

SYNTHESIS AND APPLICATIONS OF NANO-STRUCTURED IRON OXIDES/HYDROXIDES-A REVIEW

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Abstract

The nano iron oxides have been synthesized by almost all the known wet chemical methods which include precipitation at ambient/elevated temperatures, surfactant mediation, emulsion/micro-emulsion, electro-deposition etc. Iron oxides in nano-scale have exhibited great potential for their applications as catalytic materials, wastewater treatment adsorbents, pigments, flocculants, coatings, gas sensors, ion exchangers, magnetic recording devices, magnetic data storage devices, toners and inks for xerography, magnetic resonance imaging, bioseparation and medicine. Nano sized magnetite Fe_3O_4 , and maghemite $\gamma\text{-Fe}_2\text{O}_3$ exhibiting excellent magnetic properties find applications for biomedical purposes and as soft ferrites. Iron hydroxides and oxyhydroxides such as ferrihydrite, goethite, akaganeite, lepidocrocite are being evaluated for their applications in water purification for the removal of toxic ions. Hematite, $\alpha\text{-Fe}_2\text{O}_3$ in the nano range has been used to obtain transparent paints. In catalysis both iron oxides and hydroxides find application in numerous synthesis processes. This review outlines the work being carried out on synthesis of iron oxides in nano form and their various applications.

Keywords: nano iron oxides, synthesis, catalysts, magnetic properties, biomedical application

1. Introduction

Iron oxides are one of the most important transition metal oxides of technological importance. Sixteen pure phases of iron oxides, i.e., oxides, hydroxides or oxy-hydroxides are known to date. These are $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$, Fe_3O_4 , FeO , five polymorphs of FeOOH and four of Fe_2O_3 . Characteristics of these oxide compounds include mostly the trivalent state of the iron, low solubility and brilliant colors (Cornell and Schwertmann, 1996). All the iron oxides are crystalline except Schwertmannite and ferrihydrite which are poorly crystalline. These oxides can be synthesized by all known wet chemical methods but to tailor the particle size in nano range and morphology towards a particular application still remains a challenging task. Some of the synthesis techniques include chemical precipitation, sol-gel, hydrothermal, surfactant mediated-precipitation, emulsion-precipitation, microemulsion - precipitation, electro-deposition, and micro wave assisted hydrothermal technique. These oxides find applications as catalysts, sorbents, pigments, flocculants, coatings, gas sensors, ion exchangers and for lubrication (Miyata *et al.*, 1978; Lim *et al.*, 1983; Sharrock and Bodnar, 1985; Catlow, 1988; Schwertman and Taylor, 1989; Vissokov and Pirgov, 1996; Sestier, 1998; Choo and Kang, 2003). Iron oxide nano-composites have potential applications in areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging, wastewater treatment, bioseparation, and medicine (Raj and Moskovitz, 1990; Pieters *et al.*, 1992; Sun *et al.*, 1992; Ziolo *et al.*, 1992; Safarik, 1995; Häfeli *et al.*, 1997; Schütt *et al.*, 1997; Gazeau *et al.*, 1998; Denizli and Say 2001). Below a critical size, Fe_2O_3 nanoparticles can be used for niche applications like transparent iron oxide pigments, due to their durability, shade, UV absorption and added value (Silber *et al.* 2002). Careful control of the preparation process of transparent iron oxide pigments results in the formation of pigments with very small primary particle sizes. When fully dispersed, they do not scatter light and are hence completely transparent. A brief literature scan is reported in the present review considering the application of various forms of nano iron oxides in the above fields.

2. Basic structure of some of the iron oxides

The term 'ferrihydrite' is often used to describe both 2- or 6-line ferrihydrite, which have either two or six identifiable broad reflections in a diffraction pattern. Different chemical formulae for ferrihydrite are: $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$, $\text{Fe}_5(\text{O}_4\text{H}_3)_3$, $\text{Fe}_2\text{O}_3 \cdot 2\text{FeOOH} \cdot 2.6\text{H}_2\text{O}$ and $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$. The morphology of

ferrihydrite is spherical and unlike other iron oxides it exists only as nano crystals resulting in high specific surface areas ranging from 100 - 700 m²/g (Cornell and Schwertmann, 2003). The structure of ferrihydrite is still under debate as the low degree of order impedes the elucidation of the structure.

FeO, 'wustite' crystallizes in the sodium chloride structure containing four formula units in the cubic unit cell. The large O²⁻ anions form a close packed fcc sublattice with the small Fe²⁺ cations located in the interstitial sites. All iron ions are octahedrally coordinated to oxygen. Under thermal equilibrium this phase is stable only at low pressures and for temperatures above 843 K.. In this oxide the oxygen and iron (111) planes form ideal two-dimensional hexagonal lattices with an inter-atomic distance of 3.04 Å, which corresponds to the lattice constant of the hexagonal unit cell on the unreconstructed FeO(111) surface. Along the (111) direction the iron and oxygen (111) planes form the cubic ABC stacking sequence with an interlayer distance of 1.25 Å. The iron- oxygen bond length is 2.16 Å.

Goethite, α -FeO(OH) exhibits an orthorhombic symmetry, space group Pnma (N^o 62). Crystal parameters are: $a = 9.95 \text{ \AA}$, $b =$

3.01 \AA , $c = 4.62 \text{ \AA}$. The structure could be described as a three-dimensional structure built up with FeO₃(OH)₃ octahedra which form large tunnels, spreading out along the direction (010) and where hydrogen atoms are located. Each octahedron is linked to eight neighboring octahedral by four edges and three vertices. Oxygen atoms are in tetrahedral surroundings, either OFe₃H or OFe₃H(bond). Although goethite displays a range of shapes, the basic morphology is acicular. The specific surface area range from 8 - 200 m²/g (Cornell and Schwertmann, 2003).

Among the iron compounds, the iron oxyhydroxide phase 'akaganeite', \square -FeOOH, has a large tunnel-type structure where iron atoms are strongly bonded to the framework. Generally Akaganeite contains some Cl⁻ as an impurity. In akaganeite the octahedral sites are occupied by FeH, and Cl (and perhaps H₂O) is presumably located in the tunnels. Charges are balanced by substituting OH⁻ for O²⁻.

The crystal structure of 'lepidocrocite' $\square\square$ FeO(OH) is built by double layers of Fe-octahedra, with the hydroxyl groups being located on their external surfaces and providing hydrogen bonding between the layers. It is assumed that hydrogen atoms occupy the centers of inversion and are located at the same distances from two oxygen atoms of the adjacent layers, thus forming continuous O-H-O-H-O chains with symmetric hydrogen bonds. The basic morphologies of lepidocrocite are lath-like or tabular and the specific surface area range from 15 - 260 m²/g (Cornell and Schwertmann, 2003).

Magnetite (Fe₃O₄) is a black, ferromagnetic mineral containing both Fe(II) and Fe(III). In stoichiometric magnetite Fe(II)/Fe(III)

= 0.5 but magnetite is often non-stoichiometric resulting in a cation deficient Fe(III) layer. The crystal structure of magnetite is inverse spinel with a unit cell consisting of 32 oxygen atoms in a face-centered cubic structure and a unit cell edge length of 0.839 nm. In this crystal structure Fe (II) ions and half of the Fe (III) ions occupy octahedral sites and the other half of the Fe(III) occupies tetrahedral sites. Divalent iron atoms prefer to occupy octahedral sites to have a higher Crystal Field Stabilization Energy (CFSE), whilst the trivalent iron atoms has a CFSE=0 in both octahedral and tetrahedral sites. The crystal forms of magnetite include octahedron and rhombodecahedron and the specific surface area ranges from 4 - 100 m²/g (Cornell and Schwertmann, 2003).

