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Some wet routes for synthesis of hematite nanostructures

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Increased attention has been paid to the synthesis of hematite nanoparticles recently due to its properties and application in various fields of modern technology. Various methods (aqueous and non-aqueous) have been applied in order to produce hematite nanostructures of required size and morphology suitable for these various applications. The aqueous route has been found to be simpler and more versatile than the non-aqueous routes. This paper reviews some of the most commonly used wet route for the synthesis of hematite nanoparticles and shows that the sol-gel and hydrothermal methods are simple and versatile, capable of producing narrow particle size ranges with good control of morphology and high yield in contrast to precipitation and microemulsion methods.

Key words: Nanoparticles, goethite, hematite, ferrihydrite, synthesis.

INTRODUCTION

Nanoparticles refer to materials whose size in at least one dimension is between 2-99 nm (Zhang and Webster, 2009). Nano-structured materials have generated a lot of interest over the last two decades due to their attractive properties and wide range of application (Mohapatra and Anand, 2010; Li et al., 2009). The need to control the size range and morphology and hence the properties of these nanomaterials have led chemists to develop various routes for synthesis of materials with morphology suitable for application in these various fields. The most utilized transition metal oxide of technological importance are the Iron oxides with sixteen known oxide and oxy-hydroxide (that is, five polymorphs of FeOOH (that is, goethite α-FeOOH, lepodocrocite γ- FeOOH, akaganite β- FeOOH feroxyhyte, δ- FeOOH and ferrihydrite FeOOH of which goethite is the most stable), four of Fe_2O_3 (that is, hematite α- Fe_2O_3, maghemite γ- Fe_2O_3 then β- Fe_2O_3 and ε- Fe_2O_3 which are the less occurring ones) $Fe(OH)_3$, $Fe(OH)_2$, $FeHO_8 \cdot 4H_2O$, Fe_3O_4 (magnetite) and FeO (wusite)) some of which are not only crystalline but show interesting photolytic, electric and magnetic properties (Schwertmann and Cornell, 1991; Mohapatra and Anand, 2010). Hematite, an n-type Semiconductor (Energy transfer band gap = 2.1eV), being the most thermodynamically stable of these oxides coupled with its low cost and nontoxicity, has been the most investigated for application in a wide range of fields (e.g. as pigments, in catalysis, in photo electrochemical water splitting, gas sensors, electromagnetic, optical, and biomedical devices) (Guo et al., 2011; Lian et al., 2009). Various techniques have been used to fabricate hematite nanomaterials of desired morphology (e.g. nanorods, nanofibres, nanowires, etc.) for various applications. Methods that have been employed for hematite synthesis may either be solution based/ wet or non solution based /dry. Wet synthesis include methods such as thermolysis/forced hydrolysis, precipitation/co-precipitation, which in the case of hematite might involve synthesis of a precursor (A ferrihydrite or goethite or both) followed by dehydroxylation at high temperature, or Sol-gel synthesis, which involves dissolution of the Fe^{3+} and an organic compound to form the sol, concentrating

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the sol by removal of water to form the gel and subsequent thermal treatment to obtain the required product (Pandey and Mishra, 2011; Pomogailo, 2005), or hydro/solvothermal synthesis in which α-Fe$_2$O$_3$ is precipitated at high temperature (ranging from 160 to about 280°C). The dry methods could be either thermal decomposition/combustion processes (reaction occur in the vapour phase. e.g. chemical vapour condensation, laser pyrolysis and arc discharge) (Tavakoli et al., 2007) or solid state chemical reaction (reactions take place in solid state e.g. mechanochemical high energy or ball milling, it involves milling of the precursors at high energy to form nanomaterials) (Karami, 2010; Tavakoli et al., 2007). This paper reviews some of the various solution based synthetic routes that have been used to synthesize hematite nanoparticles of various sizes and morphology.
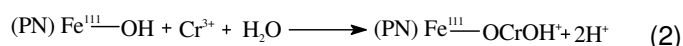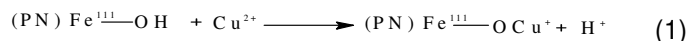
Thermolysis/forced hydrolysis

The hydrolysis of soluble metal ions in solution can be achieved by either heat (thermolysis) (Fu et al., 2011) or by the use of mild or concentrated alkali (forced hydrolysis) (Raming et al., 2002). A very simple thermolysis route for hematite synthesis was used by Plaza et al. (2001) to prepare granular nano-hematite particles of size range between 100-200 nm. FeCl$_3$.7H$_2$O (0.018 M) was dissolved in water and HCl (0.001 M) added and the solution heated at 100°C for 24 h. The suspension was washed repeatedly with milli-Q water to remove unreacted species.

