Method of metallic nanoparticles synthesis

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Abstract: The versatile family of nanoparticles is considered to have a huge effect in the various fields of material science primarily nanoelectronics, catalytic chemistry, targeted drug delivery and tissue engineering. As a result of their size and shape-dependent properties, metal nanoparticles are very attractive. Due to their unusual properties and exciting applications in photonics, electronics, biochemical sensing, and imaging, metal nanoparticles have garnered extensive attention. For the preparation of metallic nanoparticles, various approaches are used, which are classified into two main forms according to the starting material of nanoparticle preparation as bottom-up methods and top-down methods. In biomedicine and allied disciplines, the use of metal nanoparticles is continuously growing worldwide. Because of their noticeable properties, researchers are currently concentrating on metal nanoparticles, nanostructures and nanomaterial synthesis. This review selectively focuses on different methods of nanoparticle preparations by Top down and Bottom-up synthesis.

Keywords – Gold Nanoparticle, Silver Nanoparticle, Top-Down Method, Bottom-Up Method.

Nanoparticles:

Nanotechnology is a science that deals with matter at the 1 billionth of a metre scale (i.e., 10-9 m = 1 nm) and is also the study of atomic and molecular scale manipulation of matter. Nanotechnology has been a well-known research field since the last century. Nanotechnology has developed nanoscale-level materials of different types. Nanoparticles (NPs) are a broad class of materials containing particulate matter lesser than 100 nm [1]. These materials can be of different dimensions such as 0D,1D, 2D or 3D, depending on the overall shape [2]. The importance of these materials was discovered when researchers discovered that size can affect the physiochemical properties of a substance, such as optical properties. NPs are not simple molecules on their own and are thus composed of three layers, i.e. (a) a surface layer that can be functionalized with a number of small molecules, metal ions, surfactants and polymers. (b) the shell layer, which in all ways is chemically different from the core material, and (c) the core, which is basically the integral part of the NP and usually refers to the NP itself [3]. These materials have earned tremendous interest from researchers in multidisciplinary fields due to certain exceptional characteristics. Additional features in NPs are given by Mesoporosity. NPs can be used for drug delivery, chemical and biological sensing, gas sensing, CO_2 capture and other similar applications.

Synthesis:

Diverse techniques are used for the preparation of metallic nanoparticles, which are divided into two main types as bottom-up methods and top-down methods, enlisted in Table 1 [4-8]. The key difference between the two approaches is the starting material for nanoparticle preparation. In top-down methods, bulk material is used as a starting material and particle size is reduced by various physical, chemical and mechanical processes to nanoparticles, while atoms or molecules are the starting material in bottom-up methods [4-5].

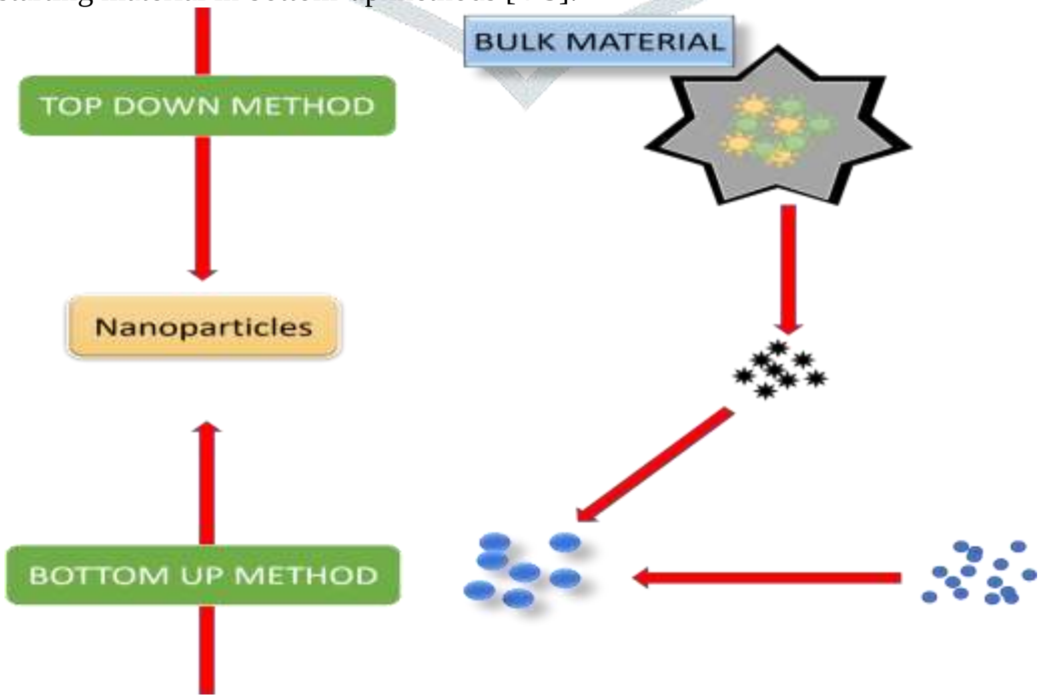

Fig. 1. An overview of top down and bottom up method.

