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Raman spectroscopy investigation of magnetite nanoparticles in ferrofluids

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ABSTRACT

Raman spectroscopy is used to investigate magnetite nanoparticles dispersed in two types of β-cyclodextrin suspensions. An approach is presented for characterization of the magnetic core in liquid surrounding at room temperature and atmospheric pressure. The effect of elevating laser power on the structural stability and chemical composition of magnetite in the ferrofluids is discussed. The data are compared with data from dry by-products from the fluids. Powder samples undergo total phase transition from magnetite to hematite at laser power of 1.95 mW. The same nanoparticles in the fluid undergo transformation at 9 mW, but no hematite positions appear throughout that investigation. The Raman spectra revealed that the main phase of the magnetic core in the fluids is magnetite. That is indicated by a strong and non-diminishing in intensity peak at 670 cm^{-1}. A second phase is present at the nanoparticle's surface with Raman spectroscopy unveiling maghemite-like and small fractions of goethite-like structures. The Fourier transform infrared spectroscopy investigations confirm deviations in the surface structure and also point to the fact that the oxidation process starts at an early stage after formation of the nanoparticles. The analyses of the infrared data also show that β-cyclodextrin molecules retain their cyclic character and the coating does not affect the oxidation process once the particles are evicted from the fluids. A Mössbauer spectroscopy measurement on a ferrofluidic sample is also presented.

1. Introduction

Since the first magnetic nanoparticles necessary to prepare a stable ferrofluid were prepared in the early 1960s [1]; they have found many interesting applications in fields like sealing, damping, heat transfer, loudspeakers, measuring devices, etc. [2]. Since then, the advances in synthesis technologies of the main magnetic component used in these ferrofluids – iron oxide, and in the methods of its analysis, had opened new wide possibilities for their application in the field of medicine [3]. Nowadays ferrofluids are extensively studied for their potential role as both diagnostic and cancer therapeutic agents [4]. This also includes studies on magnetic drug delivery systems [3], magnetic fluid hyperthermia [5], and as contrast agents for magnetic resonance imaging (MRI) [6], with currently nearly 50% of the advocated T_2-agents in MRI being based on ferrofluids containing superparamagnetic magnetite nanoparticles [7]. In all cases, the magnetic fluids used are based on superparamagnetic iron oxide nanoparticles (magnetite or maghemite) dispersed in water. Their low toxicity and suitable magnetic properties – high relaxation signal of the particles used as a contrast agent and high magnetic moment of the particles used for drugs targeting, determine the choice of these magnetic materials. But unlike the composite, which is a dry magnetic material, the chemical and structural characterization of the iron oxide particles while in liquid medium is a difficult task, due to the evident constraints of the most applied measurement techniques.

Raman spectroscopy allows characterization of many types of samples without any specific preparation [8], which encouraged our experiments with liquids. In this paper, we focus on Raman micro-spectroscopy investigation of magnetite nanoparticles dispersed in two types of ferrofluids. Contributions to Raman spectroscopy investigations of nanosized iron oxides have already been reported, with some special emphasis on the works of da Faria et al. [9] and Shebanova and Lazor [10]. Some ferrofluid investigations involving this vibrational spectroscopy have also been made, where the preparative techniques yield either dried [11], precipitated [12], or frozen [13] samples to be

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measured. In our investigations, we used a simple procedure to probe the state of the magnetic core in liquid surrounding at normal conditions.

The aim of the investigation was to obtain new information about the development towards a second, maghemite-like phase on the surface of magnetite nanoparticles [14], when dispersed in liquid using Raman spectroscopy. The role of the liquid surrounding for reducing or preventing such development was also studied. Since all ferrofluids are known to be polydisperse to some degree [5], structural deviations on the magnetic nanoparticle's surface, if present, will complicate even more the choice of exact parameters of the applied external magnetic field. FTIR (Fourier transform infrared spectroscopy) measurements on powder samples from the fluids are also presented. Mössbauer spectroscopy was performed on specially prepared sample to probe the material as closely as possible to its fluid state. The synthesis routine of the ferrofluids is also described, since, to the best of our knowledge, only two other groups are involved in combining magnetite with beta-cyclodextrin (β-CD) [15,16] – a water soluble cyclic oligosaccharide, used in many commercial pharmaceutical products [17,18].