Chen and Li (2010) used a similar method with slight modification to produce hematite nanoparticles with granular shape and size of about 75 nm. HCl (About 0.05 ml) and FeCl$_3$ (2.7 g) were added to 500 ml of deionzed water preheated to 90°C. The mixture was then transferred to an oven at 100°C for 2 days to obtain hematite nanoparticles. Size control can be achieved in this method by varying certain experimental parameters. The addition of some tri- or tetravalent cations, addition of some anions and varying the pH of the solution play an important role, the cations decouple the nucleation and growth stages leading to narrower size range, at pH $\leq$ 3, oxolation enhance metal oxide formation and chloride concentration determines which precursor (ferrihydrite/akaganite) is formed before the final product (Jolivet et al., 2008).

This method as can be seen is very simple, cost effective and can produce granular nanoparticles with size range between 75-200 nm as is evident from the microgram. The forced hydrolysis method as described by Raming et al. (2002) was developed by Matijevic and co-workers (Kandori et al., 1998b; Raming et al., 2002) and has been extensively studied and used for fabrication of hematite nanoparticles of different sizes and morphology (Kandori et al., 1998a, b; 2000, 2002, 2008; Kazuhiko and Mai, 2011; Raming et al., 2002). It involves
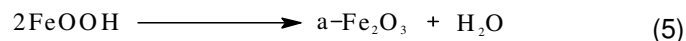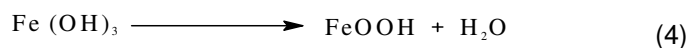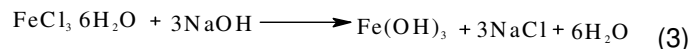
the hydrolysis of FeCl$_3$. 6H$_2$O in solution at a temperature of about 100°C with ageing which could last for a period of time (can last for several weeks depending on the period required to monitor growth) (Mohapatra and Anand, 2010). As earlier stated this method has been extensively studied and the factors effecting size and morphology have been high-lighted. Raming et al. (2002) for instance studied the effect of time and rate of precipitation/hydrolysis and showed that little changes to these parameters could lead to bigger sizes for the nanoparticles. Kandori and co-workers on the other hand have studied the effect of the presence of anions (Cl$^-$, F$^-$, NO$_3^-$ and Br$^-$), metal ions (Cu^{2+}, Co^{2+}, Ni^{2+} and Cr^{3+}), polyethylene glycol, the precipitation medium and the use of polyethylene amine surfactant and have shown variation in size and morphology of the hematite nanoparticles (Kandori et al., 1998b, 2000, 2002, 2008; Kazuhiko and Mai, 2011). The anions can influence particle morphology depending on the electronegativity of the anion and the concentration. Kandori et al. (2008) showed that the influence of anion on the particle morphology can be expressed in the following order: F$^-$ > Cl$^-$ > NO$_3^-$ $\approx$ Br$^-$. Anion presence can also lead to formation of β-FeOOH which could inhibit hematite formation. The influence of the cations on the other hand precedes via formation of surface complexes with the hydroxyl groups of polynuclear complexes (PN) (Equations 1 and 2 shows coupling of metal ion and release of hydrogen ion). Some of the metals can also be incorporated into the crystals as dopants.

$$(PN) Fe^{III}—OH + Cu^{2+} \longrightarrow (PN) Fe^{III}—OCu^+ + H^+ \quad (1)$$

$$(PN) Fe^{III}—OH + Cr^{3+} + H_2O \longrightarrow (PN) Fe^{III}—OCrOH^+ + 2H^+ \quad (2)$$

