Magnetic properties and applications of carbon nanotubes filled with Fe_3O_4 nanoparticles[1]

Svitlana KOPYL [1], Andrey TIMOPHEEV [2], Vladimir BYSTROV [3,4], Mikhail MAIOROV [5], Igor BDIKIN [1], Manuel A. VALENTE [2], Evgenij MAEVSKIJ [6], Nikolai A. SOBOLEV [2]*, Antonio C.M. SOUSA [1]

[1] *Nanotechnology Research Division, TEMA, Department of Mechanical Engineering, University of Aveiro, 3810-193, Portugal*
[2] *Physics Department and I3N, University of Aveiro, 3810-193, Portugal*
[3] *Department of Materials and Ceramic Engineering and CICECO, University of Aveiro, 3810-193, Portugal*
[4] *Institute of Mathematical Problems of Biology RAS, 142290, Pushchino, Russia*
[5] *Institute of Physics, University of Latvia, LV-2169, Latvia*
[6] *Institute of Theoretical and Experimental Biophysics RAS, 142290, Puschino, Russia*
**sobolev@ua.pt*

***Abstract* — Ordered arrays of magnetic carbon nanotubes have been obtained by means of non-catalytic chemical vapor deposition, by growing nanotubes inside porous alumina templates and subsequently filling them with Fe_3O_4 particles. Magnetic properties of the arrays have been studied at different temperatures using vibrating sample magnetometry and ferromagnetic resonance. The filled nanotubes have exhibited superparamagnetic properties with a blocking temperature of about 145 K. The average nanotube filling factor, as determined by the magnetometry, was 32%, while the ferromagnetic resonance has detected the presence of conglomerates of nanoparticles. This allowed us to conclude that the filling of the nanotubes with the magnetic phase was non-uniform. Such magnetic carbon nanotubes have the potential of being used in a wide range of applications, in particular, in the production of nanofluids, which can be controlled and steered by appropriate magnetic fields. The proposed methodology opens an opportunity for simplified fabrication of magnetic nanotubes aiming at biomedical applications and, in particular, at the production of magnetic nanofluids which can be steered by appropriate magnetic fields, e.g., as magnetic sorbents for cleaning blood from free hemoglobin. The first experimental results have shown that our proposed magnetic nanoseparation is of more than tenfold efficiency in comparison with the conventional hemosorption method.**

***Index Terms* — magnetic nanoparticles, magnetization, nanofluids, nanotubes.**

I. INTRODUCTION

The research field of carbon nanotubes (CNTs) has received a continuously growing interest since their discovery in 1991 [1] due to their unique and highly desirable electrical, thermal and mechanical properties [2]. Functionalizing CNTs with magnetic nanoparticles can combine the features of magnetic nanoparticles and CNTs, which may result in materials with novel chemical and physical properties, and thus promising applications. It has been reported that CNTs filled with Fe_3O_4 may be used as diffraction gratings, optical filters, and polarizers [3]. Other applications of these materials include cantilever tips in magnetic force microscopes, magnetic stirrers or magnetic valves in nanofluidic devices [3–5] as well as transporting drugs to specific locations in the body and for medical diagnosis without surgical invasive procedures [4].

Our motivation for creating a CNT/magnetite composite stems from the goal of creating a new generation of nanofluids, which are amenable to be controlled by appropriate magnetic fields. These nanofluids are a suspension of carbon nanotubes filled with magnetite nanoparticles, in a base fluid [4,5]. These suspensions, in general, exhibit behavior of a normal liquid coupled with superparamagnetic properties. This leads to the possibility of controlling the properties and the flow of these liquids with moderate magnetic fields.

Gogotsi's group [9] demonstrated that it is possible to fill CNTs with a diameter of 300 nm using commercially available ferrofluids. However, the level of CNTs filling, in terms of the ratio between the magnetic particles volume by that of the nanotube, was relatively low (approximately 11%).

Despite a number of previous studies, filling CNTs completely with Fe_3O_4 nanoparticles has remained a challenging task.

In this paper we report a modification of the CNTs production procedure proposed in Ref. [9] aimed at increasing the nanotube filling factor to levels that are adequate for the production of nanofluids with magnetic CNTs as nanoparticles. A detailed magnetic characterization of the CNTs filled with ferroparticles has been undertaken by means of ferromagnetic resonance (FMR) and vibrating sample magnetometry (VSM) techniques.

