

Proceedings of the European Conference Physics of Magnetism 2011 (PM'11), Poznań, June 27–July 1, 2011

# Physical Properties of Magnetite Nanoparticles Covered by 11-Mercaptoundecanoic Acid

M. TIMKO<sup>a,\*</sup>, P. KOPČANSKÝ<sup>a</sup>, M. ANTALIK<sup>a</sup>, M. SIMSIKOVA<sup>b</sup>, E. VALUSOVA<sup>a</sup>,  
M. MOLCAN<sup>a</sup> AND J. KOVÁČ<sup>a</sup>

<sup>a</sup>Institute of Experimental Physics, SAS, Watsonova 47, 040 01 Kosice, Slovakia

<sup>b</sup>Department of Biochemistry, Faculty of Sciences UPJS, Moyzesova 11, 041 54 Kosice, Slovakia

We have investigated the magnetic behavior of magnetite nanoparticles covered by the 11-mercaptoundecanoic acid around magnetite core prepared by a standard co-precipitation method. The particles show superparamagnetic behavior at room temperature, with transition to a blocked state at blocking temperature 91 K estimated from zero field cooled and field cooled at 500 Oe experiment. The hysteresis loop measured at 293 K showed magnetization 32.8 emu/g at 50 kOe without any coercivity. The mean particle size (7.1 nm) was determined by fitting a magnetization curve obtained at 295 K assuming a log-normal size distribution.

PACS: 47.65.Cb, 85.70.-w, 75.30.Cr, 75.47.Lx

## 1. Introduction

The biomedical applications of magnetic nanoparticles have experienced a rapid growth due to the benefits in molecular imaging and targeted therapy. Iron oxide nanoparticles are considered as a multifunctional platform, which can be both detected by noninvasive resonance imaging and activated at a distance by a remote magnetic field, allowing controlled manipulation or hyperthermia [1]. Applications in magnetic resonance cell tracking [2], macrophage imaging [3], cancer hyperthermia [4] or tissue engineering [5] are being explored to provide insight into disease mechanism, facilitate diagnostic imaging or design new tools for controlled therapy.

Due to combination of unique magnetic properties, low toxicity and biodegradability [6], the magnetite nanoparticles have great chance to be widely used. Several surfactants have been tested for biocompatibility. Some coatings are degraded enzymatically *in vivo* [7]. Thus, stability of the resulting particle is of critical importance for mentioned bioapplications. The covalently linked core avoids flocculation of magnetite nanoparticles due to their loss shell [8].

In this contribution we propose the surface coating with 11-mercaptoundecanoic acid around magnetite core prepared by a standard co-precipitation method. The nature of those nanoparticles as well as their innovation of physical properties has been studied. Techniques, such as attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), electrophoretic mobility measurements on Zeta Sizer Nano ZS have been used to characterize new form of magnetite in the powder and/or in the fluidic form.

## 2. Experiments

Preparation of magnetite nanoparticles covered by 11-mercaptoundecanoic acid: iron(II) chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) — 0.054 g and iron(III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) — 0.0198 g were dissolved in 10 ml distilled water. Under constant stirring was slightly yellow solution warmed up to 80°C. Then the surface covering was performed by adding dropwise a 2 mL alkaline solution of 10 mg of 11-mercaptoundecanoic acid to warmed solution stirred at 300 rpm. The resulting magnetic black nanoparticles were settled by magnet and washed 3 times with 5 ml of distilled water. In final step, settled moisture magnetic particles were dried and stored at room temperature.

The fluidic form of the above powder was prepared by its dissolving in water and then ultrasonicated the suspension at room temperature for 45 min until the suspension becomes fluid enough.

