Historical Development of Magnetite Nanoparticles Synthesis

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Summary: Top down and bottom up are two fundamental routes for the formation of magnetite nanoparticles (MNPs). These routes are generally utilized for producing technologically and economically significant MNPs. This review discusses the synthesis of MNPs and outlines methods of preparation that allow control over the size, morphology, surface treatment and magnetic properties of the nanoparticles. In the past, long grinding of bulk magnetite in the presence of stabilizing surfactants produced the first accepted ferrofluid containing MNPs. Such mechanogrinding methods were inherently time consuming and costly. Currently, perhaps the most commonly accepted approaches for creating MNPs concentrate around different forms of coprecipitation, microemulsion, biological nanoreactors, sol-gel and polyol methods. Various additional methods also exist for the controlled synthesis of MNPs including ultrasound irradiation (sonochemical synthesis), spray and laser pyrolysis.

Introduction

The fabrication of MNPs has been a field of significant interest because of their various useful applications in science and technology. In recent years, magnetic nanoparticles have found increasing interest in biomedical applications [1-3] such as myocardial tissue engineering [4], cell labeling, magnetic separation [5-8], MRI contrast agents [9-10], hyperthermia, thermal ablation [11], site-specific drug targeting, delivery and controlled release [10, 12-15]. Usually magnetic materials [16-18] comprising magnetic alloy [19], various cobalt particles as well as cobalt ferrite [20], nickel ferrites, maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) [13, 21]. Natural magnetite is found in igneous rock, bees, homing pigeons and salmon. Magnetite is also found in brain tissue of various types of bacteria [15, 22] and it has also been recognized for possessing low toxicity [11, 13, 23, 24]. A laboratory set-up can also be used for producing nanopowders of uniform size and definite shape [11, 25]. The ratio of surface area to the volume of nanoparticles is larger than their bulk counterpart [14]. MNPs of about 10 nm in size exhibit superparamagnetic phenomenon even below its Curie temperature. In this size regime each particle is considered to be a single magnetic domain. Superparamagnetism permits MNPs to be magnetized in the presence of a magnetic field, but not to preserve remnant magnetism in its absence [3, 12, 26, 27]. Superparamagnetism does not have the hysteresis at 300 K [28].

Magnetite (Fe_3O_4) is ferrimagnetic in nature and is also known as ferrous ferric oxide. So a more significant way to represent its formula would be $Fe^{2+}Fe_2^{3+}O_4$. The magnetic moment of magnetite is produced due to their iron ions located in two different valence states. Magnetite has inverse spinel crystal structure shown in Fig. 1, with 8 Iron(III) ions residing in tetrahedral sites, 8 Iron(III) ions residing in octahedral sites and 8 Iron(II) ions occupying octahedral sites. The Iron(III) ions in the octahedral sites have equal and opposite magnetic moments to the Iron(III) ions in the tetrahedral sites, thus they cancel out each other. Therefore, the overall magnetic moment comes from the sum of the magnetic moments of the Iron(II) ions in the octahedral sites [37].

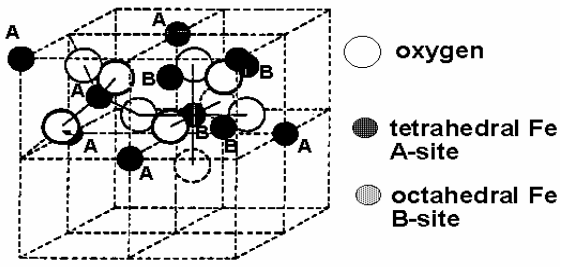

Fig. 1: Inverse spinel crystal structure of magnetite.

The magnetic properties of MNPs change considerably due to their small particle size and large surface area. A complexity of aggregation of nanoparticles with each other is produced during the synthesis of MNPs and thus reducing their surface energy by strong magnetic dipole-dipole attraction between them. The aggregation of stable MNPs during the synthesis process is prevented by coating with some suitable surfactants [29].

