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Hydrophobic magnetic nanoparticles: synthesis and LB film preparation

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Magnetic nanoparticle probes are emerging as a class of novel contrast and tracking agents for medical and other applications. The synthesis a large scale quantity of monodispersed magnetic nanoparticles is of great importance for using these materials in practice. In this work, we report the synthesis of magnetite γFe_2O_3/ Fe_3O_4. The obtained nanoparticles were investigated by IR, TEM, XRD and AFM techniques.

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1. Introduction

Nanocrystals possess a set of unusual and valuable properties which determine their high technological potential [1,2]. Magnetic nano-particle probes are emerging as a class of novel contrast and tracing agents for magnetic resonance imaging (MRI) [3]. In this paper we examine the route for obtaining lyotropic super-paramagnetic iron oxide (SPIO), as reported by Igartua and al. [4]. That synthesis consists of tree steps: the first one - obtaining of Fe_3O_4 – magnetite [5], the second step - surface modification; the last one - bioactive surface modification. In this way they obtained phospholipid modified magnetite.

We propose a shorter synthetic route by integration of the first and the second steps, using the synthesis of Jongnam Park et al. [6].

2. Materials and methods

2.1 Materials

The following materials were used from various sources: $FeCl_3.6H_2O$ (98%), oleic acid (90%), 1-octadecene 90% (Aldrich), n-hexane (Merck), $Fe(oleate)_3$ (Evipol Ingredients Ltd.). The quality of the $Fe(oleate)_3$ is was proved by IR characteristic peaks due to a metal-oleate complex

- stretching bands at 1712 cm^{-1} [7] and 627 cm^{-1} [8].

2.2. Synthesis

The synthesis was made according to reference [6]: 36 g (40 mmol) of $Fe(oleate)_3$ and 5.7 g oleic acid were dissolved in 200 ml 1-octadecene at room temperature. The reaction mixture was heated to 320 ºC with at a constant heating rate of 3.3ºC min^{-1}, and then kept at that temperature for 30 min. The brownish – black solution was cooled to room temperature and 500 ml ethanol was added to precipitate the nanocrystals. The nanocrystals were separated by centrifugation.

3. Methods for analysis of the nanocrystals

3.1. IR analysis

The obtained ground material (black fine powder) was analysed using a IR spectrometer Brucker. The IR spectrum (KBr) in sequence of wave number- assignment is as follows: 2956 (CH_3 sym. str.), 2924 (CH_2 asym. Str.), 2854 (CH_2 sym. str.)m, 1712 (C=O str.), 1641 (C=C), 1466-1378 (CH_3, CH_{32} bemd), 721 (CH_2 rock), 627 (large peak) – Fig. 1. The peak at 1641 cm^{-1} corresponds to the double stretching bond due to the oleic acid.

The little peak at 1712 cm^{-1} characterizes the metal - oleate complex. We attribute the peaks from 2854 cm^{-1} to 2956 cm^{-1} to the long fatty radicals belonging to the oleic acid. In conclusion, all of this proves the existence of the oleic radicals in the analysed black powder.

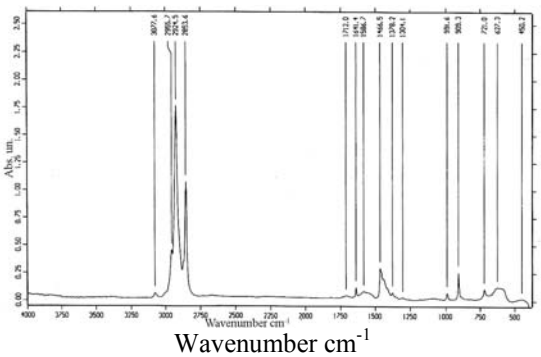

Fig. 1. The IR spectrum of black powder.

The large peak at 627 cm^{-1} is characteristic of magnetite, and was observed by Tomasovicova et al. [8] in studying biocompatible magnetic nanoparticles.

