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The Classification and Synthesis Methods of Nanomaterials

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ABSTRACT

Recently the more interesting and attracting point in research area is the synthesis and characterizations of nanomaterials because of nanotechnology field has contributed to the improvement and revolutionizing of different fields. The list of benefits and applications of nanotechnology is growing rapidly. Nanoparticles (NPs) are small particles that exist in an average size ranges between 1 and 100 nm that distinguish them from their parental bulky materials and make them ideal for diverse applications [1], [2] . Now a day's nanoscale materials, with unique properties have been widely used in different fields such as energy, engineering, biomedical and environment applications. The NPs have become an area of intensive research in the recent past because of their unique and distinguished properties which make their potential application in various fields biomedicine, catalysis, agriculture, and environment [3], [4]. We go through the various research papers and discuss the synthesis of NPs with different methods by the various authors. There are many techniques and applications are reported in the last five years but here we strictly focused on the general synthetic approaches and applications of the nanomaterials which provide a general idea to the young researchers.

Keywords : Nanoparticles, Ball Milling, Sol-Gel Method, Co-precipitation Method, CVD.

I. INTRODUCTION

In upcoming days the nanotechnology controls mankind in living, working, communication, medical, defence and many fields. Due to increasing the use of nanomaterials, this leads to the discussion of the basic and major topics of nanotechnology. The nanomaterials are usually 10^{-9} m in size that means it is one billionth of a meter. The nanomaterials show different physicochemical properties than the bulk material which inherently depends on their size and shape of the nanomaterials. In recent years nanotechnology has become one of the most important and exciting forefront fields research area. Most of the nanomaterials produce a unique character with new characteristics and capabilities by modifying the shape and size at the nanoscale level due to its large surface area to volume ratio [5].

Nanomaterials are classified as nanoparticles, nanorods/nanotubes, films/layers which can be characterized based on their dimensionality. Nanomaterials with zero-dimensional are nanoparticles, one dimensional is nanorods or nanotubes and two dimensional are generally films and layers type one. These are categorized mainly for the single isolated nanomaterials. By the interaction of two or more particles, their physical properties will alter. These particles of different constituents are called bulk or three-dimensional nanomaterials. Nanoparticles have been integrated in to various industrial, health's, food, space, chemical and cosmetic industry of consumers which calls for a green and environmental eco-friendly approach to their synthesis [6], [7].

In this review authors summarizing the recently used with recent developments in the synthesis of nanomaterials with their respective advantages and disadvantages. Authors reported an information regarding different classification of nanomaterials based on different elemental compositions and metals followed by their characterization and applications in different fields such as energy, biomedicine, biosensing, environmental, agriculture, catalysis and medical etc.

II. SYNTHESIS OF NANOMATERIAL

We studied various research papers for the synthesis of nanomaterials by the write down the mostly used methods in some of them we cannot control the size and shape of nanomaterials when it is synthesized via physical method, but in chemical method we can control the shape and size of nanomaterials. Here we discuss the method used for the synthesis of nonomaterial he synthesis of nanoparticles can be done by three different approaches. They are as 1. Physical methods 2. Chemical methods and 3. Biological methods [8 and 9]

1. Physical Methods: The synthesis of nanomaterials viva "top-down" and "bottom-up" approaches both ways are possible in this method. In the top-down approach, the bulk materials are broken into nano-sized particles. The main disadvantage of this method is the toughness of getting the desired NPs size and shape, while in bottom-up approach, the welldispersed and fine nano-scaled tiny particles can be obtained than the top-down approach. The example of bottom-up approach is laser evaporation [10 and 11]. Some other physical methods like laser evaporation, ball milling, wire explosion and inert-gas condensation method are also used to prepare NPs. Here, we will discuss three physical methods i.e. laser evaporation, ball milling, wire explosion method and RF plasma method as below

1.1 Laser Evaporation: This method is a bottom-up approach in which nanoparticles are formed through condensation from liquid or gaseous phase. The laser evaporation also called laser ablation is a simple technique in which high energy laser is applied for production of NPs. This method is also suitable for producing iron oxide NPs [10 and 11]. In this process, particles of coarse textured are selected as raw materials and are evaporated through under the focus of laser beam. The material is placed at the bottom of a cell submerged in a liquid solution and targeted by the focused laser beam. The irradiation of the material in a solution takes place by a laser beam. The vapours of the material are cooled down in a gas phase and as a result a fast condensation and nucleation takes place that lead to the formation of nanoparticles [12 and 13]. This method is low cost-effective and it do not require any expensive chemical or produce any hazardous waste as in wet chemistry methods [14 and 15].

