

Preparation and characterization of superparamagnetic magnetite (Fe₃O₄) nanoparticles: A short review

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Abstract

Magnetic magnetite (Fe₃O₄) nanoparticles have attracted a great deal of attention in both fundamental research and practical applications over the past decades. Down to the nanoscale, superparamagnetic Fe₃O₄ nanoparticles with only a single magnetic domain exhibit high magnetic susceptibility, which provides a stronger and faster magnetic response. Their superparamagnetic properties together with other intrinsic properties such as low toxicity, high surface area-to-volume ratio and simple separation methodology, making them ideal for environmental remediation, biomedical, and agricultural applications. This review discusses three conventional wet chemical methods, including chemical co-precipitation, sol-gel synthesis and thermal decomposition for the preparation of superparamagnetic Fe₃O₄ nanoparticles with controlled size and magnetic properties. Nowadays, with the growing research interest in Fe₃O₄ nanoparticles, there is a great amount of researches reported on efficient routes to prepare size-controlled magnetic nanoparticles. Thus, this review is designed to report the recent information from synthesis to the characterization of Fe₃O₄ nanoparticles as well as the discussion of future perspective in this research area.

Keywords: magnetite, nanoparticles, superparamagnetic properties

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INTRODUCTION

Nowadays, there is a widespread research on nanosized magnetic magnetite (Fe₃O₄) particles across many scientific disciplines, including both fundamental research and applications, mainly because of their unique and tuneable magnetic properties that can cater the essential needs for various applications (Ali *et al.*, 2016; Babay *et al.*, 2015; Campos *et al.*, 2015). Magnetite is one of the naturally occurring iron oxides that can be easily obtained and synthesized. In general, Fe₃O₄ nanoparticles with chemical formula of FeO.Fe₂O₃, possess ferrimagnetic properties in bulk with high magnetization saturation, M_s of 92 emu/g at room temperature and high Curie temperature, T_c of 577°C (Wu *et al.*, 2015). However, the magnetic properties of Fe₃O₄ nanoparticles are governed by their particle size. When the size of ferrimagnetic Fe₃O₄ nanoparticles is sufficiently small, they possess superparamagnetic properties with large response to the applied magnetic field (Ghazanfari *et al.*, 2016). The transformation of ferrimagnetic to superparamagnetic properties is shown in Fig. 1, where the magnetic nanoparticles transform from a multi-domain magnetism to a single-domain magnetism with the reduction of size. Fig. 1 depicts the increase of coercivity due to the reduction of size to a maximum value at a specific size called critical diameter, D_s. At this condition, all of the magnetic spins are pointed in the same direction and thus, the magnetic characteristic is improved and the magnetic nanoparticles are usually difficult to be demagnetized due to high coercivity (Scepka, 2016). However, further size reduction will rapidly reduce the coercivity value until it reaches zero and the nanoparticles in this condition are said to be in a superparamagnetic state. In general, Fe₃O₄ nanoparticles with a diameter below the threshold of 20 nm exhibit superparamagnetic properties (Baumgartner *et al.*, 2013; Hasany *et al.*, 2013; Sun, *et al.*, 2014).

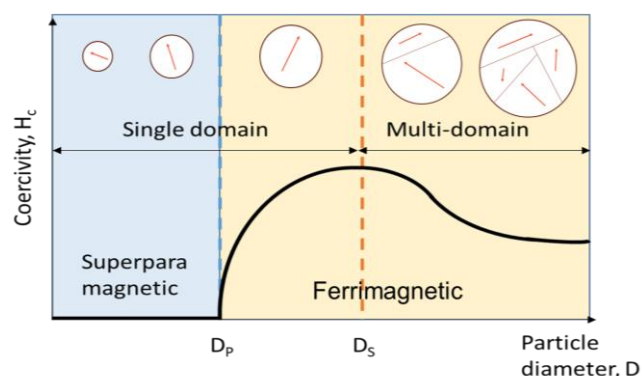


Fig. 1 Schematic diagram of the dependency of coercivity, H_c on the magnetic particle diameter, D.

As shown in Fig 2, superparamagnetic Fe₃O₄ nanoparticles are different with the ferrimagnetic particles, in which they do not have coercive force or hysteresis loop due to single-domain magnetism, thus making them can only be magnetized in the presence of external magnetic field (Laurent *et al.*, 2017; Scepka, 2016). Therefore, these superparamagnetic Fe₃O₄ nanoparticles are easily controlled using external magnetic field (Ghazanfari *et al.*, 2016; Indira & Lakshmi, 2010; Ma & Chen, 2016). It is also worth mentioning that superparamagnetic nanoparticles give stronger and faster magnetic response towards external magnetic field (Wahajuddin & Arora, 2012). Due to the superparamagnetic together with other intrinsic properties such as low toxicity, high surface area-to-volume ratio and simple separation methodology, superparamagnetic Fe₃O₄ nanoparticles have

attracted much attention in the field of environmental remediation for pollution prevention and wastewater treatment (Auffan *et al.*, 2009; Zhang, 2003; Zhao *et al.*, 2008), as well as biomedical applications for protein immobilization such as diagnostic magnetic resonance imaging (MRI), bioseparation, biosensing and drug delivery (Busquets *et al.*, 2015; Lee & Hyeon, 2012; Mahmoudi *et al.*, 2011).

