# **Recent developments in the synthesis and stability of metal ferrite nanoparticles**

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## **Abstract**

This article presents a comprehensive review on the synthesis and stability of ferrite nanoparticles such as nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>), zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>), manganese ferrite (MnFe<sub>2</sub>O<sub>4</sub>), iron ferrite (Fe<sub>2</sub>O<sub>3</sub>), cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) and also mixed nanoparticles. Different synthetic methods for ferrite nanoparticles have been reviewed such as co-precipitation, thermal decomposition and hydrothermal, microwave-assisted and sonochemical methods. The effect on the stability of different capping agents like canola oil, glycerol, sodium dodecyl, sodium citrate, oleic acid, Triton-100 and sodium dodecyl benzene sulfonates has also been studied.

#### **Keywords**

Ferrite mixed nanoparticles, capping agent, hydrothermal method

## **Introduction**

Nanotechnology includes the control and understanding of matter of 1–100nm dimensions, where distinctive physical phenomena facilitate novel applications. The chemical and physical properties of nanomaterials are largely governed by their size, shape or morphology. A deviation in the size of nanomaterials can alter their physical properties without changing their composition. When the particle size falls below 100nm, a large fraction of the component atoms is located on the surface of the nanocrystals, thus suggesting major changes in the magnetic structure and properties of the nanomaterials in contrast to their bulk counterparts. These nano- and micro-changes lead to new phenomena such as superparamagnetism, enhanced anisotropy and spin canting. Nanomaterials have been

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greatly utilized worldwide over the last 20years due to their better thermophysical properties in engineering applications.<sup>1,2</sup> This management of matter, with nanometre dimensions, has enabled the manufacture of new devices, structures and materials. Nanoparticles (NPs) offer an exceptional advance in certain sectors, as in medicine, consumer products, energy, materials and manufacturing. $3-5$  It has been shown that ferrites also act as a multifunctional detoxicant for soluble metal ions other than iron.<sup>1–3</sup> Studies published in the 80s evidenced ferrites having in vivo binding potential for metals such as  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Al^{2+}$ ,  $Zn^{2+}$  and Be<sup>2+</sup> after administration of their respective salts.<sup>4,5</sup> The production of small magnetic NPs with sizes from 2 to 20nm is important, because of their uses in multi-terabyte magnetic storage devices.6 The magnetic properties of NPs originate because of the compact sizes of isolated NPs, and the influence of interparticle interactions is insignificant. The main issues in NP production are homogeneity of particle size, size control, crystal structure, shape control and arrangement for device applications.<sup>7</sup> Ferrites are superparamagnetic, hard and brittle ceramic materials. The general formula of ferrites is  $M_1M_2O_4$ , where  $M_2$  is Fe and  $M_1$  is a transition metal which accounts for enhancing and elevating the magnetic properties of the ferrites. Depending upon coercivity, ferrites can be divided into soft ferrites and hard ferrites. Soft ferrites are distinguished as having a short period of magnetization and demagnetization, giving reduced hysteresis loss and low coercivity. The small loop area of soft ferrites opens its applications in switching circuits, magnetic drug delivery, treatment of bacterial infection and electromagnetic cores of various transformers.8 In contrast, hard ferrites have a high magnetic strength value of  $0.35T - 160kAm^{-1}$  for their cycle of magnetization and demagnetization – and have greater values of their coercivity and retentivity. These ferrites act as permanent magnets due to their high flux density and hysteresis loss, and are used for the preparation of data storage devices, microelectronics, radio formation and magnetic analysis.

## **Comparison of the syntheses of ferrite NPs**

## *The co-precipitation method*

The particles obtained with the co-precipitation method have a broad size distribution.<sup>9</sup> For the preparation of monodisperse NPs of magnetite, a number of methods are used as follows:

- 1. This is selected according to which a high temperature up to  $(265^{\circ}C)$  is to be maintained: Fe(acac)<sub>3</sub> (iron(III) trisacetylacetonate) is reacted with phenyl ether with alcohol, oleylamine and oleic acid. Using smaller NPs of magnetite as seeds, larger monodisperse magnetite NPs of up to 20 nm diameter can be synthesized and dispersed into a nonpolar solvent. The process does not require a size selection procedure and is readily scaled up for mass production.10
- 2. The co-precipitation method is modified to synthesize iron oxide NPs: 0.074 g of ferric chloride and  $0.190$  g of ferrous chloride FeCl<sub>2</sub> are used in a 2:1 ratio. These were dissolved in 20mL of deionized water, stirred and heated at 60°C. To retard any unwanted oxidation reaction, the mixture was bubbled by Ar gas. Then,



**Figure 1.** Schematic of the formation mechanism of the nanoporous polyaniline and hollow  $MnFe<sub>2</sub>O<sub>4</sub>$  nanocomposite.