[1] This work has been supported by the FCT of Portugal through projects and grants PTDC / EME-MFE / 105031 / 2008, PEst-C / CTM /LA0025 / 2011, RECI / FIS-NAN / 0183 / 2012, SFRH / BPD / 22230 / 2005, SFRH /BPD / 74086 / 2010, and REDE / 1509 / RME / 2005.

II. EXPERIMENTAL DETAILS

CNTs were produced by a non-catalytic chemical vapor deposition (CVD) technique based on the pyrolysis of ethylene. Before the growth of CNTs, the 60 μm thick alumina template membranes (Whatman® Inc., U.K.) were placed vertically inside the quartz tube. The nanotubes were formed in straight cylindrical pores which run through the whole membrane thickness. The microstructures of the alumina membrane and the CNTs samples inside the membrane were observed in a Hitachi SU-70 scanning electron microscope (SEM). The SEM images (see, e.g., Fig. 1a) reveal that the pores have varying diameters within one membrane sample. The pore diameter in our samples was in the range from 200 ± 15 nm (Fig. 1b).

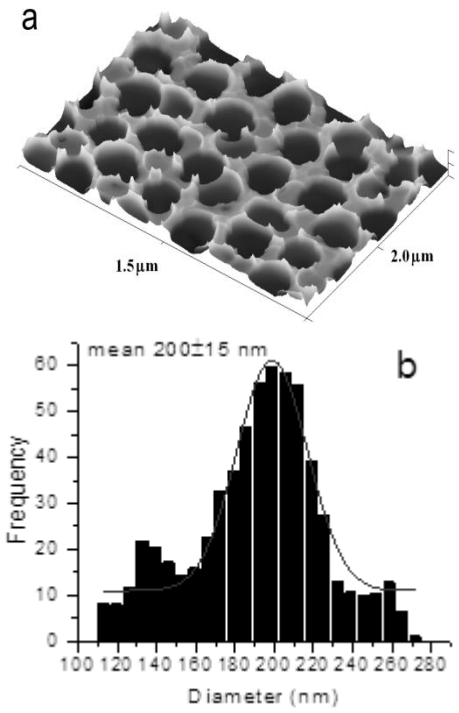


Fig. 1. (a) SEM micrograph of an alumina membrane. (b) Pore size distribution in the alumina membrane calculated from the SEM image analysis.

The resulting CNTs with an average length of 6 μm have at least one open end, and their walls are highly disordered and amorphous – this characteristic makes filling of the nanotubes with both organic and water-based fluids viable [9,11]. The size of the membrane pores with CNTs inside was characterized using atomic force microscopy (AFM, Ntegra, NT-MDT). The majority of CNTs have an inner diameter close to 124 nm [12].

The organics-based ferrofluid EMG 911 (Ferrotec Corporation) containing Fe_3O_4 nanoparticles with an average diameter of 7.5 nm was used in our experiments. To fill the CNTs sitting in the template with ferrofluid, we added a 100-fold excess (by weight) of the ferrofluid to the system; no magnetic field was used in this filling procedure. The nanoparticle-filled CNTs were characterized using transmission electron microscopy (TEM) in a Hitachi H-9000 microscope at 300 kV.

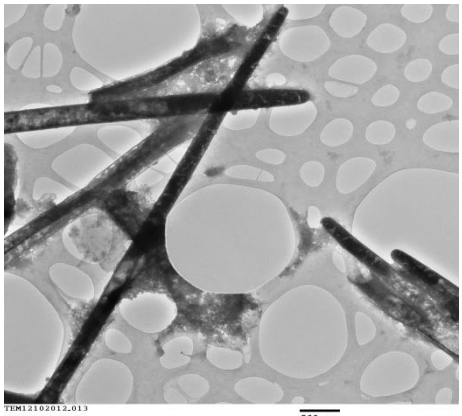
The magnetic properties of the original CNTs and samples filled with Fe_3O_4 were characterized using a vibrating sample magnetometer (VSM, Lake Shore Cryotronics, model 7404). The measurements were done at several temperatures from 78 K to 293 K in applied fields up to 10 kOe.

FMR was measured on a X-band Bruker ESP 300E EPR spectrometer. Out-of-plane angular dependences of the FMR were obtained at RT by rotating the magnetic field between the film plane and the normal to the film. The temperature-dependent measurements from 150 to 450 K were conducted for two principal magnetic field orientations, viz., for the field aligned parallel and perpendicular to the film plane.

