Influence of constant magnetic field on aggregation processes in magnetite colloids

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Abstract. Colloids of Fe3O4/SiO2 nanoparticles derived by a two-stage technique on the base of tetraetoxisilane soles were studied. Phase composition of the particles was analyzed by X-ray diffraction and Raman spectroscopy. It was found that phase transition of Fe3O4 into α-Fe2O3 occurs at a laser power exceeding a threshold value. The aggregation of the particles to linear structures in a constant magnetic field was studied by atomic force microscopy. The data on the change in resistance of Fe3O4/SiO2 colloids under an applied magnetic field were obtained.

1. Introduction

Magnetic colloids have found many applications in medicine and electronics. A variety of techniques for the synthesis of magnetic nanoparticles were developed, that can be classified into two main groups: mechanical milling of bulk material and chemical synthesis [1, 2]. Particle coating within a shell of organic and inorganic material enhances the stability of magnetic colloids. An inert coating on the surface of magnetic nanoparticles also makes them suitable for biomedical application.

Magnetic nanoparticles are very promising as contrast agents for magnetic resonance imaging (MRI). The use of magnetite-based contrast agents even at low concentrations can enhance the quality of MRI because of the high efficiency of spin-spin relaxation [3]. Besides, magnetite is nontoxic to biological tissues and can be used for targeted drug delivery [4].

Physical properties of magnetic colloids are of great interest to researchers. Magnetohydrodynamics problems and the particle aggregation under an external and induced magnetic field (dipole-dipole interaction) were considered in one of the early publications [5]. Self-assembly of nanoparticles into chain-like structures, properties of the resultant aggregates and their dependence on the particle-size distribution were described in detail in [6-9].

Magnetic colloids can be characterized by thermal conductivity and electrical conductivity measurements under an external magnetic field [10, 11]. Raman spectroscopy can be used for the analysis of chemical composition of magnetic nanoparticles. This technique enables one to locally observe coexisting phases and phase transitions between magnetite (Fe3O4), maghemite (γ-Fe2O3) and hematite (α-Fe2O3) [12].

2. Experimental methods

Magnetic colloids were synthesized by a two-stage technique. First, silica nanoparticles were prepared by sol-gel technique in alcohol solution of tetraethoxysilane (TEOS) [13-16]. The surface morphology of SiO2 powders was analyzed by nitrogen thermal desorption. The estimated mean particle size is 50-100 nm (the specific surface area is about 100 m²/g). In the second stage, magnetite nanoparticles were
precipitated from aqueous solution of Fe (II) and Fe (III) salts and superfine silica according to the reaction [17]. Fe₃O₄ nanoparticles are assumed to coat the surface of silica spheres. Thus, the formation of core-shell structures occurs. This assumption was confirmed experimentally. High conductivity was found in Fe₃O₄/SiO₂ film on dielectric substrate (magnetite is half-metal with E₉ ≈ 0.2 eV).

The aggregation of colloidal magnetic nanoparticles is intensified under a static magnetic field. Chain-like structures with different width were found to form because of the dipole-dipole interaction [6-9]. Fe₃O₄/SiO₂ layers were obtained by deposition of the colloidal solutions at different static magnetic field strength (0-150 kA/m) in order to observe these phenomena. Specimens were dried at the room temperature for 24 hours. Magnetic field was produced by Nd-Fe-B magnet that was influencing on objects for the whole time of drying. The surface morphology of layers was examined by atomic force microscopy (AFM). X-ray diffraction (XRD) and Raman spectroscopy were used to confirm the formation of magnetite phase by the reaction described in [17].

Raman spectra were recorded at room temperature using a LabRam HR800 spectrometer. A Nd:YAG laser operating at a wavelength of 532 nm was used as an excitation source. The diameter of the focused laser beam was ~ 1 µm. The laser beam was focused on the surface of the sample and the scattered radiation was collected by an X100 objective. The measurements were performed at different laser power values.

The change in resistance of magnetic colloid was measured under an alternating electric field (1 kHz) and under a constant magnetic field.

3. Experimental results

The XRD pattern of magnetite-silica powder (figure 1) indicated the presence of crystalline magnetite. The halo background at low angles is due to the amorphous phases.

![Figure 1. XRD pattern of powder obtained by drying 0.3 mM Fe₃O₄/SiO₂ solution with 10 vol. % TEOS in the initial sol](image)

Raman spectra of Fe₃O₄/SiO₂ layer recorded at different laser power values are shown in figure 2. The most intense magnetite band corresponding to the A₁g mode vibration is observed at 670 cm⁻¹ [12]. The bands at ~220 cm⁻¹ and ~280 cm⁻¹ are usually assigned to α-Fe₂O₃ lattice vibrations [12]. The analysis of Raman spectra (figure 2) revealed laser induced phase transition of magnetite to hematite via an intermediate maghemite phase at a laser power exceeding a threshold value (~1 mW). As it was stated early in works phase transition of magnetite to maghemite accomplishes at approximately 220ºC [18,19] and maghemite transforms to hematite at 500ºC [19]. So local heating over 500ºC caused by 1 µm mean diameter laser spot may be supposed that can be proved by microphotographs containing SiO₂ melted areas. The characteristic band of maghemite is observed at
When a laser power exceeds a threshold value, the intensities of bands at 390 cm\(^{-1}\) (maghemite) and 670 cm\(^{-1}\) (magnetite) decrease.