The structure of 'hematite', α -Fe₂O₃, is isostructural with corundum, \square -Al₂O₃. The structure has also a three-dimensional framework built up with trigonally distorted octahedra FeO₆, linked to thirteen neighbors by one face, three edges and six vertices. The space group is R3 c (N^o 167, rhombohedral symmetry) and the lattice parameters given in the hexagonal cell are: $a = 5.0346 \text{ \AA}$, $c = 13.752 \text{ \AA}$. The structure is similar to that of corundum, and consists essentially of a dense arrangement of Fe³⁺ ions in octahedral coordination with oxygens in hexagonal closest-packing. The structure can also be described as the stacking of sheets of octahedrally (six-fold) coordinated Fe³⁺ ions between two closed-packed layers of oxygens. Since Fe is in a trivalent state (ferric Fe), each of the oxygens is bonded to only two Fe ions, and therefore, only two out of three available oxygen octahedrons are occupied. This arrangement makes the structure neutral with no charge excess or deficit. The Fe-O sheets are held together by strong covalent bonds. The crystal system of hematite is hexagonal, but crystals appear in a wide variety of forms. The specific surface area ranges from 10 - 90 m²/g (Cornell and Schwertmann, 2003).

3. Synthesis

Synthesis of iron oxides in the nano range for various applications has been an active and challenging area of research during the last two decades. The processes include careful choice of pH, concentration of the reactants, temperature, method of mixing, and rate of oxidation (Domingo *et al.*, 1994). The morphology of the iron oxide particles depends on the competition between several processes like nucleation, growth, aggregation and adsorption of impurities (Cornell and Schwertmann, 1996). However, in many cases it is not possible to precipitate specific iron oxide particles directly in the desired size and shape. Instead, the synthesis must be done by the transformation of another iron oxide precursor particle (Baker *et al.*, 2000). The sensitivity of the preparative method complicates both the reproducibility and scale up of the process. Recently, several colloidal chemical synthetic procedures have been developed to produce mono-disperse nanoparticles of various materials. This includes the classical LaMer mechanism, wherein a short burst of nucleation from a supersaturated solution is followed by the slow growth of particles without any significant additional nucleation, thereby achieving a complete separation of nucleation and growth (LaMer and Dinegar, 1950). Synthesis procedure that combines slow, continuous nucleation and fast, autocatalytic surface growth have also been reported (Butter *et al.*, 2005). Further, in several preparative methodologies, agglomeration of the nano-oxide generated takes place on exposure to air. This is prevented by employing surfactants or by capping with organic acids. In general, for the solution-based synthesis of iron oxide colloids and nanoparticles several techniques such as chemical precipitation, sol-gel processes, forced hydrolysis, hydrothermal synthesis, electrochemical preparation methods (Ozaki *et al.*, 1984; Blesa and Matijevic, 1989; Ozaki *et al.*, 1990; Sugimoto and Sakata, 1992; Sugimoto *et al.*, 1993; Yitai *et al.*, 1994; Sahu *et al.*, 1997; Li *et al.*, 1998; Jungk and Feldmann, 2000; Butter *et al.*, 2005) surfactant mediated or template synthesis, emulsion/ microemulsion methods have been reported. The following sections briefly review the synthesis techniques.

Chemical precipitation

The precipitation technique is probably the simplest and most efficient chemical pathway to obtain iron oxide particles. Iron oxides (FeOOH , Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$) are usually prepared by addition of alkali to iron salt solutions and keeping the suspensions for ageing. The main advantage of the precipitation process is that a large amount of nanoparticles can be synthesized. However, the control of particle size distribution is limited, because only kinetic factors are controlling the growth of the crystal. In the precipitation process, two stages are involved i.e., a short burst of nucleation occurs when the concentration of the species reaches critical super saturation, and then, there is a slow growth of the nuclei by diffusion of the solutes to the surface of the crystal. To produce mono disperse iron oxide nanoparticles, these two stages should be separated; i.e., nucleation should be avoided during the period of growth (Tartaj *et al.*, 2006). Size control of mono dispersed particles must normally be performed during the very short nucleation period, because the final particle number is determined by the end of the nucleation and it does not change during particle growth. A wide variety of factors can be adjusted in the synthesis of iron oxide nanoparticles to control size, magnetic characteristics, or surface properties. A number of studies have dealt with the influence of these different factors (Sjorgren *et al.*, 1994; Weissleder, 1996; Pardoe *et al.*, 2001; Itoh and Sugimoto, 2003; Thapa *et al.*, 2004; Tominaga *et al.*, 2006). The size and shape of the nanoparticles can be tailored with relative success by adjusting pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), or the Fe(II)/Fe(III) concentration ratio.

Pure goethite was synthesized using 1 M ferric nitrate solution and 10 M sodium hydroxide solutions under controlled conditions. Ferric nitrate solution was vigorously stirred at room temperature with the simultaneous addition of 10 M sodium hydroxide solution until the pH of the solution reached 12–12.5. In order to obtain Cu, Ni or Co doped goethites, the respective sulphate solutions were mixed with ferric nitrate solution prior to alkali addition. Further studies were carried out to convert the goethite to primarily magnetite (Mohapatra *et al.*, 2003; Mohapatra *et al.*, 2005a). Cerium-doped goethite samples in the nano range were prepared through aqueous precipitation by varying Ce(IV)/Fe(III) atomic ratio in the range of 0.015 to 0.07 (Mohapatra *et al.*, 2005b; Sahoo *et al.*, 2009). Irrespective of the amount of cerium doping, all the samples showed only goethite as the crystalline phase. Doping of cerium in goethite affected the peak positions (positive shift 0.02–0.04), crystallinity and lattice parameters of goethite and perturbed the particle structure of $\gamma\text{-Fe}_2\text{O}_3$ during transformation process. The lattice image of a typical sample with Ce(IV)/Fe(III) atomic ratio 0.035:1, indicated that the goethite grew along (1 1 0) plane and there was no separate plane of cerium phases present in goethite structure. On heating the samples to 400°C, goethite was

completely transformed to hematite while the crystallization of CeO_2 was only partial. Further calcination to 800°C resulted in the formation of two distinct phases of CeO_2 and $\alpha\text{-Fe}_2\text{O}_3$ as observed from XRD pattern. Lattice image of the same sample revealed intergrowth of (1 1 1) plane of CeO_2 along (0 1 2) plane of $\alpha\text{-Fe}_2\text{O}_3$. However, CeO_2 crystallites did not separate from $\alpha\text{-Fe}_2\text{O}_3$. Nano-structures of $\text{CeO}_2\text{-}\alpha\text{-Fe}_2\text{O}_3$ oxides were retained even on calcination at 800°C .

The first controlled preparation of superparamagnetic iron oxide particles using alkaline precipitation of FeCl_3 and FeCl_2 was performed by Massart (1981). The process engineered by Massart (1981) for rapid synthesis of homogeneous $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles allowed for coating by a wide range of monomeric species, such as amino acids, R-hydroxyacids (citric, tartaric, and gluconic acids) (Fauconnier *et al.*, 1996) hydroxamate (arginine hydroxamate) (Fauconnier *et al.*, 1999), dimercaptosuccinic acid (DMSA), (Fauconnier *et al.*, 1997) or phosphoryl choline (Denizot *et al.*, 1999). Adding increasing amounts of citrate ions in the Massart process allowed for a decrease in the diameter of citrate-coated nanoparticles from 8 to 3 nm (Bee *et al.*, 1995). Through such a process of size selection using NaCl as an extra electrolyte, the size distribution of the 7 nm citrate nanoparticles obtained by the Massart process could be reduced (Massart *et al.*, 1995; Cabuil *et al.*, 1995). Jolivet (1994) studied the influence of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio on the composition, size, morphology, and magnetic properties of co-precipitated nanoscale particles. Babes *et al.* (1999) also studied the influence of different parameters, including the iron media and the iron concentration. In their setup, the most important factor is the $\text{Fe}^{2+}/\text{Fe}^{3+}$ molar ratio. The mean size increased with the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, whereas the preparation yield decreased. These results were corroborated by literature data (Massart and Cabuil, 1987; Jolivet *et al.*, 1992; Tronc *et al.*, 1992). The dependence of particle mean size of magnetite upon the acidity and the ionic strength of the precipitation medium has been reported (Vayssières *et al.*, 1998; Jiang *et al.*, 2004; Jolivet, 2000). The higher the pH and ionic strength, the smaller the particle size and size distribution width will be, because these parameters determine the chemical composition of the crystal surface and consequently the electrostatic surface charge of the particles (Tartaj *et al.*, 2006). Qiu *et al.* (2000) investigated the dependence of the ionic strength of the reaction solution on the formation of magnetite. The magnetite prepared with the addition of 1 M NaCl

aqueous solution created iron oxide nanoparticles 1.5 nm smaller than those formed without its presence. In addition, these smaller nanoparticles formed in the higher ionic strength solutions displayed lower saturation magnetization (63 emu/g) than those prepared in NaCl-free solutions (71 emu/g). Many factors may influence the size of the nanoparticles. For example, an increase of the mixing rate tends to decrease the particle size. On the contrary, injection flux rates did not seem to have a preponderant influence on the nanoparticle synthesis. Several researchers report the use of an elevated reaction temperature and suggest its significance in optimal crystal formation (Sun and Zeng, 2002). Bubbling nitrogen gas through the solution not only protected against critical oxidation of the magnetite but also reduced the particle size when compared to methods without oxygen removal (Gupta and Wells, 2004; Kim *et al.*, 2001).