III. RESULTS AND DISCUSSION

Typical TEM images of CNTs filled with Fe_3O_4 nanoparticles are shown in Figs. 2a,b. The filled nanotubes can be easily identified in the image. The table in Fig. 2a results from EDS measurements of the filled samples; these measurements confirm the presence of atomic iron in the CNTs.

The filling of the CNTs can be explained in terms of capillary forces induced during the impregnating process.



Element	Series	Net	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]	Error [%]
Iron	L-series	1789	29.54	29.54	8.91	10.3
Carbon	K-series	8371	48.24	48.25	67.69	15.6
Oxygen	K-series	2761	22.21	22.21	23.40	7.5
		Total:	100.00	100.00	100.00	

Fig. 2. TEM image of CNTs filled with Fe_3O_4 nanoparticles. Table: EDS results.

Previous studies reported in the literature [6–8,13,14] have shown that elements and compounds with surface tension lower than 200 mN/m are suitable for wetting and filling of carbon nanotubes. The EMG 911 ferrofluid has a surface tension value of 68 mN/m; therefore, as demonstrated, this ferrofluid is capable of strongly wetting and filling the nanotubes.

The empty arrays have been checked by magnetometry before filling. The original carbon nanotubes did not present any ferromagnetic properties. The magnetization curves of the CNTs samples after being filled with Fe_3O_4 nanoparticles are shown in Fig. 3.

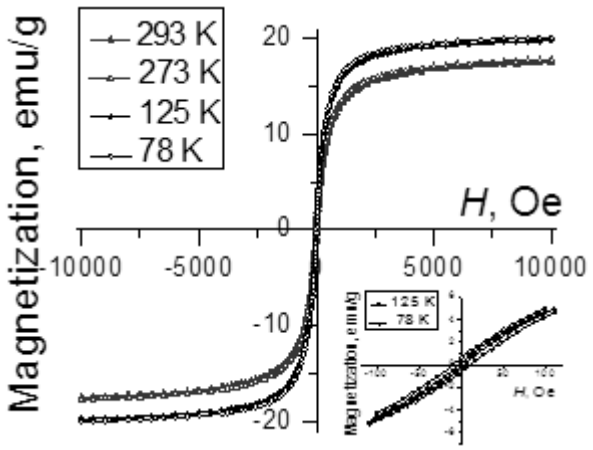


Fig. 3. Magnetization curves of CNTs filled with Fe_3O_4 at different temperatures. Inset: Enlargement of the low-field region at at 125 K and 78 K.

It is seen in Fig. 3 that the magnetic CNTs exhibit no hysteresis loops in a weak applied magnetic field at RT and at 273 K. However, hysteresis is clearly observed at lower temperatures, 125 K and 78 K. Thus, ferromagnetic properties do occur. The saturation magnetization varies with temperature from 17.53 emu/g to 20.10 emu/g. The saturation magnetization M_S, coercivity H_C, remanent magnetization M_R and the ratio $R = M_R/M_s$ measured at different temperatures are presented in Table 1.

TABLE 1. CHARACTERISTICS OF CNTs WITH MAGNETITE NANOPARTICLES.

T, K	H_C, Oe	M_s, emu/g	M_r, emu/g	$R = M_r/M_s$
293	0	17.53	0	0
273	0	17.78	0	0
175	0	19.26	0	0
125	2.75	19.78	0.2	0.01
78	9.98	20.10	0.63	0.03

At low temperatures the coercivity of a system of non-interacting and randomly oriented particles is expected to follow the relation [15]:

$$H_C = H_{C0}\left[1-\left(T/T_B\right)\right]^{1/2} \quad (1)$$

For CNTs filled with Fe_3O_4 we obtained at low temperatures the following H_C values:

$H_C \approx 3$ Oe at $T = 125$ K, and $H_C \approx 10$ Oe at $T = 78$ K.

Besides, the blocking temperature T_B was estimated. At temperatures well below T_B, the hysteresis appears and, as a result, the superparamagnetism is no longer manifested, as the thermal energy is not sufficient anymore to overcome the magnetic anisotropy energy. In our case the T_B value is equal to approximately 145 K.