AFM studies of the layers deposited at different external magnetic field strength values revealed that nanoparticles begin to form linear structures at 1 kA/m. Isolated particles together with the linear structures are observed in the AFM images of the layers obtained at larger magnetic field strength values (figure 3-5). The layers deposited without a magnetic field consist of isotropic aggregates.

Figure 2. Raman spectra of the layer obtained from the 0.3 mM Fe\(_3\)O\(_4\)/SiO\(_2\) solution with 50 vol. % TEOS in the initial sol

![Raman spectra](image)

Figure 3. AFM image of layer formed in magnetic field 150 kA/m
It was shown in [19] that the product of the reaction of magnetite formation is also ammonium chloride. The resulting colloid is known to exhibit ionic conduction. Therefore, resistance should be measured under an alternative electric field in order to avoid the adsorption of ions at electrodes. Furthermore, the assembly of Fe$_3$O$_4$/SiO$_2$ nanoparticles into linear chains leads to a decrease in resistance of magnetic colloid. The response time of the system to a static magnetic field is several seconds (figure 6). Thus, the effect of an alternative magnetic field on the electric properties of magnetic colloids was not studied. Besides, it was found that the change in resistance (after 180 s exposure) is maximal under a static magnetic field at 450 A/m and small at 150 A/m. This result is in good agreement with the observed stability of magnetic colloids in the earth magnetic field (about 40 A/m).
Figure 6. Resistance versus time dependence at various strength of magnetic field for 0.3 mM Fe$_3$O$_4$/SiO$_2$ solution with 60 vol. % TEOS in the initial sol.

To determine the influence of static magnetic field on the relative change in resistance, the samples were exposed to a magnetic field with different strength for the same periods of time (180 s). As can be seen in figure 7, this dependence is linear.

Figure 7. Relative resistance change versus magnetic field strength dependence for 0.3 mM Fe$_3$O$_4$/SiO$_2$ solution with 60 vol. % TEOS in the initial sol.

4. Conclusions

XRD analysis of Fe$_3$O$_4$/SiO$_2$ layers obtained by deposition of the magnetic colloids revealed the formation of crystalline magnetite phase. Raman spectroscopy studies showed laser induced phase transition of magnetite to hematite via an intermediate maghemite phase at a laser power exceeding a threshold value (~1 mW).
AFM results indicated that the linear structures form in magnetic colloids under an external magnetic field. This structural modification leads to the change in the conductance of magnetic colloids under a magnetic field with strength larger than 100-200 A/m.

Thus, destruction of the stability of magnetic colloids under the earth magnetic field can be caused by a variation of synthesis conditions.

References
[1] Lu A-H, Salabas E L and Schuth F 2007 Angew. Chem. Int. Ed. 46 1222-1244
[2] Hyeon T 2003 Chem. Commun. 8 927-934
[3] Rink P A Magnetic resonance in medicine 1993 Blackwell Scientific publication 246 p
[4] Nikolaev B P, Marchenko Ya Yu, Yakovleva L Yu, Zimina T M, Soloviev A V, Luchinin V V, Petrov A V, Scharafudtina T A and Dobrodimov A V 2013 IEEE Trans. on magn. 49 1 Part 2 429-435
[5] Shliomis M I 1974 Sov. Phys. Usp. 17 2 153-169
[6] Morozov K I and Shliomis M I 2004 J. Phys.: Condens. Matter. 16 3807-3818
[7] Sorokina O N, Kovarski A L, Lagutina M A, Dubrovskii S A and Dzheparov F S 2012 Appl. Sci. 2 342-350
[8] Kantorovich S and Ivanov A O 2002 J. of Magn. and Magn. Mat. 252 244–246
[9] Ivanov A O and Zubarev A Yu 1998 Physica A 251 348-367
[10] Gavili A, Zabihi F, Isfahani T D and Sabbaghzadeh J 2012 Exp. Therm. and Fluid Sci. 41 94-98
[11] Racuciu M, Creanga D E and Calugaru Gh 2005 J. Optoelectr. and Adv. Mat. 7 6 2859-2864
[12] Slavov L, Abrashev M V, Merodiiska T, Ghelev Ch, Vandenberghe R, Markova-Deneva I and Nedkov I 2010 J. of Magn. Magn. Mat. 322 14 1904-1911
[13] Gracheva I E, Olchowik G, Gareev K G, Moshnikov V A, Kuznetsov V V and Olchowik J M 2013 J. of Phys. and Chem. of Solids. 74 5 656-663
[14] Moshnikov V A, Gracheva I E, An’chkov M G 2011 Glass Phys. and Chem. 37 5 485-495
[15] Abrashova E V, Gracheva I E and Moshnikov V A 2013 J. of Phys.: Conf. Ser. 461 012019
[16] Gubin S P, Koksharov Yu A, Khomutov G B and Yurkov G Yu. 2005 Rus. Chem. Rev. 74 6 489-520
[17] Massart R 1981 IEEE Trans. on Magn. 17 2 1247-1248
[18] Haneda K and Morrish A H 1977 J. de Phys. 38 4 C1-321 – C1-323
[19] Sidhu P S 1988 Clays and Clay Minerals 36 1 31-38.