10mL of 2.5M NaOH was added at 60°C for 20min. Magnetic separation was used to remove NPs from the reaction mixture. To control particle size, the amount and concentration of NaOH solution were varied.11

 $NiFe<sub>2</sub>O<sub>4</sub>$  NPs are synthesized using the co-precipitation method. 20 mL of 0.1 M aqueous NiCl<sub>2</sub>·6H<sub>2</sub>O is added in 40mL of aqueous 0.1 M FeCl<sub>3</sub> in a round-bottomed flask. 4 g of urea and 50mL of ethylene glycol are mixed and the whole refluxed for 6 h under nitrogen at 145°C. A brown-coloured precipitate appears. Centrifugation is used to collect the precipitate. To remove excess ethylene glycol, centrifugation is repeated several times using CH<sub>3</sub>OH and CH<sub>3</sub>OCH<sub>3</sub>. By changing the heating temperature (400 $^{\circ}$ C, 500 $^{\circ}$ C, 700 $\degree$ C, 800 $\degree$ C) in air for 4h, NiFe<sub>2</sub>O<sub>4</sub> NPs of various sizes can be prepared.<sup>12</sup>

 $MnFe<sub>2</sub>O<sub>4</sub>$  NPs were prepared by the co-precipitation method with canola oil as a surfactant as presented in Figure 1. 0.2 molL<sup>-1</sup> of MnCl<sub>2</sub>·6H<sub>2</sub>O and 0.4 molL<sup>-1</sup> of FeCl<sub>3</sub>·6H<sub>2</sub>O were reacted with steady magnetic stirring. An appropriate amount of canola oil was used as a capping agent to retard particle growth. To maintain pH  $(11-12)$ , a 3M aqueous NaOH was added dropwise.6,7 The reaction mixture was heated for 1 h at 80°C under constant stirring in order to convert the co-precipitate into spinel ferrite. The resulting mixture was cooled to room temperature. The precipitates were separated and washed with water and ethanol several times. The resulting powder was heated in air at 500°C for 6 h.

Nanocrystalline  $\text{CoFe}_2\text{O}_4$  was synthesized by a simple co-precipitation method with canola oil being used as a surfactant. The stoichiometric quantities of analytical grade reagent (0.2 M CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.4 M FeCl<sub>3</sub>·6H<sub>2</sub>O) were stirred magnetically. An appropriate quantity of surfactant (canola oil) solution was mixed in the above solution, in order to limit the particle growth and act as a capping agent. A solution of 3M NaOH was added dropwise. The pH was adjusted to 11–12 during the reaction using aqueous NaOH. The details concerning the co-precipitation method have already been communicated.<sup>13,14</sup> To convert the co-precipitate into spinel ferrite, the reaction mixture was heated and maintained for 1h at 80°C with constant stirring. The reaction mixture was cooled down to room temperature. The precipitates were removed and washed with ethanol and water several times. The resulting ferrites were heated for 6h at 500°C in air.

 $ZnFe<sub>2</sub>O<sub>4</sub>$  NPs were prepared by the chemical co-precipitation method. Aqueous  $FeCl<sub>3</sub>·6H<sub>2</sub>O$  and ZnCl<sub>2</sub> solutions were prepared by mixing suitable amounts of (Fe/Zn in 2:1) in 100mL of distilled water. A 4M solution of NaOH was used as a precipitating agent. Metal chlorides and NaOH solution were added dropwise (2mLmin−1) from two different burettes in the reaction vessel containing 100mL of distilled water, and the solution was heated at  $40^{\circ}$ C with constant stirring. After 2h, the precipitates that were obtained were centrifuged at 6000 r/min, washed repeatedly with acetone and distilled water and dried.<sup>15</sup>

