

## Magnetite and maghemite nanocrystals: variation of synthesis and stabilization conditions

*O.Korovyanko, M.Sytnyk, Yu.Khalavka\* , O.Kopach*

Department of Inorganic Chemistry, Chernivtsi National University,  
2 Kotsyubynsky St., 58012 Chernivtsi, Ukraine

\*Institute of Physical Chemistry, University of Mainz,  
11 Jakob-Welderweg, 55128 Mainz, Germany

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The effect of synthesis, growth, and stabilization conditions (temperature, heat treatment duration, concentration and ratios of ions) on characteristics of magnetite and maghemite particles have been studied. The influence of the synthesis conditions on the magnetite nanoparticle surface character has been investigated. The magnetic properties of colloid solutions have been characterized.

Изучено влияние условий синтеза, роста и стабилизации на характеристики частиц магнетита и магемита: температуры, времени термообработки, концентрации и соотношения ионов. Исследовано влияние условий синтеза на характер поверхности наночастиц магнетита. Охарактеризованы магнитные свойства коллоидных растворов.

Magnetic nanomaterials, such as nanocrystals, quantum dots (QDs) or nanowires, attract attention due to their unique magnetic properties and also of great interest for biomedical applications in magnetic resonance imaging (MRI) [1, 7] cell and protein separation [2–4] and drug delivery [5]. For those applications, the stability of magnetic nanomaterials in aqueous solutions is of considerable importance.

Magnetite nanocrystals ( $\text{Fe}_3\text{O}_4$ ) are synthesized directly in water by precipitation of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts or by thermal decomposition of iron acetylacetonate in 2-pyrrolidone. However, these materials often are fine-crystalline and/or polydisperse [6]. Therefore, a reasonable task is to improve the procedure of monodisperse nanocrystals preparation with the controlled sizes and transferring thereof into a high quality organic solvent providing the dispersion of iron oxide nanocrystals in aqueous phase [1]. Among numerous published experimental results [1–15], there are only few well re-

producibile chemical synthetic procedures of high-quality magnetic nanocrystals in water solutions [12]. The aim of this work is to study the structure and stability of magnetite or maghemite nanoparticles synthesized using modified procedures from water solutions of iron ions.

The effect of synthesis, growth, and stabilization conditions on characteristics of iron oxide nanoparticles were investigated using transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis.

All the chemicals and solvents were acquired from commercial sources and used as received without further purification. The amounts of precipitant, stabilizer, and additional heat treatment conditions were varied to provide the procedure improvement (see Table).

The chemical reactions during synthesis without  $\text{Fe}^{3+}$  ions include the  $\text{Fe}(\text{OH})_2$  oxidation processes with the air oxygen. The hydrolysis processes of iron salts form the

Table 1. Synthesis conditions and characteristics of Fe oxide nanocrystals

No.	Initial component concentrations	Precipitant NH <sub>4</sub> OH	Stabilization conditions	Description of characteristics
1	0.01 M Fe <sup>2+</sup> , 0.02 M Fe <sup>3+</sup> , V = 100 ml	5 ml 20 %	15 ml oleic acid. T~100°C, t = 1 h	Fe <sub>3</sub> O <sub>4</sub> ; d ~ 5–20 nm; absorption peak ~1100–1200 nm
2	0.02 M Fe <sup>2+</sup> , 0.04 M Fe <sup>3+</sup> , V = 100 ml	14 ml 19 %	10 ml oleic acid. T~100°C, t = 1 h	Fe <sub>3</sub> O <sub>4</sub> ; d ~ 5–20 nm; absorption peak ~1100–1200 nm
3	0.02 M Fe <sup>2+</sup> , 0.04 M Fe <sup>3+</sup>	No	10 ml oleic acid. T~100°C, t = 2.5 h	Spherical of Fe <sub>2</sub> O <sub>3</sub> ; d ~ 20 nm; absorption peak ~1100 nm
4	0.01 M Fe <sup>3+</sup> , V = 100 ml	14–20 ml 19 %	10 ml oleic acid. T~100°C) for 1 h	Fe <sub>2</sub> O <sub>3</sub> ; d ~ 5–20 nm; absorption peak ~500–590 nm
5	0.02 M Fe <sup>2+</sup> , V = 100 ml	12 ml 19 %	15 ml oleic acid. T~100°C) for 2.5 h	Magnetic foam ferrofluides; Fe <sub>3</sub> O <sub>4</sub>

basis of the precipitant-free synthesis. The maghemite small nanocrystals have been obtained in a similar manner by synthesis without Fe<sup>2+</sup> ions (Fig. 1).