Alternatively, the magnetic properties of the EMG 911 ferrofluid were estimated taking into account that it shows a significant hysteresis in the presence of a weak magnetic field at 78 K and 5 K. A detailed analysis for EMG 911 (similar to that described above for the CNTs filled with Fe_3O_4) yields the following parameters:
$H_C \approx 265$ Oe at $T = 78$ K; $H_C \approx 2250 \pm 250$ Oe at $T = 5$ K.

For the EMG 911 ferrofluid $T_B = 93 \pm 6$ K. This value is much higher than that for pure magnetite nanoparticles with a diameter of 6 nm ($T_B \approx 31$ K) and for CNTs filled with them ($T_B \approx 58$ K) and is comparable with values reported in the literature [10]. This may infer that there is an increase of the interaction strength between magnetic nanoparticles and CNT walls [10,16] as well as of those among magnetic nanoparticles inside the nanotubes. It is generally accepted that the magnetic interactions that dominate magnetic nanoparticle assemblies are dipole-dipole interparticle interactions (which are always present) and exchange interactions through the surfaces of particles that are in close contact [10,16]. It is known [17] that the exchange interaction among Fe_3O_4 particles might be minimal because the average edge-edge separation between particles is large due to the presence of the surfactant. However, the tight packing of Fe_3O_4 inside CNTs can reduce the average distance between the Fe_3O_4 particles, thus enhancing the strength of the dipolar interparticle interaction. In the present case the filling level of carbon nanotubes with magnetic particles is about 32% [12,18]. This percentage corroborates our premise that there is a strong interaction among the magnetic particles inside the CNTs, which are the object of the FMR study described in the following.

FMR measurements at RT have shown relatively broad resonance lines (line width $\Delta H \sim 1$ kOe) which are typical of FMR in magnetite nanoparticles [19–24]. An in-plane FMR line is comprised of three resonance peaks each having Gaussian shape. Typical fitting using three Gaussians is shown on Fig. 4b. The main peak is practically two times wider and has an integral intensity as least one order of magnitude higher than the two others. Its angular dependence reflects easy-axis anisotropy of the system as a whole with the axis perpendicular to the film plane, which is to be expected for such a structure with a low surface density of pores (13.5%). In other words, individual magnetic properties of magnetically filled nanotubes are dominating over the collective properties of the film-shaped ensemble of nanotubes. In the following, calculations will be performed to quantitatively evaluate the filling factor and to compare its value with the data obtained from the magnetometry.

The low-intensity peaks have resonance field positions lower and higher than the main peak (Fig. 5). Both peaks have the same magnitude and line width (FWHM ~ 540 Oe). These parameters have been found to be practically independent on the angular variation of external magnetic field. The angular dependences of their resonance fields reflect different symmetry. Actually, the high-field peak evidently shows 180º symmetry. Nevertheless, it was impossible to track its angular variation with a high accuracy in the whole range of angles due to strong overlapping with the main peak. Surprisingly, the low-field peak shows the combination of 180º and 90º symmetries. It is hard to explain such a behavior from the point of view of randomly oriented and well-separated nanoparticles uniformly filling the nanotubes. On the other hand, according to previous studies [24–26], it could be attributed to the FMR of anisotropic conglomerates of nanoparticles (e.g., dimers) formed on the CNT's walls or

spontaneously appearing in the presence of the external magnetic field.

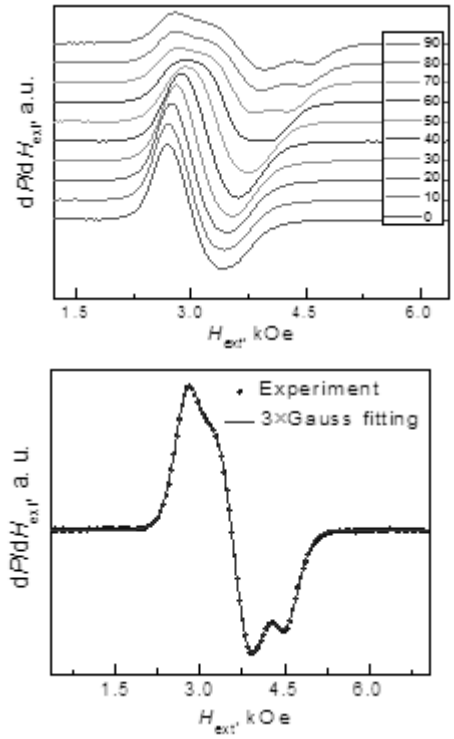


Fig. 4. (a) FMR spectra measured at different angles (indicated in the graph) between the external magnetic field and the normal to the film plane. (b) An example of the FMR spectrum fitting with three Gaussians. The spectra were measured at f_0 =9.78 GHz.

