

ATR-FTIR *VERSUS* RAMAN SPECTROSCOPY USED FOR STRUCTURAL ANALYSES OF THE IRON OXIDE NANOPARTICLES

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Received October 10, 2018

Abstract. Hereby we report the preparation of water colloidal solution of magnetic IONPs coated using perchloric acid, by application of co-precipitation method. ATR-FTIR and Raman spectroscopic techniques were used to investigate the IONPs' structure. The Raman pattern revealed that magnetic core of IONPs is given by the coexistence of magnetite and maghemite phases. Transmission electron microscopy analysis showed that IONPs are mostly spherical with the average physical diameter of 10.42 nm. Based on magnetic measurements data, the obtained average magnetic diameter was 7.12 nm. We supposed that a partial oxidation of magnetite to maghemite have been produced during the preparation of IONPs.

Key words: iron oxide nanoparticles, magnetite, maghemite, Raman spectra, ATR-FTIR spectra, TEM analysis, magnetic properties.

1. INTRODUCTION

Nanoparticles have received considerable attention in the past decades due to the unique properties mainly related to their nanometer size. Functionalized iron oxide nanoparticles (IONPs) stably dispersed in polar or nonpolar fluids represent colloidal suspensions with superparamagnetic bulk properties [1] which have been increasingly used in science, technique, biology and medicine due to their nanometric size (diameters ranging from 1 to 100 nm). Recently they have been considered promising materials for emerging fields such as cancer diagnosis and therapy [2–4]. It is well known that iron is essential in the development of all forms of life being stored in all living organisms in the ferritin form, as well as in other iron containing proteins or enzymes relevant for key biochemical processes [5].

Within the colloidal magnetic IONPs systems, the particles suspended in polar or nonpolar solvents are near-spherical magnetic grains. In order to prevent the coalescence at room temperature, particles are coated either with single or double

layers of surfactant, in relation to the type of solvent. Water-based magnetic nanoparticles suspensions were of low long-term stability compared to hydrocarbon-based ones. Some research studies suggest that oleate ion could develop one of the strongest interactions with iron ions at the surface of IONPs [6]. The mostly coating agents used for IONPs colloidal solution stabilization are synthetic and natural polyacids (*e.g.* 2,3-dimercaptosuccinic, aspartic, glutamic, citric, tartaric acids) [7–12].

For biomedical applications, magnetic IONPs are the best option due to their biocompatibility, superparamagnetic behaviour and chemical stability [13]. IONPs such magnetite (Fe_3O_4) and its oxidized form, the maghemite ($\gamma\text{-Fe}_2\text{O}_3$) have attracted more attention because they are basically biocompatible and non-toxic in low concentrations [14–16].

The magnetic properties of IONPs provide simple separation during material preparations, rendering them suitable for applications such as drug delivery or hyperthermia treatment. Biophysicists pay more and more attention to the magnetic nanoparticles functionalized with nonmagnetic molecular surfactant, that prevents the irreversible aggregation of the magnetic nanoparticles and make them suitable for biomedical applications. The suitability of magnetic IONPs for biomedical purposes requires particles size smaller than 100 nm and high magnetic properties. In the last years, more and more research studies are focused on the analysis of toxic effects of magnetic nanoparticles and their potential accumulation in plants or microorganisms [17–23].

In this work we report the application of surface Raman spectroscopy and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy in the characterization of stabilized IONPs. IONPs colloidal solution was prepared using chemical co-precipitation method using perchloric acid to stabilize magnetic nanoparticles in water.

The oxidation of magnetite to maghemite was studied in IONPs water based solution *via* Raman and ATR-FTIR spectroscopy. Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are the main forms of iron oxide. Magnetite nanoparticles are not very stable under ambient conditions, and are easily oxidized to maghemite.

