Study of colloidal particles $\text{Fe}_m\text{O}_n\text{-SiO}_2$ synthesized by two different techniques

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Abstract. Colloidal solutions $\text{Fe}_m\text{O}_n\text{-SiO}_2$ were obtained by two different techniques based on sol-gel process: silica cores partially coated by iron oxide particles and iron oxide cores coated by silica. Dried layers were investigated by atomic force microscopy and size distribution was plotted. Chemical contain of dried specimen was analysed by FTIR-spectroscopy. Magnetic properties of colloidal particles obtained by both the techniques were measured by VSM. Resistivity’s change under the influence of magnetic field was measured using LCR-meter.

1. Introduction

Composite magnetic colloids could be applied for solving biomedicine problems such as MRI diagnostics [1] or blood vessel controlled occlusion [2], including oncology [3]. Synthesis of superparamagnetic nanoparticles may be provided by sol-gel technique [1]. Using this technological route authors obtained aggregate stable specimens starting to settle under the influence of constant magnetic field [4]. Aggregation and sedimentation processes were studied by MRI relaxation times’ and AC signal resistivity measurements [1, 4]. Authors of [5] investigated process of iron oxide phase transformation from magnetite/maghemite to hematite initiated by laser radiation at wavelength of 532 nm. Also oxidation of magnetite/maghemite particles may be caused by the absence of the outer coating so using of one-stage technique based on the sol-gel process should give better result. However the biological inertness of two-stage derived colloids is probably much higher because of silica heat treatment at 300 °C for 30 minutes in comparison to the presence of 0.04 vol. % untreated tetraetoxisilane in the one-stage derived colloids.

Intensive heating of iron oxide nanoparticles by the influence of laser radiation is used in biomedical application. Photothermal effects of laser heating iron oxide nanoparticles in cartilaginous tissues are studied in work [6]. Presence of magnetite nanoparticles allowed to achieve about 41 degrees Celsius in 1.5 seconds. Wavelength of the heating laser was determined by the absorbance spectra of an aqueous dispersion of nanoparticles. Thus using the absorbance spectra of the synthesized colloidal particles it is possible to choose the optimal laser wavelength. As it was shown in the work [7] UV, visible and near-infrared spectra of colloidal particles $\text{Fe}_m\text{O}_n\text{-SiO}_2$ obtained by two-stage technique doesn’t have any intensive absorbance lines. In accordance to the work [8]
authors tried to find some appropriate wavelength in IR range. Despite of higher absorbance by the biological tissue than, for example, at the terahertz range, IR lasers now are more widespread and can generate much higher optical power.

2. Experimental methods
In present work authors investigated colloidal solutions Fe₃O₄-SiO₂ derived by two different ways. The first one is based on magnetite precipitation in the presence of colloidal silica as described in [1] and the second one assumes magnetite precipitation followed by coating iron oxide particles by tetraetoxisilane at the alkaline aqueous medium. Estimated concentration of synthesized solutions equaled 3 mM/L. Analysis of particles’ size distribution was made by NTEGRA TERMA AFM (NT-MDT). The average diameter was calculated using Gwyddion software basing on AFM images. Magnetic properties were investigated measuring DC-hysteresis curves using vibrating sample magnetometers Lake Shore 7410 and MPMS SQUID (Quantum Design). Resistivity’s change under the influence of constant magnetic field 500 A/m at 1 kHz AC signal was measured by LCR-meter E7-20 (MNIPI). To analyze chemical contain of dried specimen FTIR-spectroscopy using Nikolet 6700 spectrometer was applied.

3. Experimental results
FTIR spectra of dried specimen obtained by one-stage process (figure 1) indicated the presence of magnetite. Peaks about 1100, 1400, 1600 and 3400 cm⁻¹ are in conformity to the work [8] which describes FTIR-spectroscopy analysis of magnetite particles covered by oleic acid. The most intensive absorbance line at 1100 cm⁻¹ (9.1 μm) may be used as the laser wavelength for heating the particles. Thus quantum cascade lasers and interband cascade lasers with the radiation range of 3.42…9.60 μm (2924…1042 cm⁻¹) may be used.

![Figure 1. FTIR-spectra of dried specimen obtained by one-stage process](image1)

AFM images of the colloidal particles obtained by one and two-stage processes are shown at Figure 2.

![Figure 2. AFM image of dried specimens obtained by one (a) and two-stage (b) processes](image2)
To obtain the image of standing alone particles initial specimens of 0.3 mM/L were diluted to 0.015 mM/L solutions and dried at room temperature. Size distribution graphs plotted using AFM images are shown at figure 3. The average particles diameter is about 15 nm for both the techniques although the one-stage process allows to obtain colloidal particles with narrower size distribution and to avoid any additional filtration.

![Size distribution graphs](image)

Figure 3. Size distribution for particles based on AFM image of dried specimen obtained by one (a) and two-stage (b) processes

DC-magnetization curves are shown at figure 4. Saturation magnetization for the one-stage process derived specimen is about five times higher probably because of inhibition of oxidation process in the solution. As it was stated in the work [5] colloids consisted of silica cores partially coated by iron oxide particles could intensively oxidize even without any heat treatment and therefore significantly decrease in magnetization.

Phase transformation of magnetite/maghemite to hematite could be one of the reasons leading to an increase of protons spin-spin relaxation time $T_2$ that is described in the work [1] but the main disadvantage of colloids obtained by two-stage process is intensive aggregation of particles under the influence of constant magnetic field. Aggregates provoke rapid sedimentation process and loss of colloidal stability. Nanoparticles Fe$_3$O$_4$-SiO$_2$ obtained by the one-stage process could be more chemically and aggregate stable due to the silica coating. As it can be stated from figure 4 relative resistivity change is slightly higher for the specimen obtained by the two-stage process. The following restoration of resistivity after the release of magnetic field is different for the specimens and its rate is much higher for the one-stage derived colloid.
Figure 4. Magnetization curves of dried specimens obtained by one (a) and two-stage (b) processes.

Figure 5. Time dependence of resistance under the influence of magnetic field for solutions obtained by one and two-stage processes.
4. Conclusions
Colloidal particles Fe$_x$O$_n$-SiO$_2$ obtained by one and two-stage techniques have similar average diameter but the other properties differ significantly. One-stage process allows to achieve narrower size distribution of particles and higher saturation magnetization. According to the results of FTIR-spectroscopy silica coated iron oxide particles consist in the main of magnetite. The silica shell leads to higher aggregate stability as it was stated using the resistivity change measurements. However further experiments are needed to determine the toxicity of specimens obtained by both the techniques.

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