3.2. Qualitative XRD analysis

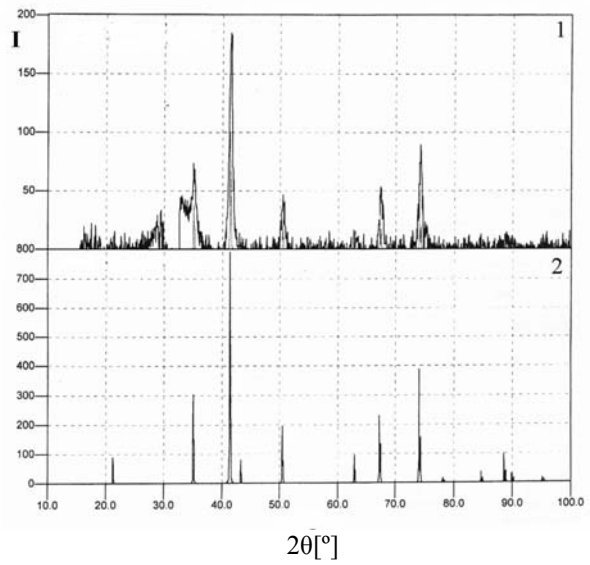

Fig. 2. XRD pattern of magnetite nanoparticles: 1-black powder, 2-reference.

The X-ray diffraction analysis was carried out using standard apparatus - a Philips- Micro 111 with Brag-Brentano geometry. Co- radiation was used. A constant measuring time was employed. The recording of the investigated specimen was done with a step of 0.08º/min. The holding time at each point was 5 seconds. For practical processing of the obtained results the Origin 5.0 Professional program and Search-Match crystallographic software were used. In Fig. 2 we see the full coincidence between the reference spectrum and that of the black powder. The reference spectrum was obtained from the Crystallographic Search-Math data base, and corresponds to magnetite, Fe_3O_4. The size of the particles cannot be determined from the spectrum.

3.3. Transmission electron microscopy (TEM).

The TEM image shows particle sizes of about 50 nm [Fig. 3]. The size statistics is indispensable, because the analysis using monochromatic light scattering shows a high poly- dispersity of the nanoparticles - between 50 and 150 nm. This is in contradiction with the next experiment in Section 3.4.

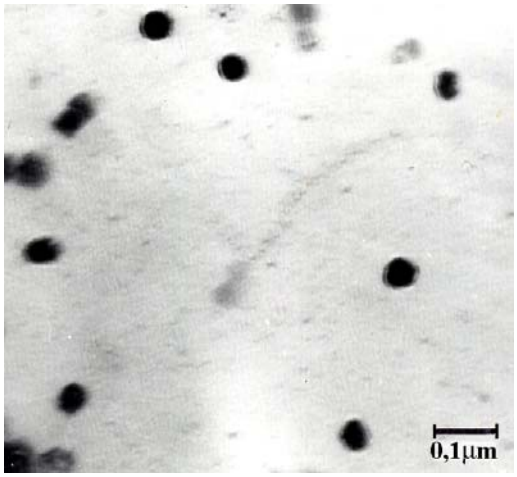

Fig. 3. TEM image of the magnetite Fe_3O_4, *JEM 7*A, *marker = 0.1.10*$^{-6}$ *m.*

3.4. LB film deposition and Atomic Force Microscopy investigations

The magnetite nanoparticles were dispersed in toluene by sonification for 30 min. A two hour sedimentation was then performed. The suspension obtained consisted of clear and dark parts. The sample from the clear part was used for these experiments. The isotherm measurement at 26 ºC (shown in Fig. 4) and the LB film deposition were performed using a Kibron (Finland) micro LB trough. In the isotherm, the area per chain is an arbitrary value. The deposition was carried out at the end of the horizontal plateau at 10 mN/m on the upstroke a silicon wafer as a substrate. In an attempt to deposit second layer on a downstroke, it was seen that the first layer began to peel off.

