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Co-precipitation in aqueous solution synthesis of magnetite nanoparticles using iron(III) salts as precursors

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Abstract An innovative quantitative synthetic method for preparing magnetite nanoparticles was achieved by co-precipitation in aqueous solution using only one single iron(III) salt as a precursor. A 2 Fe(III):1 Fe(II) mole ratio was first attained in solution by reducing iron(III) using KI solution, followed by filtering the iodine formed and hydrolyzing the filtrate by 25% ammonium hydroxide solution at pH 9–11. A high selectivity and atom economy percents were achieved indicating that the method is environmentally benign and green. The as-synthesized nanoparticles were characterized by fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), field emission transmission electron microscopy (FETEM), selected area electron diffraction (SAED), and ^{57}Fe Mössbauer spectroscopy. Magnetite nanocrystals (d: 7.84 ± 0.05 nm) and nanorods (d: 6.3 ± 0.2 nm; l: 46.2 ± 0.9) formation was evident.

1. Introduction

Synthesis, characterization and applications of iron oxide nanocrystals have received tremendous attention in recent years due to their potentials for information storage devices, rotary shaft sealing, position sensing (Raj and Moskowitz, 1990), as well as medical and pharmaceutical applications (Xie et al., 2008). Several methods are known in the art for the synthesis of magnetite, Fe_3O_4. Cornwell and Schwertmann (Cornwell and Schwertmann, 2003) have reported several synthetic methods all of which require more than one iron component as precursors, several chemical reagents, inert atmosphere, special apparatus and/or restricting conditions. Exemplary methods are shown as follows:

$$\text{(a)}\ FeSO_4 + KOH + KNO_3 \xrightarrow[N_2\ gas]{90^\circ C} Fe_3O_4 \quad (1)$$

(David and Welch, 1956).

$$\text{(b)}\ FeSO_4 + NaOH \xrightarrow[gas]{N_2} Fe(OH)_2 \xrightarrow[N_2\ gas]{100^\circ} Fe_3O_4 + 2H_2O + H_2 \quad (2)$$

(produces complicating side effect) (Schikorr, 1929).

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(c) Reduction of hematite at 400 °C in an atmosphere of 5% H_2/95% Ar, saturated with water vapour free of O_2 (Regazzoni et al., 1981).
(d) Reaction of a 1:2 Fe(II)/Fe(III) solution, under alkaline conditions at 80 °C under N_2 (Regazzoni et al., 1981).
(e) Reaction at 85 °C of Fe(II) ammonium solution (buffered to pH 7 to 8 with sodium acetate) with hydroxylamine sulfate; the suspension is held under N_2 gas (Ardizzone and Formaro, 1983), as shown thus

$$3Fe^{2+} + NH_3OH^+ + 3H_2O \rightarrow Fe_3O_4 + NH_4^+ + 6H^+ \quad (3)$$

(f) Reductive transformation in a sealed ampoule of an akaganeite suspension in the presence of hydrazine at pH 9.5 to 11.5 and 100 °C (Blesa and Maroto, 1986).

$$12\beta - FeOOH + N_2H_2 \rightarrow 4Fe_3O_4 + 8H_2O + N_2 \quad (4)$$

(g) Decomposition of an alkaline (0.2–0.4 MOH) solution of Fe(III) NTA at 217 °C in an autoclave (Booy and Swaddle, 1978).
(h) Heating of iron hydroxide acetate at 200–260 °C under N_2 (Pinheiro et al., 1987).
(i) Boiling a mixture of Fe(II) sulfate and bispyridoxylidene hydrazine phthalazine for 10 min at pH 7 (Sarel et al., 1989).
(j) Thermal decomposition of Fe(II) sulfide in air at 500 °C, which is environmentally unfriendly (Robl, 1958).

$$3FeS_2 + 5O_2 \rightarrow Fe3O_4 + 3S + 3SO_2 \quad (5)$$

(k) Holding a solution of Fe(III) acetylacetonate in 1-propanol under N_2 in an autoclave at 300 °C for several hours (Kominami et al., 1999).
(l) Reduction of nitrobenzene to aniline produces Fe_3O_4 (Laux, 1925) as shown thus:

$$4C_6H_5NO_2 + 9Fe + 4H_2O \overset{Fecl_2}{\rightarrow} C_6H_5NH_2 + 3Fe_3O_4 \quad (6)$$

Further, several Fe_3O_4 synthetic methods were patented (Michael et al., 2004; Shen, 2002; Yoshito et al., 1984; Tomio and Horoyuki, 1999; Shouheng, 2002; Maurice et al., 1978; Naoyoshi and Kenzo, 2000).

