Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Evaluation of Differences between Fe_3O_4 Micro- and Nanoparticles Properties

Z.A. Duriagina, T.L. Tepla and V.V. Kulyk*

Department of Applied Materials Science and Materials Engineering, Lviv Polytechnic National University, Bandera Str., 12, Lviv, 79013, Ukraine

Small sizes of nanoparticles lead to the appearance of new unique functional properties. Under transition to nanosizes in metals and their compounds new specific characteristics appears. In this work, the microstructural and magnetic properties of Fe_3O_4 nanoparticles (Fe_3O_4-NP) have been compared with those of commercially available Fe_3O_4 microparticles (Fe_3O_4-MP) and detailed analysis of differences has been carried out. The synthesis of Fe_3O_4-NP was carried out by means of colloidal method performed without the use of surfactants. Commercial and synthesized particles were characterized using NTEGRA Prima (NT-MDT) atomic force microscope. For magnetic properties investigations we used the method of vibrating sample magnetometer.

DOI: 10.12693/APhysPolA.133.869

PACS/topics: Fe_3O_4 micro- and nanoparticles, atomic-force microscopy, magnetization, superparamagnetism

1. Introduction

During last years, special interest is observed in the use of nano- and microsized powder materials, especially in combination with bioselective elements (ferments) to develop technologies for obtaining bionanomaterials with catalytic properties. High chemical activity of Fe_3O_4 particles enhances ability to atomic or ion exchange, adsorption and the formation of superficial connections with other adsorbed particles. This enables us to create bioparticles (particles on the surface of which there are immobilized ferments) with their further use in biosensors, as well as in enzymatic reactions [1, 2].

In solving these problems, aspects of materials science occupy the main place. In particular, the process of synthesis of ferromagnetic iron oxide powders should be directed to obtaining the powder of specific fraction both as to the size and as to the shape. Size factor of powder particles affects their adsorption characteristics, which are determined by the surface energy level. Materials science approaches to the formation of the desired shape and character of the distribution as to the powder fractions will improve their functional properties [3, 4].

Synthesis of superparamagnetic nanoparticles developed not only for the benefit of fundamental science, but also for many technologies, such as technologies of magnetic storage media, magnetic ink for printers, for biosensors and medical applications, etc. [5, 6]. Superparamagnetic iron oxide nanoparticles with appropriate surface can be used to enhance the contrast of images, tissue repair, detoxification of biological fluids, hyperthermia, for the directed delivery of pharmaceuticals, and separation of cells. All the biomedical applications require that the nanoparticles have high enough levels of saturation magnetization; their size should be less than 100 nm with a small deviation in size [7–9]. Depending on the sizes other properties of nanoparticles as toxicity, adsorption ability and magnetism also change. In particular, when the size of nanoparticles is less than 10 nm they pass into a superparamagnetic state that, when adsorbing the energy of the external high-frequency electromagnetic field, promotes conversion of the energy state into the thermal one [10–13].

Physical and chemical properties of magnetic nanoparticles are determined by their structure and method of preparation. In most cases these are particles of size from 1 to 100 nm with clearly expressed superparamagnetism. Investigation of superparamagnetic nanoparticles, especially Fe_3O_4 nanoparticles, should be aimed at establishing the interrelations between their structure and pharmacokinetics. Processes of modification of magnetic nanoparticles surface, that are used for connection of biovectors, must be improved. This is decisive in optimization of superparamagnetic nanoparticles likeness with biological objects [14].

Among the magnetic research methods in materials science the magnetic phase analysis is especially widely used. Its possibilities and effectiveness to a great extent are determined by technical characteristics of the equipment. The quantitative phase magnetic analysis uses properties of ferromagnetics, which they acquire in strong magnetic fields — in the state of technical saturation. Primary magnetic properties that are structurally insensitive are obtained from the curve of temperature dependence of saturation magnetization. Such characteristics are magnetization and the Curie point. These values give the information about phase composition of material and its changes in the process of certain thermal operations and also in the process of deformation. The Curie point and saturation magnetization are called primary magnetic properties because their values are de-

*corresponding author; e-mail: kulykvolodymyrvolodymyrovych@gmail.com

termined by the nature of the ferromagnetic phase (crystal lattice, electron structure of atoms, chemical phase composition) [15].

