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REVIEW

Research Progress of the Preparation of Nano-Ferric Oxide

ZI-QUAN LIU*, FANG-JUN KAN, SHUANG-XIN XU, RUI-CUI LIU and FU-YI JIANG

School of Environmental and Material Engineering, Yantai Universiy, Yantai 264005, P.R. China

*Corresponding author: E-mail: lzqytu@163.com

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There is a wide use of nano-ferric oxide. There are many ways to prepare iron oxide nano-particles, such as co-precipitation, micro-emulsion, sol-gel process, pyrolytic process, hydro-thermal method, forced hydrolysis, *etc*. This article started from the descriptions of the methods to prepare iron oxide nano-particles, emphasized on summing up the progress in the research on the preparing methods and technical part of nano-ferric oxide. This article also commented on the advantages and disadvantages of each method. It finally predicted the future of the trend of the research on the preparing methods of nano-ferric oxide.

Key Words: Nano-ferric oxide, Preparation methods, Magnetic, Monodisperse, Stabilizer.

INTRODUCTION

In recent years, magnetic nano-particles have attracted considerable attention not only for fundamental research, but for broad range of applications due to unique magnetic properties. Among these magnetic nano-materials, iron oxides (Fe_2O_3 and Fe_3O_4) have been extensively investigated because of its excellent magnetic properties and biocompatibility. For more than 10 years in the past, people have been doing a lot of research on the preparation of iron oxide nano-particles. Many methods have been reported to prepare monodisperse, shape-controllable and biocompatible ferric oxide nano-particle. The most commonly-used methods include co-precipitation method, pyrolytic process, hydro-thermal method, micro-emulsion and sonochemical method. There are some other methods such as electrochemical synthesis[1,2], laser pyrolysis technology[3] and microbiological or bacterial synthesis[4,5]. The commonly-used precursors to prepare mono-disperse iron oxide nano-particles include $FeCl_2$, $FeCl_3$, $Fe(CO)_5$, $Fe(NO_3)_3$, $Fe(NO_3)_2$, $Fe(SO_4)_3$, $Fe(acac)_3$, iron acetate, iron oleate, *etc*.

This article started from the descriptions of the methods to prepare iron oxide nano-particles. It summed up the progress in the research on the preparing methods of iron oxide nano-particles from recent years and finally predicted the future of the trend of the research on the preparing methods of iron oxide nano-particles.

Progress of the research on the preparation of iron oxide nano-particles

Co-precipitation method: Co-precipitation method is the most simple and effective way to prepare magnetic nano-particles. In the room temperature or rising temperature, add alkaline matter into Fe^{2+}/Fe^{3+} salt solution to prepare iron oxide nano-particles (Fe_3O_4, γ-Fe_2O_3).

In the process of co-precipitation, salt varieties [$FeCl_3$, $FeSO_4$, $Fe(NO_3)_3$, $FeClO_4$], pH value, ionic strength, temperature and Fe^{2+}/Fe^{3+} concentration ratio were used to adjust the dimension and shape of iron oxide nano-particles. In recent years, some people used co-precipitation method to produce iron oxide nano-particles with a dimension of 2-17 nm. They also studied the influence of different parameters (Fe^{2+}/Fe^{3+} concentration ratio, temperature, injection flow, the concentration of Fe^{2+}, Fe^{3+} and TMAOH) on the dimension and magnetism of the particle[6]. Another team used co-precipitation method to make superfine magnetite nano-particle with a dimension of 2-4 nm and adjusted the dimension of the particles by the temperature of the sediments. The product prepared by this method has good superparamagnetic behaviour but α-Fe_2O_3 and γ-Fe_2O_3 appeared in the process of annealing[7]. One team used $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ as metal salt, kept the ratio between Fe^{2+} and Fe^3 as 1:2, used ammonia as alkali, used co-precipitation method to prepare the mixture of goethite and magnetite. Research shows that the pH value and the concentration of the salting liquid before the reaction and the final pH value is important parameters in controlling the content of goethite and magnetite in the product[8]. This finding is very useful to make pure magnetite nano-particles without goethite.

