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Synthesis and characterization of iron oxide nanoparticles grown via a non-conventional chemical method using an external magnetic field

J. Arenas-Alatorre *, S. Tehuacanero C., O. Lukas, A. Rodríguez-Gómez, R. Hernández Reyes, C. Tapia-del León, J. Lara V.

Instituto de Física UNAM, Circuito de la Investigación Científica S/N, Ciudad Universitaria, Delegación Coyoacán, CDMX C.P. 04510, Mexico

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ABSTRACT

Iron oxide nanoparticles (NPs) were synthesized at room temperature, using a method based on a chemical reaction of iron filings, white vinegar, hydrogen peroxide, and ammonium hydroxide, in the presence of an external magnetic field (EXMF) of 1200 G. X-ray diffraction (XRD) analysis indicates that magnetite (Fe_3O_4) is the most predominant phase, with lepidocrocite (γ-FeO(OH)) in smaller proportion. The shape and average particle size is altered by the application of a magnetic field during NPs synthesis. The average size of crystallite calculated with Scherrer's equation were 30.30 nm without EXMF and 18.37 nm with EXMF. Using electron microscopy techniques (SEM, TEM), NPs with regular shapes were identified when the EXMF was applied. Meanwhile, irregular shapes were observed when the EXMF was not applied. Some NPs with nanoflake shapes and the crystalline phases γ-FeO(OH) were also identified. High-resolution transmission electron microscopy (HRTEM) showed that the NPs with regular shapes are of Fe_3O_4.

1. Introduction

Among the wide variety of superparamagnetic materials available, iron oxide nanoparticles (NPs) have received special attention due to their applicability in medicine, including in contrast agents, biosensors, and cancer treatment [1–3]. Several synthesis methods have been designed to optimize the particle size distribution, shapes, and crystalline phases [4–6]. Unfortunately, dangerous substances are often used during the synthesis process. Thus, there is currently a trend in NPs synthesis towards avoiding the use of some raw materials harmful to the environment and human health. It is possible to find reports, not only in the scientific literature but even on some web pages that make use of simple techniques for NPs synthesis; in many of these approaches, the authors employ materials that are commonly used at home [7–11]. The results shown in these reports are interesting, but they lack an in-depth analysis of the properties of the NPs synthesized. In this work, we present such results for iron oxide NPs synthesized at room temperature using a simple and low cost method based on a chemical reaction of steel wool, white vinegar, hydrogen peroxide, and ammonium hydroxide [7]. The novel aspect of our work lies in the synthesis of the iron oxide NPs being carried out under the influence of an EXMF produced by two magnets of 1200 G. Considering that the anisotropic magnetic behavior in solid materials is dependent on the crystalline structure and the direction in which the EXMF is applied, this field must exert an influence on the shapes and sizes of the NPs synthesized.

2. Experimental

2.1. Synthesis

The method proposed by the atomic salad site[10] was used as a reference, 5 g of steel wool from Fibrasmex were washed in a solution of 50% acetone and 50% isopropyl alcohol using an ultrasonic cleaner for 30 min at room temperature. After 25 ml of white vinegar (pH 1.76) was added, and was allowed to stand for 24 h to form Fe^{2+}. The resulting solution with pH 4.24 was divided into two beakers in a 2:1 ratio 5 drops of hydrogen peroxide (0.22 ml) were added dropwise to the beaker with the least amount of solution, inducing a transformation from Fe^{2+} to Fe^{3+} (pH 4.35). Fe^{3+} was added to the Fe^{2+} and ammonium hydroxide was slowly added until the substance became dark in color with pH 12.37. The reaction occurs as follows:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

* Corresponding author.
E-mail address: jarenas@fisica.unam.mx (J. Arenas-Alatorre).

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Before combining the Fe^{2+} and Fe^{3+}, the beaker with the Fe^{2+} was placed between two 1200 G magnets (from this value begin to observe changes in the NPs shape), as shown in Fig. 1. With this arrangement, we induce preferential crystalline directions for the growth of the NPs.

2.2. Characterization

The crystalline analysis was done using a Bruker X-ray diffractometer with Cu-Kα radiation (λ = 0.15405 nm) with a range of 2θ of 10–110°, in steps of 0.1°. The average size of crystallite (D) was calculated using Scherrer's equation ($D = 0.9\lambda/\beta\cos\theta$) [12].

The shape and size distributions of the iron oxide NPs were analyzed using a Field Emission Scanning Electron Microscope (FSEM), JSM7800F, equipped with an Oxford microanalysis detector (Energy Dispersive X-Ray spectroscopy, EDS).

Transmission Electron Microscopy (TEM) analysis was performed using a JEOL2010FEG instrument. Measurements of the interplanar distance were recorded in HRTEM images using the Digital Micrograph software from GATAN.