#### *The combustion synthesis*

The solution combustion synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>: 0.140 mol of 96% Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.179 mol of 99%  $D$ -(+)-C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> were mixed in 40 mL of distilled water in a roundbottomed flask. The flask was positioned in a heating mantle at 400°C. When the solution was heated, a smouldering combustion effect was observed between  $Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O$ and glucose. A huge quantity of gases was evolved during this reaction. These gases were passed into a beaker of distilled water.12 After 30min, the gas development ceased and a black voluminous powder was formed. 50% of this black powder was further reacted with  $H_2O_2$  with constant mechanical stirring, followed by evaporation to dryness. Each gram of the black powder was reacted with  $50 \text{ mL of H<sub>2</sub>O<sub>2</sub>$ . Following evaporation towards dryness, a reddish brown powder was formed. 0.7 g of the reddish brown powder was sonicated for 2h and the particles were covered with a bilayer of oleic acid. The oleic acid bilayer covering the NPs were diffused in 25mL of saline solution, to achieve a stable colloidal suspension.16

To synthesize  $\text{CoFe}_2\text{O}_4$  NPs, a combustion method applied: aqueous solutions of  $Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O$  and  $Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O$  were prepared and mixed. Then an appropriate amount of glycine was mixed in this solution.<sup>17</sup> The resultant solution was heated to a high temperature until combustion happened. Then sample was annealed at 200°C for 30min.18,19 Combustion is an easy and quick mode of preparing NPs which provides high-value products. By altering the rate of fuel and the nitrates, the magnetic coercivity, size and magnetization can be varied.<sup>18,19</sup>

 $ZnFe<sub>2</sub>O<sub>4</sub>$  NPs were prepared by the solution combustion technique with 7.43 g of  $Zn(NO<sub>3</sub>)$ <sup>2</sup>·6H<sub>2</sub>O, 7.27 g of Fe(NO<sub>3</sub>)<sup>2</sup>·6H<sub>2</sub>O and 6.05 g of urea which act as the fuel. Urea has a high heat of combustion  $\Delta H_c$ . In the first step, urea, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and  $Fe(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O$  were taken in a 1:1:4 stoichiometric ratio and a uniform paste was prepared. A thick gel was obtained by heating this paste on a hot plate at 70°C–80°C. Then the gel was auto-combusted at  $170^{\circ}$ C $-180^{\circ}$ C on a hot plate to produce nanocrystalline  $\text{ZnFe}_{2}\text{O}_{4}$  in 5 min. The nanocrystalline  $\text{ZnFe}_{2}\text{O}_{4}$  powder was annealed at various temperatures, that is,  $300^{\circ}$ C,  $500^{\circ}$ C,  $800^{\circ}$ C and  $1000^{\circ}$ C for 4h which provided a radiating powder of brown colour.20

#### *The sol–gel method*

For the synthesis of nanostructured metal oxides, the sol–gel method is an appropriate wet route.21 This process depends on hydroxylation and condensation of the molecular precursors in the solution state, initiating a 'sol' of nanometric particles. Solvent removal or chemical reaction is applied to the dried/gelled sol to obtain a three-dimensional (3D) metal oxide network. The gel properties are based on the arrangement formed in the sol phase of the sol–gel method. Water is generally used as a solvent but acid/base can also be used to hydrolyze the precursors. A colloidal gel is produced by acid catalysis, while base catalysis produced polymeric gel. Room temperature is used for these reactions but for the final crystalline state a heat treatment is applied.

The sol–gel method of preparing  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs is described as follows: 0.2M ferric nitrate was dissolved in 100mL ethylene glycol under constant stirring for 2h at 401°C, and the sol was heated and maintained at 801°C to obtain a brown gel. The gel was ripened for 2h and then dried at  $1201^{\circ}$ C for ca. 4h. Subsequent to drying, the xerogel obtained was annealed at 200°C–400°C in vacuo. Finally, various-sized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were produced.22