Top-Down Synthesis: Bulk material is converted into tiny nano-sized particles in this process. The preparation of nanoparticles is based on size reduction by different physical and chemical treatments of the starting material [9]. Methods such as mechanical milling, thermal, and laser ablation are included. While top-down techniques are simple to execute and very small size component is not ideal for preparing methods. Changes in surface chemistry and physicochemical properties of nanoparticles are a major problem associated with this process [10].

Mechanical Milling: It includes:

Ball milling- With high-energy ball milling, the working principle of mechanical milling is the reduction in particle size. In 1970, John Benjamin invented this method of reducing the size of particles. The adjustment of surface properties is the responsibility of this process. Phase variables and properties of milling powder affect the performance of mechanical milling [11]. It is classified into higher and lower energy milling processes that depend on powder mixture induced mechanical energy. Using the method of high energy ball milling, nanosized particles are typically formed. This technique is commonly preferred for synthesis of intermetallic nanoparticles. In this technique, along with several heavy balls, bulk powder is applied to a container [5]. With the help of high-speed spinning spheres, high mechanical energy is applied to bulk powder material. Various high-energy mills, such as attrition ball mill, planetary ball mill, vibrating ball mill, low-energy tumbling mill and high-energy ball mill, can be used to minimize particle size [5]. In all these approaches, heavy moveable high-energy balls may roll down in a series of parallel layers on the surface of the chamber containing bulk powder content, or they may fall freely and affect the powder [12].

Mechanochemical synthesis: The method of mechanochemical synthesis is based on repeated deformation, welding, and fracturing of the reactant mixture. During the process of milling, various chemical modifications are produced at the interface of nano-sized particles. For various purposes, such as separating reaction phases from the product phase, elevated temperatures are usually needed to precede chemical reactions. Without the use of external heating, nanoparticles can be obtained using a ball mill at low temperatures [13]. The starting materials (such as sodium carbonate and chloride hexahydrate for $Fe3O2$ nanoparticles synthesis) are stichometrically mixed and milled in a mechanochemical process of synthesis. The deformation, fractionation and welding of the reactants takes place during the process of milling. At the surface interface between substrate and reagent, several chemical reactions are generated, and therefore the reaction requiring high temperatures takes place at low temperatures without any external heat application. Various displacement reactions occur during the process which is given below;

$$SxC + yR = xS + RyC$$

Whereas. SxC and yR are reactant, xS is product and RyC is by-product.

The developed nanoparticles are surrounded by a by-product material that is dispersed in the matrix of soluble salts. The by-product is then extracted by washing with a suitable solvent and then the particles are dried for 12 hours at 105 °C [14].

Laser Ablation: Laser irradiation is used in the laser ablation technique to decrease the size of particle to nano level. The solid target material is put under a solid target material, small layer and then exposed to the irradiation of pulsed lasers. Nd: YAG (neodymium-doped yttrium aluminium garnet) laser at 106 μm output and its harmonic laser, Ti: Sapphire (titanium-doped sapphire) laser and copper vapor lasers are primarily used [15]. Laser irradiation contributes to the fragmentation of solid material in the form of nanoparticles, which stays in the liquid surrounding the target and creates a colloid solution. The relative number of ablated atoms and particles produced is determined by the laser pulse length and energy [16]. Several parameters such as laser pulse time period, wavelength, ablation time, laser fluency, and efficient liquid surrounding medium with or without surfactant affect ablation efficiency and metal particle characteristics [17].