This method is simple, effective and easy to adjust to massive production. Iron oxide nano-particles that are prepared have a wider range of dimensions, sometimes you need to have a second choice of dimensions. A wider range of dimensions of the particles will lead to a wider range of block temperature and as the block temperature depends on the dimension of the particle, ideal magnetism cannot be reached in many application fields. The product prepared by this method is not pure, there are often some impurities. It is a bit difficult to control the reaction condition. In addition, as it is not easy for some metals to have precipitation reaction, this method won't be applied in many areas.

In recent years people have improved the co-precipitation method concerning its problems. For example, using some organic additives as stabilizing agents has made some progress. Magnetite nano-particle with a dimension of 4-10 nm exist stably in the water solution of 1 wt % PVA, while form chaining cluster sediments. So that it is very important to chose suitable surface active agent. Recent research shows that oleic acid is the best stabilizer of Fe_3O_4 nano-particles[9].

Pyrolytic process: The method of pyrolysis of organic matters is widely used in the synthesizing of iron oxide nano-particles. Pyrolyzing $Fe(cup)_3$, $Fe(acac)_3$, $Fe(CO)_5$ and some other ferric precursors and oxidizing can prepare high-quality mono-disperse iron oxide nano-particles. This method doesn't need the process of size-choosing and is easy to have mass production. Direct decomposing $Fe(cup)_3$ usually makes mono-disperse γ-Fe_2O_3 nano-particles[10]. Pyrolytic process usually needs a relatively high temperature and complicated working process. Sun and Zheng[11] decomposed $Fe(acac)_3$ to make mono-disperse Fe_3O_4 nano-particles with a controllable size under high temperature (265 ºC) in diphenyl ether with ethanol, oleic acid and oleyl amine. Then, they annealed the Fe_3O_4 nano-particles for 2 h under a high temperature (250 ºC) to transform it to γ-Fe_2O_3 particles. For example, under the temperature of 100 ºC with oleic acid, Hyeon *et al.*[12] pyrolyzed $Fe(CO)_5$ to produce mono-disperse, high crystalline iron nano-particles. Then they used weak oxidizer trimethylamine to control the oxidizing and transformed iron nano-particles to γ-Fe_2O_3 nanoparticles. Pyrolyzing $Fe(CO)_5$ will produce iron nano-particles and then using chemical agent can produce mono-disperse γ-Fe_2O_3 nano-particles[13].

From the cited, it is suggested examples that pyrolytic process is easy to produce mono-disperse iron oxide nano-particles with a small range of dimension. However, the precursors such as $Fe(cup)_3$, $Fe(acac)_3$ and $Fe(CO)_5$ that are used are a little bit expensive, the needed temperature is relatively high and the process is complex. The biggest disadvantage of this method is that the nano-particles that is made usually only dissolves in non-polar solvent and it greatly confines its applied range.

Sol-gel method: Sol-gel process is a wet chemistry method to make iron oxide nano-particles. This method uses the alcoholysis and polycondensation of molecular precursors to make sol, the further polycondensation will make the 3D network wet gel and then the heat treatment will form the final iron oxide nano-particles. Many documents show that the structure of the sol in the process determines the property of gel. The solvent, temperature, the concentration and pH value of metal alkoxide are important parameters that influence the reaction kinetics, alcoholysis, polycondensation, the structure and property of the gel.

Sugimoto *et al.*[14] used sol-gel method to prepare mono-disperse α-Fe_2O_3 nano-particles. They found that adding α-Fe_2O_3 beforehand would save a lot of time for jelling and the size of the particle would be smaller. The gelation of alkoxide was achieved by the hydrolyzation of alkoxide and polycondensation.

Another example, under the temperature of 400 ºC, some researchers pyrolyzed the gel directly to prepare γ-Fe_2O_3 nano-particles with the dimension of 6-15 nm. This method has the following advantages: preparing materials with the planned structure by changing experimental conditions; preparing mono-disperse materials with controllable size and uncontrollable shapes; insert other materials in sol-gel kinetosome, the property remains the same[16].

Solnas *et al.*[17] used sol-gel process to produce Fe_2O_3-SiO_2 complex material and kept the mole concentration ratio of Fe to Si as 0.25-0.27. They studied two factors that affected the process: temperature and surface/volume (S/V). Research showed that sol-gel process determined the dimension and crystalling phase of nano-particles in silicon substrate. Adopting a high S/V ratio would produce quite fine iron oxide particles. On the contrary, if the gel process of the sol adopted a low S/V ratio, we could produce big iron oxide particles. Then in the gel process, low S/V ratio and high temperature is advantageous to producing γ-Fe_2O_3; high S/V ratio and low temperature is advantageous to producing α-Fe_2O_3.