Now commercial Fe_3O_4 microparticles are widely used, but the use of Fe_3O_4 nanoparticles has not been thoroughly studied. This limits the use of nanoparticles in many areas of medicine, including the directed delivery of pharmaceuticals and separation of cells. Therefore, the aim of our work is to step-up knowledge of the advantage properties of nanoparticles in comparison with microparticles.

2. Material and methods

The commercial microparticles of Fe_3O_4-P and nanoparticles of Fe_3O_4-NP were investigated. The synthesis of Fe_3O_4-NP was carried out by means of colloidal method performed without the use of surfactants. To eliminate oxygen, argon was blown to pass through bidistilled water for 30 min. After that, 50 ml of 1 M ammonium hydroxide NH_4OH were added. The obtained substance was introduced into the mixture of the following reagents: 10 ml of freshly prepared 1 M $FeCl_2{\cdot}4H_2O$ and 20 ml of 1 M $FeCl_3{\cdot}\ 6H_2O$. The obtained mixture was mixed by a centrifuge at 1000 rev/min. Formation of dark brown nanoparticles was observed. In 10 min, the nanoparticles were precipitated by centrifugation for 15 min. The precipitate was washed 4 times by bidistiller which contained N_2. Precipitated nanoparticles were dried at 37 °C for 12 h [16].

Commercial and synthesized particles were characterized using NTEGRA Prima (NT-MDT) atomic force microscope. We used probe sensors of NSG10-A series. Experimental data processing and calculations of parameters of surface's microgeometry were carried out using Nova 1.0.26.1443 software package.

For magnetic properties investigations we used the method of vibrating sample magnetometer [15, 17]. Such a device for investigation of the magnetic properties possesses a number of unique characteristics. At room temperature it is possible to build a hysteresis loop, partial hysteresis loops, initial curves of magnetization and demagnetization, dependence of a magnetic moment on the sample orientation. At elevated temperatures thermomagnetic measurements, high-temperature hysteresis measurements, time dependences of magnetic moment at different temperatures can be carried out. Temperature measuring interval ranges from 80 to 1100 K at power 3.5 kWt. Curves of the investigated samples over-magnetization were recorded in magnetic fields from –200 kA/m to +200 kA/m by measuring the dependence of the given magnetization I/I_{200} on the magnetic field strength H (I_{200} — magnetization at magnetic field strength 200 kA/m).

3. Results and discussion

All the biomedical applications require that the nanoparticles have high enough levels of saturation of magnetization; their size should be less than 100 nm with a small deviation in size.

Microstructure of the synthesized Fe_3O_4-NP and Fe_3O_4-MP is characterized by two types of structural inhomogeneity. It can be distinguished on the investigated Fe_3O_4-NP sample surface: conglomerates of conical-like nanoparticles and granular texture of substrate. At the same time, on the Fe_3O_4-MP surface we can see the cooperation of microparticles because of their magnetic attraction. As it known, little particles of magnetic materials attract and construct some colonies or conglomerates. This is encumbered using of this size particles in medicine or for sensitive carrier and triggered drug.

To estimate the sizes of Fe_3O_4 atomic-force microscopy was used, whose software products allowed the establishment of the scanned particles structure (Fig. 1). Surface topography is characterized by a rough relief with morphological regions of blocked structure. Blocks are characterized by non-isometric round form with no surface faceting. Their height above the substrate surface is in the range from 5 to 10 nm, base diameter — 30–50 nm. In this case the dominant size of nanoparticles is 8 nm. As it seen, sometimes there are an association and created particles conglomerates.