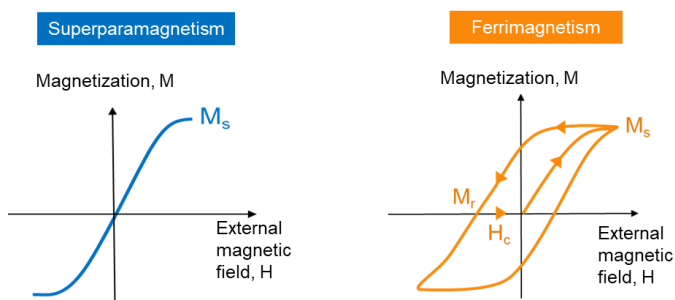


Fig. 2 Schematic diagram of the superparamagnetism and ferrimagnetism hysteresis curves.

Nanoparticles synthesizing method is one of the most challenging parts that will determine the shape, particle size, size distribution, and surface chemistry of the particles, hence defining their magnetic properties (Lopez-Perez *et al.*, 1997; Kouchi *et al.*, 1997; Sjogren *et al.*, 2014). In addition, the synthesizing method also expresses the structural imperfections or impurities in the particles to a great extent, as well as the distribution of such defects within the particles, hence affecting their sensitivity towards magnetic field (Akbarzadeh *et al.*, 2012; Majidi *et al.*, 2014). In order to rule the magnetic properties of Fe_3O_4 nanoparticles, deep understanding on the reaction parameters is of key importance. Therefore, it is well known that the researchers took advantage of the adjustable reaction parameters to synthesize Fe_3O_4 nanoparticles with different morphologies and develop thousands of functionalities. To date, numerous review papers on the synthesis, characterization and application of Fe_3O_4 nanoparticles have been published. However, up to now, the published reviews do not highlight the details of reaction parameters in synthesizing superparamagnetic Fe_3O_4 nanoparticles. Most of the reviews only discuss the synthesis of nanoparticles in general without focusing specifically on the superparamagnetic Fe_3O_4 nanoparticles. Hence, in this review, we will focus on the mechanism, process and influencing factors of three wet chemical synthetic methods for the synthesis of superparamagnetic Fe_3O_4 nanoparticles which are chemical co-precipitation, sol-gel synthesis and thermal decomposition. Not to mention, the capabilities of the abovementioned methods in controlling over particle size and magnetic properties will also be illustrated and compared.

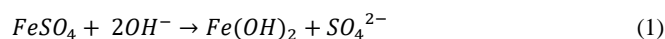
PREPARATION OF MAGNETITE NANOPARTICLES

In the last two decades, a significant amount of researches has been devoted to synthesize magnetic Fe_3O_4 nanoparticles in order to achieve proper control over its particle size, shape, crystallinity, as well as magnetic properties (Ali *et al.*, 2016). To date, there are three most important published routes for the synthesis of Fe_3O_4 nanoparticles, which are physical, chemical and biological routes. A chemical route is preferred over the other synthetic routes in terms of simplicity, efficiency and reproducibility (Ali *et al.*, 2016). Compared to physical and biological routes, chemical route has the advantages in synthesizing new materials with better chemical homogeneity by modifying the combination of precursor (Ghazanfari *et al.*, 2016), and well controlling the size, shape and composition of nanoparticles (Ali *et al.*, 2016; Xu *et al.*, 2014). Besides that, the chemical route is a time saving and cost-effective technique for synthesizing nanoparticles as it does not require expensive equipment and chemicals (Nazari *et al.*, 2014). However, there are some drawbacks in chemical route such as the formation of surplus intermediates and impurities, as well as the risk of colloidal agglomeration to happen during synthesis process (Ghazanfari *et al.*, 2016). In order to control and optimize the properties of nanoparticles such as particle size, size distribution, crystal structure and magnetic

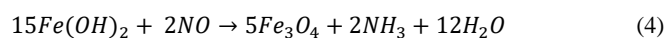
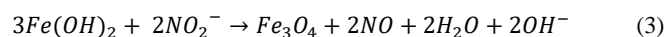
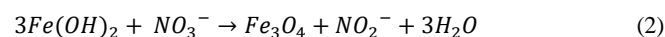
properties, the significant knowledge about the mechanism, process and influencing factors of the nanoparticles synthesizing methods is essential.

Chemical co-precipitation

Chemical co-precipitation is the most promising method in producing nanoparticles due to its ease of implementation and less hazardous chemical and procedure requirements (Cheng *et al.*, 2012; Fu *et al.*, 2012). In general, this method employs an alkaline solution to precipitate metal ions in an aqueous solution under an inert atmosphere at room temperature or elevated temperature (Chu & Hou, 2017). There are two main methods for the co-precipitation synthesis in solution of spherical magnetic Fe_3O_4 nanoparticles. The first method involves the partial oxidation of ferrous hydroxide suspensions followed by co-precipitation (Sugimoto & Matijevec, 1980). Sugimoto and Matijevec succeeded in synthesizing spherical Fe_3O_4 nanoparticles of narrow size distribution with average diameter between 30 to 100 nm by partially oxidizing Fe (II) salt with a base and a mild oxidant. Apesteguy *et al.* (2015) prepared Fe_3O_4 nanoparticles with average particle size of 58 nm and M_s of 75emu/g by partially oxidizing $FeSO_4$ with KOH and KNO_3 which acted as a base and an oxidant agent, respectively. The reaction mechanism for this method is shown in the following equation, where Eq. (1) shows the mechanism of partial oxidation of $FeSO_4$ to $Fe(OH)_2$ (Sugimoto & Matijevec, 1980).