Infrared ATR spectra were recorded on a Nicolet 8700 Fourier transform infrared (FTIR) (Thermo Scientific) spectrometer equipped with Smart OMNI-Sampler (diamond crystal), deuterated triglyceride sulfate (DTGS) detector and a KBr beamsplitter. All spectra were collected for 64 scans at a resolution of 4  $\text{cm}^{-1}$  in range of 4000–400  $\text{cm}^{-1}$  with a 150 cm aperture. Spectra were referenced to a background spectrum previously recorded on the crystal without the nanoparticles and cleaned under the same conditions as for the covered crystal. The electrophoretic mobility of coated nanoparticles was determined using a Zeta Sizer Nano ZS from Malvern Instruments.

The magnetization properties were measured by SQUID magnetometer of Quantum Design in a magnetic field (up to 50 kOe) and in a temperature range 2–300 K.

\* corresponding author; e-mail: timko@saske.sk

### 3. Experimental results

#### 3.1. ATR FT IR spectroscopy

The ATR FT IR spectra of mercaptoundecanoic acid, magnetite nanoparticles and modified particles by mercapto-undecanoic acid are presented in Fig. 1a, b and c. Spectrum of mercaptoundecanoic acid (Fig. 1a) displayed very broad signal at  $3094\text{ cm}^{-1}$  due to the stretching vibration of hydroxyl groups and two bands at  $2928$  and  $2847\text{ cm}^{-1}$  arising to the  $\nu_{\text{as}}$  (C-H) and  $\nu_{\text{s}}$  (C-H) vibrations of  $\text{CH}_2$  groups. Signals at  $1540$  and  $1402\text{ cm}^{-1}$  due to symmetric and asymmetric  $\nu$  (C=O) vibrations, which are consequence of ionisation of carboxylic groups into carboxylic anions in alkaline pH.

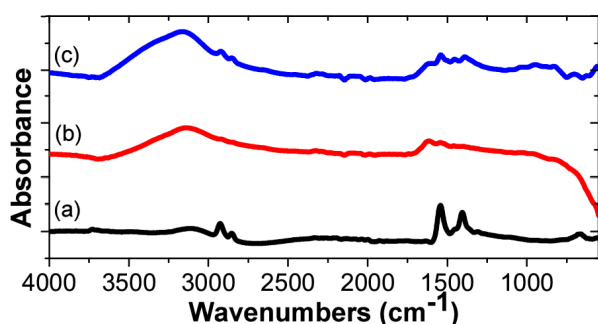


Fig. 1. The FTIR spectra of solid samples: (a) 11-mercaptoundecanoic acid; (b) pure magnetite nanoparticles; (c) mercaptoundecanoic modified particles.

For spectrum of magnetite nanoparticles (Fig. 1b) are characteristic peaks at  $3132\text{ cm}^{-1}$  and  $1625\text{ cm}^{-1}$  which indicates the presence of hydroxyl groups on the surface of nanoparticles.

When compared with pure nanoparticles, the spectrum of capped sample contains new peaks at  $2918$  and  $2850\text{ cm}^{-1}$  corresponding to the stretching vibrations  $\nu_{\text{as}}$  (C-H) and  $\nu_{\text{s}}$  (C-H) of alkane groups and  $1540$  and  $1397\text{ cm}^{-1}$  which belong to  $\nu_{\text{s}}$  ( $\text{COO}^-$ ) and  $\nu_{\text{as}}$  ( $\text{COO}^-$ ) vibrations. These changes confirmed successful surface modification of magnetite nanoparticles via covalent linking with mercaptoundecanoic acid.

#### 3.2. Measurement of zeta potential of modified magnetite nanoparticles

The electrophoretic mobility of coated nanoparticles was determined using a Zeta Sizer Nano ZS from Malvern Instruments and transformed into zeta potential using the Smoluchowski equation. For all experiments  $1.28\text{ mM}$  solutions of sample at temperature  $25^\circ\text{C}$  in the water were used. For the titration of the samples to appropriate pH, the concentrated HCl and aqueous NaOH were used. The pH values (pH 2.0–12.0) measured using the SENSOREX glass electrode before and after the data had been recorded.