The angular dependence of the resonance field (Fig. 5) for the main peak demonstrates a comparatively low variation amplitude: the highest and the lowest resonance fields are 3600 and 3100 Oe, respectively, which gives a magnitude of the perpendicular anisotropy field of ~250 Oe. If one considers a 100% filling of nanotubes by the magnetite phase, and that the average CNT length is orders of magnitude larger that the average diameter, then, in the absence of dipole-dipole interaction between the nanotubes, one has to obtain $H_a = 2\pi M_s = 2\pi \cdot 480 \approx 3$ kOe, which is one order of magnitude higher than the observed value. This discrepancy may be theoretically explained as a decrease of the perpendicular anisotropy due to the dipole-dipole interaction in the ensemble or by the fact that the filling factor is much lower than 100%, and the filling inside the nanotubes is non-uniform. The possibility of non-uniform filing is also supported by the analysis of the angular dependence of the line width for the main peak (Fig. 5). The angular dependence shows a 37% increase for the in-plane magnetic field orientation as compared to the out-of-plane orientation, where H_{ext} is parallel to the nanotubes axes. Such a behavior is understandable if the particles are able of moving inside the nanotubes: when the magnetic field is oriented along the nanotubes, the particles have to gather together to minimize the magnetostatic energy. In contrast, for the magnetic field oriented perpendicularly to the nanotubes, the minimization of the magnetostatic energy should lead to a spreading of the particles over the nanotube as much as any possible. In the latter case, the non-uniformity of the internal field will be higher, which will be reflected by a larger line width of the FMR absorption peak.

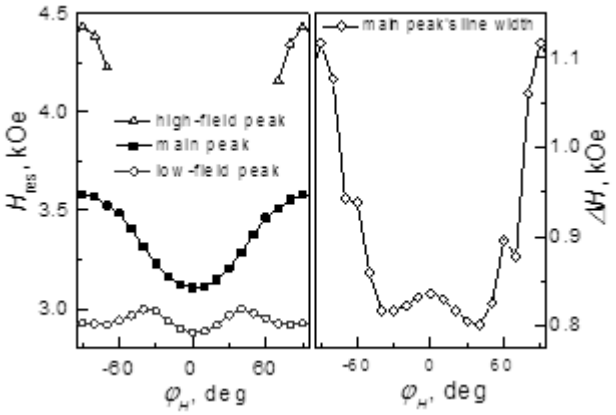


Fig. 5. Angular dependences of the resonance peak positions (left panel) and for the line width of the main FMR peak (right panel). The spectra were measured at f_0 =9.78 GHz.

The temperature dependence of the main resonance peak for the in-plane and out-of-plane magnetic field orientations is shown in Fig. 6. A continuous decrease of the resonance fields for both orientations with reducing temperature is supplemented by an increasing line width. This is a classical superparamagnetic behavior in FMR measurements [19–24]. A constant ratio $\Delta H_{\parallel} / \Delta H_{\perp}$ = 1.3 ± 0.06 is preserved in the whole range of temperatures. At the same time, a decrease of the resonance fields, is accompanied by an increase of the distance between the resonance fields for the in-plane and out-of-plane magnetic field orientations. This effect is linked to a slight growth of the particles' saturation magnetization which typically occurs when the temperature decreases down to the Verwey transition point [27].

To evaluate the nanotube filling factor from the FMR angular dependences, one has to start with a description of the considered system's magnetic energy. If the nanoparticles are considered as magnetically isotropic, the total magnetic energy density will have two contributions:

$$E_{tot} = E_d + E_Z, \quad (2)$$

where E_Z is the Zeeman energy term expressing the interaction of the net magnetic moment with the external magnetic field H:

$$E_Z = -M_s H_{ext} \left(\cos\theta_m \cos\theta_h + \cos(\phi_m - \phi_h)\sin\theta_m \sin\theta_h\right). \quad (3)$$