Sol-Gel and forced hydrolysis techniques

Sol-gel processing route is a wet chemical process for the synthesis of colloidal dispersion of inorganic and organic inorganic hybrid materials. The synthesis of metal oxides by sol-gel synthesis has proven extremely versatile since it allows the formation of a large variety of metal oxides at relatively low temperatures via the processing of metal salt or metal alkoxide precursors. The structure and composition of nano oxides formed by sol-gel method depend on the preparation condition, the nature of the precursors, the ion source and pH. It offers advantages such as: (i) tailor-made materials due to good process control, (ii) homogeneous multicomponent systems due to mixing in liquid medium, (iii) low temperature for materials processing. This process is based on the hydroxylation and condensation of molecular precursors in solution, originating a sol of nanometric particles. Further condensation and inorganic polymerization leads to a three dimensional metal oxide network denominated wet gel. The main parameters that influence the kinetics, growth reactions, hydrolysis, condensation reactions, and consequently, the structure and properties of the gel have been reported (Cannas *et al.*, 1998; Ennas *et al.*, 1998). The Sol-Gel synthesis of iron oxide particles was carried out from condensed ferric hydroxide gels, obtained from FeCl_3 solutions in NaOH. After aging the gel at 100°C for 8 days, mono-disperse pseudo-cubic $\alpha\text{-Fe}_2\text{O}_3$ particles were obtained (Sugimoto and Sakata, 1992; Sugimoto *et al.*, 1993). The particles were poly-crystals composed of much smaller subunits. The reaction proceeded through a two-step phase transformation from precipitated $\text{Fe}(\text{OH})_3$ gel to a fibrous $\alpha\text{-FeOOH}$ and finally to $\alpha\text{-Fe}_2\text{O}_3$ (Sugimoto and Sakata, 1992).

The widely used method to synthesize iron oxy-hydroxide consists of the hydrolysis of Fe^{3+} cations. However, aging of the sol prepared by pouring fresh ferric solutions into concentrated NaOH or KOH solutions has to take place at 60–80°C for a period of time ranging from a few days to several weeks (Pascal *et al.*, 1999). As referred by Cornell and Schwertmann (1996), particles formed by the oxidation of Fe^{2+} solutions at neutral conditions are usually much less developed and the crystals are smaller than those obtained in alkaline Fe^{3+} solutions. Moreover, oxidation of the ferrous salt solutions by air bubbling yields one or several of the following products: goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). The crystallization of Fe-oxides are strongly affected by the anions or cations adsorbed by ligand exchange. Furthermore, various phases formed during the oxidation of aqueous ferrous systems suggest that the oxidation rate, which can be influenced by pH, temperature and other additives (anions or cations) present in the system, is the dominant factor in determining the hydrolysis product. For the advanced particulate materials, size and shape are often as crucial as crystal structure in determining the performance. Using the forced hydrolysis technique $\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$, and Fe_3O_4 with different morphological properties were produced under a wide variety of synthesis conditions (Domingo *et al.*, 1994). Acicular goethite particles were obtained after aerial oxidation of iron(II) solutions at 20°C – 80°C in acidic conditions. Depending on the temperature, the length of the particles varied between 0.1 – 0.5 μm and the aspect ratio lay between 5 and 10.

Polydisperse magnetite micro crystals were prepared in neutral or basic pH at 90°C by the addition of KNO_3 to FeCl_2 and KOH solution. Spindle-type colloidal hematite particles of narrow size distribution were prepared in a similar way by forced hydrolysis of ferric chloride solution in the presence of phosphate and hypophosphate at 100°C for 2 to 7 days (Ozaki *et al.*, 1984). These hematite particles can easily be converted in maghemite particles of the same size and shape by heating under hydrogen gas flow followed by re-oxidation with air (Ozaki and Matijevic, 1985). Plate-like hematite particles of about 5 – 10 μm in diameter were obtained by aging basic ferric salt solutions in the presence of either EDTA or KNO_3 or triethanolamine and hydrazine or hydrogen peroxide (Ozaki *et al.*, 1990).

Hydrothermal technique

Hydrothermal technique is defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions. Hydrothermal treatment of iron salt could generate iron oxides when the applied conditions are appropriate. The hydrothermal preparation of goethite and hematite from amorphous iron(III) hydroxide was studied at various pH values in the temperature range 100–200°C. In the pH range 8.0–10.0, goethite and hematite were formed. In the range 10.5–10.8 only goethite was formed, and in the pH range 0.8–2.6 hematite was the only reaction product (Christensen, 1968). The decomposition of $\alpha\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$ in neutral and weakly alkaline hydrothermal solution was observed at $150^\circ\text{C} \pm 20^\circ\text{C}$, and this temperature was suggested to be the upper temperature for the formation of the $\alpha\text{-FeOOH}$ minerals. However, the transformation is also strongly pH dependent so that the transformation temperature increased by 25K per pH unit (Robins, 1967). The first in situ investigation of the rate of crystallization of amorphous iron(III) hydroxide to $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ was made at hydrothermal conditions using neutron powder diffraction (Axel *et al.*, 2007). Chen *et al.* (1998) have reported a facile and environmental friendly ultrasonic-assisted hydrothermal route for preparation of goethite flower structures using Fe nano-powders at low temperature (85°C). The flower structure consisted of tens of hundreds of nano wires and such structures could further self- assemble with the flake with micro size area. Structural, morphological, and elemental analysis revealed that the products consisted of flower-like structures with high structural uniformity, good crystal quality, and high yields. Magnetic measurements showed that the as-obtained goethite flowers exhibited weakly ferromagnetic characteristics at room temperature, which were quite different from those of the corresponding bulk materials.

Šaric *et al.* (1998) discussed the effects of urotropin on the chemical and microstructural properties of Fe-oxide powders prepared by the hydrolysis of aqueous FeCl_3 solutions. Hydrothermal treatment of an iron chloride solution together with iron powder in the presence of urea yielded after 20 hours at 130°C – 150°C ultrafine, short and rod-shaped magnetite particles of about 80 nm in size and an aspect ratio of about 2 (Yitai *et al.*, 1994). By varying the pH in the range 3 to 10 and by increasing the reaction temperature up to 180°C, hematite particles of various shapes and sizes were obtained (Sahu *et al.*, 1997). It was observed that the particle size decreased with an increase in the pH. The prepared particles were all

polycrystalline at pH of ≤ 7.0 . Transmission electron microscopy investigations revealed that the particle morphology strongly depended on the pH value: at pH 3 very uniform pseudocubic particles of about 0.65 nm were obtained, and at pH 4.5 the particle size decreases; whereas at pH 7 a change in the shape of the particle took place. Ultrafine powders of α -Fe₂O₃ and Fe₃O₄ were hydrothermally prepared at 150°C in the presence of hydrazine (Li *et al.*, 1998). Also in this case, the morphology of the iron oxide particles was strongly influenced by the pH value. The non-agglomerated and spherical particles were homogeneous in morphology with an average size of about 70 nm. α -Fe₂O₃ nanowires were successfully prepared by a hydrothermal method and subsequent heat treatment using isopropanol and nitrilotriacetic acid. Liang *et al.* (2010) synthesized iron oxides using hydrothermal and solvothermal processes. In hydrothermal preparation, α -Fe₂O₃ was obtained. The α -Fe₂O₃ crystal was suggested to grow in sub-critical water via dissolution and precipitation processes. The α -Fe₂O₃ particles synthesized at 420°C had a particle size of nearly 40 nm, which is much smaller than particles produced at 350°C (60 nm). Crystalline Fe₃O₄ was formed in a solvothermal preparation due to the reducing atmosphere resulting from the oxidation of IPA into acetone. The acetone molecules adsorbed on the Fe₃O₄ surfaces were suggested to suppress crystallite growth.