 $NiFe<sub>2</sub>O4$  *NPs*. In the sol–gel method, aqueous 0.4mol NiNO<sub>3</sub> and 0.8 mol ferric nitrates were prepared and mixed in peracetic acid (PAA) solution. Phase separation occurred. A suitable amount of  $HNO<sub>3</sub>$  was added dropwise to this solution till a clear green solution of pH 3.0 was obtained. The solution was evaporated at 50°C to obtain a transparent sol. Water was evaporated from the sol by heating at 50°C for 10h as a result of which the sol changed into a thick brown gel. By varying the molar ratio of PAA and metal ions (0.5, 1.0, 1.5 and 2), different gels were prepared. To remove the organic content, the gels were calcined at 300°C/400°C for 2 h at a rate of 5°Cmin−1 and spinel  $NiFe<sub>2</sub>O<sub>4</sub>$  NPs were obtained.<sup>23</sup>

The sol–gel technique was used for the lower temperature preparation of glass, ceramics and others. In this technique, the precursor materials,  $Mn(CH_3CO_2.4H_2O)$  and  $Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O$ , were mixed in deionized water and ethylene glycol with constant stirring until a uniform mixture was obtained, which was then heated at 70°C for 12 h and dried at 80°C for 24h. The resultant gel was finally ground, reheated at 900°C for 2h and slowly cooled down to obtain MnFe<sub>2</sub>O<sub>4</sub> NPs. Finally, sintering was conducted at  $1200^{\circ}$ C for 3 h at a rate of 2°Cmin−1 followed by slow cooling at room temperature at the same rate.24

A solid-state technique was used to prepare  $\text{ZnFe}_2\text{O}_4$  NPs. An appropriate quantity of 99.6% Fe<sub>2</sub>O<sub>3</sub> and 99% ZnO powder were ground and calcined at 1200 $^{\circ}$ C for 2 days. In the sol–gel technique, a clear solution of iron and zinc nitrates was prepared by dissolving in a small amount of deionized water. To prepare the gel, polyvinyl alcohol was used. An aqueous solution of polyvinyl alcohol was mixed with the solution of nitrates, and water was evaporated at 60°C–80°C. The gelation process was stopped and a dull red– coloured gel-type precursor was formed.  $ZnFe<sub>2</sub>O<sub>4</sub>$  NPs were obtained on calcination of this precursor at 350°C–450°C.25

Using the sol–gel method, stoichiometric amounts of  $Co(CH_3CO_2)$ , 4H<sub>2</sub>O (1/200 mol) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1/100 mol) were dissolved in 100 cm<sup>3</sup> of 2-methaoxyethanol and

2cm3 of diethanolamine with the help of an ultrasonic cleaner. The reaction mixture was refluxed at 70 $\degree$ C for 12 h. The crystallization temperature of CoFe<sub>2</sub>O<sub>4</sub> was determined by drying some portion of the solution for Mossbauer spectroscopy.  $\text{CoFe}_2\text{O}_4$  films were spin-coated onto thermally oxidized Si wafers of  $\sim$ 700Å at 4000 r/min for 30 s. The substrate was washed with the standard cleaning silicon process before spin coating.<sup>26</sup> After spin coating, thin films were pyrolysed to 120°C and 270°C for 3 and 10min, respectively. To gain the required thickness, the process of deposition was repeated. Spincoated powders and samples were annealed at different temperatures from 350°C to 950 $\rm{^{\circ}C}$  for 3 h in air.<sup>27</sup>

#### *The sonochemical method*

In the sonochemical method, structural hosts, polymers or organic capping agents, are applied to reduce NP growth.<sup>21</sup> Cavities are produced in the aqueous medium due to the ultrasonic irradiation, and the formation, growth and collapses of microbubbles take place.28 The high temperatures and pressures generated by cavitations facilitate the occurrence of a number of remarkable chemical reactions. In some cases, thermally induced processes give crystalline NPs, while ultrasonic reactions produce amorphous products.

