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Synthesis of magnetite (Fe_3O_4) nanoparticles without surfactants at room temperature

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Abstract

Iron oxide nanoparticles in the interval of 4–43 nm were synthesized by a colloidal method at room temperature, without use of surfactants and using precursors like $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$; deionizated water free of dissolved oxygen and ammonia solution (29% vol.) and using several aging times (2, 5 and 10 min). A detailed study by X- ray diffraction (XRD), Conventional Transmission Electron Microscopy (CTEM), High-Resolution Transmission Electron Microscopy (HRTEM) and electron diffraction patterns showed that with a reaction time less than 5 min nanoparticles of magnetite phase (Fe_3O_4) were synthesized, and with a bigger time of reaction the lepidocrocite phase (FeO(OH)) was identified. The minor particle average size measured was 6 nm in the sample, 0.0125 M with 2 min of aging time (0.0125M2 m). In addition it was possible to obtain a narrow nanoparticle size dispersion from 4 to 10 nm for small aging times.

Keywords: Magnetite nanoparticles; Magnetic materials; Microstructure; Nanomaterials; HRTEM; XRD

1. Introduction

Advances in nanoscience and nanotechnology are centered in the control of the size and shape of nanoparticles, as well as obtainment of the extended arrangement of nanoparticles in 1D, 2D and 3D. Their physical properties depend on these variables and their anisotropy from which it may be possible to find new nanostructured systems with novel and specific properties [1]. New optimized methods of synthesis are necessary to allow for the control of the shape and size distribution of nanoparticles. In particular, systems made of iron oxides nanoparticles, have an enormous potential towards applications in several areas such as magnetic recording technology, pigments, catalysis, photocatalysis and medical uses. In medicine, these systems have been applied as part of cancer therapy, as well as in diagnosis, where the magnetite nanoparticles are used as contrast agent for studies of nuclear magnetic resonance (NMR) [2]. Commercial products in the market for these medical treatments exist in the market nowadays. However, they have wide size distributions (120–180 nm) and their particle size is bigger than the extracellular space (<50 nm) [3]. Hence it is necessary to obtain magnetic nanoparticles with smaller and narrower size distribution than the ones manipulated with external magnetic fields. Another potential application of these nanoparticles is their use as tertiary treatment of residual waters acting as powerful reducer agents of organic and inorganic material, with the advantage that it could be possible to recycle and separate the magnetite particles by an external magnetic field [4].

Concerning the synthesis of magnetite, Gribanov et al. [5] have used a colloidal method with NH_4OH as hydrolyzing agent in substitution of NaOH or KOH. They obtained a high saturation of magnetization and avoided impurities as α-FeOOH and other iron compounds. They report that a the temperature of 20 °C is ideal for magnetite formation and suggest the use of an excess of alkali and iron salts concentration of about 0.1 M. On the other hand, Murray et al. [6] synthesized

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metallic nanoparticles made of Fe, Ni, Co and Pt by the same method. In particular they synthesized Fe nanoparticles with a range size of 2–20 nm at 200 °C, using pentacarbonile iron (Fe$(CO)_5$) as precursor and surfactants as stabilizing agents. Finally, the particles size distribution was controlled by selective stabilization.

Other reports indicate the use of several synthesis routes for the formation of magnetic nanoparticles. For example, a microemulsion route was employed for the synthesis of magnetite nanoparticles smaller than 10 nm [7]. Vollath et al. [8] reported a microwave plasma synthesis technique in which they obtained particles with sizes up to below 10 nm, using $FeCl_3$ and $Fe_3(CO)_{12}$ as precursors materials. Other techniques have been used for the iron oxide nanoparticles synthesis such as sol–gel, freeze-drying, laser pyrolisis and vaporization condensation methods [9–11]. However, one of the main challenges of these numerous and novel techniques lie in their capacity to obtain a narrow dispersion in particle size together with the desired compositional, structural and crystalline uniformity.

In consequence, the aim of this work is to explore the feasibility of synthesizing magnetite (Fe_3O_4) nanoparticles by a colloidal method at room temperature and without the use of surfactants. The characterization of the synthesized nanoparticles was carried out with CTEM, HRTEM and XRD techniques.

2. Synthesis and characterization

Reagents as ferric chloride hexa-hydrate ($FeCl_3{\cdot}6H_2O$, Aldrich 98%), ferrous chloride tetra-hydrate ($FeCl_2{\cdot}4H_2O$, Aldrich 99%) and ammonium hydroxide (NH_4OH, Aldrich 28–30% of ammonia) were used for the synthesis as well as deionized–deoxygenated water with conductivity between 0.6 and 1 μS/cm. A solution of ferric chloride 0.0125 M was added to a ferrous chloride solution 0.0125 M and a solution 1 M of ammonium hydroxide.