1.2 Ball Milling: This method was first developed in 1970 [16]. In this nanomaterials are produced by top-down approach. It is a simple and convenient process which involves the mechanical grinding of coarse-textured particles into fine-textured particles [17]. The working principle is very simple; the raw materials are enclosed in a small hollow cylindrical jar containing many steel balls as a grinding medium. The balls apply kinetic energy to the solid material as a result of continuous collisions between steel balls and solid materials which results in nano/micro-sized powder. The ball to powder ratio, ball size, vibration speed, and milling time are the main factors that affect the formation process of nano/micro size crystals. The main disadvantage of this process is the contamination of the product [18, 19].

1.3 Wire Explosion Method: The wire explosion technique is a new physiochemical technique which is a safe and clean process for synthesizing MNPs. This method is a one-step highly productive process which requires no additional steps like separation of NPs from solution and retreatment of by products. This method was previously used to prepare iron oxide MNPs for removal of arsenic from water [20, 21]. It is environmentally safe and requires minimum energy for making less contaminated nano powders [22, 23]. The NPs produced through this method are not monodispersed [24].

1.4 RF plasma method: This method requires a high temperature. By using high voltage RF coils encased around the evacuated system the metal is heated beyond its evaporation point. Helium gas is then passed into the system and the coils in the region form high temperature. On the He gas atoms, the nucleation of metal vapour occurs. Through diffusion, it enters in to the colder collector rod and the nanoparticles are formed [9].

2. Chemical Methods: These methods consist of different bottom-up approaches. Some common methods that are widely used to synthesize nanomaterials is mentioned below

2.1 Sol-Gel Method: The combination of Sol that a colloidal form of suspended solid particles and gel that is solid macromolecules dissolved in solvent. This method completed through three steps as Hydrolysis, Polycondensation and Drying. Sol is the formation of stable solution of the metal oxide with distilled water or non aqueous solvent such as ethanol, alcohol, ketoses etc. Which were stirred for some time depending upon the precursor, after well mixing of solution, titrated with ethanol drop wise after the condensation reaction precipitation formed. [25, 26]. The Van-der Waals forces between the particles occur and the interaction between particles increases by stirring and increasing the temperature. The mixture is heated until the solvent is removed and the solution is dried, which finally results in the formation of gel [27]. For the sol-gel method, no special equipment is needed and can be done at room temperature which makes it a cheaper technology. This method is very simple in controlling the composition, shape, and size of NPs. The solid materials produced through this method are highly pure with good crystallinity and tenability. This method is useful in the production of various types of NPs. The MNPs can be produced in large quantities with control size and well-defined shape by Lu et al. in 2007 [28 and 29].

2.2 Co-precipitation Method: Co-precipitation is the most commonly used method for producing nanomaterials of controlled size and some properties [30] The synthesis of NPs through co-precipitation is very convenient and facile when we need nanocrystals in large quantities. This method is very common for the production of NPs of controlled size with good magnetic properties. Specially for the different metal ions are used to dissolve in a solvent to produce magnetic NPs. NPs of manganese ferrite

($MnFe_2O_4$) were formed by using ferric chloride ($FeCl_3$) and manganese(II) chloride ($MnCl_2$) as the metal ions and salts of sodium hydroxide (NaOH) as precipitant and the nanocrystals of $MgFe_2SO_4$ can be formed by Fe^{3+} and Mg^{2+} ions, co-precipitated by adding NaOH [31 and 32]. During the process of co-precipitation, different factors like pH, metal ions, and their concentrations, the nature of salt, the reaction temperature can affect the composition of MNPs, particle size, and shape. The MNPs synthesis through co-precipitation is quite simple to obtain uniformly dispersed small size NPs [33, 34 and 35]. Authors observed that, this method is preferred because of its simplicity but, sometimes it is difficult to control the shape of NPs.

