

Raman Spectroscopy of Iron Oxide of Nanoparticles (Fe_3O_4)

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Abstract

Nanoparticles of iron oxide (Fe_3O_4) were obtained by Coprecipitation with synthesis time of 30, 60 and 90 min. The morphology of the samples was investigated by scanning electron microscopy (SEM) and structural characteristics were obtained by X-ray diffraction (XRD). The crystallite size was calculated from the spectrum X-ray diffraction with the application of the Scherrer equation and Winfit. The crystallite size varied from 4.6 to 14.4 nm when calculated by Scherrer equation and when calculated by the single line ranged from 7.5 to 22.3 nm Winfit. The degree of graphitization was studied by Raman spectroscopy where spectrums were analyzed with different lasers: 514 nm (0.75 mW power used) and 785 nm (1.2 mW power used). The dominant structures of the spectra are in 215, 276, 398, 487, 654 and 1300 cm^{-1} when using the laser 514 nm. The spectrum produced with laser 514 nm is characteristic peak of magnetite in 654 cm^{-1} . The spectrum produced by laser 785 nm has a peak at 670 cm^{-1} , shifted relative to the laser 514 nm. The spectrum generated by laser 785 nm peaks characteristic of maghemite encountered due to possible oxidation of the sample caused by the high power laser. The experimental results were satisfactory and are according to the survey.

Keywords: Nanoparticles; Coprecipitation; Raman Spectroscopy; Magnetite

Introduction

The nanoparticles of iron oxide are a major focus of research in physics, chemistry, engineering and materials science, among others. Research is because their main magnetic properties such as superparamagnetism, high coercivity, low Curie temperature, high magnetic susceptibility, among others, which occur due to the nanometric size. The Fe_3O_4 nanoparticles can have various applications in nanotechnology, such as pigment, drug delivery, targeting, magnetic resonance imaging for clinical diagnosis, recording material, hyperthermia, catalyst, etc., [1,2]. These nanoparticles have an ability to interact in different ways with different biological molecules due to their properties such as high specific area and wide variety of surface functionalization.

Many methods have been developed for preparing magnetic nanoparticles, such as polyols, microemulsions, laser pyrolysis, sonochemistry, coprecipitation, hydrothermal, etc., [3]. Coprecipitation method is suitable for low cost; this method has great potential due to direct production of nanoparticles Fe_3O_4 (water-based). Techniques for the synthesis of nanoparticles determine the particle size, which can be controlled by a surfactant. There are important conditions for the synthesis, such as pH of the solution, temperature and time of reaction, stirring speed, solute concentration and surfactant. All features are important in order to obtain particles of desired size and shape [1-3].

This work has focused on the preliminary results of the synthesis process of the nanoparticles of iron oxide by the coprecipitation method in which the particles can be well controlled. Subsequently characterizations were conducted by XRD, TEM and Raman spectroscopy.

Experimental

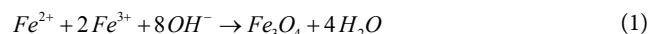
Materials

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), were obtained from Sigma Aldrich (EUA), tetramethylammonium hydroxide (25-28%, w/w) was obtained from Vetec (Brazil). Distilled water was used for preparation

of the solutions after deoxygenation with dry argon for 10 min. The divalent ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), trivalent ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) iron salts and aqueous ammonium hydroxide (25-28%, w/w) were also deoxygenated with dry argon before use. All the other chemicals used in this work were analytical reagent grade from commercial market without further purification.

Preparation of iron oxide magnetic nanoparticles

Method previously published by Kim was chosen for the iron oxide magnetic nanoparticles preparation. Nanoparticles were prepared by coprecipitation of Fe^{2+} and Fe^{3+} salts solution and NH_4OH solution using peristaltic pump. The principle of reaction is given by:



According to the results of thermodynamic model of this system, a complete precipitation of Fe_3O_4 is expected while maintaining a molar ratio of 1:2 to a non-oxidizing environment [4].

Salts, ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) and ferrous chloride tetrahydrate $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (>99%) obtained from Aldrich were dissolved in deionized water (40 ml) previously degassed. During the reaction the pH must be controlled at the beginning and end. Besides these, the temperature and agitation rate should also be controlled in reaction [5,6]. The following is performed to pass the inert gas (argon) in the system under stirring and heating $75^\circ\text{C} \pm 15^\circ\text{C}$. Starts dripping of 100 ml of ammonium hydroxide (NH_4OH) (25%) obtained from Vetec. Just after mixing the solutions, the color of the solution changed from light brown to black, indicating the forming of Fe_3O_4 .

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nanoparticles, which was allowed to crystallize completely for another 30, 60 and 90 min under rapid stirring. After this time period, the magnetic nanoparticles were washed three times with pure water with the help of a magnet [1].