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There are two fundamental methods for the synthesis of MNPs; (a) top down (size reduction) and (b) bottom up. Interest in the synthesis of these particles of uniform size and definite morphology has been grown enormously in the recent years due to their promising applications. The preparation methods play a key role in determining the particle size, shape, size distribution, surface chemistry and so the applications of the nanomaterial [30]. Many synthesis pathways have been developed to accomplish appropriate control of particle size, polydispersity, shape, crystallinity and magnetic properties [3, 31-36]. Magnetic nanoparticles often display a wide range of particle sizes and morphologies indicating that nucleation and crystal growth took place in the synthesis reaction.

Production of Magnetic Nanoparticles

In the recent years, attention has been focused on the production of MNPs with different shapes and also with a narrow size distribution. This interest has been encouraged by the fact that magnetic, optical, electronic and catalytic properties can change obviously with particle size and shape. Monodispersed magnetic nanoparticles form ideal system for basic investigation into these properties [34, 35].

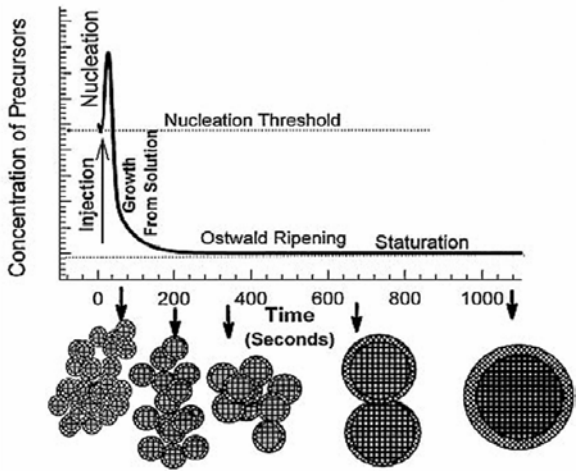

Fig. 2: Diagram depicting the stages of nucleation and growth for the synthesis of monodispersed nanoparticles based on the work of LaMer and Dinegar.

The mechanisms by which magnetic nanoparticles form, are still incompletely understood although much is known about their methods of preparation [35]. Formerly, it was considered that the necessary requirements for synthesis of monodispersed particles are the separation of nucleation and crystal growth during the synthesis process. The present nucleation theory for size control was derived on the basis of the traditional LaMer model. Nucleation and growth were explained via this model shown in Fig. 2, which was originally proposed for schematic explanation for the formation of monodispersed particles [37]. The separation of nucleation and crystal growth can be accomplished by arranging the reaction conditions so that there is slow creation of growth units until the critical supersaturation for nucleation is exceeded. The supersaturation is reduced by the burst of nucleation at that point. Subsequently, the growth units are taken up by the nuclei. The rate of generation must be sufficiently slow so that they are removed completely by the nuclei i.e. the concentration never reaches a high enough level for more nuclei formation. Slow generation of growth units can be readily achieved by controlling the decomposition of a soluble iron complex [3].

The recrystallization of primary particles during the synthesis process must be prevented for the production of nanoparticles system [35]. Synthetic magnetic particles are usually produced in the size of micro or nano scale. MNPs with dimensions in the nanometer range frequently require more specialized techniques than do the larger crystals.

Methods of Preparation

All most all the iron oxides and hydroxides can be prepared by several methods (bottom-up and top-down). The bottom-up approaches are superior to top-down approaches because of their easier and more effective ways of producing MNPs of the better quality and quantity [3]. The most common chemical synthesis methods such as coprecipitation, oxidation of ferrous ions, microemulsions, biological nanoreactors, sol-gel, spray pyrolysis, laser pyrolysis and polyol methods are used for the formation of magnetic nanoparticles. The important methods/techniques for the production of uniform MNPs are given in the proceeding sections.

Size Reduction Process

The size reduction approach involves heating selected iron oxides or iron salts in rotary kilns under oxidizing atmosphere. The resulting product is first suspended in water, filtered, washed and dried. It is then ground to the appropriate size in mill [38]. The milling time, milling materials and atmospheric medium affect resultant properties of

nanoparticles [39]. The top-down approach is based on the size reduction techniques, such as machining, templating or lithographic. This approach reduces the size of the bulk materials to the size of the nanoscale via ball milling or mechanical grinding devices. Ball mill grinding of the magnetite micropowders was one of the first method, introduced and developed by Papell in the late 1960s, for producing particles in the nano regime [40]. Historically, long-term grinding of bulk magnetite in the presence of solvents and stabilizing surfactant created the first recognized ferrofluid; the procedure is sketched in the flow chart shown in Fig. 3 [41].