Zheng *et al.* (2006) reported the synthesis and magnetic properties of hydrothermally prepared Fe₃O₄. The hydrothermal synthesis of size controlled Fe₃O₄ nanoparticles was carried out by Mizutani *et al.* (2010) using the starting solution containing lactate and sulfate ions at various concentrations in order to control the particle size. The particle size was controlled by means of the coexistence effects of lactate and sulfate ions. Depending on their concentration, the particle size could be varied from 9.5 to 38.6 nm. Size-controlled and coated magnetite nanoparticles with glucose and gluconic acid were synthesized by Sun *et al.* (2009) via a simple and facile hydrothermal reduction route using a single iron precursor, FeCl₃. The particle size could be easily controlled in the range of 4-16 nm. Sucrose was required for the formation of nanoscale and coated magnetite instead of the much larger hematite. Sucrose acts as a bifunctional agent (i) it decomposes into reducing species, causing partial reduction of the Fe³⁺ ions to Fe²⁺ ions as required for the formation of Fe₃O₄ and (ii) acts as the source of a capping agent to adjust the surface properties and enable the formation of nanoscale particles.

Selective synthesis of α -FeOOH and α -Fe₂O₃ nanorods was developed by Dong *et al.* (2009) using ferrous sulphate and hydrogen peroxide as raw materials. Only by adjusting the reaction temperature in hydrothermal synthesis, the α -FeOOH nanorods (at 150°C) and α -Fe₂O₃ nanorods (at 200 °C) were obtained. A facile one-step hydrothermal approach was made by Ge *et al.* (2009) for the synthesis of iron oxide (Fe₃O₄) nanoparticles (NPs) with controllable diameters, narrow size distribution, and tunable magnetic properties. The iron oxide NPs were synthesized by oxidation of ferrous chloride in basic aqueous solution under an elevated temperature and pressure. The particles were highly crystalline and that the diameters of the particles could be tuned from 15 to 31 nm through the variation of the reaction conditions. The NPs exhibited high saturation magnetization in the range of 53.3- 97.4 emu/g and their magnetic behavior was either ferromagnetic or superparamagnetic depending on the particle size. Nanoparticles with a high level of mono dispersity and size control were obtained by high-temperature decomposition of iron organic precursors, such as Fe(Cup)₃, Fe(CO)₅, or Fe(acac)₃, using organic solvents and surfactants (Hyeon *et al.*, 2001). For example, iron oleate could be formed from decomposition of iron carbonyl in the presence of octyl ether and oleic acid at 100°C followed by cooling to room temperature. Then (CH₃)₃NO was added and the solution was refluxed (Hyeon *et al.*, 2001). Highly crystalline and mono-disperse maghemite crystals were obtained at 100°C by thermal decomposition of iron pentacarbonyl in the presence of oleic acid and then aging at 300°C the iron oleic complex. This two-step process allowed for the production of selected particles sizes from 4 to 16 nm. Hydrophobic magnetite particles with a narrow size distribution were prepared by thermal decomposition of Fe(CO)₅ in octyl ether solution of oleic acid and consecutive aeration (Woo *et al.*, 2005). The nanoparticles were converted into a magnetite core/silica shell with hydrophilic and processible aminopropyl groups on their surfaces. Sun *et al.* (2004) have described a high-temperature reaction of iron(III) acetylacetonate with 1,2-hexadecanediol in the presence of oleic acid and oleylamine to obtain monodisperse magnetite nanoparticles. The particle diameter could be tuned from 4 to 20 nm, and the hydrophobic particles could be transformed into hydrophilic ones by adding a bipolar surfactant. The thermal decomposition of iron pentacarbonyl and iron oleate at different temperatures affords monodisperse nanoparticles ranging from 4 to 11 nm, dispersible in organic solvent (Park *et al.*, 2005).

The use of nontoxic iron chloride salts as a precursor has been proposed by different groups (Jana *et al.*,

2004; Park *et al.*, 2004). The nanoparticles obtained are dispersible in different organic solvents (hexane and toluene) but probably not in water, and sophisticated post preparative methods are required to make these nano crystals water-soluble. Li *et al.* (2004 a, 2004b, 2005a, 2005b) have described synthesis route of water-dispersible magnetite in acidic or basic media by thermal decomposition of $\text{Fe}(\text{acac})_3$ or inexpensive FeCl_3 in refluxing 2-pyrrolidone. Magnetite nanocrystals were synthesized from thermal decomposition of $\text{Fe}(\text{acac})_3$ in high boiling organic solvents with a controlled size of 4, 6, 9, and 12 nm. An efficient route for simultaneous synthesis and self-assembly of 3D layered $\beta\text{-FeOOH}$ nano rods was reported by Fang *et al.* (2010). The nature of particles depended on a pH-induced strategy, in which the continuous change of pH was achieved by hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the presence of urea under hydrothermal conditions. The electron microscopy observations revealed that the square-prismatic $\beta\text{-FeOOH}$ nano rods were self-assembled in a side-by-side fashion to form highly oriented 2D nano rod arrays, and the 2D nano rod arrays were further stacked in a face-to-face fashion to form the final 3D layered architectures. On the basis of time-dependent experiments, a multistage reaction mechanism for the formation of the 3D layered $\beta\text{-FeOOH}$ nano rods architecture was presented, involving the fast growth and synchronous self-assembly of the nano rods toward 1D, 2D, and 3D spontaneously.

Surfactant mediated /template synthesis

Supramolecular surfactant-controlled method for the synthesis of mesostructured iron oxides has acquired more importance in recent scenario, which uses neutral or charged template molecules. Hexa-decylsulfonic acid mixed at room temperature with an aqueous solution of FeCl_2 yielded a hexagonal structured iron oxide with a d-spacing of 3.75 nm (Ciesla *et al.*, 1994). In a similar approach, lamellar iron oxide/surfactant composites were produced by the controlled precipitation and hydrolysis of aqueous iron cations into self-assembled iron/surfactant arrays (Tolbert *et al.*, 1997). These composites were obtained by mixing iron(II) or iron(III) salt solutions with diluted aqueous solutions of sodium n-alkyl sulfates at room temperature. Lamellar iron(hydro) oxyhydroxide-surfactant composites were also prepared by adding ammonia to a FeCl_3 solution followed by mixing with the sodium n-alkyl sulfate template (Wirnsberger *et al.*, 1998). By adjusting the reaction conditions, composites with inorganic walls from about 10 – 26 Å were produced in a controllable manner. Not only long-chain surfactant templates can influence the morphology of the iron oxide particles, it is well known that inorganic anions like chloride, phosphate or sulfate have a strong influence on particle size and shape (Livage *et al.*, 1988; Reeves and Mann, 1991). $\alpha\text{-Fe}_2\text{O}_3$ nanorods and nanotubes have been synthesized (Liu *et al.*, 2006) using different surfactant i.e., polyisobutylene bissuccinimide (L113B) or surfactant Span80. High- quality one dimensional products were obtained with aqueous butanol solution as the solvent and carbamide as the base, giving rise to single-crystalline products at 150°C.

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A microbial-derived surfactant (MDS) (Iijima *et al.*, 2006) with a high carboxyl density and low molecular weight or an artificially synthesised polyacrylic acid sodium salt (PAA) was added to the raw material aqueous solution before iron oxide particle synthesis by gel-sol method. Pseudo-cubic haematite particles with a diameter of 500 nm were prepared without surfactant addition while spherical size iron oxide nanoparticles of 20 nm diameter were prepared by MDS addition. Nevertheless, needle shaped iron hydroxide nanoparticles with a length of 100 nm along the long axis were prepared by PAA addition. The morphology of the iron hydroxide nanoparticles depended on the molecular structure of the surfactants.

A hybrid nano crystalline surfactant modified akaganeite ($\beta\text{-FeOOH}$) sorbent was prepared (Deliyanni *et al.*, 2006) by using iron(III) chloride as the precursor and a cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA) to chemically modify the adsorbent surface by co-precipitation. Yue *et al.* (2010) demonstrated a CTAB-directed synthesis method for synthesizing well-crystalline goethite nano rods.

