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Iron oxide nanoparticles modified with oleic acid: Vibrational and phase determination

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ABSTRACT

A simple path methodology to detect the phase composition of iron oxide nanoparticles modified with oleic acid based on vibrational spectroscopy is present here and applied on three different nanoparticles prepared by co-precipitation method. Firstly, the phase composition, magnetite, maghemite, and hematite, is determined using a reference intensity ratio methodology on X-ray diffraction pattern. Also, the size of each sample was calculated by Scherrer equation. Scanning, transmission electron microscopy, microanalysis and electron diffraction show a core magnetite particles size of around 10 nm for all particles. Based on lattice vibrations, we find a concentration of around 80% of magnetite and a hematite phase lower than 5%. Whereas, the magnetite composition from X-ray diffraction shows 76%. We also investigate the metal-organic interaction and disorder degree of organic molecule conformation by infrared and Raman spectroscopy analysis. Hematite lattice vibrations show more alterations as it interacts with the organic acid. Finally, magnetic measurements at room temperature of the modified particles, suggest a superparamagnetic behavior and high saturation magnetization.

1. Introduction

Many groups are working with magnetic nanoparticles (MNPs) focusing on several applications, as fillers in nanocomposites [1], cleaning up oil spills [2], environmental sciences for metal separation [3], integrated nano-devices for cancer detection and screening [4] among others.

Hematite, magnetite, and maghemite are outstanding phases of iron oxide. Hematite (α-Fe_2O_3) crystallizes in a rhomboid structure and is used as a catalyst for water oxidation [5] and as a paint pigment [6]. On the other side, maghemite (γ-Fe_2O_3) forms a cubic structure, is used as a contrasting agent in magnetic resonance [7,8] and as magnetic recording medium [9]. The control of iron oxide particles composition regarding the quantity of each phase seems to be a crucial issue to improve the magnetic behavior of the particles focusing on further uses as magnetic resonance imaging (MRI) contrast.

Several methodologies have been reported to produce iron oxide nanoparticles as micro-emulsion [13], co-precipitation [14], reduction-precipitation [15], hydrothermal [16], spray pyrolysis [17] and chemical liquid deposition [18]. All these methods produce particles with a size in the order of 50–1000 nm [19]. Colloidal chemical precipitation methodology was widely studied to produce small size particles [10]. Nonetheless, Ostwald ripening mechanism helped by organic surfactant, and the use of polymers of different nature leads to monodisperse iron oxide nanoparticles [11,12].

On precipitation-co/precipitation methodology [2–5,16], variables as stirring level, pH, heating and Fe^{3+}/Fe^{2+} ratio influence on shape, size, and phase of iron oxide particles. As a result, different magnetic behaviors can be obtained according to these variables and that influences directly the main application of the particles [20].

X-Ray Diffraction is a well-established characterization technique on material science to determine the nanoparticles composition. However, is time-consuming to have a quantitative analysis. Vibrational spectroscopy provides essential information about the organic molecule conformation and the interactions with the iron oxide, enabling to go further in the inorganic spectral region characterization. To accomplish this, we proposed a different way from the infrared spectra analysis to calculate the iron oxide phase composition by using a deconvoluted peak, showing how the particles are affected by the organic surfactant.

Another information in the infrared spectrum related to the organic-inorganic interface could provide the second derivative function spectrum that allows more accurate identification of small absorption peaks not well resolved in the original spectrum [21,22]. Rieppo and coworkers [23] reported the importance of the second derivative analysis by infrared spectroscopy [24]. So this signal allows some specific absorption peaks on the sample to be analyzed. Although the derived signal appears with lower

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intensity, one order of magnitude, and increment by a factor 61/2 of signal-to-noise ratio [23,25].

In this report, we present a simple and straightforward methodology, based on vibrational spectroscopy, to detect the phase composition of iron oxide particles modified with oleic acid. As well, a metal-organic interaction of the nanoparticles is detected by Raman and infrared spectroscopy. To understand the accuracy of the result present here, we use as internal reference the data provided by X-Ray diffraction technique together with semi-quantitative analysis. Also, are discussed by us electron diffraction, electron microscopy and magnetization measurements on the three different co-precipitation synthetic methods performed.

2. Materials and methods

Iron (III) chloride ($FeCl_3 \cdot 6H_2O$), Iron (II) chloride ($FeCl_2 \cdot 4H_2O$), ammonium hydroxide (NH_4OH) and hydrochloric acid (HCl), all of them in analytical grade, were purchased from Vetec (*Rio de Janeiro, Brazil*), and used without further purification. Magnetite (Fe_3O_4) nanoparticles were prepared by chemical co-precipitation method of aqueous Fe^{+2} and Fe^{+3} salt solution and basic solution. To ensure the stoichiometric formation of the Fe_3O_4 and based on chosen literature reports [19–22], we use a molar ratio of Fe^{+2} and Fe^{+3} equal to 1:1.8 to sample termed as ***MAO$^-$1*** and a ratio of 1:1.45 on termed ***MAO$^-$2***, ***Zero***, and ***MAO$^-$3*** samples. On Supplementary information there are describe each of the nanoparticles modified synthesis conditions.