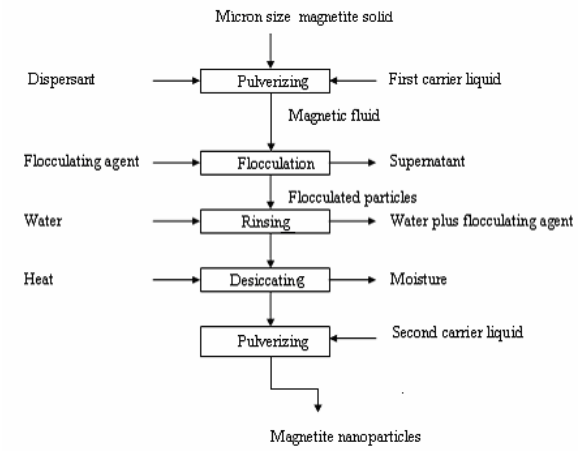

Fig. 3: Pulverization of bulk magnetite in the presence of solvent and surfactants.

Mechanical grinding methods used for producing nanoparticles are intrinsically time consuming (500- 1000 hours) and expensive, so they have been replaced by chemical methods [41]. Electron beam lithography is complicated method for producing particles below 100 nm in size [31-33].

Coprecipitation

The coprecipitation method has been widely used for producing magnetic nanoparticles. MNPs can also be prepared via this method by addition of an alkali to an aqueous mixture of divalent and trivalent iron salts at a definite molar ratio, the synthesis process is represented in the flow chart shown in Fig. 4 [42-51, 58-60]. This synthesis route can be performed with or without surfactants such as dextran, polyethylene glycol (PEG), polyvinyl alcohol (PVA) and oleic acid. Surfactants are often applied during the synthesis process to provide colloid stability and biocompatibility to the synthesized nanoparticles. Bare MNPs (without coating with the surfactants) are produced following the addition of alkali solution to a mixture of Iron(II) and Iron(III) salt solutions [50]. The produced precipitate is isolated through magnetic decantation or centrifugation. The precipitate is then treated with nitric or perchloric acid, centrifuged and peptized (colloidally dispersed) in water. This produces an acidic magnetic solution. Similarly, alkaline magnetic solution can be prepared on substituting the perchloric or nitric acid by tetramethyl ammonium hydroxide [42]. MNPs thus produced are black in colour, polydispersed and nearly sphere-shaped [50, 54, 55]. The nature of salts, divalent and trivalent iron ratio, temperature, pH and ionic strength of the media could be manipulated for the size, shape and composition of nanoparticles [52, 53]. The main synthesis processes are carried out in the inert atmosphere for controlling the reaction kinetics. Inert atmosphere not only shields against oxidation of the MNPs but also decreases the particle size as compared to open atmosphere methods [29, 36].

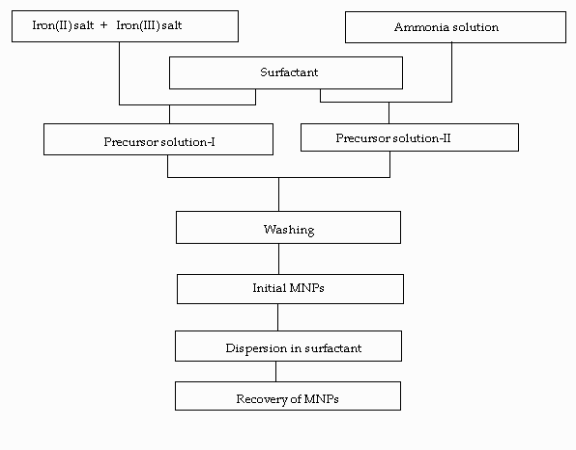

Fig. 4: Procedure for the synthesis of MNPs by chemical coprecipitation method.