3. Results and discussion

Before the synthesis of the NPs, the steel wool was analyzed by EDS, and the results indicated a content of 93.40% at Fe and 6.60% at O.

Fig. 2 shows the XRD analysis of one of the samples synthesized without the presence of a EXMF (Fig. 2a) and one synthesized between the two magnets (Fig. 2b). In both cases, the main crystalline phase identified was Fe_3O_4 (PDF file 87-2334). However, in the first case also exhibited the α-Fe_2O_3 (PDF file 88-2359). The sample with the EXMF also contained some reflections of γ-FeO(OH) phase (PDF file 762301).

Using the Scherrer equation, we obtained an average crystal size of 30.30 nm when the EXMF was not applied and 18.37 nm when was applied.

In Fig. 3a, a typical image of iron oxide NPs obtained using FSEM with secondary electrons is shown, for the case where the EXMF was not applied. The presence of NPs less than 100 nm in size and with irregular shapes are observed at 33,000×. Fig. 3b shows iron oxide NPs obtained at the same amplification when an EXMF of 1200 G was applied. FSEM images show NPs have a size range of 20–213 nm, an average size of 61.03 nm, as shown in the particle size distribution histogram (Fig. 3d). In both cases, the analysis using EDS indicates a stoichiometry near to the Fe_3O_4 phase (43.50% at Fe, 56.50% at O). In a similar work, Ismali et al. [4] analyzed the effects of applying a magnetic field of 0.5 T on the shape and size of Fe oxide NPs grown using an ablation laser in dimethylformide, and found a decrease in the particle size. Although, in our case, the synthesis is done through a simple chemical method, the results are similar in terms of the effects on the characteristics of the NPs when applying an EXMF.

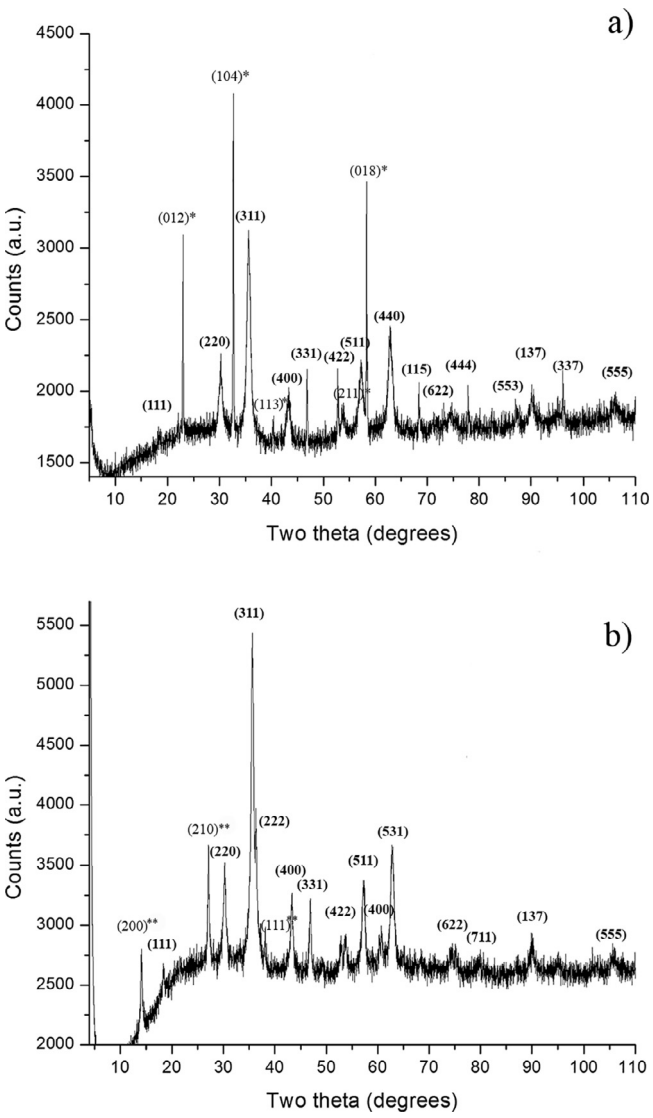

Fig. 2. (a) The XRD pattern of iron oxide nanocrystals grown without the presence of an EXMF. Fe_3O_4 is the main crystalline face identified but $(hkl)^*$ of α-Fe_2O_3 were also observed. (b) A diffractogram of the iron oxide nanocrystals grown in the presence of an EXMF. Fe_3O_4 (77.3%) was identified but some reflections $(hkl)^{**}$ of γ-FeO(OH) (22.7%) were also detected (percentages were obtained with Rydberg analysis, done with PANalytical X'Pert HighScore Plus v3.0 software).