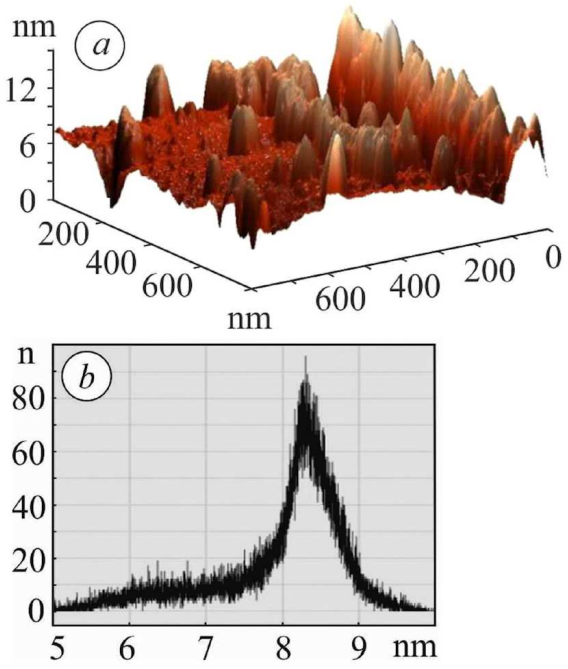

Fig. 1. Distribution of the synthesized Fe_3O_4-NP on the surface (a) and histogram of their height distribution (b).

It is established that the size of the commercial Fe_3O_4 microparticles is greatly increased and is about 1 μm, which was regulated by the manufacturer (Fig. 2). As is seen, with increasing particle size microparticles combined and created large conglomerates. This can be explained due to the presence of exchange interaction

in magnetic materials, a spontaneous (without external magnetic field, but for internal reasons) magnetic ordering can be established. If in nanoparticles these are the single cases, in the case of microparticles we can see that most of particles are united.

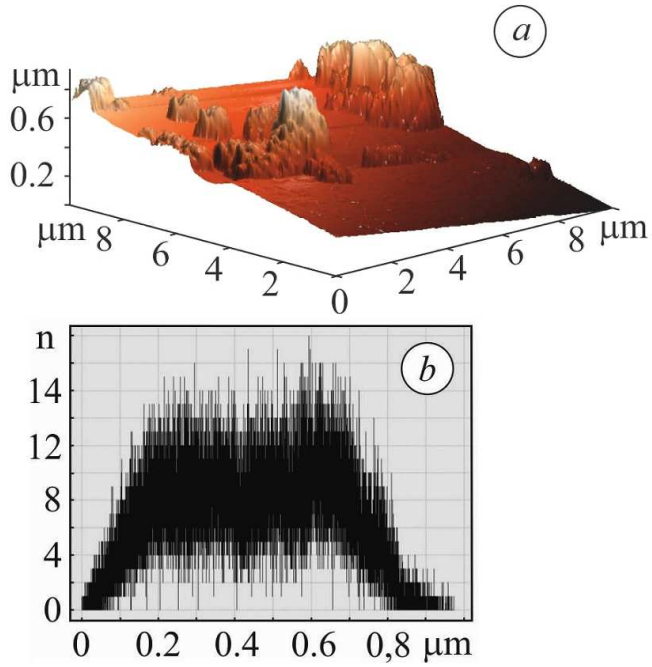

Fig. 2. Distribution of the synthesized Fe_3O_4-MP on the surface (a) and histogram of their height distribution (b).

This information is very useful for further use of particles as carriers of drugs. As it shown, the Fe_3O_4 nanoparticles are characterized by a rough relief with morphological regions of blocked structure. In the case of Fe_3O_4 microparticles the form of particles is different, their relief is not linear, we can obtain cavities and protrusions, the surface looks porous. But in the same time the volume of functionalized particles increases several times and this makes it difficult to use them to transfer drugs.