Precipitation/co-precipitation

Precipitation/co-precipitation refers to the addition of alkali to a solution of soluble metal salts to form precipitates which are then aged at certain temperatures to obtain the required product. Fabrication of hematite nanoparticles through this method proceeds via ferrihydrite or goethite nanoparticles (Equations 3-5) which are then converted to hematite nanoparticles by ageing for a period of time. The method has been described in details by Atkinson et al. (1967) and has been adopted and modified by other researchers. Coprecitation has two basic advantages, first is its simplicity and second is the fact that the yield is usually very high, but size and morphology control is however, difficult (Atkinson et al., 1967; Mohapatra and Anand, 2010; Schwertmann and Cornell, 1991; Yue et al., 2010). Three different stages can be identified in the fabrication of hematite via coprecipitation. (1) Nucleation stage which is normally rapid and (2) the growth stage which is

slow and at temperatures between 60 to 80°C. Both these stages constitute the precipitation leading to goethite nanoparticles formation (Varanda et al., 2002; Mohapatra and Anand, 2010). A third stage would involve dehydroxylation of the prepared goethite to form hematite according to Equation (2).

$$FeCl_3\,6H_2O + 3NaOH \longrightarrow Fe(OH)_3 + 3NaCl + 6H_2O \quad (3)$$

$$Fe(OH)_3 \longrightarrow FeOOH + H_2O \quad (4)$$

$$2FeOOH \longrightarrow a-Fe_2O_3 + H_2O \quad (5)$$

Hematite formation from ferrihydrite would involve dehydration/dehydroxylation followed by some structural rearrangement (Cornell and Schwertmann, 2006).

In a typical co-precipitation synthesis, a soluble iron salt (e.g. $Fe(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$, $Fe_2(SO_4)_3.H_2O$ etc.) is dissolved in aqueous medium and then precipitated using concentrated base (KOH, NaOH, TMAH etc.). The precipitates are then aged in the oven for about 24 to 48 h to obtain a mixture of goethite and hematite. Dry heating the product in a muffle furnace at a temperature higher than 250°C (250-400°C for 4 h) would yield pure hematite (Atkinson et al., 1967; Mohapatra and Anand, 2010; Nagano et al., 1992; Schwertmann and Cornell, 1991; Prasad et al., 2006). A simple coprecipitation procedure for goethite synthesis as described by Mustafa et al. (2009) and Mohapatra and Anand (2010) is as follows:

NaOH (10 M) was added to ferric nitrate (1 M) solution drop wise. The suspension obtained was aged at 70°C for 48 h in a polyethylene bottle. As earlier stated, controlling the size and morphology of nanoparticle in the coprecipitation synthesis is complicated and hematite morphology and size control is determined by the control of the morphology and size of the goethite precursor. Some researchers have developed ways to try to control growth and sometimes morphology of goethite prepared by coprecipitation.

Varanda et al. (2002) modified the Atkinson et al. (1968) route introducing two important modifications. The first was that they outlined the stages in goethite formation as (1) ferrihydrite precipitation, (2) goethite nucleation (at 40°C for 48 h) to allow for maximum goethite nuclei formation and more uniform final particles, (3) the growth of the goethite nanorods (at 60°C for 3 days). The second was the addition of sodium carbonate to adjust the pH to 10 and also to control the OH^- concentration to allow for more uniform growth. The result is a reduction in the axial ratio by a factor of about 0.5 and 0.25 for the length (Varanda et al., 2002). Subsequent calcinations (> 300) (Yue et al., 2010) would lead to formation of hematite with same morphology (Cornell and Schwertmann, 2006).

A surfactant, cetyltrimethylammonium bromide (CTAB) assisted synthesis of monodispersed α-FeOOH nanorods at ambient temperature was described by Yue et al. (2010) and with other surfactants (tetraethylammonium chloride (TEAC), polyvinylpyrrolidone (PVP), ethylene glycol (EG) sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS) together with simulation by Yue et al. (2011). The effect of temperature, pH, and surfactant type were studied. CTAB was found to be most effective and an optimum condition for monodispersed goethite and hence, hematite nanorods synthesis with size and morphology control can be described accordingly as follows:

Dissolve Iron(III) sulphate monohydrate (0.01 M) and CTAB (0.015 M) in 50 ml of de-ionized water and then heat at 80°C for about 20 min to dissolve the CTAB into a homogenous solution. Cool down the solution to room temperature (about 25°C) and then adjust the pH to between 8-12 using NaOH (1 M) to form precipitates (that is, $Fe(OH)_3$ or ferrihydrite (Equation 6). Leave suspension until it turns clear with brown precipitates at the bottom for over 24 h. Wash precipitates several times with HCl (0.1 M), then with distilled water and ethanol. Dry heat in a muffle furnace at above 300°C to convert to hematite.