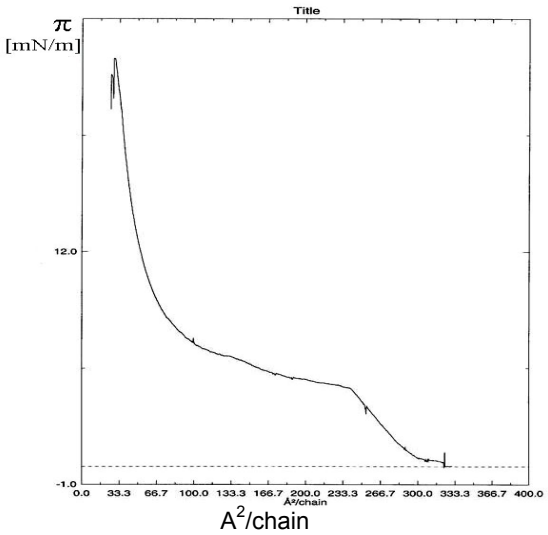

Fig. 4. The isotherm π – surface pressure, A^2 –area per chain (arbitrary value) of a monolayer at the air-water interface.

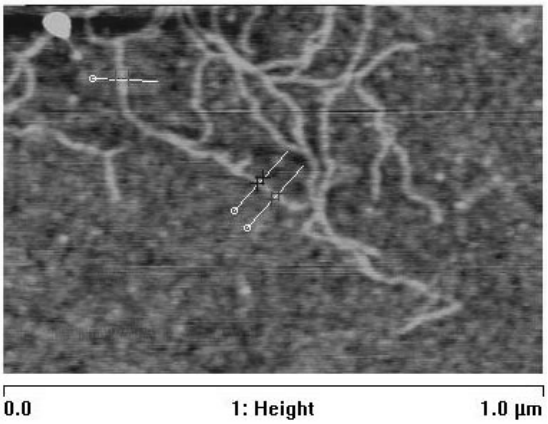

Fig. 5 AFM of an LB monolayer. A chain of "hills" can be seen.

Monolayers from the magmetic nanoparticles are very difficult objects for observation by Atomic Force Microscopy. Hence the monolayer was observed by the highest resolution AFM on the market – MultiMode by Veeco (USA) using sharpened tips with an approximately 1 nm apex of the tip. It can be seen that apart from large areas of tightly compressed spheres there are also some chains of "hills" which have a maximum height of 0.5 nm above the average value. The width of these hills was measured to be ranging from 16 to 23 nm. This corresponds to spheres of 50 nm diameter of which only the top is seen. Friction and elasticity measurements suggest there are holes in the sample as in none of the measurements the silicon substrate was observed.

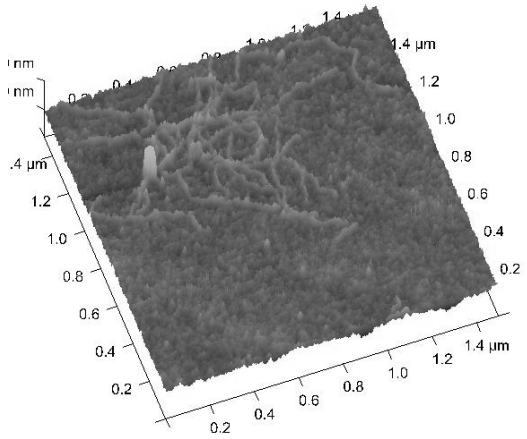

Fig. 6. Larger size of the same scan as in Fig. 5 in 3D view.

4. Conclusions

The synthetic procedure developed provides the possibility of obtaining nanosized magnetite possessing a hydrophobic surface, as a precursor for the contrast agent used in MRI. The average size of the nanoparticles was of about 50 nm. A schematic cross section of one particle is shown in Fig. 6.

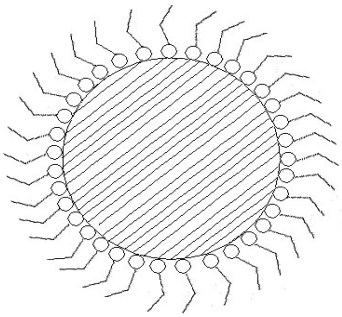

Fig. 7. Schematic cross section of one particle of modified magnetite.

A homogeneous LB film monolayer was obtained with no obvious holes in it and a roughness of 0.5 nm corresponding to the protruding magnetic nanoparticle spheres. The quality of the film offers the possibility for technological applications.

Acknowledgements

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