The synthesized MNPs via coprecipitation process were kept for 19 months and found that their magnetic properties and original shapes were retained [56]. Jeong *et al.* [57] prepared MNPs using chemical coprecipitation method through a typical pipette drop and piezoelectric nozzle technique. The MNPs oxidized to maghemite nanoparticles by aeration at 573K.

Monodispersed magnetite has been prepared by high-temperature solution-phase reaction of Iron(III) acetylacetonate in phenyl ether with alcohol, oleic acid and oleylamine. The particles of controlled size and shapes have been synthesized by addition of seed particles. Magnetite powders of 5 nm in size were prepared by non-toxic chemical coprecipitation route and their size tuned by the reaction temperature [61].

The demerit of coprecipitation methods is that the pH value of the reaction mixture has to be adjusted in the preparation and purification steps. The progress toward uniform and monodispersed nanoparticles has only limited success. MNPs of smaller size have been prepared by organic solution-phase disintegration of the iron precursor at high temperature [62]. Coprecipitation methods are however, extensively used due to their simplicity and capacity for large-scale production. The nanoparticles thus produced are fairly polydispersed. As a consequence, numerous other methods are currently being developed for producing the nanoparticles with more uniform dimensions.

Oxidation of Ferrous Ions

Oxidation of ferrous ions for producing magnetic nanoparticles is a very versatile approach. Careful control of pH, rate of oxidation, suspension concentration, synthesis temperature and concentration of foreign species are required for obtaining a pure product. MNPs are produced by oxidation of Iron(II) salts such as $FeSO_4.7H_2O$ and KNO_3 at pH > 8 and the pH must be held constant by continual addition of alkali to the system. This is achieved most conveniently by using an automatic burette and pH-state titration technique [54, 63, 64]. Sugimoto *et al.* [64] proposed magnetite preparation is accomplished by means of crystallization of amorphous ferrous hydroxide. Gardineer *et al.* [65] proposed the oxidation of ferrous hydroxide to ferric hydroxide by thermal aging with oxygen purging. The ferrous hydroxides and ferric hydroxides react with one another to form magnetite during the aging process [65].

Douglas *et al*. [66] customized the oxidation method to investigate the effects of a carboxylate functionalized poly (amidoamine) dendrimers on the formation of ferric oxide. The reaction utilized trimethylamine N-oxide as an oxidation agent, while maintaining a pH of 8.5 at 338K [66]. The rate of reagent addition is an essential reaction parameter in the oxidation of ferrous ions to magnetite or maghemite. A slow controlled process avoids the formation of pure Fe^{2+} phases, which may compete and limit the desired iron oxide formation [66, 67]. MNPs were produced with the same molar concentration of Iron(II) and Iron(III) salts in the presence of a base and with or without the polysaccharide [68]. The quality of the oxidation of Iron(II) system is that a crystalline product can be obtained in a few hours at room temperature.

MNPs Production under Controlled Atmospheres

The spherical MNPs of various sizes are formed through precipitation of hydrated iron ions in the restricted environment. Synthetic and biological nanoreactors have been used for the synthesis of MNPs of the controlled size and shape. The controlled atmosphere comprises amphoteric surfactants [69-73] apoferritin protein cages [4, 74, 75] and phospholipid membranes [80, 81]. The amphoteric surfactants create water swollen reversed micellar structures in nonpolar solvents. The phospholipids membranes that form vesicles with MNPs are serving as solid supports. The synthesis of MNPs was carried out in a closed system under N_2 gas flow via controlled chemical approach. Using of a polymeric starch network as coating agent prevented the aggregation of the magnetic nanoparticles [78]. Liu *et al*. [79] synthesized MNPs with different molar ratios of the citrate to iron ions under the closed environment with N_2 gas flowing at 323K. The methods such as sol–gel [80], polymer matrix-mediated synthesis [81], precipitation using microemulsions [82, 83] and vesicles [84] have been developed on the principle of precipitation in extremely controlled domains. MNPs have been produced in apoferritin cages and laboratory-grown bacteria on very small scale in constrained environment [85]. MNPs produced through different chemical methods illustrated different characteristic features are shown in Table-1.