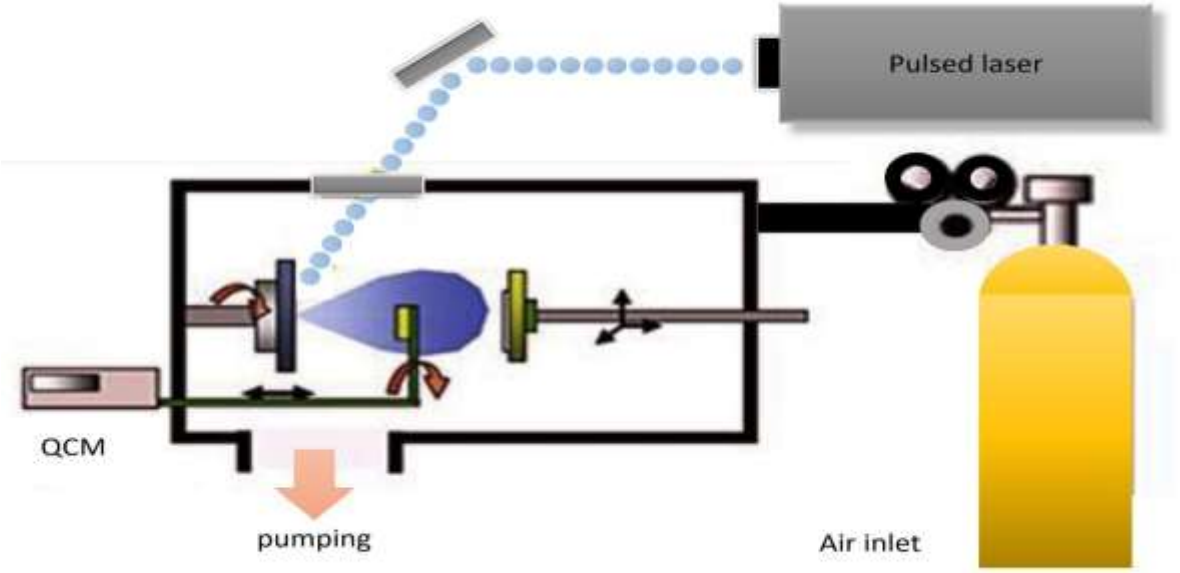

Fig. 2. Pulsed laser deposition of ablated species.

Ion Sputtering: The technique of Ion sputtering involves the vaporization of a solid by sputtering using an inert gas ion beam. This process has recently been used for the preparation of multi-metal nanoparticles using magnetron sputtering of metal targets. Collimated beams of nanoparticles are formed in this process and the mass nanostructured films are deposited on the substrates of silicon [18]. The deposition of the sputter is carried out in an evacuated vacuum chamber where sputtering gas is accepted and the working pressure is preserved (e.g., 0.05 and 0.1 mbar). In the target (cathode), a very high voltage is applied and free electrons are moved in a spiral direction using a magnetic device where they collide with atoms of sputtering gas (argon) and lead to gas ionization. This ongoing process creates a discharge of glow (plasma) to ignite. The positively charged gas ions were drawn to the target, where they were continually impacted. This recurrent event occurs and reaches the target surface with energy above the binding energy of the surface, and an atom can be expelled. Collisions occur continuously in the vacuum chamber between metal atoms and gas molecules, which contributes to the dispersion of atoms that form a dispersed cloud [19].

Bottom-up methods: Using a bottom-up approach, nanoparticle synthesis is based on the creation of nanoparticles from smaller molecules such as atom, molecular or small particle joining. Nanostructured building blocks of the nanoparticles were first developed in this technique and then assembled to create the final nanoparticle [20].

Physical vapor deposition method: In the process of physical deposition, material is deposited either as a thin film or as nanoparticles on a surface. Highly regulated vacuum methods such as thermal evaporation and sputtered deposition result in material vaporization, which is further concentrated on a substrate [21]. In general, physical vapor deposition techniques such as pulsed vapor deposition are used to prepare lanthanum strontium cobalt thin film [22]. Laser ablation is used on a solid target for pulsed laser deposition that induces plasma formation of ablated species, and these ablated species are further deposited on a substrate to create a film [23].

Chemical vapor deposition method: CVD is a well-known process in which, via a chemical reaction from the vapor or gas phase, a solid is deposited on a heated surface. The CVC response needs activation energy to continue. This energy can be provided by several approaches. In thermal CVD, a high temperature above 900oC triggers the reaction. A typical apparatus consists of a gas supply system, an exhaust system and a deposition chamber. In plasma CVD, at temperatures between 300 and 700°C, the reaction is activated by plasma. In laser CVD, when laser thermal energy heats an absorbing substrate, pyrolysis occurs. In photo-laser CVD, to break the chemical bond in the reactant molecules, the chemical reaction is induced by ultra violet radiation that has sufficient photon energy. Nano composite powders have been prepared by CVD [24].

Sol gel method: The sol gel system for the synthesis of nanoparticles includes either;
(a) mixing of preformed metal (oxide) colloids with soles containing a matrix forming species, accompanied by the formation of gel,
(b) Direct blending inside a pre hydrolysed silica sol of metal and metal oxide or nanoparticles.
(c) Complexion of metal with silon and reduction of metal before hydrolysis [25].
In this process, the formation of a network is implemented using colloidal suspension (sol) and gelatin to create a continuous liquid phase network (gel). As a precursor for colloid synthesis, the ions of metal alkoxides and aloxysilanes are used. Most generally, tetramethoxysilane (TMS) and tetraethoxysilane are used to form silica gel. The sol-gel formation involves four main steps; hydrolysis, condensation, particle growth and agglomeration of particle [5].

