Materials Science-Poland, Vol. 28, No. 1, 2010

Preparation and characterization of SiO_2 microspheres doped with $CoFe_2O_4$ nanocrystals

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Main goal of the reported work was to fabricate silica microspheres doped with magnetic nanocrystals. Cobalt ferrite nanocrystals were fabricated separately via surfactant-assisted coprecipitation. The sol -gel method in microemulsion was subsequently used for encapsulating of the magnetic nanonanocrystals into the silica microspheres. Final products were characterized by various techniques and magnetic measurements. The obtained silica microspeheres doped with $CoFe_2O_4$ were of average diameter 11 μm.

Keywords: *sol-gel; microemulsion; cobalt ferrite; microspheres; nanocomposite*

1. Introduction

Fabrication of new functional materials tailored for specific applications is a challenge for chemistry and material science. Magnetic nanoparticles have been of a great interest ever since pioneer works of their simple preparation, reported for example in [1]. The sol-gel chemistry, mainly of silicate precursors has been undergoing through a renaissance since 1980 [2–4]. Combination of ever more progressive techniques leads to a variety of new materials based on magnetic or superparamagnetic (SPM) nanoparticles with functionally modified surface. The presence of a silica gel surface layer could shift the point of zero charge (p.z.c.) into acidic one, while an amino-modified silica layer could shift it in a basic range [5, 6]. A silica layer could be introduced by a number of preparation methods, two of them being widely used. The Stöber method uses ammonia catalyzed gelation of tetraalkoxysilane [7, 8], and the so-called microemulsion method is based on the formation of droplets of the emulsion,

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stabilized by surfactants, that acts as a micro-reactor for the sol-gel process [5, 9]. The advantages of the microemulsion method are, for example, independence of a catalytic mechanism (acidic or basic) of the sol-gel process, easy variation of the droplet size (by changing the amount of the water phase or changing the surfactant type), thermodynamic stability of the system, etc.

The paper concentrates on the fabrication of silica microspheres with the diameter of a few micrometers containing nanocrystals of $CoFe_2O_4$. The magnetic Co-ferrite nanoparticles were prepared by coprecipitation of cobalt(II) and iron(II) dodecylsulpahate solution using methylamine as the precipitant [10]. By this preparation route, many types of ferrite nanoparticles were synthesized, for example Fe_3O_4 [11], $NiFe_2O_4$ and $MnFe_2O_4$ [12]. Dodecylsulphate (an anionic surfactant) controls the shape and size of nanocrystals during the precipitation. A micellar system of water/CTAB (cetyltrimethylammonium bromide)/*n*-hexanol was used for encapsulation of the magnetic particles into silica spheres via the sol-gel microemulsion method. The proper pH acidic solution) of droplets and temperature around 40 °C, caused gelation of the silica precursor TMOS (tetramethoxysilane). In general, microemulsion, containing droplets of an acidic cobalt ferrite ferrofluid, is a suitable system for gelation of TMOS at higher temperatures.

Nowadays, a micro-scale processing is slightly ignored due to the greater emphasis placed on the nanosized features. However, this work is an illustrative example of a bottom-up approach, where the micro-objects are formed from molecular and nanoparticle building blocks.

2. Experimental

Syntheses and materials. All chemicals were of 98% purity or higher. Nanoparticles of $CoFe_2O_4$ were prepared by the coprecipitation method as described earlier [10]. Cobalt(II) and iron(II) dodecylsulphate, respectively, were prepared by crystallization of 1:1 volume mixture of 0.1 M cobalt acetate (Merck) or 0.1 M iron(II) chloride (Merck) solution, with 0.1 M sodium dodecylsulphate (Merck) at 2 °C. After adding of 2 M methylamine into the mixture of $8\cdot10^{-3}$ M $Co(DS)_2$ and $2{,}6.10^{-2}$ M $Fe(DS)_2$, the mixture was stirred vigorously for 2 h. Co-ferrite particles were purified by several cycles of centrifugation and decantation.

A schematic diagram of the synthetic routes of $CoFe_2O_4/SiO_2$ microspheres is shown in Fig. 1. The non-aqueous part of the microemulsion consisted of 5 g of *n*-hexanol (Aldrich), 1.5 g of ethanol and 0.3 g of CTAB (Aldrich). Few droplets of distilled water (maximum 0.5 cm^3) were added to form appropriate emulsion. Furthermore, 3.87 g of TMOS (Aldrich) were pre-hydrolyzed with 3.6 g of 0.03% HNO_3 (Lachema) for 1 h at 40 °C. 1 g of formamide (Merck) with 30 mg of ultrasonically dispersed $CoFe_2O_4$ particles were added, and stirred for 1 h at room temperature. 1.5 g of this mixture was slowly added into stirred nonaqueous part and evenly heated up to 60 °C. Final product was washed with acetone and ethanol, and finally dried at 100 °C.