Use of Fe_3O_4 nanoparticles with the aim of their functionalization (application of shells, medical aids and markers on them) or introduction in a living organism for hyperthermia, foresees the application of surface coating. In this case the analysis of the dimensions and properties of nanoparticles using a simple method becomes more complex [18]. In such cases magnetic methods become one of the methods of particles categorization.

As one can see, curves of Fe_3O_4-NP samples re-magnetization has a non-hysteresis form with a zero coercive force H_c and residual magnetization I_r (Fig. 3a). Probably particles of Fe_3O_4 due to a high degree of dispersivity are in a superparamagnetic state — state that is typical of microscopic and nanoscopic particles of ferromagnetic materials. In this case a magnetic moment of the like particle changes its orientation spontaneously and randomly or due to thermal fluctuations. When external magnetic field is absent superparamagnetics have on average a zero magnetic moment, i.e. they behave like paramagnetics with a high magnetic susceptibility. As known, superparamagnetic properties of Fe_3O_4 particles at room temperature are exhibited, when reaching an average diameter $D < 25$ nm [7, 19, 20]. In our case the particles size is 5–10 nm.

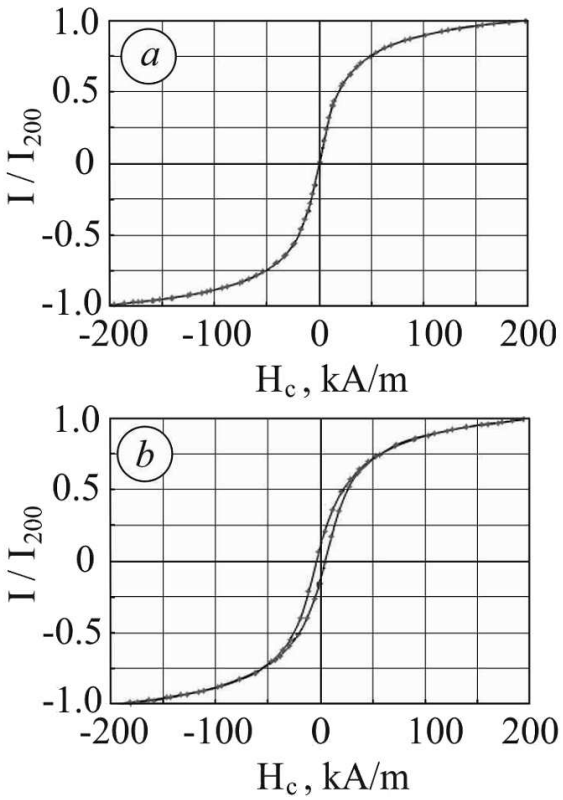

Fig. 3. Curves of re-magnetization of Fe_3O_4-NP (a) and Fe_3O_4-MP (b) samples.

With increasing sizes of Fe_3O_4 particles to microsizes we have already a hysteresis loop (Fig. 3b). These particles sample coercive force $H_c = 4$ kA/m, ratio $I/I_{200} = 0.1$.

4. Conclusion

Surface topography of Fe_3O_4-NP is characterized by a rough relief with morphological regions of blocked structure. Blocks are characterized by non-isometric round form with no surface faceting.

With increase of size Fe_3O_4-MP combined and created large conglomerates. This can be explained due to the presence of exchange interaction in magnetic materials, a spontaneous (without external magnetic field, but for internal reasons) magnetic ordering can be established.

Particles of Fe_3O_4-NP due to a high degree of dispersivity are in a superparamagnetic state. It is shown in

the paper that identification of synthesized nanoparticles can be realized most effectively by the change of their magnetic properties. Success of the proposed approach formed the basis of the vibrating sample magnetometer use for monitoring the stability of nanoparticles microstructure and their functional properties in application in medicine.

In addition, the parameters of the porous structure and the state of the surface are important for the immobilization of biological objects on magnetic nanoparticles. Therefore, in the future we plan to conduct some experiments to obtain additional information about this. This will be very useful for a better understanding of the content of the article.