Biomimetic mineralization

Bio-mimetic mineralization within protein cages provides an attractive alternative approach for synthesizing mono-disperse nano-sized particles. Since maximum particle sizes are limited by the cage inner diameter, reactions carried out in cages can lead to highly mono-disperse size distributions, particularly if nucleation rather than growth is the rate-limiting stage of the synthesis. Control of the size and shape of the

particles can be obtained through the use of various distinct protein cages in an expanding library of structures (Douglas and Young, 1998; Douglas and Stark, 2000; Allen *et al.*, 2003; Rice *et al.*, 2004). Finally, the protein shell surrounding particles synthesized by this method provides a framework of amino acid side-chains for further synthetic processing, useful, for example, for forming uniform spatial arrays (Klem *et al.*, 2003).

Precipitation by anhydrous solution

To overcome the limitations introduced by aqueous solution reactions, some researchers have developed anhydrous solution approaches for the production of metal oxide nanoparticles and in particular iron oxide (Rockenberger *et al.*, 1999; Hyeon *et al.*, 2001; Sun and Zeng, 2002; Jing and Wu, 2004; Li *et al.*, 2004c; Nicola *et al.*, 2005). Hyeon *et al.* (2001) have successfully fabricated highly crystalline and mono-disperse γ -Fe₂O₃ nanoparticles with a particle size of 13 nm by direct oxidation of iron pentacarbonyl in the presence of oleic acid with trimethylamine oxide as an oxidant. Jing and Wu (2004) have synthesized acicular γ -Fe₂O₃ nanoparticles with a particle size of around 10 nm using lauric acid as an anhydrous medium. Rockenberger *et al.* (1999) have also reported that the reaction of FeCup₃ with trioctylamine at 300 °C leads to 6–7 nm maghemite nanocrystals. Recently, the production of high quality water-soluble iron oxide (WSIO) nanocrystals (Jun *et al.*, 2005) has been reported by thermal decomposition of Fe(CO)₅ in hot dioctyl ether. Some of the main difficulties in in-vivo MRI lie in lack of high quality biocompatible magnetic nanocrystals. Therefore, one of the current challenges is how to develop well defined magnetic nanocrystals with optimal nanoscale magnetism, high bio-stability to withstand harsh biological conditions, and the ability to

escape from the reticulo-endothelial system (RES). For biological application, robust water-soluble nanostructures are necessary, so several synthesis strategies have been used, such as surface functionalization with water-soluble ligands (Chan and Nie, 1998; Jun *et al.*, 2005), silanization (Bruchez Jr. *et al.*, 1998), and encapsulation within block-copolymer micelles (Dubertret *et al.*, 2002; Lee *et al.*, 2005a). On the other hand, adsorption-resistant coatings such as PEG (polyethylene glycol) are often used to minimize recognition by the RES (Gref *et al.*, 1994).

Microemulsion technique

The microemulsion system consists of an oil phase, a surfactant phase and an aqueous phase. Microemulsions are transparent solutions consisting of small droplets of an immiscible phase (non-polar or polar) dispersed in a continuous phase. Surfactants are added to lower the interfacial tension between the immiscible dispersed and continuous phases to stabilize the droplets. Microemulsions may consist of oil-in-water or water-in-oil, depending on the concentration of the different components. By varying the concentration of the dispersed phase and the surfactant, it is possible to tailor the size of the droplets in the range 1–100 nm, approximately. Self-assembled structures of different types can be formed, ranging, for example, from (inverted) spherical and cylindrical micelles to lamellar phases and bicontinuous microemulsions, which may coexist with predominantly oil or aqueous phases (Solans *et al.*, 2005). Microemulsion and inverse micelles route can be employed for obtaining the shape- and size-controlled iron oxide NPs. Geng *et al.* (2006) synthesized α -FeOOH nanorods at room temperature by using Pluronic triblock copolymer P123, poly (ethyleneoxide)-*block*-poly(propyleneoxide)-*block*-poly(ethyleneoxide) (EO₂₀PO₇₀EO₂₀, M_{av} = 5800), and ferric nitrate. The single-crystalline orthorhombic α -FeOOH nanorods, growing along (0 0 1) direction, were 8.2 ± 1.5 nm in diameter and 106 ± 16 nm in length. A corresponding mechanism of the formation of α -FeOOH nanorods was suggested and it was proposed that the surfactant and high basic condition play important roles in the directed growth of α -FeOOH nanorods. Monodisperse maghemite was synthesized (Vidal-Vidal *et al.*, 2006) by capping with a monolayer coating of oleylamine (or oleic acid). It exhibited narrow size distribution of 3.5 ± 0.6 nm and displayed high saturation magnetization values (76.3 Am²/kg for uncoated NPs, 35.2 Am²/kg for oleic acid coated NPs, and 33.2 Am²/kg for oleylamine coated NPs). Chin and Yacob (2007) reported the synthesis of magnetic iron oxide NPs (less than 10 nm) via w/o microemulsion. Furthermore, in comparison to the particles produced by Massart's procedure (Tourinho *et al.*, 1990), particles produced by microemulsion technique were smaller in size and showed higher values of saturation magnetization (Chin and Yacob, 2007). Zhang *et al.* (2008) fabricated hollow magnetite NPs of 200 to 400 nm in diameter by the microemulsion route, however these NPs may not be useful for drug delivery purposes. This method suffers from the preparation of adequate

crystalline SPIONs on a large scale as the temperature used for such synthesis is low. Lee *et al.* (2005b) reported synthesis of crystalline maghemite particles with well-defined nanometer sizes by the microemulsion method at high temperature using iron (III) acetyl acetonate as an iron precursor. Sun and Zeng (2002) reported the size controlled synthesis of ultra-small magnetite (12 and 16 nm) NPs using $\text{Fe}(\text{acac})_3$ as an iron source by the microemulsion route. However, despite the presence of surfactants, the aggregation of the produced NPs usually needs several washing processes and further stabilization treatments.

Flow injection syntheses

Reaction zone confinement in different “matrices”, such as emulsions, etc., has been used to produce particles with narrow size distributions and, in some cases, to tailor the particle morphology. However, a specific design of the reactor can serve as an alternative to the “matrix” confinement. Alvarez *et al.* (2006) have developed a novel synthesis of magnetite nanoparticles based on a flow injection synthesis (FIS) technique. The technique consisted of continuous or segmented mixing of reagents under laminar flow regime in a capillary reactor. The FIS technique has some advantages, such as a high reproducibility because of the plug-flow and laminar conditions, a high mixing homogeneity, and an opportunity for a precise external control of the process. The influence of chemical parameters and conditions on the properties of the material was investigated. The obtained magnetite nanoparticles had a narrow size distribution in the range of 2-7 nm.

Electrochemical methods

In this method electrons act as reactant. It is an environmental friendly process with no pollution. However, the costly platinum is used as an electrode and not for reuse in aqueous solution. The electrochemical synthesis of nanosized particles of $\gamma\text{-Fe}_2\text{O}_3$ of about 20 nm in non-aqueous medium was reported by Zhang *et al.* (2007). They used stainless steel plate as anode and cathode respectively, the solvent used can be re-used. Pascal *et al.* (1999) prepared 3-8 nm maghemite particles by electrochemical method from an iron electrode in an aqueous solution of DMF and cationic surfactants. Here current density controlled the particle size. Electrochemical deposition under oxidizing conditions has been used to prepare nanowires of by Kahn and Petrikowski (2000).