The angular variables θ_h (polar angle read from a certain direction in the film plane) and ϕ_h (azimuthal angle read from the film normal) determine the external magnetic field orientation, while θ_m and ϕ_m give the film's net magnetic moment orientation, respectively, and M_s stays for the particles saturation magnetization. The second term,

$$E_d = \left(M_s^2/2\right)\left(f_v f_p 4\pi - f_p(1-f_v)N_{eff}\right)(\cos\phi_m \sin\theta_m)^2,$$ is

the magnetostatic energy which, according to Refs. [28,29], describes a thin film having an array of perpendicularly oriented pores filled by nanoparticles:

$$E_d = \left(M_s^2/2\right)\left(f_v f_p 4\pi - f_p(1-f_v)N_{eff}\right)(\cos\phi_m \sin\theta_m)^2, \quad (4)$$

where f_v is the relative volume occupied by the pores in the film, f_p is the relative volume occupied by the particles in each pore, and N_{eff} is an effective demagnetization factor of the filled nanotube as a whole: for a uniformly filled tube N_{eff} will be equal to 2π, while $N_{eff} < 2\pi$ will characterize the non-uniformity of the filling.

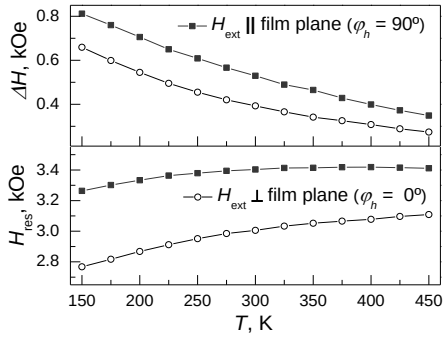


Fig. 6. Temperature dependences of the main peak's resonance field (H_{res}) and its line width (ΔH) measured for the in-plane and out-of-plane magnetic field orientations. The spectra were measured at f_0 = 9.465 GHz.

To calculate the resonance field of a FMR line, we applied the Smith-Beljers formalism:

$$\left.\begin{aligned} &\frac{\partial E_{tot}}{\partial\theta_m}=0, \qquad \frac{\partial E_{tot}}{\partial\varphi_m}=0; \\ &\left(\frac{\omega}{\gamma}\right)^2 = \frac{1}{\left(M_s\sin\theta_m\right)^2}\left(\frac{\partial^2 E_{tot}}{\partial\theta_m^2}\frac{\partial^2 E_{tot}}{\partial\varphi_m^2}-\left(\frac{\partial^2 E_{tot}}{\partial\theta_m\,\partial\varphi_m}\right)\right) \end{aligned}\right\}. \quad (5)$$

Here $\gamma = ge/(2mc)$ is the gyromagnetic ratio (g – spectroscopic Landé g-factor, e – electron charge, m – electron mass, c – light velocity). Kittel's resonance conditions for two main orientations of the magnetic field, i.e. those in-plane ($\theta_h = \varphi_h = \pi/2$) and out-of-plane ($\theta_h = \varphi_h = 0$), can be found from Eq. (5) directly:

$$\begin{aligned} &(\omega/\gamma)^2 = H_{\perp}(H_{\perp} + N_{sys}M_s), \quad (\theta_h = \varphi_h = \pi/2), \\ &\omega/\gamma = H_{\perp} - N_{sys}M_s, \qquad (\theta_h = \varphi_h = 0). \end{aligned} \quad (6)$$

Here $N_{sys} = f_p(4\pi f_v - N_{eff}(1-f_v))$ is the net demagnetization parameter of the system as a whole. For intermediate orientations, Eqs. (5) have to be solved numerically.

Fig. 7 shows the best fit of an angular dependence of the resonance field for the main peak. The literature value of saturation magnetization for the bulk magnetite (480 emu/cm^3) was used [30]. The filling parameters f_p and f_v were also set fixed, as f_v has been determined from the microscopy and f_v, from the VSM magnetometry. The fitted model parameters were the g-factor and N_{eff}, yielding 2.043 and $0.69\cdot 2\pi$, respectively. The g-factor value obtained for T = 300 K is slightly lower than that for bulk magnetite (2.10–2.12) [30], which is reasonable from the viewpoint of superparamagnetic resonance [19–23]. From the temperature dependences of H_{res} for the main peak (Fig. 6) we obtain using Eqs. (6) that, with the temperature lowering from 450 to 150 K, the g-factor decreases from 2.04 to 2.18. The second fitting parameter, representing an effective demagnetization factor of a nanotube non-uniformly filled with a magnetic phase, has been found to be 30% lower than those estimated for completely and uniformly filled nanotubes whose shape is approximated by an infinite cylinder. This proves the aforementioned assumption about the non-uniform nanotube filling.