$$Fe_2(SO_4)_3\,H_2O + 6NaOH \longrightarrow 2Fe(OH)_3 + 3NaSO_4 + H_2O \quad (6)$$
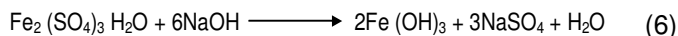
Another goethite route with good control of morphology for fabrication of hierarchical hematite was developed by Tong et al. (2011). They co-dissolved various ratios of D-(+)-glucose and $FeSO_4.7H_2O$ in 400 ml of deionized water in a 3-necked conical flask and refluxed at about 100°C for 12 h with stirring and constant air flow of 1.0 $Lmin^{-1}$. The goethite obtained was filtered off and washed with distilled water, dried in the oven at 90°C for 12 h and annealed at different temperatures (≥ 300°C) to produce hematite.

Sol-gel method

The sol-gel route of synthesis of metal oxides and other organic-inorganic hybrid materials has been shown to be extremely handy as well as flexible and can be used to fabricate nanomaterials with very good control over size and morphology (Pandey and Mishra, 2011; Pomogailo, 2005). The sol-gel method involves the addition of organic molecules (OMs) or polymers to colloidal dispersions of metal ions to form the sol, concentration of this sol by removal of the solvent (e.g. water) molecules to form the gel, followed by thermal treatment to obtain the product.

The forces (that is, van der Waals) hydrogen bond and hydrophobic interactions within functional groups (Pomogailo, 2005) acting between the ions, the OMs or polymers serve to control the reaction rates by controlling
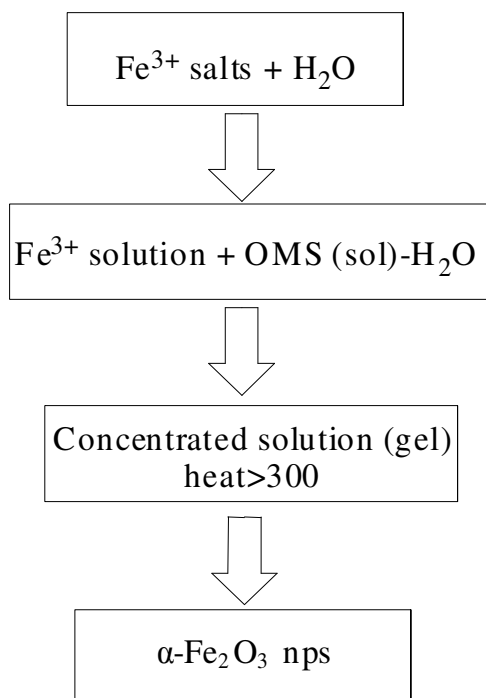
$$\boxed{Fe^{3+} \text{ salts} + H_2O}$$

$$\downarrow$$

$$\boxed{Fe^{3+} \text{ solution} + OMS \text{ (sol)-}H_2O}$$

$$\downarrow$$

$$\boxed{\text{Concentrated solution (gel)} \\ \text{heat}>300}$$

$$\downarrow$$

$$\boxed{\alpha\text{-}Fe_2O_3 \text{ nps}}$$

Figure 1. Flow chart of a sol-gel synthetic route.

the flow and homogeneity of the reactants within the reaction mixture and hence the nucleation process, they can also serve as templates and hence control the morphology of the material (Pandey and Mishra, 2011; Pomogailo, 2005). The following scheme (Figure 1) illustrates a simple sol-gel route for metal oxide synthesis.

Zhang et al. (2003) used the sol-gel route to prepare hematite nanoparticles starting from a 1:1.1 ratio of $Fe(NO_3)_3$ and citric acid. $Fe(NO_3)_3$ was dissolved in water followed by citric acid. The mixture was refluxed at 343K for 30 min with continuous stirring, the gel was obtained by rotary evaporation and then heat treated at various temperatures (423, 523, 623 and 800 K) in air for 2 h to obtain the product.