2.3 Hydrothermal Synthesis Method: Hydrothermal also referred to as Solvothermal is one of the successful solution reaction-based approaches through which nanomaterials are produced. This method is used to prepare NPs in an aqueous solution, under high pressure and temperature. One of the most used methods for synthesis of nanoparticle is hydrothermal method. It is solution reaction based approach and water is used as solvent. In this case mixture of precursor heated in autoclave above the boiling point of water, consequently pressure within the reaction is increases above the atmospheric pressure [26 and 36]. The crystal formation depends on the extent of the solubility of minerals in the water. Particles of various magnetic nanomaterials of uniform size were obtained through this method [37]. There are number of researchers prepared NPs using this method for example, Chitosan-coated Fe_3O_4 NPs of 25 nm size were prepared and applied in enzyme immobilization by Li et al. [38]. The morphology and crystallinity of synthesized MNPs depend on the appropriate mixing of solvent, time, amount of pressure, and temperature. Following this approach can yield more NPs as compared to the microemulsion method. But this process needs high temperature and pressure; therefore, it is done with great care and carried out in special equipment. Comparatively, hydrothermal method is preferred over sol-gel and other methods because of its advantages of producing NPs of desirable shape, size, with high crystallinity and consistent composition [39].

2.4 Thermal Decomposition Method: The process of decomposition of organometallic precursors is carried out under the presence of organic surfactants to produce NPs of desired size and shape [40]. The stabilizers used in the decomposition process can slow down the nucleation of NPs which control the growth of NPs and help in producing a spherical shape and desirable size. The stabilizing agents used for the synthesis of MNPs include fatty acids, hexadecylamine and oleic acid. This method has been reported as one of the best methods to produce NPs on a large scale in uniform size and homogeneous shape, the degree of temperature, reaction time, type of surfactants and solvents, and aging period is adjusted according to the desired shape and size [41, 42]. Some of the examples of developed by this method are listed as the thermal decomposition of zero-valent metal precursor Fe $(CO)_5$ leads to the formation of metal nanoparticles, but if oxidation occurs it may form iron oxide MNPs of high quality. While on the other hand if the decomposition of precursors occurs with cationic metal centres can result in the direct formation of metal oxide NPs by Frey et al. [40, 43]. The risk factor associated with this method is the production of toxic organic-soluble solvents, which limits its application in the biomedical field. The thermal composition is comparatively more useful than co-precipitation for synthesizing magnetic particles of smaller size [44].

2.5 Microemulsion Synthesis Method: This is the turbid systems of lipophilic and hydrophilic phases that involve surfactants or sometimes co-surfactants. This is an isotropic transparent liquid system of water, oil, and amphiphile. In this process, oil is mixed with a surfactant and water is magnetically stirred at ambient temperature. There are three kinds of microemulsions; i) oil in water, which is the aqueous phase with some oil droplets, ii) water in oil, which is oil as a dominant phase with some droplets of water and iii) both oil and water are present in a comparable amount. For example, microemulsion of type, droplets of water in organic solvent were coated by a surfactant reducing the size of NPs [45]. The shape and size of NPs prepared through this method depends on what kind of surfactant is used. Some iron oxide MNPs were prepared through the water in oil type of microemulsion, in which they used two microdroplets, one with metal percussor and another with a precipitating agent This method was used to prepare NPs with silica-coating and were further modified with amino, which was useful for tumour cell separation [46, 47]. The MNPs prepared by microemulsion are of low quantity and uniformly dispersed.

3. Biological Synthesis Method: Biological synthesis is well-known method to synthesize NPs by using living organisms like plants and microorganisms such as fungi, viruses and bacteria. The NPs produced by this method are comparatively biocompatible and useful application in the biomedical field. The benefits of this method are its efficiency, eco-friendly and clean process and the disadvantage is its poor dispersion of the NPs [48, 49]. The following are main method used for the synthesis of NPs.

3.1 Synthesis by plant extract: The synthesis by plant extract is free from toxicity and the plants tender the superior option for the synthesis of nanoparticles. The gold and silver nanoparticles can be produced from the plant extracts like Geranium, aloe vera, sun dried cinnamon camphora, azadiracta indica etc. [50]

3.2 Synthesis by bacteria or fungi: The synthesis of NPs in last few years has enlarged comprehensively due to its immense applications. Bacillus species are widely used in the production of NPs or metal nanoparticles, since this bacterium has ability to fabricate extracellularly with the size ranges from 10 to 20 nm. The nanoparticles can be produced by using various species of fungi like aspergillus niger, aspergillus orizae, fusarium solani. Phoma globerta has been traced to produce silver nanoparticles [51, 52].