2. Synthesis

Using different approaches for magnetite stabilization, two general types of ferrofluids were prepared. The first type (type A) was based on hybrid coating of TMAOH/β-CD on magnetite superparamagnetic particles, where the tetramethylammonium hydroxide – $N(CH_3)_4OH$, was the surfactant. Some investigations were performed on this type of ferrofluids – for MRI response [19] and for hyperthermia effect [20]. In the second type of ferrofluids (type B), the coating was solely of β-CD. The difference between them is elimination of the surfactant from the process of particle stabilization. In such way, the cyclodextrin capability to absorb onto magnetite surface can be assessed and compared with the surfactant specifically designed for that purpose. For both types, magnetite was obtained via a co-precipitation routine described elsewhere [21].

For fluids type A (A-MFs), magnetic material with high water content was transferred into 0.2 ml of TMAOH, homogenized, and subsequently diluted with water solution of β-cyclodextrin (Table 1). For fluids type B (B-MFs), the magnetic material obtained was transferred directly into the β-cyclodextrin solution. For all ferrofluid samples, we used 10^{-2} M water solution of β-cyclodextrin. All experiments were conducted at atmospheric pressure and room temperature. Some initial precipitation in B-MFs was used to obtain composite samples for measurements. Minor precipitation was observed in the A-MFs. After 3-day period, all fluids were separated from the sediment fraction; and the stability period observed is given in Table 1. The powder samples subject to measurements in this paper were obtained as follows:

- Sample **MAG** is magnetite, precursor for all ferrofluids, dried at 70 °C for 24 h.
- Samples **pB1**, **pB2**, and **pB3** are the precipitates dried at 70 °C for 24 h, respectively, from B1, B2, and B3 (Table 1).

Due to the small quantity of sedimentation, such dry samples cannot be obtained non-aggressively from the A-MFs.

3. Results and discussions

The Raman spectra were obtained using a LabRAM HR visible single spectrometer equipped by a microscope and a Peltier-cooled CCD detector. The 633 nm He–Ne laser line was used for excitation. The power was adjusted using a set of neutral filters. The spectral slit width at the conditions used was 1 cm^{-1}. In our investigations, around 3 ml from each ferrofluid sample were placed by a pipette in an open, homemade, container of Al-foil. The laser beam was focused on the fluid surface by an X20 long working distance objective. The acquisition time for all liquid samples in Fig. 1 was 60 s ($\times 2$ – times per scan) for all optical excitation intensities. This time was chosen in order to minimize the drop of level due to evaporation and at the same time to get signal sufficient for analyses from the nanosized magnetic core. For powder samples, the laser beam was focused on a flat surface by an X100 objective with 150 s ($\times 2$)-acquisition time. The Raman measurements were performed at room temperature and atmospheric pressure.

By raising the laser power from 0.9 to 9.0 mW, we tested the magnetite structural stability in the fluids. The characteristic peak positions of magnetite (Fe_3O_4) and its possible oxidation by-products, maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) determined the Raman region of interest in this investigation: 100–1200 cm^{-1}. In all spectra in Fig. 1, we include a spectrum of β-cyclodextrin, crystallized from 10^{-2} M water suspension, since it is present in every sample measured. Its most intense peak positions are shown in Table 2. Also in Table 2 are the wavenumbers for the strongest peaks found in all ferrofluid samples at different laser excitation intensities.

For correct assignment of the band positions present in our samples and for phase identification, we used combined Raman data for key iron oxides bands [8,9,11,22], from where:

- Fe_3O_4: 193 (week), 306 (week), 538 (week), 668 (strong);
- γ-Fe_2O_3: 350 (strong), 500 (strong), 700 (strong); and
- α-Fe_2O_3: 225 (strong), 247 (week), 299 (strong), 412 (strong), 497 (week), 613 (medium).

Table 1
Synthesis and colloidal stability data for the samples investigated.

Ferrofluid sample	Surfactant TMAOH (ml)	Concentration β-cyclodextrin/H_2O (mg/ml)	Concentration Fe_3O_4/solution (mg/ml)	Precipitated fraction (%)[b]	Colloidal stability (days)
A1	0.2	11	3	Minor	90
A2	0.2	11	4	Minor	90
B1	No	11	0.6[a]	18 (sample **pB1**)	60
B2	No	11	1.5[a]	18 (sample **pB2**)	60
B3	No	11	2.5[a]	16 (sample **pB3**)	60

[a] Recalculated taking into account the percentage of magnetite fraction precipitated.
[b] Relative to the initial magnetite concentration.