



Magnetite Nanoparticles: Synthesis Methods – A Comparative Review

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Abstract:

Iron oxide-based nanoparticles have gathered tremendous scientific interest towards their application in a variety of fields. Magnetite has been particularly investigated due to its readily availability, versatility, biocompatibility, biodegradability, and special magnetic properties. As the behavior of nano-scale magnetite is in direct relation to its shape, size, and surface chemistry, accurate control over the nanoparticle synthesis process is essential in obtaining quality products for the intended end uses. Several chemical, physical, and biological methods are found in the literature and implemented in the laboratory or industrial practice. However, non-conventional methods have emerged in recent years to bring novel synthesis performances in terms of better-controlled morphologies, sizes, and size distribution. Particularly, microfluidic methods represent a promising technology towards smaller reagent volume use, waste reduction, precise control of fluid mixing, and ease of automation, overcoming some of the major drawbacks of conventional bulk methods. This review aims to present the synthesis methods of magnetite and future aspects, together with the newest advancements in this field.

Keywords:

Magnetite nanoparticles, Magnetite synthesis, Conventional methods, Microfluidic methods, Novel synthesis routes.

Introduction:

The development of biocompatible, functionalized ferromagnetic nanoparticles has opened the way for new biomedical applications, like medical diagnosis and therapy [1-3], target drug delivery [4-6], magnetic resonance imaging [7-9]. Biocompatibility demands the use of magnetic particles dispersed in or encapsulated in a polymer matrix.

These magnetic polymer nanoparticles have been produced from both natural and synthetic polymers [10-13]. This process decreases the percentage of magnetic material in the magnetic carriers and increases the particle diameter. The size control of magnetic nanoparticles is very important. For biomedical applications, nanoparticles of about 5–20 nm diameter should form ideal particles [14]. An alternative of the magnetic polymer nanoparticles is the chemical modification of the magnetic particle surface by small molecules that ensures the possibility for complementary attachment to functional biomolecules and sol stabilization [15]. The successful synthesis of the modified magnetic particles requires two important steps: – the size-controlled synthesis of magnetite nanoparticles; the chemical modification of the magnetic particle surface.

The physical and chemical properties of magnetite nanocrystals are greatly affected by the synthesis route. For this reason, various methods have been reported in the literature [16-23]. The chemical modification of the magnetic particle surface is the second step for the preparation of the functionalized magnetic nanoparticles. Many studies are realized on this process, used amino acids as chelating agents for maghemite ($\gamma\text{-Fe}_2\text{O}_3$), (which has a dual advantage when used in water treatment applications) and magnetite (Fe_3O_4) [24-26]. Also, the amino acids are non-toxic compounds. In all these studies, the synthesis of the modified magnetic particles is achieved in these two steps.

Main Synthesis Methods Of MNPs:

The past decade has witnessed extensive research in the development of different approaches for the synthesis of MNPs. Different synthetic methods are used to obtain MNPs of desired size, morphology, stability and biocompatibility. The most common methods include the ball milling method, coprecipitation, thermal decomposition, hydrothermal, microemulsion, sol-gel method, and biological methods to produce MNPs. A graphical illustration of MNPs prepared through various routes (physical, chemical, and biological) are given in Figure 1.

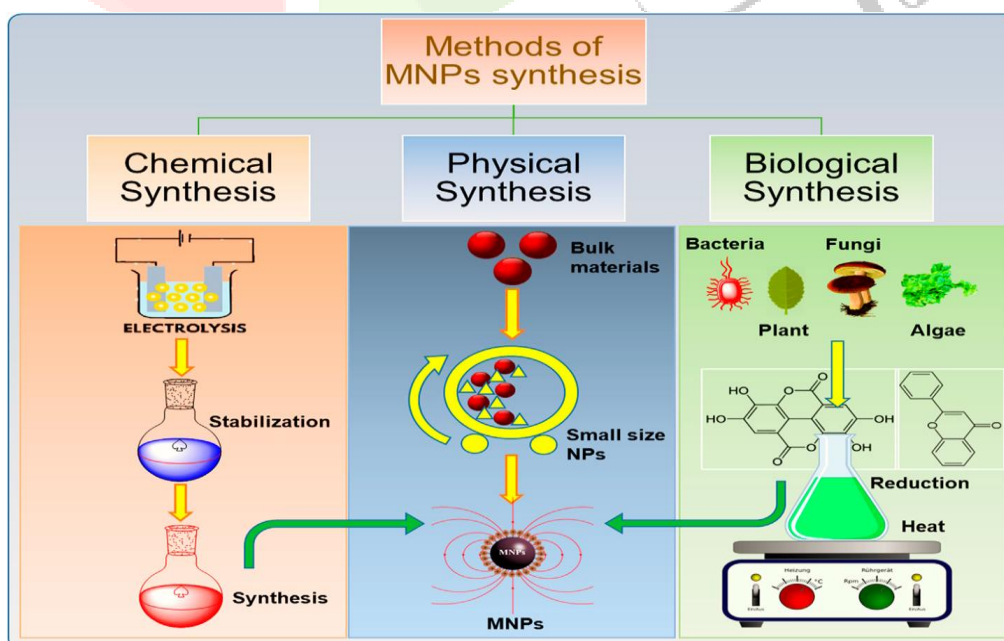


Figure1: General methods of MNPs synthesis.