Using this method, the volatile organometallic compound,  $Fe(CO)$ <sub>5</sub>, was sonochemically decomposed with the addition of the stabilizer to prepare nanosized iron colloid. Ultrasonic irradiation of 0.2 mL of Fe(CO)<sub>5</sub> in 20 mL of octanol with 1 g of polyvinylpyrrolidone (PVP) with ( $M \approx 40,000$ ) was performed. The reaction mixture was heated at  $20^{\circ}$ C in an O<sub>2</sub>-free Ar atmosphere, creating a black colloidal solution. Oleic acid can be used as a colloid stabilizer.<sup>29</sup> The tail of oleic acid (stabilizer) has a double bond, which is significant to its usefulness, as stearic acid cannot be used as a stabilizer. A hexadecane solution of 2 mol Fe(CO)<sub>5</sub> and 0.3 mol oleic acid was sonicated at 30°C for 1h, as a result of which the initial yellow-coloured solution changed to black. The resultant black solution of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was evacuated to 50<sup>o</sup>C for 1 h to remove unreacted Fe(CO)<sub>5</sub> and its isolation of an inert atmosphere system for further characterization.30

The sonochemical method was used to prepare NiFe<sub>2</sub>O<sub>4</sub> by reacting Ni(CO)<sub>4</sub> and  $Fe(CO)<sub>5</sub>$ . Ni $(CO)<sub>4</sub>$  is a very poisonous liquid with an elevated vapour pressure. It is highly sensitive to moisture and so has to be handled carefully. Pentane (Fluka) and decalin (Sigma) were carefully dried with Na metal/4Å molecular sieve and stored in a glovebox. Ar gas was used to degas the precursor solution. The NiFe<sub>2</sub>O<sub>4</sub> NPs were synthesized by ultrasonic irradiation of Ni(CO)<sub>4</sub> and Fe(CO)<sub>5</sub> in decalin at (273 K, 100–150 kPa) with a high-intensity ultrasonic probe. 3h of irradiation provided a black powder which was then centrifuged and washed repeatedly with dry pentane in the glovebox.<sup>31</sup>

In the sonochemical process,  $Fe(CO)$ <sub>5</sub> was used without any purification.  $Co(CO)_{3}(NO)$ was synthesized by the usual procedure. Pentane and decalin were dried by Na metal/4Å molecular sieve. The  $\text{CoFe}_2\text{O}_4$  NPs were synthesized by ultrasonic irradiation of a solution of  $Co(NO)(CO)$ <sub>3</sub> and  $Fe(CO)$ <sub>5</sub> at 0°C, with 100–150 kPa pressure of  $O_2$  gas, by a high-strength ultrasonic probe (20kHz, 100Wcm−2). A black powder was obtained after 3h of irradiation; this was centrifuged and washed five times with dry pentane under vacuum.32



**Figure 2.** Illustration by the IR spectra of the formation of larger monodisperse magnetite nanoparticles using smaller nanoparticles of magnetite as seeds.

Conductive polymer composites, materials encoded by inorganic NPs such as  $\text{Al}_2\text{O}_3$ ,<sup>33</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>33</sup> RuO<sub>2</sub><sup>34</sup> and TiO<sub>2</sub>,<sup>35</sup> are important due to their interactions with polymeric matrices to give novel properties. An  $MnFe<sub>2</sub>O<sub>4</sub>$  nanocomposite was synthesized using  $4 \text{ mL of aniline } (0.044 \text{ M})$  and  $10 \text{ mL of the distribution of the field.}$  The mixed and stirred for 15min. In a separate container, 10mL of deionized water was used to dilute 5 g of dodecylbenzenesulphonic acid (DBSA) to give a pulpy mixture. The pulpy mixture was then poured into aqueous aniline solution and the emulsion was agitated for 1 h to form a homogeneous phase. Next, 5mL of an aqueous solution of 0.6 g hollow ferrite spheres was ultrasonicated for 10min and poured into the above suspension. The mixture was sonicated for a further 15 min and agitated by stirring for 15 min; 10 mL of an aqueous solution of 5 g of ammonium persulphate  $(0.022 M)$  as an oxidizing agent was gradually added (for 15min) with mechanical stirring to start the polymerization reaction. The green precipitate of polyaniline (PANi) and the MnFe<sub>2</sub>O<sub>4</sub> nanocomposite was filtered, washed with distilled water and dried for 24 h in an oven at 601°C.36 The formation of larger monodisperse magnetite NPs using smaller NPs of magnetite is illustrated in Figure 2.

#### *The microwave-assisted method*

Microwave-assisted chemistry has gained much attention in recent years. The greatest benefit of microwave-assisted irradiation is its uniform heating of a substance in a glass or plastic reaction vessel, which is responsible for homogeneous nucleation and a smaller crystallization time as compared to conventional heating. This leads to the development of homogeneous colloidal materials.