#### 3.3. Physical characterization of the surface charge

Figure 2 shows the change in zeta potential of the magnetite nanoparticles modified by mercaptoundecanoic acid at different pH values in the range of 2.00–12.00. The positive zeta potential at pH 2 ( $+17\text{ mV}$ ) was slightly decreased to value  $+11\text{ mV}$  for pH 7. The negative zeta-potential value of nanoparticles was obtained at pH 8 and became practically constant at higher pH values (pH 8–12). This observation confirmed that the carboxylic acid groups assembled on the nanoparticle surface are completely dissociated around pH 8. This type of pH-ionizable group underwent protonation below the pH 7 due to obtained positive sign of zeta potential. Thus, the isoelectric point (IEP) of sample can assume the pH value of 7.2.

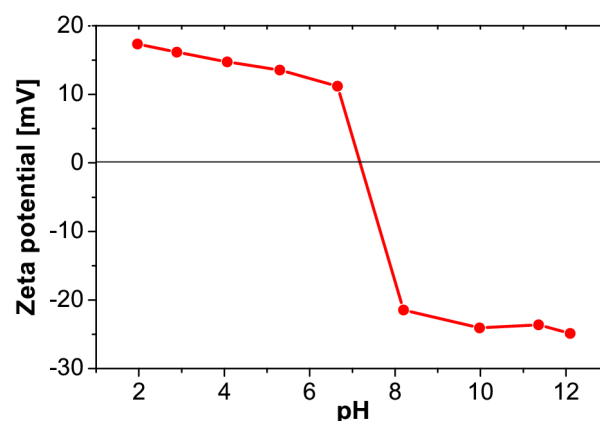


Fig. 2. Zeta potential at different pH values of coated magnetite nanoparticles by mercaptoundecanoic acid.

#### 3.4. Magnetic properties

The magnetization at room temperature and applied magnetic field  $50\text{ kOe}$  for prepared sample is  $32.8\text{ emu/g}$ . The mean diameter of magnetite core  $D = 7.1\text{ nm}$  was estimated from magnetization curve at room temperature (Fig. 3) by the Chantrell method [9]. The hydrodynamic size of nanoparticles (magnetic core + surfactant layer) was estimated to be  $10.1\text{ nm}$ . Assuming the core shell structure with a shell of thickness  $d$  which does not contribute to the magnetization this smaller value of magnetization can be understood. According to the relation  $M_s = 92(1 - 2d/D)^3$  assuming core shell structure with  $M_s = 92\text{ emu/g}$  for bulk magnetite and  $D = 7.1\text{ nm}$  as a mean particle diameter the value for thickness of shell was obtained as to be  $d = 1.03\text{ nm}$ . This value of shell thickness is higher but comparable with another values obtained for magnetite nanoparticles covered by oleic acid [10].

The zero field cooled and field cooled curves (Fig. 4) for prepared sample at an applied field  $500\text{ Oe}$  indicate the superparamagnetic behaviour with blocking temperature at  $91\text{ K}$ . The ZFC curve exhibits the typical features of an assembly of magnetic particles

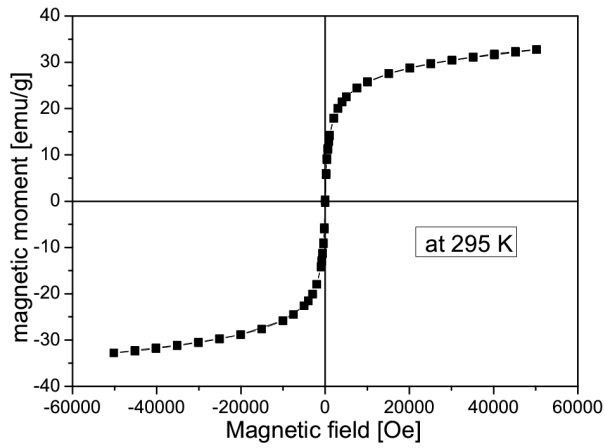


Fig. 3. Hysteresis loop at room temperature.

