A direct synthesis of water soluble monodisperse cobalt and manganese ferrite nanoparticles from iron based pivalate clusters by the hot injection thermolysis method

Khadijat O. Abdulwahab [a], Mohammad A. Malik [a], Paul O'Brien [a,b,*], Grigore A. Timco [a]

[a] School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK
[b] School of Materials, University of Manchester, Grosvenor Street, Manchester M1 7HS, UK

ARTICLE INFO

ABSTRACT

Highly monodisperse water soluble cobalt ferrite ($CoFe_2O_4$) and manganese ferrite ($MnFe_2O_4$) nanoparticles were synthesised by the hot injection thermolysis of pivalate clusters as single source precursors. The precursors [$Fe_2CoO(O_2C^tBu)_6(HO_2C^tBu)_3$] **(1)** and [$Fe_2MnO(O_2C^tBu)_6(HO_2C^tBu)_3$] **(2)** were decomposed in a mixture of polyvinylpyrrolidone (PVP) (capping agent) and triethylene glycol (TREG) (solvent) at 285 °C to produce cobalt ferrite and manganese ferrite nanoparticles, respectively. The effect of the PVP on the size and morphology of the nanoparticles synthesised was investigated. Smaller sized nanoparticles of cobalt and manganese ferrite nanoparticles were obtained at higher PVP concentration and larger nanoparticles were produced at lower PVP concentrations. The ferrite nanoparticles produced are monodisperse, directly dispersible in water without any further size selection/postsynthesis procedure. The nanoparticles were characterised by powder X-ray diffraction (p-XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED).

1. Introduction

Ferrite nanoparticles have attracted a lot of attention recently due to their wide range of applications including in drug delivery [1,2], magnetic resonance imaging [1,3–5], hyperthermia treatment [1,4,6], data storage [7], ferrofluids [8], environmental remediation [9,10] and catalysis [11,12]. Ferrite nanoparticles are well suited for biomedical applications because their sizes can be manipulated and also their surface can be functionalised with appropriate molecules to make them highly selective towards their targets [13,14]. In addition, their superparamagnetic properties make it possible to control their movement under the influence of an external magnetic field.

Various synthetic and functionalisation methods have been employed for ferrite nanoparticles. The co-precipitation method is commonly used for the synthesis of magnetite and other ferrite nanoparticles because it is easy to use and scalable [9,10,15–29]. However, nanoparticles obtained from this method tend to have a broad size distribution and poor crystallinity. Other non-hydrolytic methods have hence been employed to synthesise these nanoparticles including sol-vothermal methods and thermal decomposition of iron-based complexes [30,31].

The biological methods have been used to synthesise water soluble ferrite nanoparticles including iron [32–42], cobalt [43–45], manganese [45], nickel [44,45] and zinc [45,46]. Although this approach could be exploited for industrial scale, the success of getting monodispersed nanoparticles depends on environmental parameters such as temperature, redox potential and pH [47]. Thermal decomposition methods have produced monodisperse crystalline nanoparticles [48,49] but the shortcoming of this method is that the capping agents usually employed are hydrophobic and thus not dispersible in aqueous medium. This in turn has hampered its applications in producing nanoparticles for biomedical and environmental applications. Ongoing research into preparing water dispersible ferrite nanoparticles with desirable properties has appeared. Methods proposed to achieve this goal are either direct synthesis or postsynthesis by ligand exchange to obtain the desired surface modification.

Numerous postsynthesis surface modification/ligand exchange techniques have been employed including surface exchange of amine modified poly(acrylic acid) [50], glucosaminic acid [51], α-cyclodextrin [52], dimercaptosuccinic acid [53,54], silesquioxane ligands [55], modified polyethylene glycol [56,57], modified polymaleic anhydride [58,59], citrate [60], hydroxamic acid [61] and tetramethylammonium 11-aminoundecanoate [62] to disperse the highly crystalline nanoparticles produced from non-hydrolytic routes in aqueous medium. A major shortcoming of post-synthesis surface modification is incomplete replacements of ligand that reduces stability in aqueous solution; also often the ligand exchange procedures are often tedious, requiring prolonged reaction times and excess of the new ligand to disrupt the established surface coat and as such may require further purification after ligand exchange. Consequently, the direct synthesis of highly-crystalline ferrite nanoparticles that can be dispersed in water is a preferable alternative.