EDX analysis shows that C, O, Fe, Cu elements are present in the samples. The C and O presence is due to organic solvent and stabilizer. The oxygen is due to both stabilizer and the oxide itself. Iron content is in conformity with that in the oxide.

The optical absorption spectra of the samples (Fig. 2) were measured in the spectral range 450–1200 nm.

The magnetic properties of nanocrystalline magnetite solutions were studied by measurements of magnetization and of solution meniscus depth in electromagnetic field (Fig. 3). The magnetization was measured as a function of temperature in weak (0.01 T) magnetic field (Fig. 3, a). At T = 5 K and at T = 300 K, the magnetization was measured as a function of magnetic flux density (Fig. 3, b).

The magnetite and maghemite colloidal solutions were prepared using the sol-gel technique by modified procedure [12] which is based on thermal precipitation of iron oxide from aqueous solution and extraction it into oleic acid. Variation of precipitant and stabilizer amounts as well as an additional heat treatment were used to improve the synthesis. The precise size of obtained iron oxide nanocrystals were determined using TEM.

The preliminary experiments were carried out to reproduce the literature protocol [12]. The first attempts of the procedure modification consisted in the concentration variation of the initial solutions and in the removal of the nitrate acid neutralization stage. The

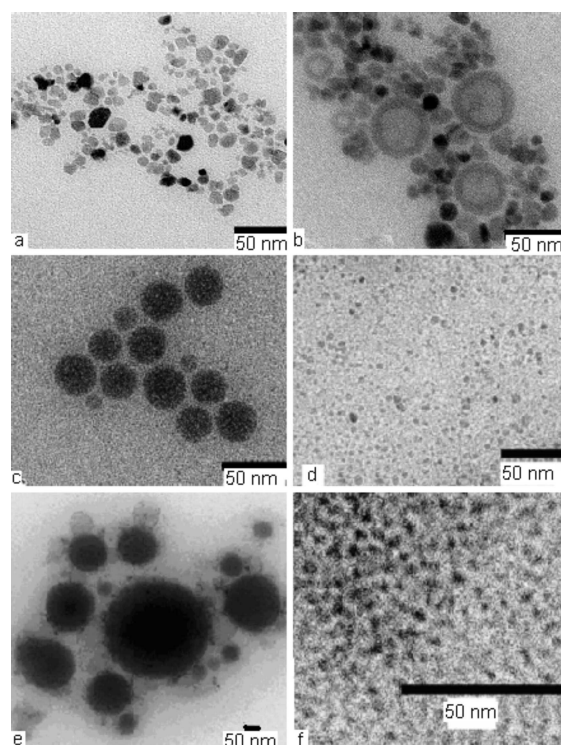


Fig. 1. TEM images of magnetite nanoparticles: (a) modification of procedure [12]; (b) procedure based on the concentration variation of iron ions; (c) synthesis without precipitant; (d) synthesis without Fe<sup>3+</sup> ions after first hour treatment; (e) the same after 2.5 h treatment; (f) TEM images of maghemite nanocrystals. Scale bar is 50 nm.

TEM images of obtained samples (Fig. 1, a) are similar to the published ones [12].

The next modification attempt consisted in the increase of of iron ions and precipitant amounts while decreasing the stabilizer