The most popular methods for the synthesis of the spinel structured Fe_3O_4 include co-precipitation in aqueous solution by adding hydroxides into iron salt solutions (Hui et al., 2008; Fried et al., 2001) and the thermal decomposition of iron organometallic compounds in high boiling organic solutions in the presence of stabilizers (Sun and Zeng, 2002; Xu et al., 2010).

Recently, Xu et al. (2010) reported on the organic phase synthesis of mono dispersed iron oxide nano crystals using iron chloride as a precursor.

In this paper, a report was made on an innovative invention (Khalil, 2012) that relates to a process of preparing magnetite nanocrystals by the co-precipitation method using iron(III) chloride or nitrate salts as precursors. The objective of this invention was to provide a process of preparing magnetite (Fe_3O_4) and derivatives thereof, not reported herein, which overcomes the drawbacks of the prior art, especially a process which only requires one iron compound as the starting precursor, a limited number of additional chemical reagents, and a process which can be carried out under simple reaction conditions, preferably at room temperature, with easy work-up of the product obtained.

2. Experimental

2.1. Starting material

Iron chlorides ($FeCl_3$ and $FeCl_3{\cdot}6H_2O$) were purchased from WINLAB, Leicestershire, England. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) sodium hydroxide (NaOH) and 25% ammonia solution were all purchased from BDH, Poole, England. And potassium iodide (KI) and polyvinyl alcohol (PVA 72000) were purchased from MERCK, Darmstadt, F.R. Germany.

2.2. Characterization

The FTIR spectrum was recorded on a Shimadzu FTIR-8400S, Prestige-21 spectrophotometer in a KBr matrix. Powder X-ray diffraction (XRD) pattern was obtained with an Ultima IV X-ray diffractometer using copper-monochromatized Cu Kα 1 radiation under the acceleration voltage of 40 kV and a current of 40 mA. The morphology of the Fe_3O_4 nanocrystals was examined by a JEOL JSM-6380 LA scanning electron microscope and a JEOL, TEM-2100F transmission electron microscope with an acceleration voltage of 200 kV. ^{57}Fe Mössbauer spectra were recorded in the Institute des Molecules et Matériaux du Mans (IMMM), Université du Maine, France.

2.3. Synthesis of magnetite nanoparticles

The work-up consists of mixing iron(III) salt solution with potassium iodide aqueous solution in a 3:1 mol ratio, filtering out the iodine formed, hydrolyzing the filtrate with either sodium hydroxide or ammonia solution, filtering the black magnetite precipitate, washing with water and drying at 250 °C.

An exemplary experiment is carried out as follows:

19.46 g (0.119 mol) of anhydrous $FeCl_3$ was completely dissolved in 150 ml distilled water to prepare aqueous solution A. Further, 6.584 g (0.0396 mol) of potassium iodide was dissolved in 50.0 ml of distilled water to prepare aqueous solution B. Solutions A and B were then mixed together at room temperature, stirred and allowed to reach equilibrium for one hour. The precipitate of iodine was filtered out, washed with distilled water, dried at 100 °C and weighed (yield: 5.076 g, 86.6%). The washing was added to the filtrate. The whole volume of filtrate was then hydrolyzed using 25% ammonia solution which was added drop-wise with continuous stirring until complete precipitation of the black magnetite was achieved (pH 9–11). The set up was then left to settle, filtered, washed with distilled water, dried at 250 °C and weighed (yield: 9.2 g, 99.0%).

The same procedure was repeated using $FeCl_3.6H_2O$ as a precursor. 27.03 g $FeCl_3{\cdot}6H_2O$ dissolved in 150.0 ml distilled water was reacted with 5.533 g (0.033 mol) KI aqueous solution. Iodine yield was 3.15 g, 75.53%. Magnetite was precipitated from three 50.0 ml portions of the filtrate. The average yield was 1.40 g, 91.61%.

The yield of magnetite from $Fe(NO_3)_3.9H_2O$ precursor was low (52.8%) when a 3Fe(III): 1.0 KI mole ratio was used.