In the microwave-assisted preparation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs, polyethylene glycol (PEG)-20000 (60 mg) and FeCl<sub>3</sub>·6H<sub>2</sub>O (76 mg) were mixed in 10 mL of distilled H<sub>2</sub>O. Then

0.4mL of hydra and 1mL of  $H_2O_2$  were dissolved in this solution (note that heat is evolved during the reaction), and a red-coloured product was obtained. This suspension was heated at  $100^{\circ}$ C by microwave heating for  $10 \text{ min}$  and the resultant product was separated through centrifugation, washed twice with distilled  $H_2O$  and absolute ethanol. The microwave oven used for the preparation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs (2.45 GHz, maximum power 300W) was a fixed single-mode microwave system (Discover; CEM). The exclusive, spherical single-mode cavity makes sure that the sample was in very concentrated microwave field. The system featured a magnetic stirrer and a watercooled condenser. The temperature was maintained by automatic adjustment of the microwave system.37

An aqueous solution of vinyl pyrrolidone was prepared by mixing 4 g in 100mL of deionized water at 363 K. 0.2 mM of Fe(NO<sub>3</sub>), 6H<sub>2</sub>O and 0.1 mM of Zn(NO<sub>3</sub>), 6H<sub>2</sub>O in the ratio of 2:1 were added to the polymer solution which was stirred vigorously for 2 h to give a colourless and transparent solution. A glass electrode was used to maintain the pH of solution at  $1-2$ . The reaction mixture was annealed at  $353 \text{ K}$  in an oven for 48 h to evaporate H<sub>2</sub>O. The orange-coloured  $\text{ZnFe}_2\text{O}_4$  was powdered in a mortar and calcined at 723, 773, 823 and 873 K for 3 h to decompose organic matter and crystallized.38

## *The thermal decomposition method*

The thermal decomposition method was used to synthesize NiFe<sub>2</sub>O<sub>4</sub>. 1 mM of Ni(acac)<sub>2</sub> in 15mL benzyl ether and  $2 \text{ mM of } Fe(aca)$  in 15mL of oleylamine were dissolved under constant stirring to prepare a homogeneous solution. Water was evaporated at 110°C for 1 h under N<sub>2</sub> (g), then the temperature was raised to 300°C for 1 h. The solution was then cooled to room temperature. The spinel ferrite was removed from the ethyl acetate–ethanol mixture, followed by centrifugation at 14,000 r/min for 30min. The final product was washed with ethanol and centrifuged. The sample was dried at 150°C. In this procedure, oleylamine plays three roles, namely, as a reductant, as a solvent and as a surfactant.<sup>39</sup>

## *The electrochemical method*

 $NiFe<sub>2</sub>O<sub>4</sub>$  was also prepared by an electrochemical method utilizing iron and nickel anodes of 99.5% purity. Ni $(CH_3)_4$ Cl was used as a supporting electrolyte. The currents functional to the Ni and Fe anodes were 50 and 100mA, respectively. The reaction proceeded for 30min at 60°C. The resultant precipitate was magnetically separated, washed with distilled H<sub>2</sub>O and dried in vacuum at  $60^{\circ}$ C for 12 h.<sup>40,41</sup>

## *The solvothermal synthesis*

A 15 mL solution of 0.54 g of  $FeCl<sub>3</sub>·6H<sub>2</sub>O$  and 0.14 g of  $ZnCl<sub>2</sub>$  was prepared in glycerol and deionized  $H_2O$  in a volume ratio of 1:1 and then 0.8 g of CH<sub>3</sub>COONa was agitated in the solution by stirring. The mixture was poured into a 40mL Teflon-lined autoclave and heated at 200°C for 24 h in an oven. Then the autoclave was cooled to 25°C. The solid



**Figure 3.** General scheme for schematic synthesis of metal ferrite nanoparticles.

products were centrifuged and washed with ethanol and distilled water and dried in the oven at  $60^{\circ}$ C for 6 h.<sup>42</sup>

#### *The refluxing method*

For the preparation of nanocrystalline Ni–Zn ferrite powders, the refluxing method was used. Ferric chloride, nickel sulphate and zinc sulphate were used as the starting agents in the aqueous solution. The salts were mixed in stoichiometric quantities  $(Ni:Zn:Fe = 1:1:4)$ . An aqueous solution of NaOH was added to the starting solution under constant magnetic stirring until the pH became 9.5–12. The reaction mixture was constantly refluxed at about 107°C for a definite time. The precipitates formed were filtered after repeated washing with alcohol and water, and alcohol, respectively, and dried at 100 $^{\circ}$ C for 6 h.<sup>43</sup> A schematic of the synthesis of metal ferrites is shown in Figure 3.