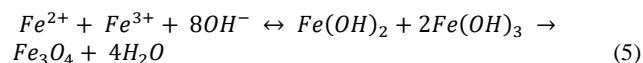


Equations below show the possible summary reactions, including the intermediate steps, for the precipitation of $Fe(OH)_2$ to Fe_3O_4 by interacting with NO_3^- .



The other method involves aging stoichiometric mixtures of ferrous and ferric hydroxides in aqueous solution, yielding magnetic Fe_3O_4 nanoparticles (Massart & Cabuil, 1987). In addition, it has been proven that by adjusting the pH and the ionic strength of the precipitation medium, it is possible to control the mean size of the particles over the magnitude of one order (from 2 to 15 nm) (Tartaj *et al.*, 2003). Hariani *et al.* (2013) prepared superparamagnetic Fe_3O_4 nanoparticles through the co-precipitation of ferric and ferrous ions with a molar ratio of 1:2 under the presence of N_2 gas for dye removal. The synthesized Fe_3O_4 nanoparticles presented narrow size distribution in the range between 5 to 20 nm with relatively high M_s of 89.46 emu/g at room temperature which was very close to the M_s value of bulk Fe_3O_4 (92 emu/g). The reaction process was carried out by precipitating the $FeCl_3$ and $FeCl_2$ with NaOH under vigorous stirring at 30°C, followed by aging process at 70°C for 5h and the pH of solution was kept at ± 12 .

The reaction mechanism of the latter method is simple as shown in Eq. (5). The reaction simply involves the precipitation of iron hydroxides, followed by the formation of iron oxides due to low water activity. The overall reaction mechanism is a dynamic equilibrium equation in which the formation of Fe_3O_4 nanoparticles is based on $[Fe^{2+}]$, $[Fe^{3+}]$ and $[OH^-]$ (Mascolo *et al.*, 2013). Typically, the precipitation reaction is designed to mix Fe^{2+} and Fe^{3+} in a molar ratio of 1:2, which is the exact stoichiometry for Fe_3O_4 (Gorski & Scherer, 2010). Moreover, the final $[OH^-]$ concentration is related to the pH and amount of alkaline solution used, where the pH range between 8 and 14 is necessary for complete precipitation.



The concentration and size of the magnetic nanoparticles of this method are much depended on the type of iron salts used (such as chlorides, nitrates and sulfates), ratio of ferric to ferrous ions, pH value, reaction temperature, ionic strength of the media, as well as other influencing factors such as stirring and dropping rates of alkaline

solution (Chu & Hou, 2017; Majidi *et al.*, 2014). By controlling the reaction parameters, it is possible to synthesize superparamagnetic nanoparticles in the range between 2 and 15 nm (Majidi *et al.*, 2014). It is also essential to ensure the reaction is carried out under inert gas protection in which it does not only protect the Fe₃O₄ nanoparticles against critical oxidation but also reduce the particle size (Laurent *et al.*, 2008).

Table 1 summarizes the influencing parameters of co-precipitation method which can control the nucleation and growth of Fe₃O₄ nanoparticles and thus, affecting the Fe₃O₄ nanoparticles properties such as particle size and M_s. It can be observed that the increase in pH of solution with amount of base can restrain the growth of Fe₃O₄ nanoparticles, resulting in smaller particle size and lower M_s (Mahdavi *et al.*, 2013; Mascolo *et al.*, 2013). Moreover, the particle size can be reduced with lower reaction temperature due to the expedition movement of particles that caused the growth rate to slow down (Khan *et al.*, 2011). In addition, Madhavi and his research team studied the synthesis of Fe₃O₄ nanoparticles with different starting reaction temperatures ranging from 25 to 85 °C. The team successfully synthesized the smallest Fe₃O₄ nanoparticles (8.3nm) with the starting reaction temperature of 45 °C. They claimed that the extent of aggregation of Fe₃O₄ nucleus was reduced by increasing the starting reaction temperature from 25 to 45 °C, thus smaller Fe₃O₄ nanoparticles were obtained. However, the growth of Fe₃O₄ nucleus was promoted when the starting reaction temperature was higher than 45 °C,

resulting in larger particle size of Fe₃O₄ nanoparticles (Mahdavi *et al.*, 2013).

On the other hand, Khan *et al.* (2011) and Mahdavi *et al.* (2013) also found that the particle size of Fe₃O₄ nanoparticles was decreased with increasing stirring rate due to a higher degree of agitation that caused the energy to be transferred efficiently to the suspension medium and dispersed the reaction solution into smaller droplets. In addition, Pereira and coworkers (2012) discovered that isopropanolamine (MIPA) and diisopropanolamine (DIPA) could be employed as both alkaline and complexing agents in co-precipitation process to restrain the particle growth and provide higher surface spin order. In summary, particle size of Fe₃O₄ nanoparticles could be well controlled by replacing the alkanolamines (such as MIPA and DIPA) with a traditional base to obtain pH solution of around 12, as well as by employing lower reaction temperature (from 25 to 45 °C) and higher stirring rate (from 600 to 800 rpm).