Acknowledgments

We are infinitely grateful to Mykhailo Gonchar and Tetiana Prokopiv from the Institute of Cell Biology of the National Academy of Sciences of Ukraine, Department of Analytical Biotechnology, for kindly provided samples of Fe_3O_4 powders for our research. Also we would like to acknowledge financial support of the Ministry of Education and Science of Ukraine under Grant 0116U004142 and partially by funds of 543994-TEMPUS-1-2013-1-BE-TEMPUS-JPCR MMATENG (Modernization of two cycles (MA, BA) of competence-based curricula in Material Engineering according to the best experience of Bologna Process — EU).

References

[1] C. Xu, S. Sun, *Adv. Drug Deliv. Rev.* 65, 732 (2013).

[2] N.V. Long, C.M. Thi, Y. Yong, Y. Cao, H. Wu, M. Nogami, *Recent Pat. Nanotechnol.* 8, 52 (2014).

[3] N. Arsalani, H. Fattahi, M. Nazarpoor, *Express Polym. Lett.* 4, 329 (2010).

[4] S. Sun, S. Zhou, P. Hou, Y. Yang, J. Weng, X. Li, M. Li, *J. Biomed. Mater. Res. A* 80, 333 (2007).

[5] [I.A. Vedernikova, *Rev. J. Chem.* 5, 256 (2015).

[6] S. Ubizskii, O. Buryy, L. Pavlyk, I. Syvorotka, O. Kravchuk, R. Savytskyy, P. Demchenko, S. Navrotskyi, N. Mitina, O. Zaichenko, *OMEE-2014*, 87 (2014).

[7] Wahajuddin, S. Arora, *Int. J. Nanomed.* 7, 3445 (2012).

[8] D.J. Huang, H.-J. Lin, J. Okamoto, K.S. Chao, H.-T. Jeng, G.Y. Guo, C.-H. Hsu, C.-M. Huang, D.C. Ling, W.B. Wu, C.S. Yang, C.T. Chen, *Phys. Rev. Lett.* **96**, 096401 (2006).

[9] I. Radisavljevic, B. Kuzmanovic, N. Novakovic, H.E. Mahnke, L.J. Vulicevic, S. Kurko, N. Ivanovic, *J. Alloys Comp.* 697, 409 (2017).

[10] Q. Husain, *Biointerface Res. Appl. Chem.* 6, 1585 (2016).

[11] C. Fang, M. Zhang, *J. Mater. Chem.* 19, 6258 (2009).

[12] M. Filippousi, M. Angelakeris, M. Katsikini, E.C. Paloura, I. Efthimiopoulos, Yu. Wang, D. Zamboulis, G. Van Tendeloo, *J. Phys. Chem. C.* 118, 16209 (2014).

[13] G. De Crozals, R. Bonnet, C. Farre, C. Chaix, *Nano Today* 11, 435 (2016).

[14] H.Y. Huang, J.F. Lovell, *Adv. Funct. Mater.* 27, 1603524 (2017).

[15] I. Martínez-Mera, M.E. Espinosa-Pesqueira, R. Pérez-Hernández, J. Arenas-Alatorre, *Mater. Lett.* 61, 4447 (2007).

[16] A.I. Kondyr, A.K. Borysyuk, I.P. Pazdriy, S.H. Shvachko, *Vibratsii v tekhnike i tekhnolohiiakh* 34, 41 (2004) (in Ukrainian).

[17] Z.A. Duryagina, R.L. Holyaka, A.K. Borysyuk, *Usp. Fiz. Met.* 14, 33 (2013) (in Ukrainian).

[18] V.N. Nikiforov, A.N. Ignatenko, V.Yu. Irhin, *Izv. Akad. Nauk SSSR Ser. Fiz.* 78, 1336 (2014) (in Russian).

[19] S.R. Dave, X. Gao, *Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol.* 1, 583 (2009).

[20] R.H. Kodama, *J. Magn. Magn. Mater.* 200, 359 (1999).