2.1. Characterization techniques

(1) Scanning electron microscopy (SEM) images were obtained directly from the powder samples using an EVO LV Carl Zeiss. A thin film of Pd/Au (30 nm) was deposited by sputtering over the films before the measurement. (2) FTIR spectra were obtained by Varian 640-IR equipment; using a number of scans 16, and resolution of 8. (3) Zeiss Libra 120 transmission electron microscope (TEM) was used to get electron images and electron diffraction (EDS) of the samples. A LaB_6 filament and accelerating voltage of 80 and 120 keV were used. (4) X-ray diffractometer was carried out on Rigaku Dengi D-Max 2000 equipment, using a Cu K_α radiation, generating a current and voltage of 30 kV, 15 mA respectively. (3) Raman spectra were measured with a Raman microspectrometer (wavelength=632.8 nm), with simple monochromator (Jobin Yvon; iHR — 320 model) and a CCD detector. The spectra acquisition time was 60 s to increase the signal/noise ratio. The laser source used as excitation light was He-Ne, with beam energy of 10 mW, focused on a spot of ~3 μm diameter. (4) Magnetic measurements were made using a vibrating-sample magnetometer (EZ9 model VSM, MicroSence). Magnetization curves were measured at room temperature, with a magnetic field of 2 T. This way, coercive field (H_c) and remnant magnetism (m_s) could be obtained.

3. Results and discussion

3.1. Morphological analysis

All the experimental procedures were done by the co-precipitation/precipitation methodology. As a result, the samples named ***Zero***, ***MAO$^-$1***, ***MAO$^-$2*** and ***MAO-3*** were prepared. A Fe^{2+}/Fe^{3+} stoichiometry ratio of 1:1.45 and HCl addition were used for samples ***Zero***, ***MAO-2***, and ***MAO-3*** and a higher ratio of 1:1.8 without HCl addition for ***MAO-1*** sample procedure. Except sample ***Zero***; iron oxide nanoparticles were modified with oleic acid, which acts as a surfactant to improve surface tension and modification approaches. Where the organic functional carboxyl group could have interactions with the iron oxide phases, as a result, stabilize the modified particles. It is noteworthy that agitation speed was not the same with all the procedures, and inert atmosphere and NaOH were only used on samples ***MAO-3*** and ***Zero***. So each synthesis procedure resulted in different particle compositions. In all the experiments, the final pH (after oleic acid addition) was around 7, but different pH values were obtained during the preparation as described in the experimental section. The literature describes that iron oxide phase composition is mainly dependent on pH and particle size distribution [2,15]. At pH > 10 the particle suspension showed a black color characteristic to the presence of magnetite phase. On the pH range from 9.7 to 10.6, the particulate material presented a maghemite phase. However, at pH lower than 8.5, red hematite phase is present, resulting in a red-brownish color suspension.

The color of each sample goes from dark black due magnetite to slight red-brownish of hematite phase as the pH goes down to neutral, meaning that magnetite should undergo the majority phase on the particles. Electron scanning microscope image of sample ***MAO-3*** shows agglomerated modified particles with the size of 126 ± 22 nm, with a regular and homogeneous texture, see Fig. 1.

Scanning electron image of the modified particles shows that ***MAO-3*** sample has a better homogeneity level and lower diameter values when compared with the other modified particles (see Fig. S1 in Supplementary information). Electron dispersive spectroscopy performed in different sample regions (Fig. 1C), indicates the presence of a ratio Fe:O ~ 1:1. The presence of sodium and chloride elements is related to washing procedure and carbon of oleic acid. We note that ***MAO-3*** sample preparation conditions produce iron oxide particles with a lower size and a more homogeneous distribution of the modified particles than the others. Thus, its procedure was used for the preparation of the ***Zero*** sample as an internal reference.

Electron microscope transmission of ***MAO-3*** shows the presence of inorganic particles with a spherical shape of 10 ± 3 nm in diameter. Around the oxide particle is observed the presence of organic material that came from the oleic acid. Electron diffraction spots taken at different zones show the presence of magnetite planes (220), (311), (400), (422), (333), and the rings presence shows a polycrystallinity nature, see Fig. 2.

Dark-field images of the same sample show the presence of some crystallinity degree confirmed by the X-ray diffraction pattern measurements. The histogram shows a modal shape, suggesting an Ostwald ripening driving mechanism as mainly growing process, which agrees with literature data, see Ref. [23].

3.2. XRD diffraction

XRD patterns of the iron oxide modified particles with the oleic acid show wide peaks in all samples. Fig. 3 displays sample pattern of magnetite (*JCPDS 19–629*) phase [26], with presence of (111), (220), (311), (400), (422), (440), and (511) planes. Those were present in all samples. As well maghemite (*JCPDS 39–1346*) [27] phase is observed.

From the patterns, we could visualize that reaction´s conditions of sample ***MAO-3*** produce a produce a single phase with some crystallinity degree intensity. Indeed, magnetite is the one phase present. On the other hand, sample ***MAO-1*** shows magnetite, maghemite and hematite phases.

To determine the crystalline samples size, Scherrer Eq. (1) was used on (311) plane of X-ray diffraction of each pattern.