Fig. 3c shows particles with different shapes, including nanoflakes of size ~200 nm in diameter and less than 50 nm in

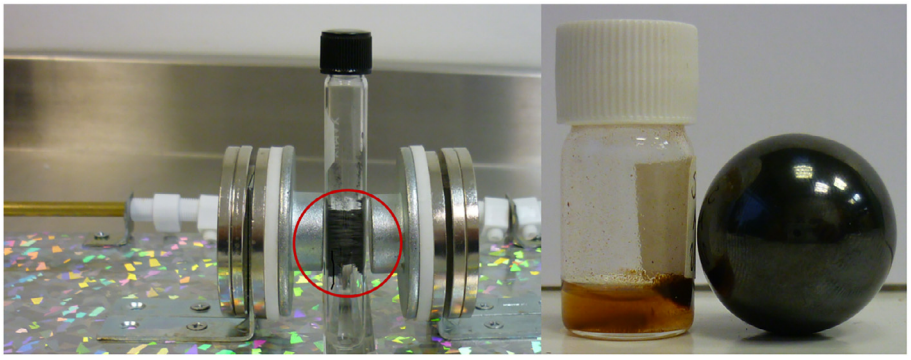

Fig. 1. The device designed to synthesize magnetic NPs under the influence of an EXMF. The lines of magnetic flux (enclosed in the circle) are parallel.

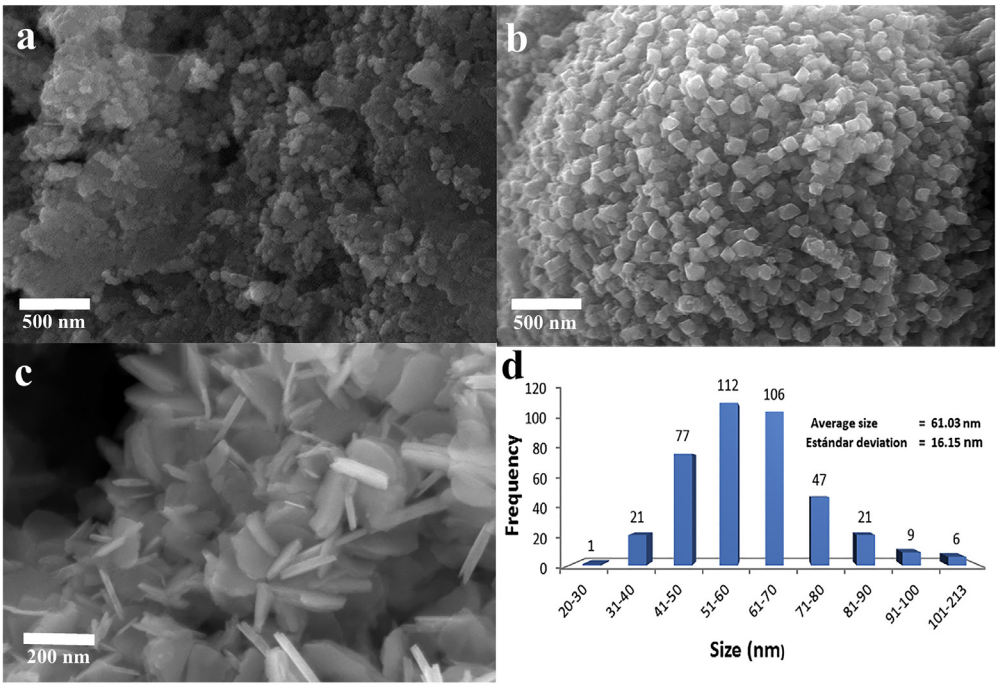

Fig. 3. (a) An SEM image of Fe_3O_4 NPs grown without the presence of an EXMF. (b) Fe_3O_4 NPs with regular shapes, grown in the presence of an EXMF. (c) Nanoflake particles of γ-FeO(OH) on the order of 200 nm are shown. (d) A histogram of the particle size distribution of the NPs shown in (b).