Table-1: Comparison of various characteristic features of MNPs fabricated through different chemical techniques.

Characteristics of The MNPs	Pyrolysis Methods	Bulk Solution Methods	Sol–Gel Methods	Microemulsion Methods
Morphology	Spherical	Spherical (large aggregates)	Spherical with high porosity	Cubic or spherical (no aggregation)
Size	5–60 nm	10–50 nm	20–200 nm	4–15 nm
Size Distribution	Broad	Broad	Broad	Narrow
Magnetization Value	10–50 emu/g	20-50 emu/g	10–40 emu/g	>30 emu/g
Magnetic Behaviour	Desired magnetic property	Superparamagnetic	Paramagnetic	Superparamagnetic
Merits	High production rate	Large quantities can be synthesized	Particles of desired shape and length can be synthesized, useful making hybrid nanoparticles	Uniform properties and also size of the nanoparticles can be modulated
Demerits	Large aggregates are formed	Uncontrolled oxidation of magnetite to maghemite	Product usually contains sol–gel matrix components at their surfaces	Surfactants are difficult to remove, only a small quantities of iron oxide can be synthesized

Microemulsion

A microemulsion is a stable isotropic dispersion of two immiscible liquids. The microdomain of either one or both liquids has been stabilized by an interfacial film of surfactant [86]. In water-in-oil (W/O) microemulsions, the liquid phase is dispersed as microdroplets ranging 1–50 nm in size, encircled by a single layer of surfactant molecules in a continuous oil phase [87]. When the aqueous phase of the microemulsion consists of soluble metal salt, it will be located in the aqueous microdroplets encircled by oil. These microdroplets will constantly collide, combine and separate again [88].

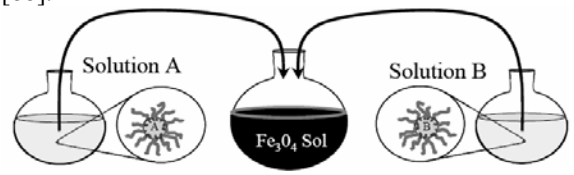

Fig. 5: W/O microemulsion method for producing MNPs in nonpolar solvents (solution A and solution B contains Iron(II)/Iron(III) and ammonia solutions respectively).

When metals A and B are liquefied in two identical W/O microemulsions, they form an AB precipitate on amalgamation shown in Fig. 5. The development of these materials in microemulsions can be considered as a process of interdroplet exchange and nuclei agglomeration [89-91].

Reactors for the production of MNPs through W/O microemulsions have been recently developed. This technique has capability to control the size and morphology of the nanoparticles [92]. MNPs were prepared in oil-in-water (O/W) microemulsions by suspending the Iron(II) salt-surfactant precipitate in reaction solution. An alkali is then added to aqueous solution to create a magnetic ferrofluid [93]**.** In another incarnation, surfactant such as oleic acids was used as coating agents for nanoparticles. This hot visible phase when dispersed in cold water accomplished lipid coating of the MNPs [94].

The W/O route is suitable for biomedical applications, is a familiar microemulsion method used for the production of nanoparticles. Nanodroplets of aqueous iron salts are surrounding surface active agents that separates them from the adjacent organic solution, thus to form reverse micelles [95-97]. The MNPs were prepared and oxidized within the micelle. The shape and size of MNPs depend on the reaction temperature as well as concentration of metal salts and the base [98]. Microemulsion is an efficient technique for producing MNPs, as the size of the formed particles can be strongly controlled between 2-12 nm [99]. Thus, this synthesis route produces somewhat uniform production of MNPs. Some microemulsion methods produce nanoparticles which are only soluble in organic solvents. These MNPs can be given water-soluble coatings that would avoid aggregation [100]. It is commonly recognized that microemulsion can produce MNPs with uniform sizes which are dependent on the synthesis technique and precision. The precision of this method has been criticized, as an approach, for producing larger nanoparticles with weak crystallinity [101].