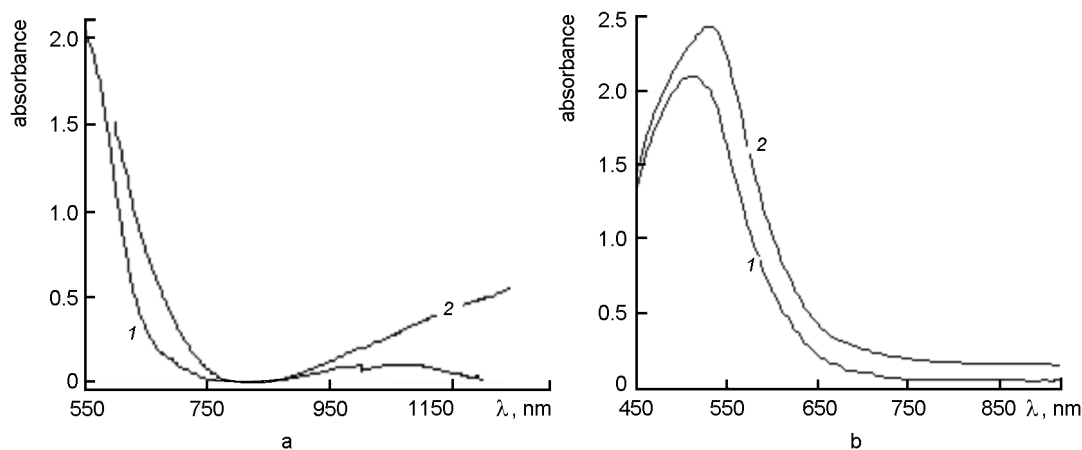


Fig. 2. Absorption spectra of iron oxide nanoparticles (time evolution): (a) magnetite nanocrystals; (b) maghemite nanocrystals (1, the first time moment; 2, the second one).

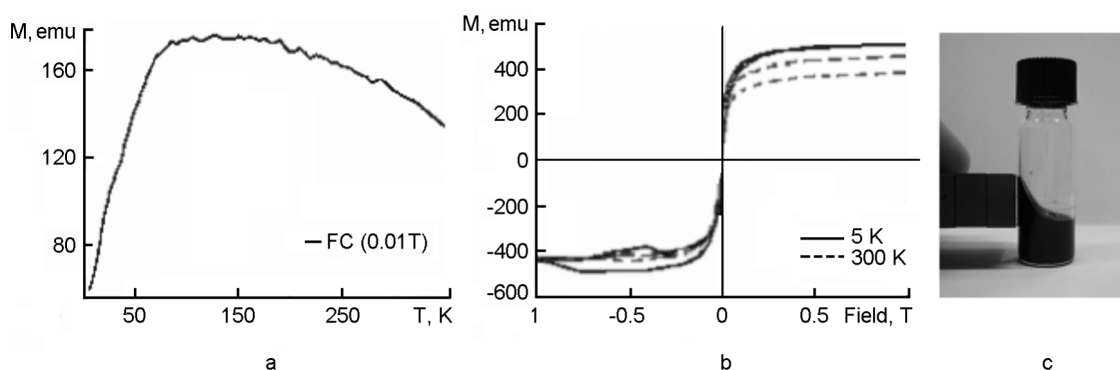


Fig. 3. Influence of magnetic field on the solutions of magnetite nanocrystals.

concentration. The TEM images of the obtained precipitates show large spherical objects together with cubical and octahedral magnetite nanocrystals (Fig. 1b).

Moreover, we have shown that the method [12] can be significantly simplified by avoiding the precipitation step itself. In this case, the heterophase hydrolysis and nanocrystal formation at the solution-stabilizer phase interface occurred more slowly. Therefore, nanocrystal growth and ripening caused spherical shape of obtained particles. The TEM images of these magnetite nanocrystals illustrate spherical shape of particles and narrow size distribution (Fig. 1, c).

The next change of the procedure consisted in the exclusion of  $\text{Fe}^{3+}$  ions. TEM images of magnetite nanocrystals obtained without  $\text{Fe}^{3+}$  ions show that after first hour of heating (about  $100^\circ\text{C}$ ) of the growth solution in water bath we can get nanocrystals of  $30 \pm 5$  nm diameter (Fig. 1, d). The magnetite crystals then form micelles of 100–200 nm size after heat treatment for 2.5 hours (Fig. 1, e). We also observed that

the magnetic nanoparticles show a trend to spontaneous assembling around the formed micelles. By slow  $\text{Fe}^{2+}$  oxidation on the nucleus surface, we have obtained magnetite nanocrystals with hollow structure. These micelles are coated with small particles and oleic acid as the core-shell type. Magnetite nanoparticles of similar structure but of considerably smaller size were obtained in organic solvents by other technique in [14]. Theoretical models of such foam structure formation are developed in [15]. These micelles are stable under air and room temperature for a long time (at least 30 days) and collapsed only under electron beam irradiation (Fig. 4).