Aerosol/vapor methods

Aerosol technologies, such as spray and laser pyrolysis, are attractive because these technologies are continuous chemical processes allowing for high rate of production (Veintemillas-Verdaguer *et al.*, 2002). In spray pyrolysis, a solution of ferric salts and a reducing agent in organic solvent is sprayed into a series of reactors, where the aerosol solute condenses and the solvent evaporates. The resulting dried product consists of particles whose size depends upon the initial size of the original droplets. Maghemite particles with size ranging from 5 to 60 nm with different shapes have been obtained using different iron precursor salts in alcoholic solution (Veintemillas-Verdaguer *et al.*, 2001; Veintemillas-Verdaguer *et al.*, 2002). Laser pyrolysis can be used to reduce the reaction volume. Laser heats the gaseous mixture of iron precursor and a flowing mixture of gas producing small, narrow size, and non aggregated nano particles. It is a well studied method of obtaining maghemite with particle sizes smaller than 10 nm (Morales *et al.*, 2003; Veintemillas-Verdaguer *et al.*, 2003). Oscar *et al.* (2008) reported synthesis of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles by in-situ hard and soft laser decomposition of gaseous $\text{Fe}(\text{CO})_5$ in air and by changing the initial Fe/O_2 ratio in the system the particle size could be controlled. Julian-Lopez *et al.* (2007) have reported the synthesis and characterization of hybrid silica-spinel iron oxide composite microspheres built with superparamagnetic nanoparticles for MRI, hyperthermia, and a hybrid mesoporous matrix, enabling the transport of bioactive molecules. These multifunctional platforms can be obtained by spray drying a sol of tunable composition, allowing for the control of the size and amount of magnetic particles embedded in the matrix.

Sonochemical technique

The sonochemical method has been extensively used to generate novel materials with unusual properties. The chemical effects of ultrasound have been found to be beneficial to form the new phases and are helpful to synthesize highly monodispersive NPs. At very high temperatures, hot spot generated by the rapid collapse of sonically generated cavities allows for the conversion of salts into nanoparticles. Bang and

Suslick (2007) reported sonochemical synthesis of nanosized hollow hematite. Vijayakumar *et al.* (2000) reported a sonochemical synthesis route for preparing pure nanometer-size Fe_3O_4 powder with particle size of 10 nm. The prepared Fe_3O_4 NPs were superparamagnetic and the magnetization at room temperature was very low (1.25 emu g^{-1}). Recently Pinkas *et al.* (2008) developed a sonochemical method for preparing amorphous nanoscopic iron oxide by sonolysis of $\text{Fe}(\text{acac})_3$ under Ar with a small amount of added water. The organic content and the surface area of the Fe_2O_3 NPs could be controlled with the amount of water in the reaction mixture, and it increased from $48 \text{ m}^2 \text{ g}^{-1}$ for dry solvent to $260 \text{ m}^2 \text{ g}^{-1}$ when wet Ar was employed. The sonolysis of an aqueous solution of $\text{Fe}(\text{CO})_5$ in the presence of sodium dodecyl sulfate led to the formation of a stable hydrosol of amorphous Fe_3O_4 nanoparticles (Abu and Gedanken, 2005). Superparamagnetic iron oxide nanoparticles (SPIO) having high magnetization and crystallinity have also been synthesized using a sonochemical method (Kim *et al.*, 2005). Ferro- fluids from these nanoparticles coated with oleic acid as a surfactant were prepared following the sonochemical methods. The coated SPIO could be easily dispersed in chitosan. The hydrodynamic diameter of the coated SPIO in the chitosan solution was estimated to be 65 nm, and they had a good stability. Shafi *et al.*, (1997) and Kumar *et al.*, (2001) used sonochemical technique to prepare nanoparticles of Fe, Fe_3O_4 , and Fe_2O_3 .

As presented in various subsections on synthesis, it can be observed that with time the synthesis procedures for preparation of iron oxides in nano range have gone through innovation. The major efforts have been devoted to obtain purpose specific particles. With the advancement in development of precision instruments for characterization of surfaces and particle size, it has now become possible to understand the nature of particles in much more details as compared to earlier times. Newer techniques and reagents have been employed for synthesizing nano iron oxides. The advancement has taken place from simple precipitation to surfactant mediation, emulsion, micro-emulsion, hydrothermal Sol-Gel etc. techniques, for obtaining monodispersed nano particles for different applications. Cost effectiveness of any synthesis procedure would depend on the final product and its application, for example, for high end use such as in drug delivery systems, comparatively higher cost of production is tolerable but when the product is to be utilized in mitigation of toxic ions from waste waters, it is essential to use low cost chemicals during synthesis.

4. Applications

As a colouring and coating material

The use of hematite and other iron oxides as natural red ceramic pigments has been practiced since prehistoric times. The iron oxides such as magnetite, hematite, maghemite and goethite are commonly used as pigments for black, red, brown and yellow colours respectively. Predominantly natural red iron oxides are used in primers for steel constructions and cars reducing corrosion problems. World consumption of iron oxide pigments comprises of 63% in synthetic form and 37% from natural resources. The construction sector – roof tiles, paving slabs and other concrete products – accounts for a major chunk of total world consumption. By reducing the particle size to nano range, transparent iron oxide pigments can be obtained. Manufacturing process of transparent iron oxide pigments depend on the control of physical and surface chemistry properties. Particle size is optimized to ensure that minimal light interference occurs thus maximizing transparency. In general particle size from 2 to 10 nm increases transparency 3- 10 time when compared to the bulk form (Elizabeth, 1992). Now a days such transparent iron oxide pigments are preferably used. These have good stability to temperature, the red can resist up to 300°C while the yellow, black, green and brown can withstand upto 160°C . These are strong absorbers of ultraviolet radiation (Sreeram *et al.*, 2006) and mostly used in automotive paints, wood finishes, construction paints, industrial coatings, plastic, nylon, rubber and print ink. The excellent weather fastness, UV absorption properties, high transparency and color strength makes trans-oxide to enrich the colors, increase color shades when combined with organic pigments and dyes.

As catalyst

Iron oxide-based materials have been found to be good candidates as cheap and efficient catalysts, especially in environmental catalysis. Miyata *et al.* (1978)) studied the catalytic activity of several iron oxides and oxide hydroxides of various particle sizes

for the reduction of 4-nitrotoluene using hydrazine hydrate as reducing agent, and found β -FeOOH was the most effective catalyst. For oxidation/reduction and acid/base reactions, the most applied iron oxides as catalyst are magnetite and hematite. Nano-particle iron oxide is significantly more effective than conventional micron-sized iron oxide (Walker *et al.*, 1988; Li *et al.*, 2003) for the oxidation of CO and the oxidative pyrolysis of biomass (Li *et al.*, 2003) or biomass model compounds (Li *et al.*, 2004; Shin *et al.*, 2004). These effects could be derived from the high activity of nano-particles that have high BET surface areas and more coordination of unsaturated sites on the surfaces. Chemical and electronic properties, such as phase changes, OH content, band gap changes etc., could also have contributed to their high reactivity. Iron oxide (usually mixed with other metal oxides) in particular, has been shown to be a very active (although unstable) catalyst for the oxygen evolution process as well as other related processes, such as water splitting, chlorine evolution, the oxidation of organic molecules, the oxygen reduction process and for the hydrogen peroxide decomposition. Even more important are iron oxide-based catalysts in non-electrochemical processes. In nature, nano- particulate hydrous iron oxide is the iron source for metallo-proteins and therefore stored in form of ferritins in the cells of animals, plants, fungi, and bacteria. The effects of heterogeneous catalyst with iron oxide as one of the phases were used in many important fields. Catalytic activity of nano sized Au/Fe₂O₃ at low temperatures on a CO oxidation reaction was investigated (Hutchings *et al.*, 2006). The catalytic activities of the Fe₂O₃-promoted catalysts for acid catalysis, 2-propanol dehydration, and cumene dealkylation with relation to Fe₂O₃ content were investigated by Sohn and Jim (2006). Heterogeneous catalysts based on magnetic mixed iron oxides (MO·Fe₂O₃; M: Fe, Co, Cu, Mn) were used for the discoloring of several synthetic dyes (Baldrian *et al.*, 2006). Multi-walled carbon nanotubes were synthesized employing a Cr_{2-x}Fe_xO₃ solid solution as a catalyst (Lima *et al.*, 2006). The Fe–Ce–O solid solutions (Fe, 5–50 mol%) are promising systems for improved N₂O decomposition catalysts (Perez- Alonso *et al.*, 2006). Iron and titanium mixed oxides have been found catalytically active for the reactions of cyclohexane oxidation (Perkas *et al.*, 2001), α -pinene oxide isomerization (Neri *et al.*, 2004), O-Cresol photo-degradation (Pal *et al.*, 2001) and formation of dimethyl ether from methanol (Wang and Ro 2006). Fe₂O₃ based nano materials have been developed for the selective catalytic reduction (SCR) of NO_x by NH₃ in diesel exhaust (Apostolescu *et al.*, 2001).

