



Magnetic properties of ultrasmall iron-oxide nanoparticles



Dušan Milivojević^{a,*}, Branka Babić-Stojić^a, Vukoman Jokanović^a, Zvonko Jagličić^b, Darko Makovec^c, Nataša Jovič^a

^a Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

^b Institute of Mathematics, Physics and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia

^c Department for Materials Synthesis, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 22 November 2013

Received in revised form 15 January 2014

Accepted 16 January 2014

Available online 24 January 2014

Keywords:

Nanostructured materials

Magnetic fluids

Magnetic measurements

Ultrasmall superparamagnetic iron oxide

USPIO

ABSTRACT

The work presents structural and magnetic properties of ultrasmall magnetic nanoparticles consisting of inorganic iron oxide core and organic ester shell, dispersed in an organic fluid, synthesized via polyol route. The structure analysis shows that nanoparticles are crystalline, less than 3 nm in size, mutually clearly separated. The magnetic properties are in accordance with the size of the nanoparticles and do not indicate interparticle interactions. The particles show pure superparamagnetic behavior with very low blocking temperature. ZFCFC bifurcation and *ac* susceptibility peaks are at temperatures $T_B < 12$ K. The properties of fluid were compared with dried powder sample. Drying of fluid brings about interactions between the magnetic nanoparticles that considerably affect spin dynamics of the particles. The surface of nanoparticles has a significant influence on their behavior. The Mössbauer parameters indicate existence of γ -Fe₂O₃ core and non-stoichiometric surface layer. Magnetic field dependent magnetization analysis suggests smaller apparent size of the particles $d_0 = 0.56$ nm. High magnetic anisotropy due to surface layer anisotropy was measured to be of the order 10⁶ erg/cm³ that is two orders of magnitude higher than that in bulk material.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Magnetic nanoparticles (MNPs) and their dispersions in various media have been for a long time of scientific and technological interest. Magnetic dipole and van der Waals interactions have tendency to agglomerate the particles. In order to prevent agglomeration the magnetic particles should be small enough (usually about 10 nm in size) and coated with a shell of an appropriate material. This coating can be a surfactant made of long chained molecules, or ionic if it is an electric shell [1–3]. The particles are usually made of maghemite γ -Fe₂O₃, magnetite Fe₃O₄, and other ferrites of the type MFe₂O₄, where M = Mn, Co, Ni, Cu. The carrier liquid is usually an organic solvent or water.

Besides wide range of technological applications [1], in recent years a lot of research work has been devoted to various biomedical applications of dispersions of magnetic nanoparticles. Biocompatible nanoparticles dispersed in aqueous or physiological medium [4] can be used in Magnetic Resonance Imaging (MRI) as contrast agents [3,5,6], as drug carriers [3,7] and in magnetic hyperthermia treatment [3,5,7,8].

Iron oxides are known as T2 MRI contrast agents but ultrasmall nanoparticles can act as both T1 and T2 contrast agents [9–11]. Ultrasmall iron oxide/ferrite nanoparticles having longer circulation half-life in the body can avoid fast uptake by the macrophages and provide better contrast [9,12,13]. Commonly used iron oxide nanoparticle contrast agents with a hydrodynamic size of over 50 nm remain primarily intravascular which severely undermines their targeting specificity.

The characterization of ultrasmall iron oxide nanoparticles (USPIO) is rather difficult task. The ultrasmall particles have high surface to volume ratio. They may be considered to be a less-ordered system which is neither completely crystalline nor completely amorphous [13]. This property is reflected in discordant data obtained using different experimental methodologies. Other problem is that some experimental methodologies require drying of samples.

In the present work we have synthesized USPIO in organic carrier fluid and studied magnetic properties. We compared it to the dried powder form. Microstructure, morphology, static and dynamic magnetic properties of the prepared fluid were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic light scattering (DLS), *dc* magnetization, *ac* susceptibility measurements and Mössbauer spectroscopy.

* Corresponding author. Tel.: +381 11 3408694; fax: +381 11 3408607.

E-mail address: dusanm@vinca.rs (D. Milivojević).