The X-ray diffractogram of the products annealed at different temperatures shows that γ-Fe_2O_3 appears to be dominant for products calcined at lower temperature while the α-Fe_2O_3 is the most stable at higher temperatures. The researchers concluded that with increase in the annealing temperature maghemite changes to hematite and particle size also increases (Zhang et al., 2003). Pawar et al. (2012) used similar method to synthesize hematite nanoparticles with slight modification and tested the effect of calcination temperatures on the Brunauer, Emmett and Teller (BET) surface area and photocatalytic properties of the materials. In this case they used a mixture of citric acid and oxalic acid in 1:1 ratio.

Produced gels were calcined at temperatures ranging between 450 and 650°C, the sizes of particles prepared was about 12.7 nm average and a rise in BET surface area was recorded for the particles with increase in temperature which peaks at 600°C (34.27, 37.75, 39.34 and 91.54 m^2/g for 400, 450, 500, 550 and 600°C respectively) and drops for materials prepared at 650°C (34.76 m^2/g), good photo catalytic activities were also observed for the particles at pH = 10 for the degradation of malachite green (Pawar et al., 2012). Other organic solvents that have been used in place of citric acid and/or oxalic acid are ethylene glycol EG (Ramesh et al., 2011; Gajovic et al., 2011) and polyvinylpyrrolidone (PVP) (Gupta et al., 2011), tetrahydrofuran (THF), pyridine, propylene with ethanol as solvent (Walker and Tannenbaum, 2006), methoxyethanol and ethanolamine (Aydin et al., 2012).

Hydrothermal/Solvothermal method

Hydrothermal synthesis refers to chemical reactions taking place at high temperature and pressure in a sealed vessel (usually in an autoclave or a Parr bomb) and in water as the solvent or other organic solvents in which case the term solvothermal becomes more appropriate (Burda et al., 2005; Feng and Xu, 2000; Mohapatra and Anand, 2010; Tavakoli et al., 2007). It is a well known method for synthesis of zeolite, molecular sieves, microporous ceramic nanocrystals and a host of other very important materials (Feng and Xu, 2000). Hydrothermal synthetic route exploits the fact that the physical and chemical properties of substances change at elevated temperatures, as reactants dissolve and become fluid various techniques are applied to control the size and morphology of the synthesized materials. These techniques could include templating, the use of structure directing agents, growth through crystal seeds and complexing (Feng and Xu, 2000). Several surfactants have been used to control the growth of crystals in the hydrothermal synthesis route, surfactants like cetyltrimethyl ammonium bromide (CTAB), polyvinyl pyrrolidone (PVP), sodium dodecyl sulfate (SDS), bis (2-ethylhexyl) sulfosuccinate (AOT), Igepal and Triton-X (Tavakoli et al., 2007), the pH of the reacting mixture can determine the final product (Li et al., 1998). Numerous investigations have been done on fabricating hematite nanostructures of different shapes and sizes which are suitable for various applications. A simple hydrothermal route for hematite synthesis can be described as follows:

Ammonium ferrous sulfate (100 ml, 0.1 M Fe) was placed together with 10 ml of 50% hydrazine hydrate in a Teflon lined autoclave of 200 ml capacity, the pH was adjusted to between 3-5 using 1.0 M H_2SO_4. The autoclave was maintained at 150°C for 4 h then cooled to room temperature naturally; red precipitates were obtained,

Table 1. Showing additives and conditions for some published hydrothermal synthetic routes for hematite nanoparticles.