As gas sensing material

A number of studies have also been focused on iron oxide (Fe₂O₃), which, especially in the gamma, cubic phase, exhibits good sensing characteristics towards hydrocarbon gases, carbon monoxide and alcohol (Lee and Choi 1990; Peng and Chai, 1993; Siroky *et al.*, 1994; Tianshu *et al.*, 1996; Tao *et al.*, 1999; Lim *et al.*, 2001; Neri *et al.*, 2006). The sensitivity of iron oxide-based sensors can be enhanced by various doping schemes and a number of different dopants such as Pd, Sn, Ti, Zn etc have been used (Kanai *et al.*, 1992; Neri *et al.*, 2002; Reddy *et al.*, 2002; Vasiliev 1992; Tan *et al.*, 2003). While doping is an important factor for controlling the sensing characteristics, the sensor structure, and especially the thickness of its active layer, also has a great influence on the sensitivity. In fact, bulk and thick-film type sensors exhibit a relatively low sensitivity, which substantially improves when the same sensing material is used in a thin-film type sensor. Kaushik *et al.* fabricated a new glucose biosensor and a urea sensor based on iron oxide nanoparticles-chitosan nano composite (Kaushik *et al.*, 2008; Kaushik *et al.*, 2009). Wang and Tan (2007) have developed a novel amperometric glucose biosensor by immobilizing ferritin antibody on the surface of Fe₃O₄ nanoparticles. (Fe₃O₄NPs)/chitosan (Cs) composite film modified glassy carbon electrode (GCE) for determination of ferritin. A practical glucose biosensor was developed by Yang *et al.* (2009) by combining the intrinsic peroxidase-like activity of Fe₃O₄ nanoparticles and the anti-interference ability of the nafion film. The modified electrode could virtually eliminate the interference during the detection of glucose. Furthermore, the biosensor was successfully applied to detect glucose in human serum sample. Recently iron oxide nano-particles have also been tested for sensing different toxic biological drug like dopamine (Abolanle *et al.*, 2010). An efficient electro catalytic detection of dopamine was reported using electrodeposited Fe₂O₃ nano-particle catalyst supported on a SWCNT (single walled carbon nanotubes)-modified edge-plane pyrolytic graphite electrode (EPPGE) platform (EPPGE-SWCNT–Fe₂O₃).

As impurity control agent

Iron oxides have relatively high surface area and surface charge, therefore, often regulate free metal and organic matter concentrations in soil or water through adsorption reactions (Barrow *et al.*, 1989; Manceau

et al., 2000; Clausen and Fabricius,

2001; Randall *et al.*, 2001). Many toxic cations (Co, Zn, Pb, Cd, Cs, U, Sr etc.) and anions like AsO_4^{3-} , CrO_4^{2-} , PO_4^{3-} , CO_3^{2-}

etc. are removed by using various phases of iron oxide (Benjamin and Leckie, 1981; Todorovic *et al.*, 1992; Ding *et al.*, 2000; Zhou *et al.*, 2001; Luengo *et al.*, 2006; Mohapatra *et al.*, 2006). The adsorption properties of the iron oxide is due to combination of both surface complexation by inner or outer sphere bonding with adsorbate and ion exchange by van der Waal forces. Again the small size of nano particle also gives a high surface area-to-volume ratio, which facilitates interaction with several kinds of chemical species, both gaseous and aqueous (Hiemstra *et al.*, 2004). At the nanoscale these materials are potentially highly efficient for binding metal ions. By tailoring the composition of the metal oxides, one can induce selective adsorption of different metal ions. Use of iron oxide nanoparticles is thus becoming very attractive in the area of adsorption or recovery of metal ions from industrial wastes or natural water streams. Again magnetic separation has been shown to be a useful solid–solid phase separation technique. The problem with magnetic materials is that the particles interact with each other forming large aggregates. However, if the size of the magnetic nanoparticles is reduced to below a few nanometers, they become superparamagnetic. When a magnetic field is applied, the particles acquire a certain magnetization but, because of the high thermal energy, the long range

order is lost when the field is removed, and the particles have no remanent magnetization (Uheida *et al.*, 2006). This makes magnetic nanoparticles excellent candidates for combining metal binding and selective adsorption properties with ease of phase separation. Recently studies have been reported on removal of cations Pb(II), Cd(II), Cu(II) or Zn by nano structured goethite (Khatun *et al.*, 2007), doped goethite (Mohapatra *et al.*, 2009), ferrihydrite (Mohapatra *et al.*, 2010a) and akaganeite (Mohapatra *et al.*, 2010b) synthesized following different precipitation techniques. Nano goethite (Mohapatra *et al.*, 2010c), nano powders of mixed iron oxides (Mohapatra *et al.*, 2010d) and nano aluminum/iron mixed and pure oxides (Sujana *et al.*, 2009; Sujana *et al.*, 2010) have been reported to be good adsorbents for the removal of fluoride from aqueous solutions and contaminated groundwater. Cu, Ni, or Co doped nano goethites were found to be quite effective for arsenic removal from aqueous solutions (Mohapatra *et al.*, 2006).

As electro magnetic material

Nanoparticles of magnetic oxides, including most representative ferrites, have been studied for many years for their application as magnetic storage media and ferro-fluids. Over the recent years, gamma iron oxide ($\gamma\text{-Fe}_2\text{O}_3$), a ferromagnetic material is widely used as magnetic storage media in audio and video recording (Tsakalakos 2003), magneto-optical devices (Goya *et al.*, 2003; Kawanishi *et al.*, 1997), magnetic refrigeration (McMichael *et al.*, 1992) whereas $\alpha\text{-Fe}_2\text{O}_3$ in nano-size is a potential candidate for photo anode for possible photo-electrochemical cells (Prosini *et al.* 2002; Wang *et al.*, 2004a). Fe-based nano compounds as positive cathode materials for Li-ion secondary batteries are of interest due to the low-cost and non-toxicity (Lindgren *et al.*, 2002; Wang *et al.*, 2004b; Liu *et al.*, 2009). Cheng *et al.* (2006) prepared a nano-sized iron oxy-hydroxide (FeOOH) via a hydrolyzing route under mild and facile synthesis condition which delivered a capacity of about 237 mAh/g in the voltage range from 1.5 V to

4.2 V, and showed a very good cycling performance in the voltage range from 1.6 V to 3.3 V with a capacity of 170 mAh/g. A novel "sacrificial template-accelerated hydrolysis" (STAH) approach to the synthesis of iron oxide-based nanotube arrays including hematite octahedral- Fe_2O_3 and magnetite Fe_3O_4 was reported by Liu *et al.* (2010). By introducing glucose into the precursor solution, they obtained carbon/hematite($\text{C}/\alpha\text{-Fe}_2\text{O}_3$) composite nanotube arrays on large-area flexible alloy substrate, with a large number of pores and uniform carbon distribution at a nanoscale in the nanotube walls. These arrays have been demonstrated as excellent additive-free anode materials for lithium ion batteries in terms of good cycling performance up to 150 times (659 mA h g^{-1}) and outstanding rate capability.