2. Experimental details

2.1. Synthesis

The synthesis was carried out using tris(acetylacetonate)Fe(III) (FeIII(acac)₃), diethylene glycol (DEG) and propionic acid. The Fe precursor compound, 34 g of FeIII(acac)₃, was dissolved in 200 ml of DEG. The solution was autoclaved at 120 °C for 2 h, than temperature was increased to 165 °C to obtain esters of diethylene glycol acetylacetonate. The reaction was promoted by iron ions which catalyzed this reaction. After this procedure the mixture was rapidly cooled to 100 °C by flow of water through the wall of autoclave. Finally, 37.63 g of propionic acid was added with a small quantity (0.9 ml) of sulphuric acid as catalyst and reaction was done at 145 °C for 2 h to obtain well dispersed iron oxide nanoparticles inside ester shell. The obtained colloid solution was brown and very stable. Besides the fluid sample, a powder sample was also prepared by drying the fluid at 200 °C for 10 h.

The idea of this route is to enable networking around iron oxide nanoparticles, to lower toxicity of DEG by making esters and prolong circulation time by covering USPIO with esters, (diethyleneglycolacetylacetonate and diethyleneglycolpropionate).

2.2. Experimental technique

X-ray characterization of the samples was carried out on a Philips PW 1050 powder diffractometer using Cu K α radiation. High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDXS) were carried out using transmission electron microscope JEOL 2010 equipped with an energy-dispersive X-ray spectrometer (EDXS) microanalysis system (LINK ISIS EDS 300) operated at 200 kV. The samples were prepared by drying a drop of the diluted suspension on a copper-grid-supported transparent carbon foil. The size distribution of the nanoparticles was measured by dynamic light scattering (DLS) using Zetasizer Nano ZS (Malvern, UK) equipped with green laser (532 nm). Intensity of scattered light was detected at the angle of 173°. All measurements were conducted at room temperature. Ten measurements were performed for each sample. All data processing was done by the Zetasizer software 6.20 (Malvern instruments). Magnetic measurements were carried out on a SQUID magnetometer (MPMS XL-5, Quantum Design) equipped with an *ac* option. Zero-field-cooled (ZFC) and field-cooled (FC) measurements of magnetization were performed at applied magnetic fields from 50 to 1000 Oe in the temperature range from 2 to 300 K. Magnetic field dependence of magnetization was measured at applied magnetic fields up to 50 kOe. The *ac* magnetization measurements were made under an *ac* exciting field with amplitude of 6.5 Oe using different frequencies in the range 1–1500 Hz. ⁵⁷Fe Mössbauer spectrum was recorded at room temperature using a conventional transmission Mössbauer spectrometer operating in constant acceleration mode. The source was ⁵⁷Co in Rh matrix. Experimental data were fitted to Lorentzian absorption lines by using a least-square based method. The spectrometer was calibrated using α -Fe foil at room temperature. All the isomer shifts are given relative to the center of the α -Fe spectrum.

3. Results and discussion

3.1. Structure analysis

The X-ray diffraction lines of the samples are very broad and no information about structure can be obtained. Estimation of average crystallite size from the width of the X-ray diffraction lines using Scherrer's formula gives sizes lower than 1.6 nm, which is the size of only two crystal lattice parameters or the material is amorphous.

The morphology, particle size and chemical composition were characterized by HRTEM and EDXS. TEM analysis (Fig. 1) shows that after drying the suspension on the TEM support, the sample deposited in the form of small deposits containing small nanoparticles of uniform, but various sizes. The nanoparticles of one size are always deposited together. The majority of the nanoparticles are below 3 nm, but also larger nanoparticles around 5 nm in size were observed. HRTEM shows that the nanoparticles are crystalline. EDXS shows presence of Fe and O.

The AFM micrographs reveal the well separated nanostructures of around 50 nm in size (Fig. 1(d)).