Igartua *et al*. [102] synthesized colloidal MNPs from warm emulsions. A two-stage technique was employed to get the sphere like nanoparticles of 62 nm following (a) preparation of a transparent phase by heating the O/W emulsion formed by liquid surfactant solution melted with a lipid phase and (b) production of the nanoparticles by dispersing hot transparent phase in cold water under stirring.

Yaacob *et al*. [103] synthesized MNPs via precipitation of mixtures of single-tailed cationic and anionic surfactants in 7:3 molar ratios. The other researchers synthesized MNPs from Iron(II) hydroxide precipitate at room temperature. It was found that the right range of intravesicular pH was a significant factor and necessary for controlling the synthesis of nanoparticles by means of suitable ratios of cationic to anionic surfactants [104-106].

Reverse Micelle Solutions

Reverse micelle solutions are translucent, isotropic, thermodynamically established aqueous media. The liquid phase is dispersed as microdroplets ranging 1–50 nm in size, encircled by a single layer of surfactant molecules in the continuous oil phase.

Reverse micelle solutions are produced by using ionic and nonionic surfactants. In nonpolar, organic solvents the polar head cluster correlates and creates micellar structures in the form of a thermodynamically stable dispersion. These micellar structures serve as controlled nanoreactor atmosphere for the coprecipitation of aqueous iron salts with the appropriate ionic surfactants such as sodium bis(2-ethylhexyl sulfosuccinate) or cetyltrimethyl-ammonium bromide [107-110].

Reverse micelle solutions have been used for producing MNPs in small size distribution with homogeneous chemical and physical properties [111]. Pileni *et al* [112] prepared superparamagnetic

MNPs using reverse micelle solutions in small size range. A ferrous dodecyl sulfate micelle solution was employed to synthesize MNPs, while size and shape were controlled by the factors such as the surfactant concentration and temperature. MNPs have been prepared by mixing ammonia solution with iron salt solutions within the reverse micelle nanocavities produced using sodium bis(2-ethylhexyl sulfosuccinate) as a surfactant and heptane as a continuous organic phase[113]. Tang group prepared smaller and more uniform particles of magnetite at low temperature in the inert atmosphere [114]. The size of the reverse micelle cavities is in nanometer range, so MNPs synthesized inside these nanoreactors were found to be very small in size(less than 15 nm) with narrow size distribution [115]. The colloidal MNPs demonstrate superparamagnetic behaviour with high magnetization values. The primary advantage of employing this type of reverse micelle system for MNPs formation is to control size of nanoparticles by adjusting the size of aqueous micellar core [116].

The approach of reverse micelle is new, however higher concentration of surfactants are necessary for making water solubilized nanoreactors. Furthermore, the ionic surfactants assembly in the hydrated core appears to inhibit the potential of creating highly crystalline MNPs [117, 118]. Moreover, it is not yet apparent how the compositions of the MNPs and their crystal structures associate to the conditions used in these reactions. Reverse micelle nanoreactor routes using cationic surfactants circumvent the difficulty of the existence of a complexing-functional group and presents great future prospectives [119-120].

Biological Nanoreactors

Magnetoferritin, a biological nanoreactor is an analogous approach to the reverse micelle employing utilization of ferritin which is a spherical polypeptide shell to create MNPs inside a biological iron storage protein core of 8 nm in diameter [121-123]. The external diameter of ferritin is about 12 nm with two internal subchannels and an inner chamber which consists of antiferromagnetic hydrated MNPs [123]. The inside chamber of the ferritin consists of ferrihydrite which is removed by reductive dissolution in acidic media by dialysis to leave apoferritin, the vacant protein cage. MNPs can be synthesized via magnetoferritin by the stepwise additions of iron(II) solutions. Wong *et al.* [122] made suitable amendments such as stoichiometric oxidation of the iron(II) ions using a mild, one electron oxidant in an anaerobic environment, to optimize the magnetoferritin approach.

Magnetoliposome is another biological approach for synthesizing stabilized MNPs, using liposomes which are phospholipids membranes [124]. This magnetoliposome structure materializes to imitate biological membranes and therefore has potential uses in biomedical applications, such as magnetic resonance imaging and magnetically controllable bioreactors [125].