Physical Methods:

The physical methods consist of “top-down” and “bottom-up” approaches. In the top-down approach, the bulk materials are broken into nano-sized particles i.e., through high energy ball milling. It is difficult to obtain NPs of desired shape and size through mechanical crushing [27]. While in bottom-up approach, the well dispersed and fine nano-scaled tiny particles can be obtained than the top-down approach. The example of bottom-up approach is laser evaporation [28]. Some other physical methods like wire explosion method and inert-gas condensation method are also used to prepare MNPs. In this review, we will discuss three physical methods i.e., ball milling, laser evaporation, and wire explosion method.

Ball Milling Method/Mechanical Method:

Ball milling is a top-down approach of producing MNPs from the bulk material. It is a simple and convenient process which involves the mechanical grinding of coarse-textured particles into fine-textured particles [29-30]. This method was first developed in 1970 [31]. 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 ball 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 [32]. The particles have wide size distribution as compared to synthesized by chemical methods.

Laser Evaporation:

Laser evaporation 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 MNPs. This method is also suitable for producing iron oxide MNPs [33]. In this process, particles of coarse textured (in μm or mm size ranges) 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 led to the formation of nanoparticles [34]. This method is low cost-effective and it do not require any expensive chemical or produce any hazardous waste as in wet chemistry methods [35-36].

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 [37]. It is environmentally safe and requires minimum energy for making less contaminated nano powders [38]. The NPs produced through this method are not monodispersed [39].

Chemical Methods:

The chemical synthesis methods consist of different bottom-up approaches. A comprehensive description of some common methods that are widely used to synthesize MNPs are discussed below.

Coprecipitation Method:

Coprecipitation is the most commonly used method for producing MNPs of controlled size and magnetic properties [40]. It includes the use of less harmful materials and procedures, and widely practiced in biomedical applications [41]. The synthesis of MNPs through coprecipitation 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. Different metal ions are used to dissolve in a solvent to produce MNPs. 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 [42]. The nanocrystals of MgFe_2SO_4 can be formed by Fe^{3+} and Mg^{2+} ions, coprecipitated by adding NaOH [43]. Similarly, in another study, Fe^{2+} and Fe^{3+} ions are coprecipitated to get Fe_3O_4 NPs [44-45]. During the process of coprecipitation, 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 [46]. The MNPs synthesis through coprecipitation is quite simple to obtain uniformly dispersed small size NPs [47]. Moreover, this method is preferred because of its simplicity but, sometimes it is difficult to control the shape of MNPs via coprecipitation.

Thermal Decomposition Method:

In this method, organometallic precursors are used to produce mono dispersed NPs under extreme temperature. The MNPs prepared by this method have high crystallinity, controlled size and well-defined shape. The process of decomposition of organometallic precursors is carried out under the presence of organic surfactants to produce MNPs of desired size and shape [48]. The stabilizing agents used for the synthesis of MNPs include fatty acids, hexadecyl amine, and oleic acid. The stabilizers used in the decomposition process can slowdown the nucleation of NPs which control the growth of MNPs and help in producing a spherical shape and desirable size of less than 30 nm. The nanocrystals of Fe_3O_4 and magnetically active composites of iron were reported to produce by this approach [49-50]. The thermal decomposition of zero-valent metal precursor $\text{Fe}(\text{CO})_5$ leads to the formation of metal NPs, 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 [51]. Monodispersed iron oxide MNPs ranging from 6 to 20 nm were previously synthesized through polymer-catalysed decomposition of $\text{Fe}(\text{CO})_5$ [52-53]. The temperature requirement depends on the type of precursor used. The degree of temperature, reaction time, type of surfactants and solvents, and aging period is adjusted according to the desired shape and size [54-55]. To date, this method has been reported as one of the best methods to produce MNPs on a large scale in uniform size and homogeneous shape [56]. The risk factor associated with this method is the production of toxic organic-soluble solvents,

which limits its application in the biomedical field [57]. The thermal composition is comparatively more useful than coprecipitation for synthesizing magnetic particles of smaller size.

Microemulsion Synthesis Method:

Microemulsions are 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; 1) oil in water (O/W), which is the aqueous phase with some oil droplets, 2) water in oil (W/O), which is oil as a dominant phase with some droplets of water, 3) Both oil and water are present in a comparable amount. For example, microemulsion of w/o type, droplets of water in organic solvent were coated by a surfactant reducing the size MNPs [58-59]. The shape and size of MNPs prepared through this method depends on what kind of surfactant is used. Some iron oxide MNPs were prepared through the w/o type of microemulsion, in which they used two micro droplets, one with metal precursor and another with a precipitating agent [60]. This method was followed to prepare MNPs with silica-coating and were further modified with amino, which was useful for tumour cell separation [61]. The MNPs prepared by microemulsion are of low quantity and uniformly dispersed.