Biological applications

Biomedical applications of iron based magnetic nanoparticles (MNPs) are classified according to their application inside (in vivo) or outside (in vitro) the body. In vivo applications could be further separated in therapeutic (hyperthermia and drug- targeting) and diagnostic applications (nuclear magnetic resonance (NMR) imaging), while for in vitro applications the main use is in diagnostic (separation/selection and magneto-relaxometry). Aqueous magnetic fluids composed of small magnetic particles about 5–20 nm covered with biocompatible functionalized shells are well known for their use in hyperthermia, as immuno

assays, as imaging for the magnetic mapping of organs, as magnetic carriers for identification and isolation of blood cells and antibodies and for transportation of drugs to the places of diseases (Reimer and Weissleder, 1996; Bonnemain, 1998; Rogers *et al.*, 1999; Babincova *et al.*, 2001; Portet *et al.*, 2001; Wang *et al.*, 2001; Wunderbaldinger *et al.*, 2002; Arbab *et al.*, 2003; Pankhurst *et al.*, 2003). Every application needs its own tailored magnetic core/shell composition. Magnetite, Fe_3O_4 , has a cubic inverse spinel structure where electrons can hop between Fe^{2+} and Fe^{3+} ions in the octahedral sites at room temperature, rendering it an important class of half-metallic materials. With proper surface coating, these magnetic nanoparticles can be dispersed into suitable solvents, forming homogeneous suspensions, called ferrofluids (Babincova *et al.*, 2001). Such a suspension can interact with an external magnetic field and be positioned to a specific area, facilitating magnetic resonance imaging for medical diagnosis and AC magnetic field-assisted cancer therapy. Again the nano size of magnetic particle with large surface area change some of the magnetic properties and exhibit superparamagnetic phenomena and quantum tunneling of magnetization which offer a high potential for several biomedical applications (Reimer and Weissleder, 1996; Bonnemain, 1998; Arbab *et al.*, 2003; Pankhurst *et al.*, 2003). Several iron oxide based cell labeling techniques have been developed including conjugation with antigen-specific internalizing monoclonal antibody, modification of USPIO (ultra small super paramagnetic iron oxide) or MION (mono crystalline iron oxide nanoparticles) with tat-proteins facilitating the incorporation into the cells (Häfeli *et al.*, 1997; Josephson *et al.*, 1999; Lewin *et al.*, 2000; Bulte *et al.*, 2001).

Active research work is continuing in finding suitable biomedical applications of versatile iron oxides in the nano scale both for drug release and drug delivery (Kubo *et al.*, 2001; Frank *et al.*, 2003; Gonzales *et al.*, 2005; Cengelli *et al.*, 2006; Aslam *et al.*, 2007; Naka *et al.*, 2008; Piao *et al.*, 2008; Guo *et al.*, 2009; Mahmoudi *et al.*, 2009; Zheng *et al.*, 2009; Tran *et al.*, 2010). Engineered fluorescent SPIONs have been developed by Cengelli *et al.* (2006) for drug delivery and imaging of brain-derived structures. These SPIONs were coated with PVA functionalized with a fluorescent reporter molecule and were administered to a microglial cell culture containing immune cells of the nervous system. Mahmoudi *et al.* (2009) prepared iron oxide NPs with a cross-linked poly (ethylene glycol)-co-fumarate (PEGF) coating. The cross-linked PEGF coating reduced the burst release by 21% in comparison with the noncross-linked tamoxifen loaded particles. Mono-disperse SPIONs with a mesoporous structure were prepared via simple solvothermal method by Guo *et al.* (2009) for studying loading and release behaviour of anticancer drug, (Doxorubicin, Dox). The release behaviour of Dox indicated that these SPIONs had a high drug loading capacity and favourable

release kinetics for this drug. Similar studies have been carried out for targeted delivery applications (Kubo *et al.*, 2001; Gonzales *et al.*, 2005). Most of polymeric coatings in SPIONs are selected from hydrogel categories. Permeability, temperature sensitivity, pH sensitivity, osmolarity sensitivity, surface functionality, swelling, biodegradability, and surface biorecognition sites are recognized as major factors for controlled drug release applications of hydrogels (Meyers *et al.*, 1963).

Naka *et al.* (2008) have reported the synthesis of methylimidazolium cation-modified iron oxide nanoparticles and estimated their potential biological application. The modified iron oxide nanoparticles of 7.6 to 11.3 nm were well-dispersed in water. The iron oxide nanoparticles modified with N-methylimidazolium cation can turn their water-miscibility and binding capacity for DNA by exchanging the counter anions by MRI. Aslam *et al.* (2007) demonstrated a simple one-step process for the synthesis of iron oxide nanoparticle aqueous colloids using the multifunctional molecule dodecylamine (DDA), which electrostatically complexes with aqueous iron ions (one precursor Fe^{2+} from FeCl_2), reduces them, and subsequently caps the nanoparticles. The iron oxide particles thus synthesized were of the face-centred cubic (FCC) phase with a high degree of monodispersity and an appropriate concentration of the amine-capping molecular layer. The magnetic nanocrystalline particles obtained were of average diameter 30 ± 10.5 nm size and were tested for potential application in magnetic resonance imaging (MRI). Piao *et al.* (2008) reported a novel wrap–bake–peel process, which involves silica coating, heat treatment and finally the removal of the silica layer, to transform the phases and structures of nanostructured materials while preserving their nanostructural characteristics. They described the fabrication of water-dispersible and biocompatible hollow iron oxide nanocapsules by applying this wrap–bake–peel process to spindle-shaped akaganeite ($\beta\text{-FeOOH}$) nanoparticles. Depending on the heat treatment conditions, hollow nanocapsules of either haematite or magnetite were produced. The synthesized water-dispersible magnetite nanocapsules were successfully used as a drug-delivery vehicle, and also as a T_2 magnetic resonance imaging contrast

agent. Doxorubicin (DOX), a chemotherapeutic agent, was used as a model drug and was incorporated into the nanocapsules.

Modified magnetic starch nanoparticles (FA-StNP@ Fe₂O₃) were synthesized by conjugating folic acid (FA-PEG-NH₂) onto the surface of magnetic starch nanoparticles (StNP@ Fe₂O₃) prepared by reverse microemulsion method (Zheng *et al.*, 2009). The average size of its well dispersed particles was 250 nm. Placing FA-StNP@ Fe₂O₃ nanoparticles in the alternating magnetic field for 30 min resulted in an increase in the suspension temperature from ambient temperature (37°C) to a value between 42°C and 43°C.

Magnetic nanoparticles (Tran *et al.*, 2010) have recently been used to treat bone diseases (such as osteoporosis and infection) by using surface modified magnetic nanoparticles. Magnetite (Fe₃O₄) and maghemite (Fe₂O₃) were coated with calcium phosphate (CaP).

Various applications of iron oxides/hydroxides/oxyhydroxides in nano form can be attributed to the difference in behaviour of particles in nano scale as compared to their bulk counterparts. The nano particles usually have much larger surface area due to their smaller size and can reduce the volume required to achieve same effect when used as a catalyst. In case of mitigation of anions

/cations from aqueous solutions, iron oxides in nano form will have higher number of active sites for adsorption, thereby reducing the amount required per liter of solution. The adsorption process involves surface hydroxyl group interaction with adsorbents. Nano iron oxides exhibit very different magnetic properties which can be used for soft ferrites and biomedical applications including drug delivery and magnetic resonance imaging. Down to the nanoscale, superparamagnetic iron oxide nanoparticles can only be magnetized in the presence of an external magnetic field, which makes them capable of forming stable colloids in a physio-biological medium. Their superparamagnetic property, together with other intrinsic properties, such as low cytotoxicity, colloidal stability, and bioactive molecule conjugation capability, makes such nanomagnets ideal in both *in-vitro* and *in-vivo* biomedical applications (Lin *et al.*, 2010).

Considering numerous applications of iron oxides in various emerging fields, tremendous efforts on synthesis of nano-dispersed particles are continuing. The biggest challenge in this field is to economically produce iron oxide nano particles of desired characteristics for specific application in large scale. There has been a lot of progress in understanding the basic science of nano iron oxides but evaluation of economic viability for commercial application needs much more attention.

5. Conclusions

1. Iron oxide nano-particles (NPs) are of considerable interest due to their wide range of applications in fields such as magnetic storage, medicine, chemical industries and water purification.
2. Typical nano-particle synthesis methodologies involve routes including precipitation, sol-gel, hydrothermal, dry vapordeposition, surfactant mediation, microemulsion, electro-deposition and sonochemical.
3. The above mentioned synthetic methods have several advantages and disadvantages for preparing iron oxide nano particles (NPs). While these methods often furnish particles with narrow size distributions they tend to require re-optimization for each desired particle size, shape, or surface functional groups.
4. In terms of size and morphology control of the iron oxide NPs, thermal decomposition and hydrothermal synthetic route seems the optimal methods. For obtaining the water-soluble and biocompatible iron oxide NPs, co-precipitation was often employed, but this method presents low control of the particle shape, broad distributions of sizes and aggregation of particles. As a time competitive alternative, sonochemical route can also be used to synthesis iron oxide NPs with unusual magnetic properties.
5. The magnetic nano-crystals are receiving much attention as these are now emerging in biomedical applications with new possibilities.

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