The demerit of these biological synthesis methods is that the pH value of the reaction mixture has to be adjusted in both the preparation and decantation steps. Consequently, the production of MNPs in uniform size and shape remains a considerable challenge through these methods. The critical difficulty is that these particles form aggregates and grow to minimize the overall surface free energy, so that free precipitation is not a viable technique [126].

Sol-Gel Method

The most commonly used chemical synthesis technique is characterized by the sol-gel approach. The sol-gel is a colloidal suspension (sol) that can be gelled to form a solid (gel), has been used in the preparation of wide range of nanomaterials. This technique is generally better than the other techniques for controlling the final shape of the particles and its preparation procedure for production of magnetic nanoparticles shown in Fig. 6 [127, 128, 133]. A greater control on the size, shape and composition of the nanoparticles could be achieved through this method. Among the available techniques for fabrication of MNPs, sol-gel is undoubtly the simplest and engineered chemical techniques [130, 131].

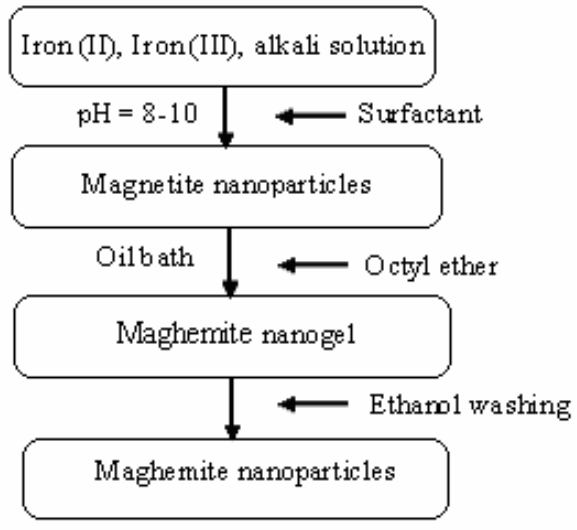

Fig. 6: Scheme for the synthesis of MNPs via sol-gel method.

The attraction and advantages of this method are due to (a) its low temperature processing, (b) its versatility and the possibility to obtain high purity materials and (c) its perfect control on its shape, size and composition of the final products [132]. Prakash *et al*. [128] prepared monodispersed MNPs by sol–gel method. It was found that the nanoparticles prepared by this method had a very high area enhancement. Hiroyoki and Tadao Sugimoto prepared monodispersed hematite (α-Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) particles in uniform size and shape via gel-sol method [127].

Polyol Technique

Polyol technique is a very capable technique for the fabrication of homogeneous MNPs of definite shape and size. Magnetic nanoparticles can be achieved by reduction of dissolved metallic salts and direct metal precipitation from a polyol solution [134, 135]. This process was first used to produce metals nanoparticles such as Ru, Pd, Pt, Au, Co, Ni or Cu [136, 137]. These days, this approach has been extended to the preparation of other nanomaterials such as iron-based alloys [138, 139], which could be utilized for biomedical purposes. In this technique, the liquid polyol can perform in different ways; (a) as the solvent of the metal precursor, (b) as the reducing agent and (c) as a complexing agent for the metallic cations. The metal precursor can be made completely or only to some extent soluble in the polyol. Monodispersed MNPs with definite shape and size can be achieved by this process by controlling the kinetic of the precipitation. The average size of the MNPs can be achieved by seeding the reactive medium with outside nucleating agents. In this fashion, nucleation and growth processes can be entirely separated and gives definite and uniform particles. Iron nanoparticles can be achieved by disproportionation of Iron(II) hydroxide in continuous oil media [137]. Iron(II) chloride and alkali hydroxide reacts with PEG and the reaction occurs in a temperature range as low as 353–372K. As a result monodispersed magnetic nanoparticles with mean size around 100 nm have been obtained without seeding [139].