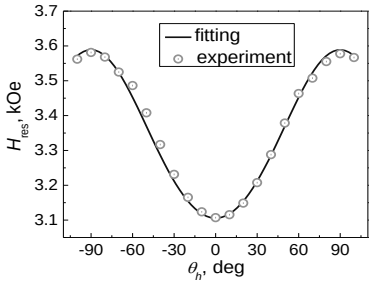


Fig. 7. Model fitting with the fixed parameters: $\omega = 2\pi\cdot 9.78\times 10^9$ rad/s, f_p = 0.32, f_v = 0.135, M_s = 480 emu/cm^3. Fitted parameters: $N_{eff} = 0.69\cdot 2\pi$, g = 2.043.

The magnetic nanotubes have a tremendous application potential in magnetics, functional nanomaterials and nanodevices. As an application example, we used the magnetic carbon nanotubes as a magnetic sorbent in a magnetic field for cleaning biological fluids from the extracellular hemoglobin and myoglobin, which appear in the blood plasma during pathology (hemolysis of red blood cells and massive damage of muscle tissues) [31].

Hemoglobin (Hb) is the major erythrocyte protein consisting of four subunits, where each subunit is a combination of a polypeptide chain and a heme group. The heme group consists of an iron atom (Fe^{2+} or Fe^{3+}) attached to a planar organic structure belonging to the porphyrin compounds.

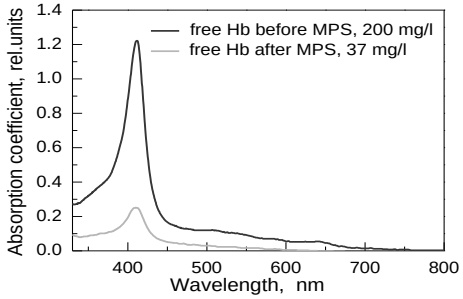


Fig. 8. The optical absorption spectrum of hemoglobin before and after magnetic nanoseparation (MPS).

Hemolysis is the rupturing of erythrocytes and the release of their contents (free Hb) into the surrounding fluid (e.g., blood plasma). The free Hb is extremely toxic.

In the present work we have determined on model systems the sorption selectivity of the magnetic CNTs for the purification of the blood plasma and whole blood from the hemoglobin and myoglobin. For the cleaning of the liquid from CNTs loaded with toxins, we have developed a special device – a magnetic separator.

The first experimental results have shown that the content of free Hb was reduced from 200 mg/l to 30...37 mg/l for 4 min of separation processing (Fig. 8). Thus, we may conclude that the efficiency of our proposed magnetic nanoseparation (MPS) is more than 10 times higher as compared to the conventional hemosorption method: the clearance of free Hb by our method is 79–150

ml/min, while by the conventional method it is only 3–15 ml/min, with the price for one procedure being the same.

IV. CONCLUSION

We propose an *ad-hoc* modification of a previously published procedure for the fabrication of magnetic CNTs. The new procedure is based on capillarity effects using a wetting fluid. It employs CNTs with a large diameter (above 100 nm) which are loaded with magnetic Fe_3O_4 particles. The magnetic properties of the loaded CNTs were investigated at various temperatures. A combination of the magnetometry and ferromagnetic resonance techniques has allowed us to determine the filling factor and uniformity, as well as the magnetic state of the system as a whole. The resulting composite shows excellent superparamagnetic properties at RT. The blocking temperature T_B was estimated to be around 145 K.

The proposed methodology opens an opportunity for simplified fabrication of magnetic nanotubes aiming at biomedical applications and, in particular, at the production of magnetic nanofluids which can be steered by appropriate magnetic fields, e.g., as magnetic sorbents for cleaning blood from free hemoglobin.

The first experimental results have shown that our proposed magnetic nanoseparation is of more than tenfold efficiency in comparison with the conventional hemosorption method.

REFERENCES

[1] S. Iijima, Nature **354**, 56, 1991.