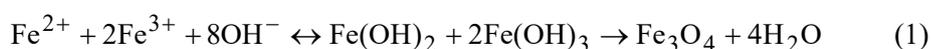
Co-precipitation is a simple and unexpensive method for the synthesis of iron oxide nanoparticles (either Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$) from aqueous $\text{Fe}^{2+}/\text{Fe}^{3+}$ salt solutions through the addition of a base, either at room or at elevated temperature. The main characteristics of the IONPs (size, shape, composition) are influenced by different factors, such as: (i) the type of salts used during synthesis, *e.g.* sulfates, chlorides, nitrates; (ii) the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio; (iii) the temperature of chemical reactions; (iv) the pH value, and (v) the ionic strength of the reaction medium.

Raman spectroscopy is a powerful tool for investigating the vibrational and structural properties of materials. This technique allows characterisation of samples without requirements of specific sample preparation [24] so that we considered it for the analysis of prepared IONPs liquid solutions. There are several studies reporting Raman spectroscopy investigations of IONPs [25–27].

ATR-FTIR spectroscopy is a nondestructive and simple method, often being preferred for liquid analysis in natural state of samples. Therefore this spectroscopic method has been used more and more to investigate the coating substance adsorption on the IONP surface [28–29].

2. MATERIALS AND METHODS

IONPs were synthesized by chemical co-precipitation of FeCl_3 and FeCl_2 in alkaline medium according to described method [30]. The co-precipitation reaction equation is presented below:



The technological approach of IONPs stabilized with perchloric acid and dispersed in water, synthesis is presented in Figure 1.

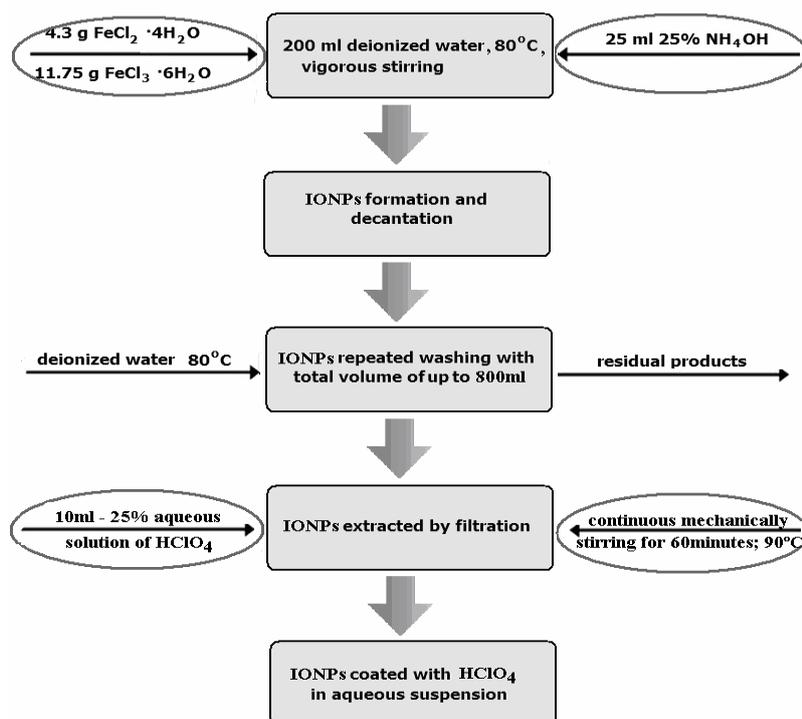


Fig. 1 – Schematic presentation of IONPs water suspension preparation technology.

Typically hydrated ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 70% perchloric acid, 25% ammonium hydroxide (NH_4OH) and all

other chemicals (J.T. Baker) were used as received, being of high purity. Distilled water produced using DEST3 – BOECO (Germany) water still was used in all experimental procedures.

IONPs water based solution was characterized by transmission electron microscopy (TEM), Raman spectroscopy, ATR-FTIR spectroscopy and magnetic measurements.

TEM was performed using a TESLA device with a resolution of 1.0 nm (sample deposition of collodion sheet after 10^4 dilution) for the assessment of the physical diameter size of studied IONPs.