Other Supplementary Methods

Advancement in the use of magnetic particles for biomedical applications depends on the new synthetic methods with better control on the size distribution, magnetic properties and the particle surface characteristics. Organized assemblies or complex structures have been used as reactors to obtain ultrafine magnetic iron oxide particles [140-141]. Stable aqueous magnetic suspensions can also be fabricated using various saturated and unsaturated fatty acids as primary and secondary surfactants [41]. In practice, however, little control can actually be exercised over the size distribution of the nanostructures. The small quantities of iron oxide can be obtained owing to the constraints of low reagent concentrations employed for this synthetic procedure. Several other techniques also exist for the controlled preparation of MNPs such as sonochemical synthesis, spray pyrolysis, laser pyrolysis and thermal decomposition [140].

Sonochemical synthesis is the rapid disintegration of sonically created nanocavities providing nanosecond lifetime hot spots of 5000K where Iron(II) salts are immediately driven to produce monodispersed MNPs which are stabilized through oleic acid [142]. MNPs were prepared from Iron(II) alkoxides by sonochemical technique under inert atmosphere [143].

Spray and laser pyrolysis are using aerosol which is the colloidal dispersion of solid or liquid particles in a gas (air). These approaches are suitable for the formation of MNPs at high-production rate [144, 145]. Spray pyrolysis is a process in which solution is sprayed into series of reactors where the solute condenses as the solvent evaporates [144]. MNPs are formed by reduction of iron(II) ions into a mixture of iron(II) and iron(III) ions in a continuous oil media [145]. A microporous solid is then sintered to a proper particle size at high temperature. Uniform iron oxide particles in alcoholic solutions can be prepared with various particles size and shapes, depending on the nature of the iron salt precursor [146]. Gonzalez *et al.* [147] has given details of the process used for the synthesis of MNPs and the schematic presentation of spray pyrolysis device, used for the synthesis of MNPs shown in Fig. 7.

Laser pyrolysis like spray pyrolysis can be utilized to decrease the reaction volume and thus uniform and high crystallized nanoparticles are synthesized just in one step [148, 149]. The higher manufacture rates of this technique can be materialized by thorough control over experimental environment and expensive apparatus. The MNPs of 5 nm in size with very narrow size distribution have

been achieved under diverse experimental conditions [150-151].

Spray and laser pyrolysis have been shown to be brilliant methods for the direct and continuous manufacture of definite MNPs under extensive control of the experimental set up. In spray pyrolysis, the nanoparticles are usually agglomerated into larger particles, while in laser pyrolysis the nanoparticles are less agglomerated due to lesser reaction time.

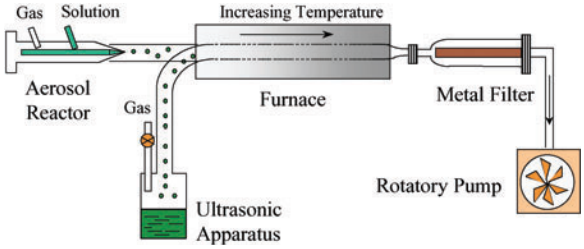

Fig. 7: Schematic demonstration of the spray pyrolysis device, used for the synthesis of MNPs.

Thermal decomposition technique has been developed for producing high-quality MNPs by thermal disintegration of diverse iron precursors. Alivisatos *et al.* [152] used N-nitroso-N-phenyl hydroxylamine ammonium salt (cupferron) in octylamine and trioctylamine at 523–573K to create a monodispersed precipitate of magnetic nanoparticles. The people of nanotechnology are working on the utilization of thermally decomposed nanoparticles for biomedical uses [153]. The other synthesis routes which are using in the production of MNPs are layer-by-layer and colloidal templates [154].

Conclusion

Different approaches were commonly employed for synthesizing MNPs. In the past, MNPs were produced by means of top down approach in the presence of stabilizing surfactants. At present, the synthesis routes such as coprecipitation, microemulsion, sol-gel and polyols are accessible for producing MNPs. Various supplementary methods including sonochemical, spray & laser pyrolysis and thermal decomposition also existed for the controlled synthesis of MNPs. Various factors for example purity of reagents, stoichiometric ratio and ionic strength, nature of the cation of the base, pH and temperature could be adjusted in the production of MNPs for controlling size, shape, magnetic characteristics and surface properties. A major challenge for all methods is the design of MNPs with effective surface coatings that provide optimal performance in biomedical applications.

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