Chemical reduction method: In the process of chemical reduction, ionic salt is reduced in the presence of surfactants using various reducing agents in a suitable medium [26]. A reduction agent such as sodium borohydride is used in the preparation of metal nanoparticles in an aqueous solution. Using trisodium citrate (TSC) or sodium lauryl sulphate, formed metal nanoparticles are capped by (SLS) [27]. Reducing agents used for synthesis of nanoparticles are sodium borohydrate ($NaBH_4$), glucose, ethylene glycol, ethanol, citrate of sodium, and hydrazine hydrate etc [28].

Hydrothermal method: The hydrothermal method is based on the reaction at high pressure and temperature of aqueous solution vapours with solid material, leading to the deposition of small particles. In this process, cation precipitates in the form of polymeric hydroxide and further dehydrates these hydroxides and accelerates the formation of the structure of metal oxide crystals. The second formed metal cation is advantageous for regulating the process of particle formation by preventing complex hydroxide from forming when the base is applied to the metal salt solution [29].

Solvothermal method: For the preparation of nanophase in the presence of water or other organic chemicals such as methanol, ethanol and polyol as a solvent, the Solvothermal process is used. Reaction is produced in a pressure vessel that allows the heating of solvents (water and alcohol) above the temperature of their boiling point [30]. By using microwave aided reactions, the kinetics of crystallization (crystal formation) can be improved by one to two orders of magnitude (microwave solvothermal) [31].

Spray Pyrolysis: Nanoparticle precursors in vapor form are delivered into the hot reactor in the spray pyrolysis process. A nebulizer is used for the delivery of the precursor that delivers the precursor directly into the hot reactor at the minute small droplets shape. As metal precursors, metals such as acetate, nitrate and chloride are widely used. The apparatus used by the spray pyrolysis process for nanoparticle preparation consists of three main components [32].

1)A fluid nebulizer for metal precursor solution atomization
2) A vertical tubular reactor, operated thermostatically (200 °C to 1200 °C)
3) A nanoparticle array precipitator [33].

Ultrasonic spray pyrolysis is an improved method of producing atomized droplets from precursors using ultrasound. The solution and the formed aerosol droplets are further transported by the carrier gas for the formation of nanoparticles that are later collected by the collection device from the atomizer to the reactor furnace. The highly diluted precursor solution is converted to a small 1-10 μm aerosol droplet, which depends on the ultrasound frequency and solution properties [34].

Laser pyrolysis: The technique of laser pyrolysis requires the application of laser energy to prepare nanoparticles. In this technique, to cause homogeneous nucleation reactions, the precursor is allowed to absorb laser energy. This, as opposed to heating the gas in a furnace, is responsible for extremely localized heating and cooling. Infrared CO_2 lasers, whose energy is absorbed by sulfur hexafluoride, which is an inert photo-sensitizer, are most widely used for heating laser energy. The formation of nanoparticles in CO_2 pyrolysis starts immediately as a sufficient degree of condensable product super saturation is achieved in the vapor phase [18].

Flame pyrolysis: The working theory of the flame pyrolysis process is the creation of nanostructures by means of direct spraying of liquid precursors into the flame. This method enables the distribution of precursors that, in the form of vapor, do not have sufficiently high vapor pressure [35]. The flame is exposed to gases (vapor-fed aerosol flame synthesis), fluids (flame-assisted spray pyrolysis: FASP and flame spray pyrolysis: FSP) or solid precursors and the formation of nanoparticles is permitted [36].

Table: Top down methods and bottom up methods of nanoparticle preparation.

Sr. No	Top down methods		Bottom up methods	
	Methods	Examples	Methods	Examples
1	Mechanical milling	Ball milling Mechanochemical method	Solid state methods	Physical vapor deposition Chemical vapor deposition
2	Laser ablation		Liquid state synthesis methods	Sol gel methods Chemical reduction Hydrothermal method Solvothermal method
3	Sputtering		Gas phase methods	Spray pyrolysis Laser ablation Flame pyrolysis

4			Biological methods	Bacteria Fungus Yeast Algae Plant extract
5			Other methods	Electrodeposition process Microwave technique Supercritical fluid precipitation process Ultra sound technique

Conclusion: Increasing awareness based on the actions and effects of NPs has been accompanied by the optimism regarding the use of NPs in the biomedical field. There are various methods to prepare gold and silver nanoparticles which are used in different fields including drug delivery, sensing, and detection. Due to their wide range of uses, nanomaterials have been extensively studied over the last decade. The field of nanomaterial synthesis is found to be very complex. Generally, there are two approaches for the synthesis of AuNPs: the "bottom-up" approach and the "top-down" approach. Several approach such as physical vapor deposition, chemical vapor deposition, sol gel methods, chemical reduction, hydrothermal method, solvothermal method, spray pyrolysis, laser ablation, flame pyrolysis etc have been made to synthesize nanoparticles of correct morphology. While many nanoparticle methods have been successfully established, to address the limitations of existing methods and to properly implement them at a commercial level, synthesis requires more precise techniques.

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