ATR-FTIR and Raman spectroscopies were used without any specific samples preparation, in order to investigate the structural characteristics of IONPs. The Raman spectrum was registered using a commercial micro-Raman spectrometer Lab Ram HR800 from Jobin Yvon Horiba, while ATR-FTIR spectrum using ATR-FTIR Alpha spectrometer (Bruker, Germany). The micro-Raman spectrometer works with three interchangeable lasers. The most used is a solid state Nd:YAG laser of 520 nm wavelength [31]. The ATR-FTR spectrometer works with a versatile high throughput ZnSe crystal for the analysis of powders, solids, pastes and liquids.

Magnetic measurements were carried out by Gouy method using an air-tight nonmagnetic cylindrical sample holder with 3 mm diameter and 25 cm length placed perpendicularly to the magnetic field. All measurements were performed at constant temperature of sample (295 K). Magnetic field intensity was measured with the Walker Scientific MG 50D Gaussmeter with Hall probe. Sample weight was measured using an ACULAB-200 electronic balance with 10^{-4} g accuracy.

3. RESULTS AND DISCUSSIONS

The TEM analysis demonstrated that the synthesized IONPs are mostly spherical with their size distribution of 10.42 ± 2.99 nm in diameter. In Figure 2 are presented the physical diameter distribution histogram and one of TEM images registered for IONPs sample.

For the prepared magnetic IONPs water based suspension, the saturation magnetization value of 18.4 emu/cm^3 was obtained from magnetization (M) versus $1/H$ curves by extrapolating to $1/H = 0$. The obtained value for saturation magnetization was not high. The oxidation of magnetite to maghemite influenced the IONPs magnetic properties.

The average size of magnetic diameter (a_m) was calculated following the Langevin's equation (2) [32] using the magnetization measurements data (Fig. 3), as follow:

$$a_m = \left[\frac{18k_B T}{\pi \mu_0 M_s \cdot M_b} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \right]^{1/3} \quad (2)$$

where a_m is the magnetic particle diameter, k_B is Boltzmann's constant, T is the absolute temperature, M_s is the saturation magnetization of the sample, μ_0 is the vacuum permeability and M_b is magnetization value of bulk magnetite ($4.8 \cdot 10^5$ A/m) [1].

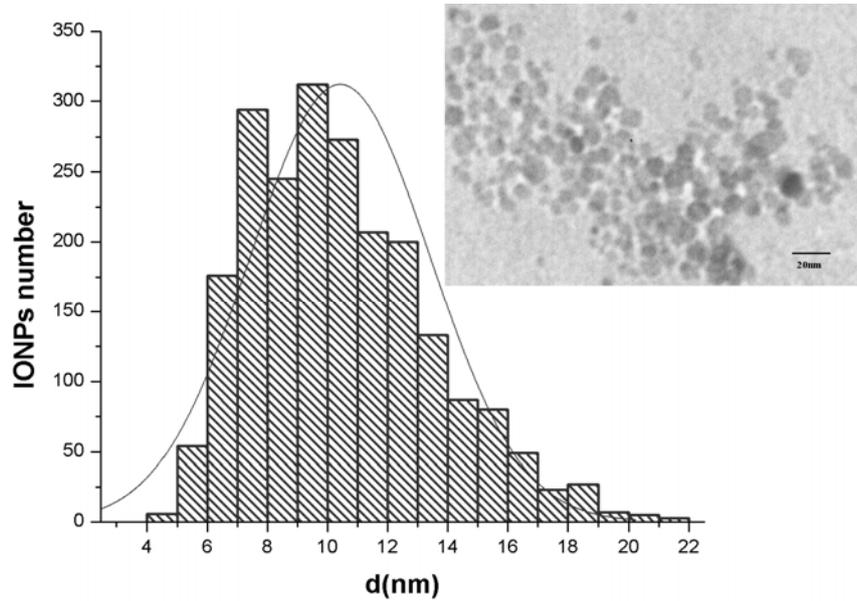


Fig. 2 – Distribution histogram and TEM image of IONPs coated with perchloric acid.