Sol-gel synthesis

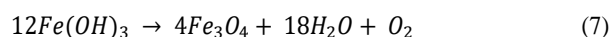
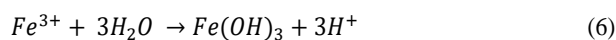
Sol-gel synthesis is a conventional wet chemical method that widely used for the preparation of nanosized metal oxides. In sol-gel processing, a 'sol' of nanometric particles is prepared through the hydroxylation and condensation of the molecular precursor (Chu & Hou, 2017; Hasany *et al.*, 2013; Teja & Koh, 2009). The further aging process of the nanodispersed 'sol' will lead to the growth of particles and

Table 1 Summary of the influencing parameters of chemical co-precipitation method for magnetic Fe₃O₄ nanoparticles synthesis.

Influencing parameters	Base solution	Reaction conditions		Ageing conditions		pH	Particle size (nm)	M _s ^{300K} (emu/g)	H _c (kOe)	Note	Ref							
		Stirring rate (rpm)	Temp. (°C)	Temp. (°C)	Time													
pH values	NH ₄ OH	800	45	80	1 h	8.0	11.8	-	Nil	Smallest particle size occurred at pH 11	(Mahdavi <i>et al.</i> , 2013)							
						9.0	9.0	-	Nil									
						10.0	7.8	-	Nil									
						11.0	9.3	-	Nil									
Reaction temp.	NaOH	500	r.t.	r.t.	3 h	10.3	11.5	75.3	Nil	↓particle size with ↑pH value	(Mascolo <i>et al.</i> , 2013)							
						11.9	11.2	71.6	Nil									
						12.1	11.0	69.8	Nil									
						12.2	10.9	69.4	Nil									
						12.6	10.7	68.3	Nil									
						12.0	7.5	-	-			↑particle size with ↑reaction temp.	(Khan <i>et al.</i> , 2011)					
600	60	60	30 min	12.0	10.3	-	-											
600	80	80	30 min	12.0	11.6	-	-											
Stirring rate	NaOH	600	80	80	30 min	12.0	11.6	-	-	↓particle size with ↑stirring rate	(Khan <i>et al.</i> , 2011)							
						1100	80	80	30 min			12.0	8.0	-	-			
						NH ₄ OH	400	45	80			1 h	11.0	9.4	78.0	Nil	↓particle size with ↑stirring rate	(Mahdavi <i>et al.</i> , 2013)
							600	45	80			1 h	11.0	8.3	70.0	Nil		
Type of base solution	NaOH	-	r.t.	r.t.	2 h	11.0	8.6	58.0	Nil	Alkanolamines good in control particle size	(Pereira <i>et al.</i> , 2012)							
						MIPA	-	r.t.	r.t.			2 h	11.0	6.3	64.8	Nil		
						DIPA	-	r.t.	r.t.			2 h	11.0	4.9	60.4	Nil		
						-	-	r.t.	r.t.			2 h	11.0	4.9	60.4	Nil		

Abbreviations: NH₄OH, Ammonium hydroxide; NaOH, Sodium Hydroxide; MIPA, Isopropanolamine; DIPA, Diisopropanolamine

form a three-dimensional metal oxide network, denominated as 'gel'. Additional heat treatment to the 'gel' is necessary to achieve the final crystalline state. For the preparation of Fe₃O₄ nanoparticles, Fe³⁺ ions of the precursor are hydrolyzed and condensed, based on reaction mechanism shown in Eq. (6) and (7) respectively. From the equation, Fe³⁺ ions are readily hydrolyzed and condensed to form ferrous hydroxides or oxides.



Previously, the starting chemical solution or precursor employed for sol-gel synthesis is the metal alkoxides of the desired metal oxides. Metal alkoxides have high endurance towards hydrolysis process and give highly crystalline and uniform size of metal oxides nanoparticles

(Qi et al., 2010; Xu et al., 2007). However, this alkoxides sol-gel synthesis method is not applicable to large-scale and economical production because of the complicated synthetic procedures and the commonly used reagents are poisonous and expensive (Owens et al., 2016). In order to solve the limitations of alkoxides sol-gel synthesis method, metal salts such as chlorides, nitrates and acetates are used as the precursor in the later sol-gel synthesis method. Gash et al. prepared nanostructured iron (III) oxides (Fe_2O_3) monoliths through sol-gel synthesis method with an inexpensive reagent of iron (III) chloride as starting material (Gash et al., 2001). A few years later, Tang et al. (2004) synthesized nanostructure magnetite (Fe_3O_4) thin film using the same synthetic procedures and reagents. However, they found that pure magnetite could not be obtained by using iron (III) chloride as the precursor due to the formation of impurities such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) during synthesis process, thus restricting its usefulness in applications.