In all cases, the micelles are spherical and rather homogeneous in size. It has been confirmed in experiment that the particles are spherical and insensitive to the grid surface. Therefore, a detailed TEM study of these nanoscale structures has been carried out. Using a prealigned 120 keV electron beam, it was possible to capture images of the particles as a function of time. We observed that the micelles appeared to evolve

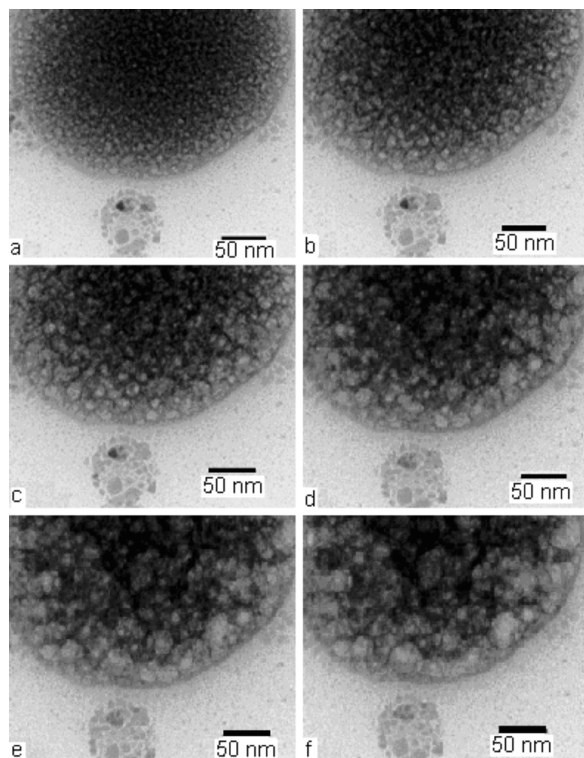


Fig. 4. TEM images series of foam nanocrystals ferrofluids after 0 (a); 300 s (b) exposure in the 120 keV beam. Scale bar is 50 nm.

into larger, two-dimensional structures while exposed to the electron beam. Fig. 4 shows sequential TEM images of the same area of the grid taken over 300 s. The increasing of hollow bubble volume under electron beam irradiation was observed. This process is very similar to that described in [14].

The magnetic properties of magnetite nanocrystals were studied using the depth of solution meniscus in magnetic field (Fig. 3). The magnetization values are in fact only relative, as the absolute amount of material in the powder sample is unknown. Peaks at 1050 nm were observed in the infrared absorption spectra of magnetite (Fig. 2, a) due to charge transfer transitions between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , which is in agreement with [13], where the synthesis was based on the decomposition of pre-synthesized iron oleate.

To extend the technique potential, we have prepared maghemite ( $\text{Fe}_2\text{O}_3$ ) nanocrystals by a similar procedure without  $\text{Fe}^{2+}$  ions. The TEM images (Fig. 1, f) show that the synthesized maghemite particles are fine-crystalline and the size distribution of the particles is about 10 nm. The absorption spectra show (Fig. 2, b) that there is a grad-

ual shift towards the UV region with a long tail of the spectrum in the long-wavelength region for different sols prepared. The absorption peak position agrees well with the literature data for  $\gamma\text{-Fe}_2\text{O}_3$  nanocrystals. The prepared nanoparticles can be easily separated and purified by size-selective precipitation with ethanol and water as nonsolvent and solvent, respectively.

To conclude, the synthesis procedure of magnetite and maghemite nanocrystals has been improved. Colloidal solutions of magnetite nanocrystals with different type of particles were synthesized using the modified technique and the trend thereof to self-assembling into spherical micelles has been studied. The ferrofluid magnetite foam has been shown to consist of hollow micelles coated with oleic acid and small particles. Being very stable, these micelles can find applications for targeted drug delivery.

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## **Нанокристали магнетиту та магеміту: варіювання умов синтезу і стабілізації**

***О.Коров'янка, М.Ситник, Ю.Халавка, О.Копач***

Вивчено вплив умов синтезу, росту і стабілізації на характеристики частинок магнетиту та магеміту: температури, тривалості термічної обробки, концентрації та співвідношення іонів. Досліджено впливу умов синтезу на характер поверхні наночастинок магнетиту. Охарактеризовано магнітні властивості колоїдних розчинів.