Assuming a spherical particle shape, we obtained the value of 7.12 nm as average magnetic diameter of IONPs. The surfactant layer of the magnetic core can be evidenced by means of value difference between physical diameter and magnetic diameter. For perchloric acid coated magnetic IONPs, the 1.65 nm thicknesses of the organic surface layers was obtained.

In addition, the density of IONPs water based suspension (n) synthesized in our study and determined using equation (3) was $2 \cdot 10^{23} \text{ m}^{-3}$.

$$n = \frac{6M_s}{\pi \cdot a_m^3 \cdot M_b} \quad (3)$$

Raman spectroscopy was used to determine the nature of the iron oxide core. Raman spectroscopy can be a convenient tool to differentiate maghemite and magnetite [33]. These two phases are ferrimagnetic and have identical crystal structures but have very distinct bulk Raman spectra. The Raman spectrum of IONPs revealed that the magnetic core of nanoparticles is given by the coexistence of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phases (Fig. 4).

According to Wang *et al.* (2009), the 668 cm^{-1} peak of Raman spectrum is the vibrational mode characteristic to magnetite (Fe_3O_4), while the 700 cm^{-1} peak is characteristic to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [34]. Shebanova and Lazor (2003) have asserted that 700 cm^{-1} peak indicates the first stage of magnetite oxidation [26]. Raman vibration peak observed at 380 cm^{-1} wavelength can be also associated with bulk maghemite spectra (Tang, 2003) [35]. On the other hand, Slavov *et al.* (2010) have asserted that the appearance of the band at 380 cm^{-1} might be due to the link between hydroxyl groups from the surfactant molecule with surface Fe^{3+} atoms of the nanoparticles [27].

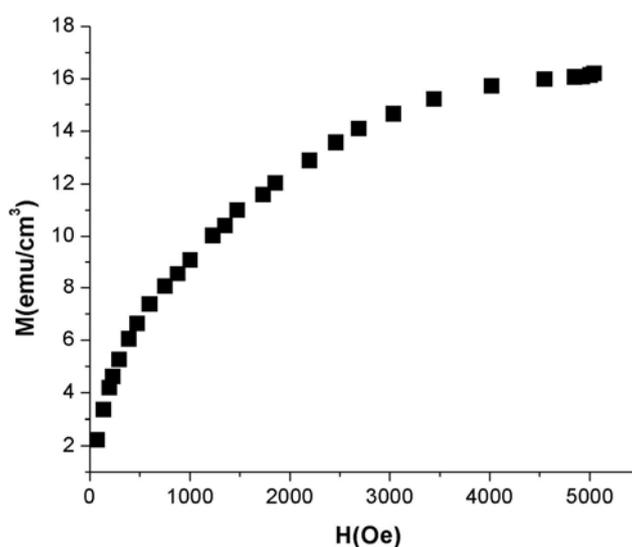
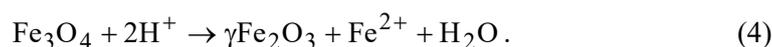


Fig. 3 – Magnetization curve of IONPs coated with perchloric acid.

The Raman peak observed around 3500 cm^{-1} can be associated with OH stretching mode (Kolesov, 2006) indicating the state of water in IONPs [36]. The intense peak at 933 cm^{-1} can be attributed to perchlorate (ClO_4^-) ion Raman vibrational modes (Patel *et al.*, 1983) [37], being the characteristic peak of perchlorate in its aqueous form (Mosier-Boss *et al.*, 2003) [38]. Weak Raman peaks were also observed at 1412 cm^{-1} and 1580 cm^{-1} , possibly due to an accidental contamination of the IONPs samples with carbon related species, following Chourpa *et al.* (2005) suggestion [24].