The synthesis of NPs by using plant tissue, extracts, exudates, and other parts of the plant has become an area of great interest for researchers for example, particles with an average size of 60 nm ferromagnetic magnetite were reported to biologically synthesize by Lenders et al. [53, 54]. but the mechanism of formation of NPs by using microorganisms and plants is not well understood and still under investigation for example, some investigations suggested possible mechanisms for the mycosynthesis of metal NPs. Biologically synthesized Fe_3O_4 magnetic material was used in Suzuki-Miyaura reaction and photo-catalysis as a catalyst [55, 56]. Some shortcomings associated with this method like yield and NPs dispersion still need to be investigated.

Table 1 : Synthesis methods with its merits and demerits are listed in the below table

Sr. No.	Synthesis Methods	Merits	Demerits	References
1	Laser Evaporation	Low experimental cost, no use of chemicals, no pollutant products	High price of laser system, needs high amount of energy	*[10-15]*
2	Ball milling	Simple, widely used, produce fine	Contamination of	*[16-19]*

	method	powder	product	
3	Wire explosion method	Ecologically safe, clean, and highly productive v	A little contamination of product may occur	*[20-23]*
4	Sol-gel method	Highly pure, good crystallinity	Longer time, toxic organic solvents	*[26-29]*
5	Co-precipitation Method	Simple, large quantity	Impurities, time consuming	*[30-35]*
6	Hydrothermal/ Solvothermal	Good crystallinity	Needs high temp. and pressure	*[26, 36-39]*
7	Thermal Decomposition	Controllable size, high yield	Toxic solvents	*[40-44]*
8	Microemulsion synthesis	Thermodynamically stable	Low yield	*[45-47]*
9	Chemical Vapor Deposition	Wide range production of materials	Low productivity, impurities	*[48]*
10	Biological method	Efficient, clean process, eco-friendly	Poor dispersion of NPs	*[49-52]*

III. CONCLUSION

Conclusion: The different techniques have been developed for the synthesis of NPs. here synthetic approaches are categorized into three different methods i.e. physical methods, chemical methods, and biological methods. We have already briefly discussed different routes of synthesis for NPs in former sections. A comparison of these methods is summarized with merits and demerits are given in Table 1, which can help researchers to select the suitable method for synthesis of NPs.

It is little difficult to adjust the particle size and shape through the physical mode of synthesis, while through chemical methods, the size and shape can be controlled by adjusting different conditions of reaction. However, when a comparison is made between physical and chemical methods, the size of NPs in nanometre range is difficult to attain through physical methods.

In chemical methods, the hydrothermal method is considered as the most convenient approach to synthesize NPs. The hydrothermal method is versatile and is superior over other methods such as sol-gel, microemulsion because of its advantages in terms of producing NPs of desirable size, shape, high crystallinity and homogenous composition.

The co-precipitation method is preferred because of its simplicity and ease in the synthesis of NPs. The yield is high but the shape control is sometimes not that good. The sol-gel method has its advantages of high purity and crystallinity, homogeneous composition, and cost-effective because the process can be completed at room temperature.

The microemulsion is suitable for the synthesis of monodisperse NPs with various morphology but of low yield.

The thermal decomposition method is preferred for attaining NPs of a smaller size as compared to the coprecipitation method. Among different methods, thermal decomposition is considered the best method so far for producing NPs of controlled size and morphology.

On the other hand, the biological method is an acceptable approach and is opted for its environmentally friendly, costeffectiveness, sustainability, reproducibility, and high yield. Biological synthesis through plants is under developmental stages and researchers are still investigating to understand the mechanism. The NPs synthesized through microbes are not monodispersed and the synthesis process takes a lot of time as compared to chemical and physical methods. Therefore, opinions on the selection of methods may vary from researcher to researcher based on their findings and purpose of application. That is why not a single method is referred to as the optimal method for the synthesis of NPs. Every method has its limitation and its selection depends on many other factors like the yield of NPs, its morphology, size, shape, and experimental cost etc.

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