 2004, 1-155.
37. Swati Tyagi., Vinay Kumar Pandey. (2016), "Nanoparticles: an overview of preparation", *Rev. Pharmceutics and Nanotech.,* 4(2), 1-12.
38. Subbaiya, R., Shiyamala, M., Revathi, K., Pushpalatha, R., Masilamani Selvam, M. (2014), "Biological synthesis of silver nanoparticles from *Nerium oleander* and its antibacterial and antioxidant property", *Int. J. Curr. Microbiol. Appl.Sci.,* 3(1), 83-87.
39. Yelil Arasi, A., Hema, M., Tamilselvi, P., Anbarasan, R. (2012), "Synthesis and characterization of SiO_2 nanoparticles by sol-gel process", *Ind. J. Sci.,* 1(1), 6-10.
40. Amudha, M., Krishnakumari, S. (2014), "Biosynthesis and characterization of silver nanoparticles using the aqueous extract of *Vitex negundo,* Linn"., *World J. Pharm. Pharm. Sci.,* 3(8), 1385 1393.
41. Vyas, S.P., Khar, R.K. (2012), Various characterization tools and methods for nanoparticles, Targeted and Controlled Drug Delivery, CBS Publishers and Distributers, New Delhi, 1, 331-343.
42. Shobha, G., Vinutha, M., Ananda, S. (2014), "Biological synthesis of copper nanoparticles and its impact", *Int. J. Pharm. Sci. Invent.,* 3(8), p6-38.
43. Lue Juh Tzeng. (2007), Physical properties of nanomaterials, Encyclopedia of Nanoscience & Nanotechnology, 10, 1-46.
44. Asim Umer., Shahid Naveed., Naveed Ramzan. (2012), "Selection of a suitable method for the synthesis of copper nanoparticles", *World Sci. Publ. Com.,* 7(5), 230005-1230023.