Thereby, Raman spectrum indicated that magnetite nanoparticles could be converted to maghemite. It was shown that magnetite (Fe_3O_4) is not very stable and is sensitive to oxidation [39], following the reaction which leads to maghemite ($\gamma\text{Fe}_2\text{O}_3$):



We presumed that the applied increased temperature during the IONPs synthesis might favour oxidation of magnetite to maghemite. The Raman spectrum could show peaks of magnetite and maghemite due to one of a partial oxidation by the incidence of high power laser, also. Shebanova *et al.* (2003) investigated magnetite using various powers of the laser Raman spectrum. They concluded that due to some critical value of the laser power, the characteristics of maghemite bands have been indicated by the Raman spectra, due to the effects of oxidation of the magnetite [26].

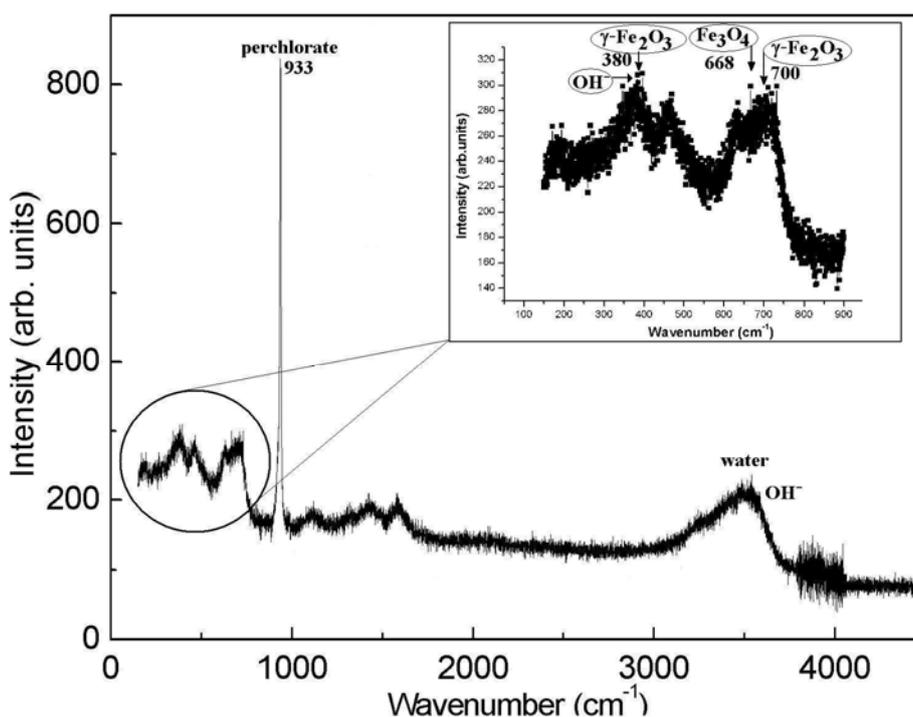


Fig. 4 – Raman spectrum of IONPs aqueous liquid solution.

The ATR-FTIR spectrum of IONPs aqueous liquid solution is presented in Fig. 5. Based on the registered ATR-FTIR spectrum of IONPs coated with perchloric acid (Fig. 5), the absorption peak (broad) at 3362 cm^{-1} can be assigned to stretching vibrations of OH^- groups, while the intense band around 1625 cm^{-1} reflects the OH^- vibration mode and may include some contribution from molecules trapped onto the magnetic colloidal nanoparticles.

The ATR-FTIR pattern showed a band at 620 cm^{-1} which corresponds to the stretching vibration $\nu(\text{Fe-O})$ of tetrahedral iron atom [40] and a band around 871 cm^{-1} which represents the C-H deformation vibrations [41]. According to Cornwell and Schwertmann 2003 [42], the 620 cm^{-1} peak is attributed to magnetite.

The appearance of a weak band at 687 cm^{-1} could indicate the maghemite presence as oxidation product of magnetite during the IONPs synthesis [43].