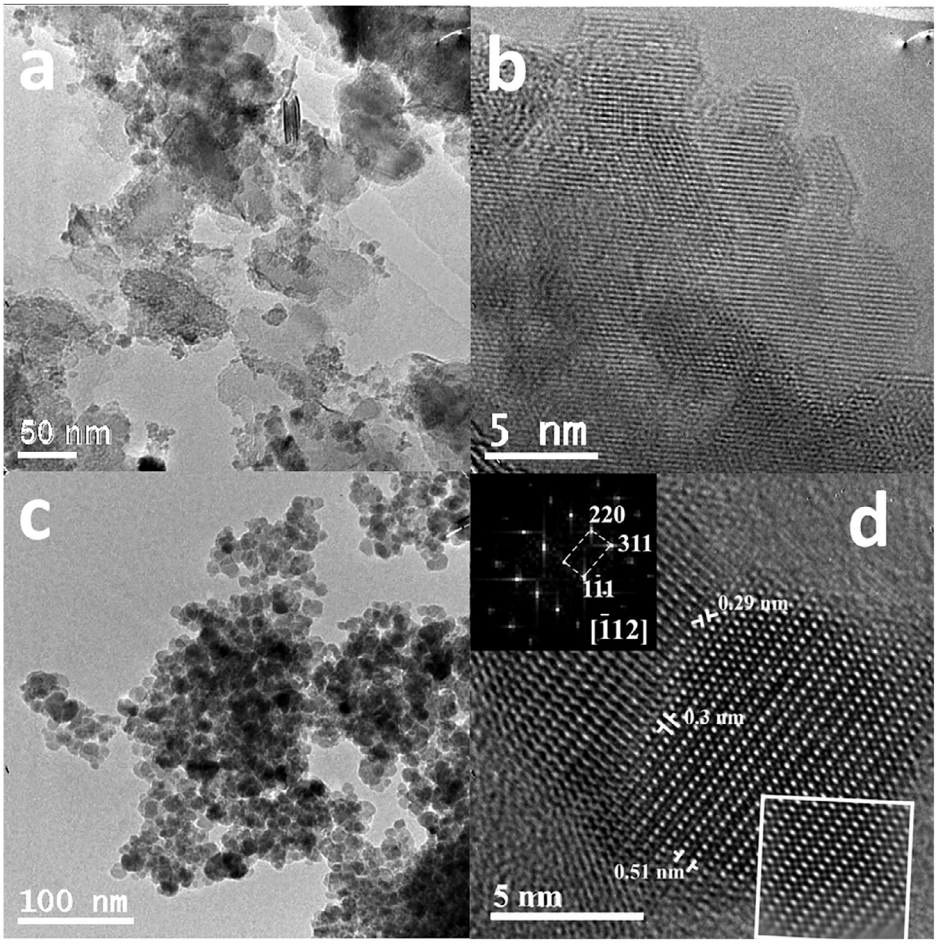

Fig. 4. (a) A TEM image of iron oxide NPs synthesized without the presence of an EXMF. Irregular shapes including nanoflakes are observed. (b) A HRTEM image of iron oxide NPs showing irregular shapes. (c) Regular shapes NPs smaller than 25 nm grown under the influence of an EXMF. (d) A Fe_3O_4 particles of size ~10 nm in the $\left[1\ 1\ 2\right]$ direction with its respective FFT and TEM image simulation (inset).

thickness. According to stoichiometry obtained by EDS analysis (62.37% at 0, 37.63% at Fe) and XRD analysis, these types of structures correspond to the γ-FeO(OH)phase. Alqasem et al. [13] obtained similar results in the synthesis of α-Fe_2O_3 nanocatalyst using electrical resistive heating (500–850 °C) in the presence of a magnetic field (0.25 T). They obtained nanoflakes in the range 0.5–4.0 μm.

TEM analysis indicates that when the sample was not subjected to an EXMF, particles <200 nm with large particle size dispersions and irregular shapes were observed (Fig. 4a). Using HRTEM, we could observe the irregular shapes of the particles in more detail. Fig. 4c shows a typical image obtained using TEM at low amplification for NPs < 25 nm, obtained in the presence of an EXMF of 1200 G, we can identify particles with regular symmetry.

Fig. 4d shows a HRTEM image of Fe_3O_4 nanoparticles with atomic resolution of size 10 nm and zone axes $\left[\bar{1}\,1\,2\right]$. In this figure an image simulation of the HRTEM image is inset, as well as its Fast Fourier Transform (FFT) with its corresponding indexing. This simulation was performed using the software simulaTEM [14].

Other studies of simple and inexpensive methods of iron oxide NP synthesis have been reported in the literature. One example is that of Yavuz et al. [11], who synthesized magnetite NPs with cubic morphology in the range 10.84–52.69 nm, through a method they named "kitchen synthesis" that uses a rusted steel hydrated and fatty acid mixture.

4. Conclusion

Iron oxides NPs were synthesized through a simple method based on a chemical reaction of iron filings, white vinegar, hydrogen peroxide and ammonium hydroxide, under the influence of two magnets. Regular shapes NPs of average size 18.37 nm were obtained. XRD analysis indicates that Fe_3O_4 is the most predominant phase and γ-FeO(OH) as a more minor phase. At low magnifications, TEM micrographs show changes in the shapes and sizes of particles when an EXMF is applied. Without the magnetic field, the shapes are mostly irregular and have sizes in the range 2–200 nm. Some NPs with nanoflake shapes were also identified in smaller proportions.

Conflict of interest

There are no conflicts of interest in the writing of the paper.

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