With the latest synthetic technique of sol-gel synthesis combined with annealing under vacuum, pure Fe_3O_4 nanoparticles have been successfully prepared using inexpensive, nontoxic ferric nitrate and ethylene glycol as a precursor (Aftabtalab et al., 2014; Setina et al., 2013; Sundar & Piraman, 2013; Xu et al., 2007). Vacuum annealing is an additional heat treatment to the nanoparticles that yielding nanosized Fe_3O_4 powders and at the same time avoiding the oxidation of magnetite to iron (III) oxides such as maghemite and hematite. Magnetic ordering of Fe_3O_4 nanoparticles prepared by sol-gel synthesis is highly depended on the phases formed and the particle volume fraction, as well as very sensitive to particle size distribution and dispersion (Hasany et al., 2013). Therefore, parameters that influence the size distribution and dispersion of particles such as the concentration of precursor employed and annealing period and temperature, have attracted interest from many researchers.

Table 2 depicts the summary of influencing parameters of the sol-gel method for magnetic Fe_3O_4 nanoparticles synthesis. Most of the studies reported that Fe_3O_4 nanoparticles with particle size < 20nm possess superparamagnetic properties at room temperature. However, a

study by Xu et al. showed that the superparamagnetic properties could only be achieved by Fe_3O_4 nanoparticles of size < 10nm. As shown in this table, Sundar and Piraman (2013) successfully proved that the size of nanoparticles was tailored by precursor concentration, where the increase of precursor concentration would enhance the nucleation rate and promote particles growth, thus resulted in larger particle size and higher M_s . Moreover, Xu et al. (2007), Qi et al. (2010), Sundar and Piraman (2013) and Shaker et al. (2013) also reported that crystallinity was improved at higher annealing temperature and consequently, the agglomeration of particles was decreased tremendously. In addition, Qi et al. (2010) found that the size of Fe_3O_4 nanoparticles was increased and crystallinity was improved with extending annealing period. They also believed that it was possible to obtain narrow nanoparticle size dispersion by decreasing the annealing period under vacuum. In brief, magnetic Fe_3O_4 nanoparticles with smaller particle size can be synthesized through sol-gel synthesis method using higher precursor concentration (1 M solution), lower annealing temperature (from 200 to 250°C) and shorter annealing time (from 1 to 2 hours).

Thermal decomposition

Thermal decomposition is a synthesis approach that involved high temperature to prepare narrow size distribution and highly crystalline magnetic Fe_3O_4 nanoparticles. The precursors used in thermal decomposition process are categorized into two classes, which are the organometallic compounds of iron (such as iron (III) acetylacetonate and iron (III) N-nitrosophenylhydroxylamine) and the organic surfactant and solvents (such as oleic acid, oleylamine, phenyl ether, benzyl ether and 1-octadecene). One or more organic surfactants and solvents are mixed and added in the reaction process as a stabilizer to obtain monodispersed Fe_3O_4 nanoparticles. The stabilizer can decelerate the nucleation process and affect the adsorption of additives on the nuclei and growth of the nanocrystal. This may restrain the growth of particles and favor the formation of small Fe_3O_4 nanoparticles (Majidi et al., 2014).

Table 2 Summary of the influencing parameters of sol-gel method for magnetic Fe_3O_4 nanoparticles synthesis.

Influencing parameters	Precursors	Annealing temp. (°C)	Particle size (nm)	M_s^{300K} (emu/g)	H_c^{300K} (kOe)	Note	Ref
Precursor conc.	0.2M solution of ferric nitrate dissolved in ethylene glycol	200	7.8	-	-	↑particle size and M_s with ↑precursor concentration	(Sundar & Piraman, 2013)
	1M solution of ferric nitrate dissolved in ethylene glycol	200	13.8	-	-		
Annealing temp.	0.2 mol of ferric nitrate dissolved in 100 mL ethylene glycol	200	18.0	31	0.04	↑particle size, M_s and H_c value with ↑annealing temp.	(Xu et al. 2007)
		250	-	47	0.07		
		400	25.0	60	0.23		
	0.01 mol of ferric nitrate dissolved in 10 mL ethanol and mixed with 14 M solution of propylene oxide	250	-	-	-	XRD patterns showed ↑particle size, M_s and H_c value with ↑annealing temp.	(Qi et al., 2010)
		300	10.0	-	-		
		400	-	-	-		
1 M solution of ferric nitrate dissolved in ethylene glycol	200	13.8	36	Nil	↓particle agglomeration with ↑annealing temp.	(Sundar & Piraman, 2013)	
	300	21.3	48	Nil			
	400	28.7	55	Nil			
Ferric nitrate and ethylene glycol mixed with molar ratio of 6:46	200	28.7	-	-	↑particle size with ↑annealing temp.	(Shaker et al., 2013)	
	300	30.5	-	-			
	400	34.9	-	-			
Annealing period	1M solution of ferric nitrate dissolved in ethylene glycol	300; 1 h	-	-	XRD patterns showed ↑particle size and crystallinity with ↑annealing period	(Qi et al., 2010)	
		300; 2 h	10	-			-
		300; 3 h	-	-			-

Fe_3O_4 nanoparticles produced through this method are usually well-controlled in size and shape because they are well crystallized with high saturation moment at high temperature (Wu et al., 2008; Ali et al., 2016). The first report using the thermal decomposition of $\text{Fe}(\text{acac})_3$ in the presence of oleylamine and oleic acid acted as surfactants to produce Fe_3O_4 nanoparticles was reported by Sun and Zeng in 2002. Reducing agent (1,2-hexadecanediol) and organic solvents (phenyl ether and benzyl ether) with high boiling point (> 250°C) were added

in the reaction process with the purpose to partially reduce Fe^{3+} to Fe^{2+} and achieve high temperature respectively (Sun & Zeng, 2002). They successfully synthesized Fe_3O_4 nanoparticles with particle size that precisely controlled between 4 to 16 nm.