The solvothermal method has been used to produce a hydrophilic magnetite and cobalt ferrite nanoparticles using polyethylene glycol as surfactant [63]. Using the same method, Guan et al produced amine functionalised magnetite nanoparticles with a narrow size distribution which can be dispersed in aqueous media [64]. Single-crystal hollow spheres of magnetite of average diameter 200–300 nm were synthesised by Zhu and co-workers using ethylenediamine as surfactant in the presence of ethylene glycol by the solvothermal route [65]. Ferrite colloidal spheres of high saturation magnetisation and dispersibility in water have been synthesised by hydrothermal treatments of chloride salts, urea and polyacrylamide (PAM) as stabilisers [66].

The thermal decomposition method has been further developed to produce water dispersible ferrite nanoparticles by using strong polar capping agents. Li et al. synthesised magnetite nanoparticles via the thermal decomposition of iron(III) acetylacetonates ([Fe(acac)$_3$]) in the presence of 2-pyrrolidone as the capping agents and obtained a 5 nm diameter nanoparticles which were further used as seeds to grow larger particles [67]. Similarly, Li et al. produced magnetite nanoparticles using the same precursor and capping agent and in addition to that carboxyl-terminated poly(ethylene glycol) were used to coat the nanoparticles [68–70]. This same group further developed their method by using the same precursor but with N-vinyl-2-pyrrolidone (NVP) to achieve PVP coated magnetite nanoparticles [71].

Glycol and its derivatives have been used as capping agents for the direct synthesis of water soluble ferrite nanoparticles. Yang et al. used tetraethylene glycol as a stabiliser to produce water soluble manganese ferrite nanoparticles by the thermal decomposition of [Mn (acac)$_3$] and [Fe(acac)$_3$] [72]. Caruntu and his team employed the hydrothermal method to synthesise magnetite nanoparticles in the presence of diethylene glycol and N-methyl ethanolamine as surfactants [73]. Using iron pentacarbonyl as the precursor, magnetite nanoparticles have been produced with 4-methylcatechol (4-MC) as the surfactant [74]. The 4-MC coated magnetite nanoparticles were then further functionalised with a peptide, making the particles stable in a physiological environment.

To date, little or no work has been reported on the use of single source precursors to synthesise water soluble ternary ferrite nanoparticles. In this paper, we explore the use of pivalate clusters as single source precursors for the direct synthesis of water soluble ferrite nanoparticles by a hot injection thermolysis method.

2. Experimental

All preparations were performed under an inert atmosphere of dry nitrogen using the standard Schlenk techniques. All reagents were purchased from Sigma-Aldrich and used as received. Solvents were distilled prior to use.

2.1. Synthesis of precursors

Synthesis of [Fe$_2$CoO(O$_2$C^{t}Bu)$_6$(HO$_2$C^{t}Bu)$_3$] **(1)** and [Fe$_2$MnO(O$_2$C^{t}Bu)$_6$(HO$_2$C^{t}Bu)$_3$] **(2)** was carried out by the methods described in literature [30]. A brief description is given below:

$$[Fe_2CoO(O_2C^tBu)_6(HO_2C^tBu)_3] \qquad (1)$$
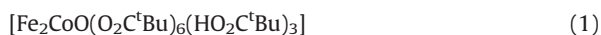
An excess of pivalic acid (30.0 g, 294 mmol) and potassium hydroxide (6.0 g, 107 mmol) were stirred in water (25 mL) at 50 °C until a clear solution was formed (∼10–15 min). To the solution, iron nitrate nonahydrate (10.0 g, 24.8 mmol) and cobalt nitrate hexahydrate (5.0 g, 17.2 mmol) dissolved in water (25 mL) and pre-heated to 50 °C were added. The mixture was stirred for 15 min; during this time two layers formed, a brown organic layer and a clear pink aqueous solution. The flask was cooled in ice water, which resulted in solidification of the organic layer. The aqueous layer was removed by decantation, and the solid was washed with cold water and then dissolved in petroleum ether (200 mL, low boiling point 40–60 °C petroleum ether). The petroleum ether solution was filtered and the residue extracted with further petroleum ether (100 mL). The two petroleum ether solutions were combined and evaporated to dryness under reduced pressure and to the residue acetonitrile (50 mL) was added, with stirring. After 15 min the crystalline product was collected by filtration, washed with cold acetonitrile (3 × 10 mL) and dried in air.