Fe source used	Solvent/Additives	Temperature/time	Hematite NPs shape/size	References
$FeCl_3$	Carbamide, water, polyisobutylene bis-succinimide, SPAN80	150°C, 12-15 h	Nanorods, nanotubes/30-50 diameter, 500-1100 nm length	Liu et al. (2006)
$FeCl_3$	1,2-propanediamine	180°C/6 h	Nanorods	Li et al. (2009)
$FeCl_3 \cdot 6H_2O$	Sodium oleate, ethanol, oleic acid	180°C/12 h	Nanocubes, broad size distribution	Wang et al. (2007)
$FeCl_3$	3,3-thiodipropionic acid (TPA)	110-200, 6 h	Nanorods, microcapsule	Guo et al. (2011)
$Fe(NO_3)_3 \cdot 9H_2O$	Sodium citrate, urea, water	160°C,/10 h	Porous nanospheres	Gou et al. (2008)
$FeCl_3 \cdot 9H_2O$	Urea, Ethylene glycol (EG)	160°C/15 h	Hollow core shell hierarchical nanostructures	Cao et al. (2010)
$FeCl_3 \cdot 9H_2O$	Urea, tetrabutylammonium bromide (TBAB), EG	195°C/30 min	Flowerlike structure	Zhong et al. (2006)
$FeCl_3 \cdot 6H_2O$	Sodium acetate, acetic acid, water	200°C/12 h	Porous nanocubes/ 20-50 nm	Hua and Gengsheng (2009)
$Fe(NO_3)_3 \cdot 9H_2O$	1:1 water/ethanol solution, oleic acid, NaOH	200°C/1 h	Plate-like particles/200 nm and above	Tadic et al. (2011)
$FeCl_3$	Water, $NaHSO_3$, $NaSO_4$,	220°C/8 h	Nanospheres, nanoellipsoids, polyhedral/50 1000 nm	Sun et al. (2010)
$FeCl_3 \cdot 6H_2O$	Water, ethanol, urea, carbon spheres	60°C/48 h	Cage-like nanospheres/30-600 nm	Yu et al. (2009)
$FeCl_3 \cdot 6H_2O$	Water, NaAcetate, PVP,	200°C/18 h	Granules/50 nm above	Zhu et al. (2012)
$FeCl_3 \cdot 6H_2O$	DI water, CH_3COOK, Ionic liquid [bmim][Cl] NaOH	150-250°C/3-8 h	Nanorods, nanocubes, nanospheres, hollow microspheres	Lian et al. (2009)

washed and dried at 100°C for 6 h. The particle size range obtained for the procedure above is 40-100 nm, adjusting the pH of the reaction between 11 to 13 would yield magnetite nanoparticles (Li et al., 1998). Note that neither surfactants nor templating agents have been added to the above reaction, Equation 7 represents the reactions and transformation of the reactants.

$$N_2H_4 + Fe^{2+} + 4H_2O \xrightarrow{pH3-5} 2NH_4 + 2H^+ + 2\alpha\text{-FeOOH} \xrightarrow{150°C} \alpha\text{-Fe}_2O_3 + H_2O \quad (7)$$
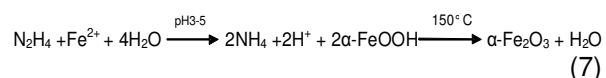
A simple surfactant-assisted solvothermal route was described by Lian et al. (2006), starting with $FeCl_3.6H_2O$ dissolved in ethanol, various morphologies (spheres, ellipsoids and peanut and various sizes ranging between 500-2000 nm) of hollow hematite nanoparticles were obtained by simply varying the concentration of CTAB additive with respect to the Fe^{3+} concentration. The particles also showed good photocatalytic properties for diethyl phthalate (DEP) photodegradation in the presence of H_2O_2. Xu et al. (2011) used sodium dodecylbenzene sulfunate

and water as solvent, heating temperature/ duration was varied between 140-220°C/12 h as well as the surfactant/Fe^{3+} ratio. Uniform nanospindles, nanoellipsoids, nanospheres and nanopolyhedra of various sizes ranging between 50-900 nm were obtained. Table 1 gives summaries of some hydro/solvothermal hematite nanoparticles synthesis showing the additives, operating temperature and duration and type of products obtained. The hydrothermal method is simple, cheap, and versatile with the possibility of fabricating a wide range of nanostructures with

Table 2. Comparison of the most used method for hematite synthesis (Lu et al., 2007; Tavakoli et al., 2007).

Method	Synthesis	Reaction temperature/time	Solvents	Size distribution /Shape control	Yield	Cost
Sol gel	Simple	70-100°C	Water/organic solvents	Relatively narrow/Good	High	High
Hydrothermal	Simple	160-250°C	Water/organic solvents	Narrow/Good	High	Medium
Precipitation	Simple	50-80°C	Water	Wide/Poor	High	Low
Microemulsion	Complicated	20-30°C	Water and organic compound	Narrow/Good	Low	High

good morphology control and percent yield (Lu et al., 2007).