Metal alkoxide first hydrolysis and then the polycondensation between molecules. These two reactions happened alternatively. In the polycondensation, the particles of the sol bonded with each other, the viscosity of the sol was on the increase. With the strengthening of polycondensation, the polymerization degree of the gel increased and finally made a 3D network. The drying of the gel is a critical part of the sol-gel process. Apart from the traditional drying under heating and reduced pressure, freezing drying and supercritical fluid drying have been used in sol-gel process to prepare iron oxide nano-particles[17].

The reaction temperature of the sol-gel process is low. The particle size of the product is small, it can be controlled in dozens of nm, it built a good basis for high-density recording and these products are apt to mass-production. But the process requires a long reaction time and high cost. The product is easy to use when it is dry.

Hydro-thermal method: Hydro-thermal method is a reaction that uses water as the medium and happens under high temperature and pressure in a closed container. Some reactions may occur according to the analysis of thermo-dynamics, but they occur slowly under normal temperature and pressure by the effect of dynamics. These reactions can perform under the hydrothermal condition. That's because under the hydrothermal condition of high temperature and pressure, especially when the temperature exceeds the critical temperature (647.2 K) and critical pressure (22.06 MPa), the water stays in a critical state. The physical and chemical property of the substance both change remarkably in the water, it prompts the ionic reaction, hydrolysis, oxidation reduction reaction, crystallization reaction, *etc*. So that hydro-thermal chemical reaction is different from a normal reaction.

As the magnetic properties of the iron oxide nano-particle depends greatly on the size and the shape, it is very important to prepare nano-particles with controllable size and shape. Micro-emulsion and high-pressure decomposing method are usually complex and require a relatively high temperature. On the contrary, hydro-thermal method is a wet chemical technology which crystallizes materials in the water solution under high temperature and pressure. This technology is used to grow mono-crystalline. Particles prepared by this method have high degrees of crystallization so that hydro-thermal method is advantageous to producing iron oxide nano-particles with high degrees of crystallization[18].

Some researchers reported to use the hydro-thermal method to produce iron oxide nano-particles[19-22]. The hydro-thermal method can be divided into two kinds, one is without surface active agent, the other is adding special surface active agent into the system.

For example, Zheng *et al.*[23] reported to use the hydro-thermal method to prepare the Fe_3O_4 nano-particle with the particle size of 27 nm with the surface active agent of AOT. This kind of particle has super-paramagnetism under room temperature. On the contrary, Wang *et al.*[24] reported that they used hydro-thermal method to produce highly-crystallized Fe_3O_4 nano-particles without surface active agent. The saturated magnetic intensity of this kind of particle is 85.8 emu g^{-1}, higher than the corresponding block Fe_3O_4, it shows that hydro-thermal method can increase the saturated magnetic intensity of Fe_3O_4 nano-particles.

Cui *et al.*[25] used a original hydro-thermal method to prepare the water-soluble Fe_3O_4 nano-particles with super paramagnetism. They put the beaker with $Fe(NO_3)_3 \cdot 9H_2O$ and glycol in the polyfluortetraethylene high-pressure autoclave with 6 mL of ammonia. They put it into microwave oven after sealing it, heated it for 10 min under the temperature of 170 ºC and then cooled it to room temperature. In this closed system, they used beaker to separate these two liquids under room temperature. When it was put into the microwave oven to be heated, the high temperature caused the ammonia to evaporate. The evaporated ammonia reacted with Fe^{3+} on the surface of gas/liquid to prepare the mono-disperse Fe_3O_4 nano-particles.

Jing and Wu[19] used FeC_2O_4 and NaOH as resources, added separately sodium dodecyl sulfate (SDS), sodium dodecy benzene sulfonate (SDBS), cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium choride pyridine as surface active agents to make mono-disperse diamond α-Fe_2O_3 nano-particles by hydro-thermal method, but mono-disperse rod-like α-Fe_2O_3 nano-particles without them. These five products all appear weak ferromagnetism.