Hydrothermal Synthesis Method:

This method is used to prepare NPs in an aqueous solution, under high pressure and temperature. Hydrothermal also referred to as solvothermal is one of the successful solution reaction-based approaches through which MNPs are produced at high pressure and temperature. Under the hydrothermal process, hydrolysis and oxidation reaction takes place to produce MNPs [62]. 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 [63]. For example, Fe₃O₄ NPs of size 15 nm and spherical shape were obtained and applied in the tumour MRI [64]. Similarly, Chitosan-coated Fe₃O₄ NPs of 25 nm size were prepared and applied in enzyme immobilization [65]. 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 a 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 [66].

Sol-Gel Method:

The whole chemistry in this process involves gel formation at room temperature by hydrolysis and polycondensation reactions of metal alkoxides. Metallic salts are dissolved in water or other solvents and are homogeneously dispersed to prepare sol or colloidal solution [67]. 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 [68]. This method is useful in the production of iron oxide MNPs and silica-coated MNPs. The MNPs can be produced in large quantities with control size and well-defined shape. Previously, MNPs were prepared by heating the mixture of FeCl₃ and NaOH solution at 50–100°C [69].

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 MNPs. The solid material produced through this method are highly pure with good crystallinity and tunability. However, in some cases, this method results in contamination from by product reactions, and the thus need to be retreated to obtain pure MNPs. The generation of three-dimensional oxide networks limit its efficiency in the production of dispersed NPs [70]. Other disadvantages of this method is to require prolong reaction time and involve toxic organic solvents.

Biological Synthesis Method:

Biological synthesis is well-known method to synthesize MNPs by using living organisms like plants and microorganisms [71] (fungi, viruses, bacteria, and actinomycetes). The MNPs produced 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. While the disadvantage is its poor dispersion of the NPs [72]. 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 [73]. Biological synthesis is a promising technique that emerged in recent years, but the mechanism of formation of NPs by using microorganisms and plants is not well understood and still under investigation [74]. For example, some investigations suggested possible mechanisms for the myco synthesis of metal NPs. Three mechanisms were suggested; 1) activity of nitrate reductase, 2) shuttle electrons quinones, and 3) mixed mechanism. However, the mechanism is not very clear to acknowledge so far as to prepare MNPs. Biologically synthesized Fe_3O_4 magnetic material was used in Suzuki-Miyaura reaction and photo-catalysis as a catalyst. Some shortcomings associated with this method like yield and MNPs dispersion still need to be investigated.

Comparison of Different Synthesis Methods:

Different techniques have been developed for the synthesis of MNPs. These 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 MNPs in former sections. A comparison of these methods is summarized with merits and demerits is given in Table 1, which can help researchers to select the suitable method for synthesis of MNPs. 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 [75]. It is difficult to adjust the particle size and shape through the physical mode of synthesis [76]. While through chemical methods, the size and shape can be controlled by adjusting different conditions of reaction [77]. Among different chemical methods, the hydrothermal method is considered as the most convenient approach to synthesize MNPs. 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 hydrothermal method allows controlling the morphology of synthesized particles by decreasing the chances of agglomeration and narrow size distribution.

The coprecipitation method is preferred because of its simplicity and ease in the synthesis of MNPs. 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. Conditions like pH, types of solvent and surfactant, ionic strength, agitation, reaction time, and stirring rate are important consideration for selection of synthesis methods.

On the other hand, the biological method is an acceptable approach and is opted for its environmentally friendly, cost effectiveness 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 [78]. 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 MNPs. 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.

CHALLENGES AND FUTURE PERSPECTIVES:

MNPs are being applied in different fields such as biomedical, environmental, agriculture, and catalysis and biosensing. In this review, we summarized recent advances in the synthesis, characterization and the potential applications of MNPs. Different kinds of MNPs showing some promising properties are being produced by using different synthetic methods. These methods include ball milling, thermal decomposition, hydrothermal synthesis, microemulsion synthesis, gas-phase condensation, sol-gel, biological synthesis method, etc. For the synthesis of the MNPs in large amount physical method such as the ball milling are being used, however, this method possess contamination from the milling jars and balls. While on the other hand, thermal decomposition or pyrolysis method is used to produce monodisperse MNPs. The pyrolysis method has advantages because of its simple and good control over the size of MNPs. The sol-gel synthesis method is used produce MNPs with uniform size distribution and superior stoichiometric control at low processing temperature. The aforementioned methods propose various kinds of MNPs for important biological and biomedical applications. Human development has been hindered by various kinds of problems such as cancer, pollution, agriculture practices, and so on. To address these problems different kinds of functionalized NPs have been developed in past decades. Nano-based cancer therapy mainly depends upon the efficient and smart design of NPs, by treating cancer more safely and effectively.

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