Microemulsion synthesis

The term microemulsion refers to a thermodynamically stable isotropic dispersion of immiscible liquids (hydrocarbon based liquid or oil and water) which is stabilized by surfactants and sometimes co-surfactants (Lu et al., 2007; Malik et al., 2012; Nagarajan and Ruckenstein, 2000), the term was originally proposed by Schulman (1959) and Malik et al. (2012). The droplet type microemulsion can either be oil-in-water (O/W, which refers to spherical oil droplets dispersed in water), water-in-oil (W/O, which refers to spherical water droplets dispersed in oil or water-in-supercritical carbon dioxide (W/sc-CO$_2$) which refers to water droplets dispersed in supercritical carbon dioxide, these have been widely studied. Some surfactants that have been used in microemulsion synthesis include cetyl trimethylammonium bromide (CTAB), sodium bis-(2-ethylhexyl) sulfosuccinate (AOT), perfluoropolyethercarboxylic (PFPE) acid, sodium lauryl sulfate (SLS), triton X, Igepal, span tween 80 and polyethylene glycol (López-Quintela et al., 2004). The water/oil droplets are dispersed as nano-sized droplets (5-25 nm) surrounded by a monolayer of surfactants in the continuous phase (reverse micelles) and allows for exchange of

reactants between these phases leading to reaction within the droplets which acts as nano-reactors (Dong et al., 2002) within which nanomaterials with narrow size range can be prepared (Gupta and Gupta, 2005).

Many metal oxide nanoparticles have been synthesized using the microemulsion route, metal oxides like SiO$_2$, GeO$_2$, TiO$_2$ and Fe$_2$O$_3$ have all been fabricated within 5-50 nm range and it has shown to be a versatile and efficient route for nanoparticles synthesis. Wongwailikhit and Horwongsakol (2011) synthesized hexagonal nanostructures of hematite in a W/O microemulsion system using n-heptane as oil phase and AOT as surfactant. They dropped FeCl$_3$ and NH$_4$OH into microemulsion systems containing different fractions of the components (that is, water, n-heptane and AOT) which has been mixed and left overnight in order to achieve equilibrium, the nanoparticles were formed and they were able to show that the particle size increased with increase in water fraction. This is expected as an increase in water fraction will lead to bigger nanoreactors been formed and therefore larger particle sizes will be produced. Han et al. (2011) used a W/n-octane system with CTAB and n-butanol as surfactant and co-surfactant respectively and a catalyst (Fe^{2+}) to study the effect of some parameter variation on particle size and rate of hematite formation. They discovered that Fe^{2+} could act as catalyst and speed up

hematite formation; they were also able to relate CTAB/n-octane ratio and water/CTAB ratio to the size of hematite formed as an increase in the former lead to a decrease in nanoparticle size while the reverse was obtained for the later. Okoli et al. (2011) have used o/w (with Iron(III), 2-ethylhexanoate as iron source, hexane as oil and synperonic 10/6 surfactant) and w/o (2:1 ferric/ferrous chloride as iron source, CTAB as surfactant, 1-butanol as co-surfactant and n-octane as oil) microemulsions to prepare iron oxide nanoparticles of about 3 nm for the o/w system and nanorods of between 20 to 50 nm length for the w/o microemulsion (Okoli et al., 2011, 2012). This illustrates that a number of combinations are possible from which a number of different morphologies of iron oxides (hematite inclusive) can be prepared (Gupta and Gupta, 2005; Petrova et al., 2006). Some disadvantages of the microemulsion method include the fact that it is an expensive method (large amount of the costly oils and surfactants are required) coupled with low yield, the product is sometimes very difficult to remove from the emulsion (Tavakoli et al., 2007) (Table 2).

Conclusion

Synthesis of hematite nanoparticles can easily be carried out in the laboratory via the wet route.

Table 2 gives a brief comparison of the four most commonly used aqueous methods for hematite synthesis. It can be seen from the table that the aqueous route of hematite synthesis is very versatile for fabricating nanoparticles of different morphologies suitable for application in various fields. It has the advantage of simplicity and size and morphology control which is difficult to achieve in the non-aqueous methods (e.g. chemical deposition method) and low energy requirements (unlike the high energy required for ball milling). The yield from aqueous methods is high and the methods have potentials for industrial application.

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