Characterization of prepared magnetic nanoparticles

For the materials characterization were used the technique of X-ray diffraction using a Philips X'equipment Pert MPD, 40 kV and 40 mA. The angular range was 5 to 75° and 0.05° and step of counting time 3 seconds for each step. The analysis of scanning electron microscopy (SEM) were performed on a JEOL microscope, model JSM 6060 with maximum operating voltage of 30 kV and nominal resolution of 3.5 nm. The voltage was 20 kV (see bar scale). Scanning Electron Microscopy (SEM) was used to determine an approximate particle size of prepared nanoparticles. The Raman spectra were recorded at room temperature by a Raman spectrometer (Renishaw brand - inVia Raman, with an Excitation laser line of 632.8 nm from a He-Ne laser.

Results and Discussion

The characterization of the resulting powders after heat treatment was performed by means of X-ray diffraction (XRD) to verify the presence of crystalline phases. The X-ray diffractometer, model Philips X'Pert MPD, was used with graphite monochromator and fixed anode operated at 40 kV and 40 mA, which uses a radiation wavelength ($\lambda=0.154056$ nm) of Cu-K α . The angular range was 5 to 75° and step of counting time 3 seconds for each step.

The XRD peaks (Figure 1) showed the formation of a spinel type crystal structure of the inverse characteristic of magnetite. We also observed a mixture of α and γ phases of Fe₂O₃ (hematite and maghemite), and magnetite (Fe₃O₄). The mean particle diameters were also calculated from the XRD pattern according to the linewidth of the (311) plane refraction peak using Scherrer equation (2)

$$D = \frac{K \cdot \lambda}{b \cdot \cos \theta} \quad (2)$$

The equation uses the reference peak width at angle θ , where λ is the X-ray wavelength (1.5418 Å), b is the width of the XRD peak at half height and K is a shape factor, about 0.9 for magnetite and maghemite [2]. The results were 9.5 nm for magnetite nanoparticles. The crystallite size was calculated from the X-ray diffraction spectrum, applying the Scherrer equation ranged from 4.6 to 14.4 nm. For calculation by single line Winfit ranged from 7.5 to 22.3 nm.

The micrographs show similar morphology as in Figure 2. The micrographs have the formation of large agglomerates of nanoscale particles, which can be attributed to the growth by coalescence of nuclei, resulting in particles that tend to aggregate toward a lower energy state free, by reduction of interfaces with the environment.

The Raman spectra were recorded at room temperature by a Renishaw Raman spectrometer mark - Raman inVia with a linear laser excitation of 514 nm and 785 nm (He-Ne). For each sample, exposed 10 sec, three distinct points were measured and displacement occurred between 100 and 1400 cm⁻¹ (Figure 3).

Raman spectroscopy was employed to determine the nature of the iron oxide core (magnetite), where the Raman Effect is caused by the molecular effects produced from certain energy irradiated on the sample. However, it is known that magnetite has a weak Raman scattering, especially for lower laser powers that are low so that there are phase transformations induced by the laser. According to Li YS, the Raman spectrum peaks of magnetite were investigated, where

from certain vibrational modes, peak 670 cm⁻¹ was identified as a band characteristic.

Shebanova conducted some experiments using various powers of the laser Raman spectrum for magnetite. And they concluded that above some critical value of the laser power, the Raman spectra passed to indicate the characteristics of maghemite bands due to the effects of oxidation of the material. Thus, in this work we used two different types of lasers 514 nm (power 0.75 mW) and 785 nm (power 1.2 mW) with different powers, which produced different Raman spectra from the same sample. The dominant structures of the spectra are in 215, 276, 398, 487, 654 and 1300 cm⁻¹ when the laser used is 514 nm [7,8].

Figure 3 shows the spectrum produced by laser 514 nm, where the characteristic peak of magnetite is 670 cm⁻¹. The laser 785 nm has a peak at 654 cm⁻¹ and shifted in relation to 670 cm⁻¹. The characteristics of the maghemite peaks occur due to high power laser, probably because the sample was oxidized.