A volume of 200 ml of deionizated water was placed in a bottom round flask, subsequently the water was deoxygenated by bubbling N_2 gas for 30 min. Later, 50 ml of ammonium chloride (IM) was added and the mixture was stirred for 10 min at 1000 rpm using mechanical agitation. Afterwards, 10 ml of ferrous chloride 0.0125 M and 20 ml of ferric chloride 0.0125 M were added; immediately a black precipitate appeared, which is separated. Three different aging times were used, 2, 5 and 10 min.

A decantation process was applied with the aid of a 0.2 T magnetic field. Finally the product was washed four times with 25 ml of deionizated and deoxygenated water and then dried at 45 °C for 4 h.

Six samples were synthesized, three of them with a concentration of 1 M and aging times of 2, 5 and 10 min (identified as 1M2m, 1M5m and 1M10m). The three remaining samples were kept constant with an aging time of 2 min and the precursors concentration were varied at 0.0125 M, 0.25 M and 0.5 M of both reactants and were identified as: 0.0125M2m, 0.25M2 m and 0.5M2m, respectively.

CTEM analysis was performed with a JEOL2010 HT electron microscope with a point resolution of 2.3 Å, HRTEM analysis was performed in a JEOL2010 FEG instrument with a point resolution of 1.9 Å. The samples were placed on holey carbon copper grids of 300 mesh. The measurements of lattice-fringe spacing and angles recorded in digital high-resolution electron micrographs were made using digital image analysis of reciprocal space parameters, according to the de Ruijter et al. method [12], with this method, the precision is 0.0001 nm for lattice spacing and 0.1° for lattice planes angles. This analysis was carried out with the aid of the Digital Micrograph software. About 100 particles were analyzed for structural characterization by HRTEM. The particle size distribution measurements were made with the Quiantikov image analyzer.

The structural phase identification of the iron oxide nanoparticles and the crystalline size calculations were done using a Siemens D5000 X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.15405$ nm) in the interval 2θ of 10 to 100°, in

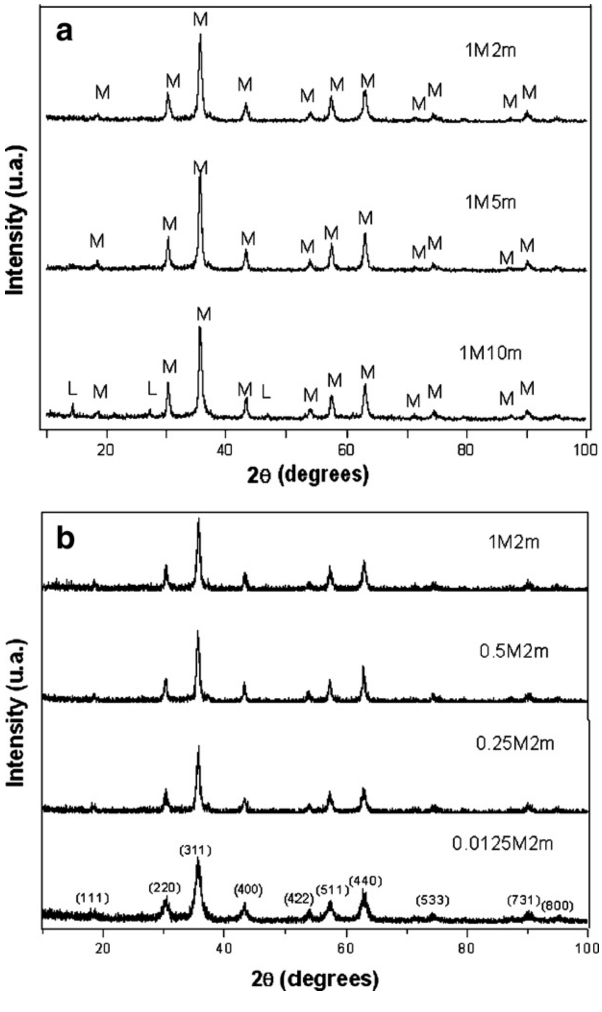

Fig. 1. (a) XRD patterns of iron oxide nanocrystals with different aging times of 2, 5 and 10 min. In all the cases (M) the magnetite phase was identified but in the sample with 10 min of aging time the lepidocrocite phase (L) was also obtained. (b) Diffractograms with different precursor concentrations, only magnetite reflections are observed in all the cases.