In 2009, this procedure was further simplified by Xu and his team. They found that oleylamine could serve as solvent, surfactant and at the same time as reducing agent, thus the reaction process could be simplified by using fewer chemicals. In this simplified procedure,

Fe(acac)₃ was heated with oleylamine and benzyl ether at 300°C for complete decomposition. Moreover, the size of synthesized Fe₃O₄ could be precisely controlled in between 7 to 10 nm by varying the volume ratio of oleylamine and benzyl ether. The latter procedure was much more cost-effective as compared to the earlier method as the oleylamine was inexpensive and strong enough to act as a reducing agent, and could be used to replace other expensive reducing agents such as 1,2-hexadecanediol (Xu *et al.*, 2009). Besides that, Fe₃O₄ nanoparticles capped with oleylamine have weaker bonding with nanoparticle surface as compared to oleic acid, thus could be easily replaced by another ligand for surface modifications (Xie *et al.*, 2006).

In thermal decomposition process, the formation of high monodispersed, narrow size distribution and highly crystalline magnetic Fe₃O₄ nanoparticles are much depended on the nucleation and particle growth steps under high temperature (Wu, *et al.*, 2008; Wu, *et al.*, 2015; Lassenberger, *et al.*, 2017). Therefore, the size, morphology and magnetic behavior of nanoparticles can be easily controlled by adjusting the reaction temperature and time as well as the concentration and ratio of the solvent-surfactant mixture (Ghazanfari *et al.*, 2016; Laurent *et al.*, 2008). The M_s of synthesized magnetic nanoparticles can be improved with higher reaction time and temperature. However, the size and size distribution of nanoparticles can also be significantly affected by higher reaction time and temperature. Therefore, the preparation of small particle size and narrow size distribution magnetic nanoparticles with high M_s through higher reaction time and temperature are challenging.

Table 3 summaries the parameters that influence the average particle size and magnetic behavior of synthesized Fe₃O₄ nanoparticles through thermal decomposition of Fe(acac)₃. Maity *et al.* (2008) studied the effects of reaction temperature and time, surfactant as well as solvent on the preparation of high M_s value Fe₃O₄ nanoparticles with particle size maintained in an acceptable range of size distribution. They found that the growth rate and crystallinity were increased with increasing reaction temperature. However, wide size distribution was observed at higher reaction temperature which was mainly caused by

uncontrolled crystal growth at the higher reaction temperature. On the other hand, increased average particle size and wider size distribution were occurred at longer reaction time. This phenomenon was known as 'Ostwald ripening' where small particles became smaller and large particles became larger with extending reaction time. Thus, it could be concluded that the particle size and M_s of Fe₃O₄ nanoparticles were increased with increasing reaction time and temperature, but at the same time induced the undesired widening of size distribution. Therefore, Maity and his coworkers adopted the effect of surfactant and solvent for the synthesis of Fe₃O₄ nanoparticle with narrow size distribution. They found that the size distribution of particles was improved in the presence of oleic acid even at the higher reaction time and temperature (Maity *et al.*, 2008). This could be due to the selective adsorption of coordinating surfactant on the particle surface, thus resulted in uniform growth of particles.

In 2009, another research team further studied the effect of solvent on the size and size distribution as well as M_s value under increasing reaction time and temperature. The particle size was increased as a result of increasing reaction time and temperature, but the size distribution of particles was well controlled in the absence of the solvent. They claimed that the growth of particles was confined in the absence of the solvent due to the reason that the particles were surrounded with very dense stabilizing surfactant environment which restrained the growth of particles. Besides that, Maity *et al.* (2009) also found that the average particle size of synthesized Fe₃O₄ nanoparticles could be controlled by varying the reaction temperature. By synthesizing Fe₃O₄ nanoparticles at a higher reaction temperature of 330°C with a reaction time of 4 h, nanoparticles with larger particle size and higher M_s were obtained. In short, smaller particle size and narrow distribution magnetic Fe₃O₄ nanoparticles with higher M_s value could be synthesized through solvent-free thermal decomposition reaction by decomposing Fe(acac)₃ with a mixture of oleic acid and oleylamine under higher reaction temperature (from 300 to 330°C) and longer reaction time (from 2 to 4 hours).

Table 3 Summary of the influencing parameters of thermal decomposition method for magnetic Fe₃O₄ nanoparticles synthesis.