To purchase these spectra we used the 785 nm laser with a power of 1.2 mW, which produced very similar spectra for all measured samples. The results confirm the formation of Fe₃O₄ since obtained Raman

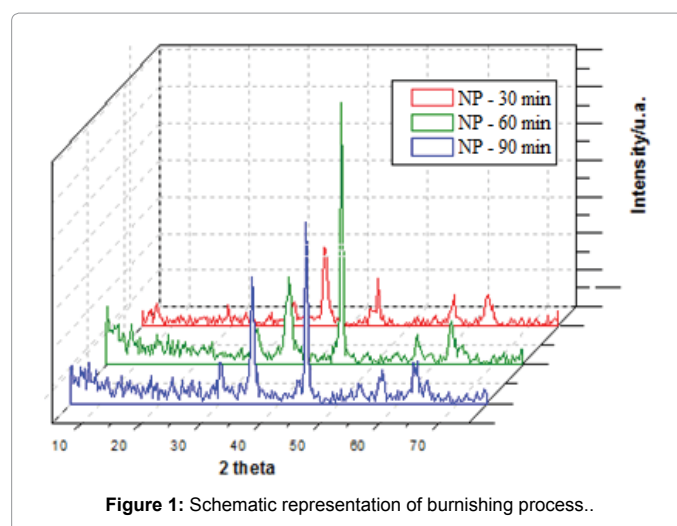


Figure 1: Schematic representation of burnishing process..

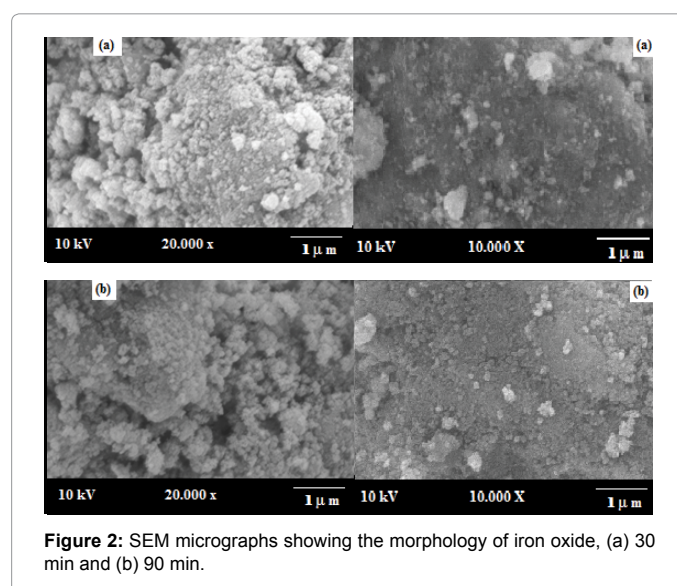
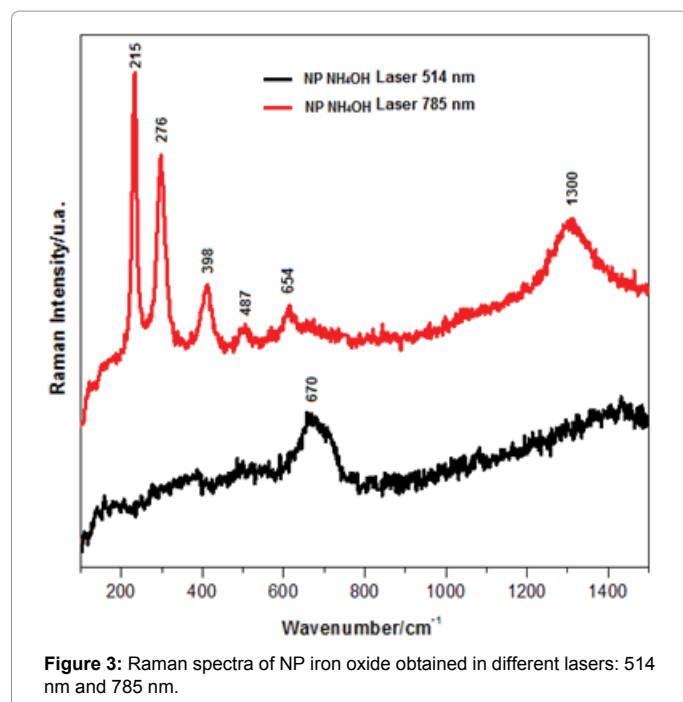


Figure 2: SEM micrographs showing the morphology of iron oxide, (a) 30 min and (b) 90 min.



spectrum has identical features to the cited work by Si H and Slavov L. The spectra show magnetite and maghemite peaks because there is a partial oxidation by the incidence of high-power laser [9].

Conclusions

Magnetic nanoparticles of iron oxide were prepared by two-step process. In the first step, magnetite nanoparticles were produced by coprecipitation of Fe^{2+} and Fe^{3+} salts solution with NH_4OH solution formed magnetite nanoparticles. Resulting samples of nanoparticles were analyzed utilizing XDR, Raman and SEM. It was found that prepared nanoparticles revealed the magnetic properties in water

suspension when external magnetic field was applied, that particles were generally spherical in shape and have particle size below 9.5 nm and that they tend to form agglomerates. When using Raman spectroscopy, the obtained one sample peaks vary with the potency and the laser 514 nm and 785 nm.

Acknowledgements

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