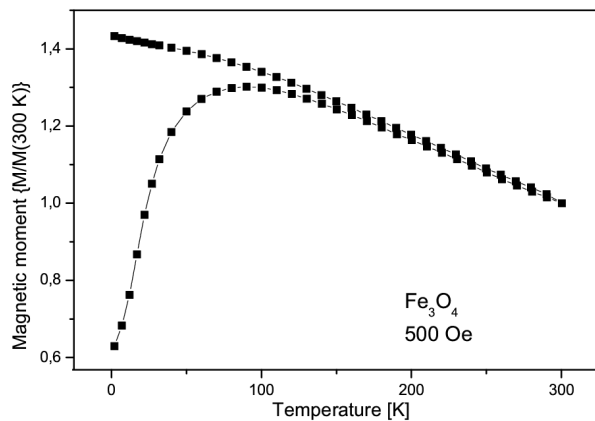


Fig. 4. Zero field cooled and field cooled curves at 500 Oe indicate the superparamagnetic behaviour with blocking temperature 91 K.

with a distribution of blocking temperatures. As the nanoparticles are cooled to very low temperature in the presence of a magnetic field (FC), the magnetization direction of each particle is frozen in the field direction. The ZFC magnetization will exhibit a maximum at the blocking temperature at which the relaxation time equals the time scale of the magnetization measurement.

#### 4. Conclusion

In summary, prepared magnetite nanoparticles covered by mercaptoundecanoic acid show typical superparamagnetic properties. Their magnetic behaviors reported here have been interpreted in terms of existence of disordered layer of surface spins, which does not contribute to the magnetization of sample. Further investigations of this disordered shell are now underway using other experimental methods.

#### Acknowledgments

This work was supported by Slovak Academy of Sciences (grants VEGA Nos. 2/0077/09, 2/0051/09, 2/0038/09, 1/4290/07 CEX — NANOFUID), Slovak Research and Development Agency under the contract No. APVV-0171-10 and Development of technology of magnetic fluids for biomedical applications Project No. 26220120021, 26220220005 and 26220120033.

#### References

- [1] Q.A. Pankhurst, N.K.T. Thanh, S.K. Jones, J. Dobson, *J. Phys. Chem. D, Appl. Phys.* **22**, 224001 (2009).
- [2] J.W. Bulte, *Am. J. Roentgenol.* **193**, 314 (2009).
- [3] Tang, K.H. Muller, M.J. Graves, Z.Y. Li, S.R. Walsh, V. Young, U. Sadat, S.P.S. Howarth, J.H. Gillard, *Atheroscler. Thromb. Vasc. Biol.* **29**, 1001 (2009).
- [4] B. Thiesen, A. Jordan, *Int. J. Hyperthermia* **24**, 467 (2008).
- [5] H. Akiyama, A. Ito, Y. Kawabe, M. Kamihira, *Biomed. Microdev.* **11**, 713 (2008).
- [6] R. Weissleder, D.D. Stark, B.L. Engelstad, B.R. Bacon, C.C. Compton, D.L. White, P. Jacobs, J. Lewis, *Am. J. Roentgenol.* **152**, 167 (1989).
- [7] A. Jordan, P. Wust, R. Scoltz, B. Tesche, H. Föhling, T. Mitrovics, T. Vogl, *Int. J. Hyperthermia* **15**, 705 (1996).
- [8] A.B. Bourlinos, A. Bakandritos, V. Georgakilas, V. Tziltzios, D. Petridis, *J. Mater. Chem.* **41**, 5250 (2006).
- [9] R.W. Chantrell, J. Popplewell, S.W. Charles, *IEEE Trans. Magn.* **MAG-14**, 975 (1978).
- [10] P. Dutta, S. Pal, M.S. Seehra, N. Shah, G.P. Huffman, *J. Appl. Phys.* **105**, 07B501 (2009).