Influencing parameters	Solvent surfactant mixture	Reaction conditions		Particle size (nm)	M _s ^{300K} (emu/g)	H _c ^{300K} (kOe)	Size distribution	Note	Ref
		Temp. (°C)	Time (h)						
Reaction Temp.	BET + OM	220	2	3	46	Nil	narrow	↑particle size with ↑reaction temp.	(Maity <i>et al.</i> , 2008)
	PET + OM	265	2	5	51	Nil	narrow		
	BET + OM	300	2	9	60	Nil	relatively wide		
	ODE + OM	330	2	24	74	Nil	wide		
Reaction time	BET + OM	300	0.5	7	57	Nil	relatively narrow	'Ostwald ripening' occurred	
	BET + OM	300	4	12	65	Nil	very wide		
Surfactant	BET + OM + OA	300	0.5	6	-	Nil	very narrow	Size distribution improved in the presence of OA	
	BET + OM + OA	300	4	14	67	Nil	very narrow		
Absence of solvent	OM	300	0.5	8	-	Nil	narrow	Growth of particles was confined	
	OM	300	4	10	65	Nil	relatively narrow		
Absence of solvent	OM + OA	300	0.5	5	-	Nil	very narrow	'Ostwald ripening' did not occur	(Maity <i>et al.</i> , 2009)
	OM + OA	300	2	6	58	Nil	narrow		
	OM + OA	300	24	11	71	Nil	narrow		
	OM + OA	330	0.5	7	-	Nil	relatively narrow		
	OM + OA	330	4	10	76	Nil	relatively narrow		

Abbreviations: OM, Oleylamine; OA, Oleic acid; BET, Benzyl ether; PET, Phenyl ether; ODE, 1-Octadecene

Table 4 Comparison of the three different synthesis methods for the preparation of magnetic Fe₃O₄ nanoparticles (Hasany et al., 2013; Maity et al., 2009; Wu et al., 2015; Xu et al., 2014; Zhao et al., 2008).

	Chemical co-precipitation	Sol-gel synthesis	Thermal decomposition
Reaction and conditions	Simple, inert atmosphere	Complicated, ambient	Complicated, inert atmosphere
Reaction temperature (°C)	25 – 70	25 - 80	100 – 350
Reaction period	Hours	Hours – days	Hours
Size distribution	Relatively narrow	Narrow	Very narrow
Shape control	Not good	Good	Very good
Yield	High/ scalable	Medium	High/ scalable
Advantages	<ul style="list-style-type: none"> • Simple and efficient • Require less hazardous chemical and procedure • Mass production possibility in industrial scale 	<ul style="list-style-type: none"> • Possible to obtain materials with a predetermined structure • Good control of the microstructure and the homogeneity of the reaction products • Possible to embed molecules • Precisely control in size, shape, aspect ratio and internal structure 	<ul style="list-style-type: none"> • Easy to control particle size and shape • High crystallinity production
Disadvantages	<ul style="list-style-type: none"> • Not suitable for the preparation of accurate stoichiometric phase • Utilization of strong base • Broad size distribution 	<ul style="list-style-type: none"> • Release large amount of alcohol during calcination process • Require post-treatment with high annealing temperature and vacuum condition • Weak bonding, low wear-resistance and high permeability 	<ul style="list-style-type: none"> • Require high reaction temperature • Require relatively expensive organometallic compound as precursor • Products dissolve in non-polar solvent

COMPARISONS

The comparison of the three synthetic methods (sol-gel synthesis, chemical co-precipitation and thermal decomposition) for the magnetic Fe₃O₄ nanoparticles preparation was shown in Table 4. Among these three approaches, chemical co-precipitation is the most effective, cheap and simplest pathway to obtain magnetic Fe₃O₄ nanoparticles. However, the particles have the tendency to agglomerate during the process which can hamper their interfacial area, thereby hindering their magnetism and dispersibility. Thus, it is difficult to obtain high crystalline and narrow particle size through chemical co-precipitation method. On the other hand, sol-gel synthesis is an alternative method for the production of Fe₃O₄ nanoparticles at low temperature and ambient conditions with good control in particle size at specific conditions. Nevertheless, the sol-gel synthesis method releases a large amount of ethanol in the reaction and thus, safety considerations are required during the synthesis process. Besides that, it also requires a post-treatment with high annealing temperature under vacuum condition which is energy consuming and expensive. Lastly, highly monodispersed, narrow size distribution and highly crystalline Fe₃O₄ nanoparticles can be synthesized through thermal decomposition. However, this synthesis method is also energy consuming because high temperature is required during reaction process.

CHARACTERIZATION OF MAGNETIC Fe₃O₄ NANOPARTICLES

For a better understanding of surface properties, comprehensive characterization techniques are used to study the morphology, particle size, size distribution, composition, and magnetic properties of superparamagnetic Fe₃O₄ nanoparticles. The fundamental techniques employed to investigate the magnetic Fe₃O₄ nanoparticles includes FTIR, EDX, XRD, SEM, TEM, DLS, VSM and SQUID. The details of characterization techniques for the assessment of the magnetic Fe₃O₄ nanoparticles physicochemical properties were shown in Table 5.