## *Effects of surfactant on metal ferrite NPs' stability*

Optical absorbance has been used to measure the stability of  $Fe<sub>2</sub>O<sub>3</sub>$  NPs in the colloidal solution. Various surfactant concentrations were used to prepare colloidal solutions in quartz cuvettes. After the preparation of the suspension, the absorbance spectra of  $Fe<sub>2</sub>O<sub>3</sub>$ NPs were obtained instantly (*True*=0h) and time (*True*=x), by keeping the colloidal suspension undisturbed. To measure the ultraviolet–visible (UV/VIS) absorbance spectra of the colloidal samples without saturation, dilutions of 1:100 and 1:200 were selected.

Initially, no specific UV–VIS peak appeared. However, with the passage of time, a decrease in absorbance was seen due to sedimentation of the  $Fe<sub>3</sub>O<sub>3</sub>$  NPs. The sedimentation occurred at a higher rate in the initial period after sonication as shown by the UV/ VIS spectrum. This effect appeared due to the absence of stabilizer in the colloidal solution, due to which aggregation of NPs occurred and their sizes increased in solution, which led to faster sedimentation. The use of a stabilizer avoids the nucleation of  $Fe<sub>2</sub>O<sub>3</sub>$ NPs as well as impeding their agglomeration and growth. A specific absorbance peak of surfactants was observed when  $Fe_2O_3$  NPs were layered with the tested surfactants; the absorbance spectra of magnetite NPs along with 8mM of surfactant oleic acid were determined at *True*=0h and *True*=24 h.

From a plot of absorbance at 224 nm (which is due to the surfactant peak) versus oleic acid concentration, a maximum absorbance was observed at concentrations greater than 50mM. However, a minor decline in absorbance occurred after 24h which might be due to some sort of agglomeration of  $Fe<sub>2</sub>O<sub>3</sub>$  NPs which were not entirely broken by sonication, and settled down in the cuvette.

At concentrations beyond 64 mM, the maximum absorbance occurred because of the effective particle disaggregation of the particles and their stability over time. This study correlates with the results published by the other authors<sup>44</sup> inferring that beyond a specific concentration a double layer of oleic acid is formed around the  $Fe<sub>2</sub>O<sub>3</sub>$  NPs to provide a highly hydrophilic surface on the NPs which stabilizes them in aqueous colloidal solutions.45 At a lower concentration of sodium citrate (1.25 mM), a greater decline in peak intensity occurs; this occurs because the concentration of surfactant is insufficient to prevent the aggregation of NPs in colloidal suspension.46 A small decline in peak intensity observed in the case of sodium citrate as compared to oleic acid, <sup>47,48</sup> which proved sodium citrate to be a better surfactant for magnetite NPs.

The structure, morphology and size of the synthesized magnetite NPs were determined before and after surfactant coating. The structure was determined by X-ray powder diffraction (XRD) spectra of  $Fe<sub>2</sub>O<sub>3</sub>$ , while transmission electron microscopy (TEM) was used to determine the size and morphology.

#### **Conclusion**

Every synthesis method for ferrite NPs such as  $NiFe<sub>2</sub>O<sub>4</sub>$ , ZnFe<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>,  $\text{CoFe}_2\text{O}_4$  and mixed NPs, from the co-precipitation, thermal decomposition, hydrothermal, microwave-assisted and sonochemical methods, has its own pros and cons, but the co-precipitation method is considered the best because of the low temperature involved and the ease of process. The effects of different capping agents, namely, canola oil, recin oil, glycerol, sodium dodecyl, sodium citrate, oleic acid, Triton-100 and sodium dodecyl benzene sulphonates, on the properties of ferrites have been studied: these capping agents help in the size stability of NPs and reduce agglomeration.

#### **Declaration of conflicting interests**

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