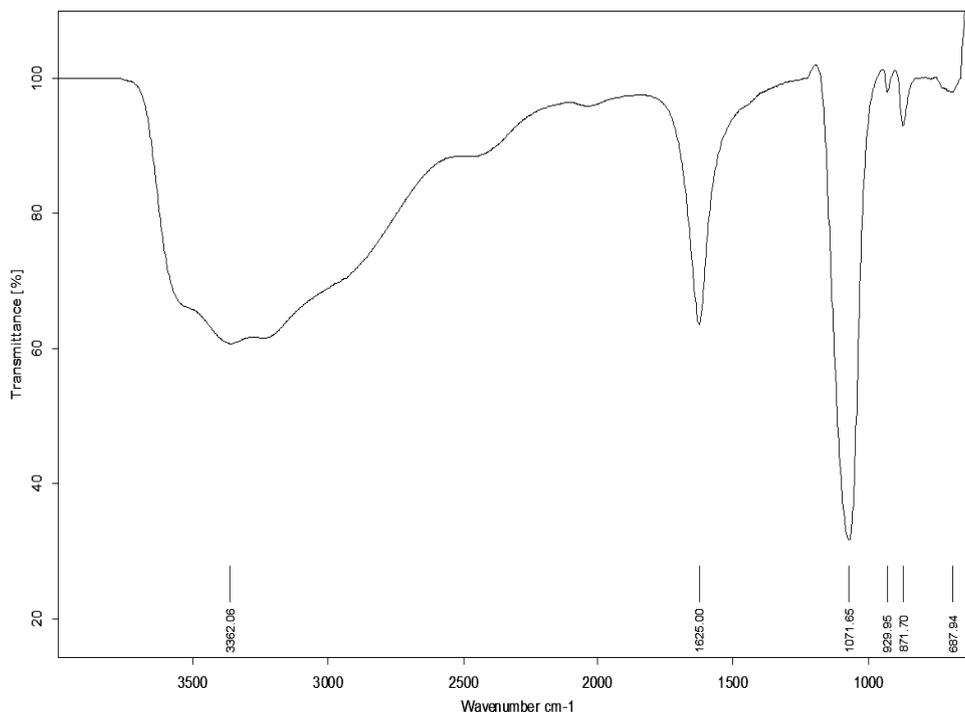


Fig. 5 – ATR-FTIR spectrum of IONPs aqueous liquid solution.

The weak band observed at $\sim 930\text{ cm}^{-1}$ can be attributed to an infrared inactive mode for free perchlorate ions as suggested by Chen *et al.* 2004 [44]. The intense peak that appeared at 1071 cm^{-1} wavelength could be due to the (C-O) stretching vibrations [45] and also to the iron perchlorate presence in the solid phase of IONPs.

4. CONCLUSIONS

Water colloidal solution of magnetic IONPs coated using perchloric acid (HClO_4) was prepared by applying the co-precipitation method. Complementary spectroscopic techniques (ATR-FTIR and Raman) applied to samples without any specific preparation was used to structurally analyse the IONPs.

The Raman spectrum revealed that the magnetic core of IONPs is given by the coexistence of two phases, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), respectively. The appearance of their characteristic peaks in Raman and ATR-FTIR

patterns could indicate a partial oxidation of magnetite to maghemite by the incidence of high power laser or temperature used during the preparation of IONPs.

Transmission electron microscopy (TEM) analysis showed that the synthesized IONPs were mostly spherical of 10.42 ± 2.99 nm physical diameter. Based on the magnetic measurements data, the obtained average magnetic diameter was 7.12 nm. The magnetic properties of synthesized IONPs were not strong, probably linked to the oxidation of magnetite to maghemite. Therefore, we suppose that a partial oxidation of magnetite to maghemite could have been produced during the preparation of magnetic IONPs at 80°C temperature.

Acknowledgements. Project financed from Lucian Blaga University of Sibiu research grant LBUS-IRG-2018-04. We greatly thank Dr. Ana Maria Racu of Institute of Condensed Matter Physics, Technical University Braunschweig, Germany, for the Raman spectra recording.

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