CONCLUSION AND FUTURE PERSPECTIVE

The recent information on the synthesis and characterization techniques for magnetic Fe₃O₄ nanoparticles have been discussed in this review. In recent years, there are many research articles have been published in this field and significant development has been achieved. This review highlights the three conventional wet chemical synthetic methods including chemical co-precipitation, sol-gel synthesis and thermal decomposition. The three methods are compared in terms of mechanism, reaction process and influenced factors that affect particle size and size distribution, hence defining the magnetic properties of Fe₃O₄ nanoparticles. However, absolute control over the structural

Table 5 Characterization techniques for the assessment of the physicochemical properties of magnetic Fe₃O₄ nanoparticles.

Modality	Analyzed physical and chemical properties	Advantages	Limitations	Ref
FTIR	Chemical bonding and functional group	<ul style="list-style-type: none"> • Rapid and cheap measurement • Suitable for gas, liquid, bulk and powdered solid samples, and thin films 	Sensitivity for nanoscale analysis is comparatively low	(Barrios <i>et al.</i> , 2012; Gaffney <i>et al.</i> , 2002)
EDX	Chemical elements, estimate chemical proportion, and overall mapping	<ul style="list-style-type: none"> • A full elemental spectrum can be obtained in only a few seconds • Can be used in semi-quantitative mode to determine the chemical composition by peak-height ratio relative to a standard • Can be employed together with other characterization technique, such as SEM and TEM 	<ul style="list-style-type: none"> • Cannot detect the lightest elements • Less commonly used for actual chemical analysis • Long analysis time 	(Joshi <i>et al.</i> , 2008)
XRD	Shape, size and structure	<ul style="list-style-type: none"> • Well-organized modalities • High spatial resolution at atomic level 	<ul style="list-style-type: none"> • Only for crystalline materials • Only one binding or conformation site is analysed • Accessibility is lower compared to electron diffraction 	(Felici, 2002; Sharma <i>et al.</i> , 2012)
SEM	Shape, size and dispersion	<ul style="list-style-type: none"> • SEM image shows the surface structure of the sample 	<ul style="list-style-type: none"> • Requirement of conducting sample or coating conductive materials • Only for dry samples 	(Cornell & Schwertmann, 2000; Leonard <i>et al.</i> , 2012)
TEM	Shape heterogeneity, size and dispersion	<ul style="list-style-type: none"> • Higher spatial resolution than SEM • Direct measurement of size and shape of nanoparticles • TEM image shows the internal structure of the sample 	<ul style="list-style-type: none"> • Ultrathin samples are needed • Samples required in non-physiological states • Equipment is expensive 	(Cornell & Schwertmann, 2000; Hurley <i>et al.</i> , 2015; Leonard <i>et al.</i> , 2012)
DLS	Particle size, size distribution, and agglomeration based on hydrodynamic	<ul style="list-style-type: none"> • Constructive way for rapid and more consistent measurement • Moderate expenses on equipment 	<ul style="list-style-type: none"> • Restricted size determination • Unable to distinguish between nanoparticles with slight differences in diameter • Unable to resolve polydisperse samples precisely 	(Ali <i>et al.</i> , 2016; Fissan <i>et al.</i> , 2014)
VSM	Magnetic properties	<ul style="list-style-type: none"> • High sensitivity up to 10⁻⁶ emu • Fully automated • Suitable for liquid or solid phase in bulk, powder, nanoparticle and thin film forms of samples 	<ul style="list-style-type: none"> • Require correction for demagnetizing field • Applicable only for small samples 	(Grössinger, 2008)
SQUID	Magnetic properties	<ul style="list-style-type: none"> • High sensitivity up to 10⁻⁸ emu • Suitable for thin and single grain sample with weak magnetic features • The most sensitive devices in analysing magnetic properties • Applicable for temperature range up to 400K 	<ul style="list-style-type: none"> • Noise sensitive • Complex handling • Time consuming 	(Grössinger, 2008; Hurley <i>et al.</i> , 2015)

Abbreviations: FTIR, Fourier-transform infrared spectroscopy; EDX, energy dispersive x-rays analysis; XRD, X-ray diffraction; SEM, scanning electron microscope; TEM, transmission electron microscope; DLS, dynamic light scattering; VSM, vibrating sample magnetometer; SQUID, superconducting quantum interference device

characteristics such as size, size distribution, shape and crystallinity remains a challenge. These structural characteristics have critical influences on the electrical, mechanical, optical and magnetic properties of Fe₃O₄ nanoparticles, which in turn will determine their performance in various applications.

Moreover, the magnetic properties such as magnetization saturation, the magnetic susceptibility of Fe₃O₄ nanoparticles are governed by their particle size and significantly affected by the size

distribution and agglomeration of particles. From the discussion above, it can be seen that the research developments on both chemical co-precipitation and sol-gel synthesis methods are focused more on size reduction of the Fe₃O₄ nanoparticles without considering the size distribution and magnetic properties. On the other hand, the development of thermal decomposition methods is based on the size reduction while maintaining the narrow size distribution and high magnetization saturation. Being the most commonly used magnetic

nanoparticles, it is utterly important to identify the magnetic properties of Fe₃O₄ nanoparticles in order to cater to specific requirements of different applications. However, there have been limited studies on the magnetic properties of the synthesized superparamagnetic Fe₃O₄ nanoparticles. Therefore, future study should be focused on the synthesis of superparamagnetic Fe₃O₄ nanoparticles with high magnetization saturation and magnetic susceptibility while retaining their desired particle size and size distribution.

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