The size distribution of the nanoparticles in the organic fluid was studied using dynamic light scattering (DLS). Number of particles as a function of hydrodynamic particle diameter can be well described by a log-normal distribution $f(d) = (1/\sqrt{2\pi}\sigma d) \cdot \exp[-\ln^2(d/d_0)/2\sigma^2]$ yielding the distribution width $\sigma = 0.22$ and median of the

distribution $d_0 = 48.82$ nm, which is related to the average hydrodynamic diameter $d_{av} = d_0 \exp(\sigma^2/2) = 50.01$ nm.

The particle diameters obtained by DLS and AFM techniques are very close to each other but are an order of magnitude larger than the values obtained by XRD and TEM. This is because DLS and AFM measure the size of possibly agglomerated particles together with the organic shell.

It is apparent in Fig. 1(a) and (b) that the particles are mutually clearly separated but clustered to form larger groups. Since TEM procedure includes drying of fluid, clusterization could be due to fluid evaporation that turns the sample into a similar to the powder sample.

Discordant structural data for USPIO nanoparticles obtained with different structural methods have been already discussed in the paper by Di Marco et al. [13].

3.2. Mössbauer spectra analysis

We have performed the Mössbauer spectrum analysis of dried USPIO in order to distinguish which iron oxide phase has been formed as a product of this synthesis. The spectrum is recorded at room temperature and shown in Fig. 2. It consists of an asymmetric doublet, which implies that two doublets should be included into refinement. The fitting of Mössbauer spectra with two symmetric doublets gave a reasonable good fit (shown in Fig. 2). The isomer shift (*IS*) of two doublets are similar, 0.36/0.38 mm s⁻¹, but their quadrupolar splitting (*QS*) and the line width (Γ) are markedly different, 0.63/1.00 mm s⁻¹, and 0.18/0.27 mm s⁻¹, respectively. It can be noticed that the component with higher *QS* is more broadened (has a larger Γ). Similar values of the Mössbauer parameters have also been obtained when fitting the Mössbauer spectra of other iron oxides in a superparamagnetic state, such as lepidocrocite (γ -FeOOH: two doublets, *QS* = 0.60/1.03 mm/s) [14] or hematite [15].

We also performed fitting of the spectrum using only a single doublet. Such model gave poorer result but the obtained values for the isomer shift *IS* = 0.38 mm/s, and the quadrupolar splitting *QS* = 0.86 mm/s of the doublet are very close to the literature data characteristic for a high spin Fe³⁺ state (*S* = 5/2) in γ -Fe₂O₃ (0.32–0.34 mm/s for *IS*, and 0.74–0.84 mm/s for *QS*) [16]. For stoichiometric γ -Fe₂O₃, the value of the isomer shift should lie within the range from 0.24 to 0.36 mm/s [17]. Slightly higher value of *IS* could be an indication of the presence of Fe²⁺ ions at the vacant positions in the cubic spinel structure of maghemite. If we now go back to a two subspectra model, we can interpret our results in accordance with the description given in the paper by Abdullah et al. [18]. In that case, the doublet-1 (~29% of total area) with narrow lines can be assigned to Fe³⁺ ions situated in the core of the nanoparticles, while the broadened doublet-2 (~71% of total area), which indicate the increase in distortion of iron coordination, can be associated with Fe³⁺ ions located at the surface of γ -Fe₂O₃ nanoparticles. Following such assumption, the surface layer of γ -Fe₂O₃ nanoparticles probably is non-stoichiometric, while the core of the nanoparticles is closer to the stoichiometric composition.

3.3. Magnetic properties

3.3.1. *dc* magnetization

The zero-field-cooled ZFC and field-cooled FC magnetic susceptibilities as a function of temperature, of USPIO fluid and powder, were measured at applied magnetic fields from 100 to 1000 Oe (Fig. 3(a) and (b)). The mass concentration of the iron-oxide phase in the fluid sample was 0.0047 g/mL, determined by drying the fluid at 750 °C.

As can be seen, the ZFC and FC magnetizations of the samples bifurcate at a certain temperature *T*_{irr} and show a broad peak in

Download English Version:

<https://daneshyari.com/en/article/1611708>

Download Persian Version:

<https://daneshyari.com/article/1611708>

[Daneshyari.com](https://daneshyari.com)