[2] M. Dresselhaus, G. Dresselhaus, A. Jorio, Annu. Rev. Mater. Res. **34**, 247, 2004.

[3] K. Kornev, D. Halverson, G. Korneva, Y. Gogotsi, G. Friedman, Appl. Phys. Lett. **92**, 233117, 2008.

[4] L. Godson, B. Raja, D. Mohan Lal, S. Wongwises, Renewable and Sustainable Energy Reviews **14**, 629, 2010.

[5] R. Saidur, K. Leong, H. Mahammad, Renewable and Sustainable Energy Reviews **15**, 1646, 2011.

[6] P.M. Ajayan, S. Lijima, Nature **361**, 333, 1993.

[7] E. Dujardin, T.W. Ebbesen, H. Hiura, K. Tanigaki, Science **265**, 1850, 1994.

[8] D. Ugarte, A. Chatelain, W.A. de Heer, Science **274**, 1897, 1996.

[9] G. Korneva, H. Ye, Y. Gogotsi, D. Halverson, G. Friedman, J. Bradley, K. Kornev. Nano Lett. **5**, 879, 2005.

[10] S. Pal, S. Chandra, M.-H. Phan, P. Mukherjee, H. Srikanth, Nanotechnology **20**, 485604, 2009.

[11] D. Mattia, Y. Gogotsi, Microfluid Nanofluid **5**, 289, 2008.

[12] S. Kopyl, V. Bystrov, M. Maiorov, I. Bdikin, A.C.M. Sousa, J. Mater. Chem. 2012 (submitted).

[13] F. Qiang, G. Weinberg, S. Dang-Sheng, New Carbon Mater.**23**, 17, 2008.

[14] J.-P. Tessonnier, O. Ersen, G. Weinberg, C. Pham-Huu, D.S. Su, R. Schlögl, ACS Nano **3**, 2081, 2009.

[15] F. Fonseca, G. Goya, R. Jardim, R. Muccillo, V. Carreno, E. Longo, E. Leite, Phys. Rev. B **66**, 104406, 2002.

[16] J. Salado, M. Insausti, L. Lesama, I.G. Muro, E. Goikolea, T. Rojo, Chem. Mater. **23**, 2879, 2011.

[17] S.A. Majetich, M. Sachan, J. Phys. D: Appl. Phys. **39**, R407, 2006.

[18] S. Kopyl, V. Bystrov, M. Maiorov, M. Valente, I. Bdikin, A.M.C. Sousa. Proc. World Acad. Sci., Eng. and Technol., Zurich, Switzerland **67**, 137, 2012.

[19] B. Zapotoczny, M.R. Dudek, N. Guskos, J.J. Koziol, B.V. Padlyak, M. Kośmider, E. Rysiakiewicz-Pasek, J. Nanomater., 2012, doi:10.1155/2012/341073.

[20] T. Bodziony, Acta Phys. Polon. A **108**, 297, 2005.

[21] O. N. Sorokina, Russian J. Phys. Chem. B **3**, 257, 2009.

[22] N. Guskos, E. A. Anagnostakis, V. Likodimos, T. Bodziony, J. Typek, M. Maryniak, U. Narkiewicz, I. Kucharewicz, S. Waplak, J. Appl. Phys. **97**, 024304, 2005.

[23] J. Typek, J. Non-Cryst. Solids **354**, 4256, 2008.

[24] M. Noginov, J. Magn. Magn. Mater. **320**, 2228, 2008.

[25] S. Russ, A. Bunde, Phys. Rev. B **74**, 064426, 2006.

[26] M. Charilaou, M. Winklhofer, A. Gehring, J. Appl. Phys. **109**, 093903, 2011.

[27] E.J.W. Verwey, Nature **144**, 327, 1939.

[28] R. Skomski, IEEE Trans. Magnetics **43**, 6, 2007.

[29] J. Dubowik, Phys. Rev. B **54**, 1088, 1996.

[30] Ü. Özgür, Y. Alivov, H. Morkoç, J. Mater. Sci.: Mater. in Electronics **20**, 789, 2009.

[31] S. Kopyl, V. Bystrov, M. Maiorov, E.I. Maevskij, A.C.M. Sousa. In: Proc. 4th Internat. Conf. on Mathematical Biology and Bioinformatics, Pushchino, Russia 2012, p. 24, Ed. V.D. Lakhno (Moscow, MAKS-Press, 2012.