The experiments mentioned above imply that this method easily produces mono-disperse iron oxide nano-particles with super paramagnetism and a relatively high degree of crystallization. The surface active agent has a relatively great influence on the particles of samples using this method. It not only changes the size and shape of the particle, but also affects the magnetism of the particle. Moreover, this method is demanding as to facilities and costs much.

Forced hydrolysis: Forced hydrolysis is a method that uses metallic salt solution to force hydrolysis. It is an important way to prepare well-distributed nano-particles. This method usually uses $Fe(NO_3)_3$ or $FeCl_3$ as resources, prepares iron oxide nano-particles with the addition of HCl or HNO_3 under the condition of closed static boiling or regurgitant dynamic boiling environment[26,27]. In order to decrease the speed of hydrolytic precipitation and the growth of crystals to make the particle grow completely and evenly, we usually put a few crystal growth substances (such as NaH_2PO_4) in the process of preparation.

Wang[26] forcedly-hydrolyzed $FeCl_3$ to prepare α-Fe_2O_3 nano-particles in HCl solution. The nucleation rate, Fe^{3+} concentration and curing time were used to control the size and shape of the particle. In the beginning period of hydrolysis, irregular structures without controllable shape were nucleated slowly, then club-shaped β-FeOOH particle was produced. Fast nucleation will produce round particles without controllable structures. With the lengthening of curing time, the club-shaped and round-shaped particles finally transformed into cubic hematite nano-particles. In this process, fast nucleation makes un-oriented iron oxide particles transform into crystallized hematite. We prepared cubic, spherical, flaky, hexagonal, discoid and tetrahedral iron oxide nano-particles by changing the nucleation speed, Fe^{3+} concentration and curing time.

Music *et al.*[27] used forced-hydrolysis with $FeCl_3$ as the resource to produce iron oxide nano-particles of different shapes. They discussed the effect of the original concentration of $FeCl_3$, the concentration of HCl, time and with quinine sulfate agent or not on the shape and component of the product. For example, 0.01 M $FeCl_3$ solution experience the forced hydrolysis for 7 days, to get an even cubic α-Fe_2O_3 particle. But on addition of 0.005 M quinine sulfate (QHS), a comparatively small α-FeOOH needle-like particle was obtained. When the concentration of $FeCl_3$ solution was 0.02 M, mixture of β-FeOOH and α-Fe_2O_3 was obtained. The cigar-like β-FeOOH particle in the mixture had irregular rims and coarse surfaces as they dissolved partly. But α-Fe_2O_3 was similar to spherical.

This method usually uses low cost and environment-friendly $FeCl_3$ or $Fe(NO_3)_3$ as resources, the prepared nano-particles have even sizes and controllable shapes. But it costs relatively more energies and is complex.

Micro-emulsion method: Micro-emulsion is a thermodynamic system that is stabilized by surface active agent. The agent forms a layer between oil and water, its water-repellent group dissolves in the oil phase and its hydrophilic group dissolves in the water phase. According to the ratio of oil to water in the system and its microstructure, we could divide it into positive phase O/W and negative phase W/O.

In this two-phase system, different types of self-assembly structures can be formed, such as sphericity, column micelle, lamellar phase and bi-continuous micelle, *i.e.* oil phase and water coexist. In a sense, micro-emulsion can be used to make iron oxide nano-particles with controllable size and shape.

Lee[28] used micro-emulsion to prepare magnetite nano-particles with even size and high crystallization. And it has super paramagnetism under room temperature. We could control the size of the particle by changing the concentration of iron salt, the kind of the surface active agent and the solvent.

Tourinho *et al.*[29] used water/oil micro-emulsion to prepare magnetic iron oxide nano-particles. Compared with Massart's method, the particle prepared by this method is smaller and has a higher saturated magnetization intensity.

The process unit of the micro-emulsion method is simple and it costs less energy. It can prepare extremely pure iron oxide nano-particles with even size. Also the experimental agents are harmless iron salt and little organic solvents, the technology is environment-friendly. But the operation of this method is difficult to control and it doesn't have a good productivity.

Phono-chemical method: Phono-chemical method is widely used in preparing new materials with special properties. Ultrasonic cavitation refers to the process of the formation, growth, shrinking and bursting of the bubbles in the liquid in the ultrasonic field. When the vacuoles blurt, the gas or steam in it is compressed to produce high temperature or local high pressure, the transient temperature of the gas can be as high as 5000 K, the pressure can reach 1800 atm, the cooling speed can reach 10^{10} K/s[30]. This extreme conditions do well to produce new phase, has a shearing effect on aglomeration. It tends to prepare mono-disperse nano-particles.

This method is widely used to synthesize all kinds of nano-phase materials. It successfully verifies its resemblance in the preparation of iron oxide nano-particles[31]. For example, in the argon atmosphere, ultrasonic iron acetate solution produces Fe_3O_4 nano-particles. Vijayakumar *et al.*[32] used phono-chemical method to prepare Fe_3O_4 nano-powder with the dimension of 10 nm successfully. The prepared Fe_3O_4 nano-particle appeared super-paramagnetic and it has a low magnetic degree under room temperature. By phono-chemical method, Pinkas *et al.*[33] used $Fe(acac)_3$ as precursor to produce amorphous iron oxide nano-particles under the argon atmosphere condition. The organic content and surface area of Fe_2O_3 nano-particles can be adjusted by the amount of water in the reacting mixtures. This method is simple, comparatively low cost, but it is not good in cystallinity.

Polyhydroxy compound method: Polyhydroxy compound method is commonly-used chemical method to produce mono-disperse nano-particles with controllable size and shape. Poly-hydroxy solvent has a high electrolyte constant and a relatively high boiling point. It can dissolve inorganic compounds and provides a wide range of temperature in the process of preparation. Polyhydroxy compound can be used as reducer and stabilizing agent to control the growth of the particle and stop the particles from aglomeration.

Laurent *et al.*[15] used a simple polyhydroxy compound method to prepare mono-disperse magnetite nano-particles. Under the high temperature, four polyhydroxy compounds including ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol separately reacted with $Fe(acac)_3$ directly. Only in the reaction with triethylene glycol, magnetite nano-particles with even sizes and a narrow, distributed range of dimension were produced. This showed that we need to choose suitable polyhydroxy solvent and reaction temperature to get mono-disperse nano-particles. Fourier transform spectroscopy and thermo-gravimetric analysis both verified the existence of hydroxyl on the surface of magnetite nano-particles.

The nano-particle prepared by polyhydroxy compound method has a small range of dimension and was covered with a layer of hydrophilic hydroxyl group, so that this kind of particle can distribute in water or polar solvents well. High reaction temperature makes the particle have good crystallinity and it has a relatively high magnetic degree. But the method requires a high temperature.

Other methods: Electrochemical process is a method to prepare nano-particles that develops from electrolysis theory. Pascal *et al.*[2] inserted the iron electrode into the mixed water solution of DMF and positive ion surface active agent and used electrochemical process to prepare hematite nano-particles with a dimension of 3-8 nm. Electrochemical process controls the dimension of the particle by controlling the current intensity. Under the oxidizing condition, we used electrochemical precipitation method to prepare Fe_2O_3 and Fe_3O_4 nano-particles successfully.

Solid phase method is a method that mixes solid reagents completely and uses grinding to have chemical reactions to prepare nano-particles. It is a new preparing method that has been developed over the last few years. For example $Fe(NO_3)_3{\cdot}9H_2O$ and NaOH with a mol ratio of 1:3 into agate mortar, mull completely for some time to make the particles make a good contact with each other, spread and react. After washing, suction filtration, drying and burning the solid products, was obtaineds iron oxide nano-particles with a dimension of 25-40 nm.

Vapour phase method can be separated into physical vapour deposition and chemical vapour deposition. Physical vapour deposition uses voltaic arc, high-frequency or plasma high-temperature heat source to heat the oxides, vaporizes it and makes it form nano-particles. However, chemical vapour deposition uses volatile metallic compound or metallic simple substance vapour to make the compound that is needed by chemical reactions.

Conclusion

The iron oxide nano-particle has a wide use. It is not only significant to fundamental researches, but also has an important application prospect in many fields. There are many ways to prepare iron oxide nano-particles, while the nano-particles made by most methods usually have such problems as low degree of crystallinity, irregular size and different appearances and so on. They seriously affect the magnetic properties of the nano-particles that are made. It should be important study to develop a technique to prepare iron oxide nano-particles with regular size and same appearance in the future. In the meanwhile, it is also a major direction and frontier to develop new especially simple methods to make nano-particle system and study its properties.

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