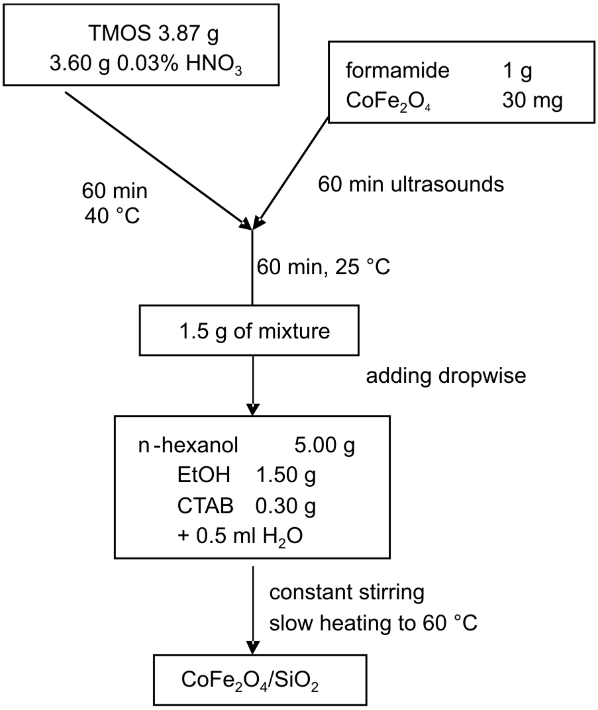

Fig. 1. The preparation scheme

Experimental techniques. Scanning electron microscopy (SEM) investigations were done on a SEM Philips XL 30 CP equipped with EDS (energy dispersive X-ray spectrometry), secondary and back-scattered electron detectors and a Robinson detector. Each powder sample was placed on the holder with an adhesive carbon slice and covered with a thin (<10 nm) Au/Pd layer. Microscale morphology was examined with a high-resolution transmission electron microscope HRTEM JEOL JEM 3010 and a conventional TEM Philips 80 kV. A copper grid coated with a perforated carbon support film was used to prepare samples for the TEM observation. The powdered sample was dispersed in ethanol and placed on the grid.

The powder X-ray diffraction (XRD) measurements were performed on the Seifert diffractometer using CuK_α radiation with a monochromator. The phase analysis was done using the PDIFF database.

Investigation of the magnetic behaviour of the final composite was performed with the PPMS 14T and PPMS 9 T devices (Quantum Design, San Diego). The temperature dependence of magnetization was recorded in the zero-field cooled (ZFC) and field-cooled (FC) regimes in an external magnetic field of 10 mT. The ac susceptibility measurements were done in strictly zero magnetic field conditions for which the amplitude of the ac field was set to 5 mT and the frequency was varied from 10 Hz to 10 kHz.

3. Results and discussion

3.1. Cobalt ferrite nanocrystals

Particles of cobalt ferrite nanocrystals had already been fully characterized earlier [10]. Briefly, the reported characteristics show the average diameter by TEM of 5 nm ($\sigma = 23\%$). Magnetization measured at 10 K is 50 emu/g and the coercive field at 10 K is 9 kOe. The TEM micrographs were made in order to confirm that the desired particle size and morphology had been achieved (Fig. 2).

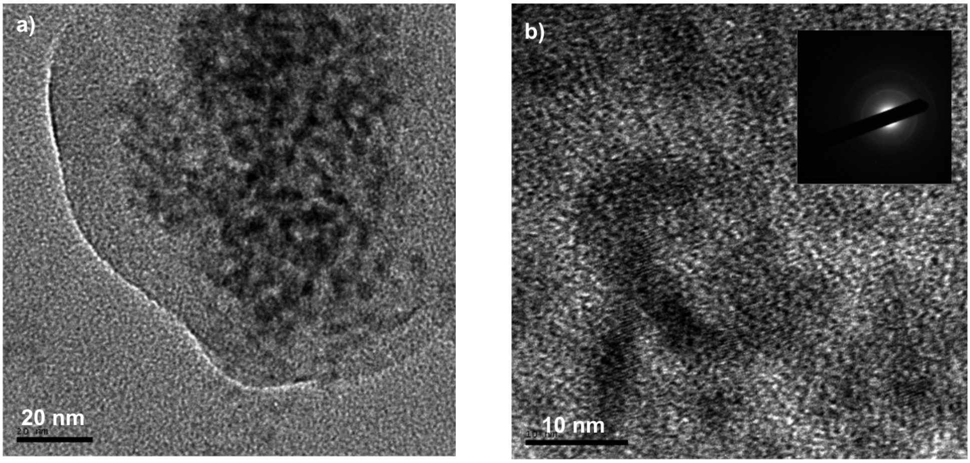

Fig. 2. TEM micrographs of $CoFe_2O_4$ nanocrystals: a) overview; b) details and electron diffraction pattern

3.2. $CoFe_2O_4/SiO_2$ microspheres

The morphology of the final composite microspheres is presented in Fig. 3. The silica particles are of regular spherical shape, as required.

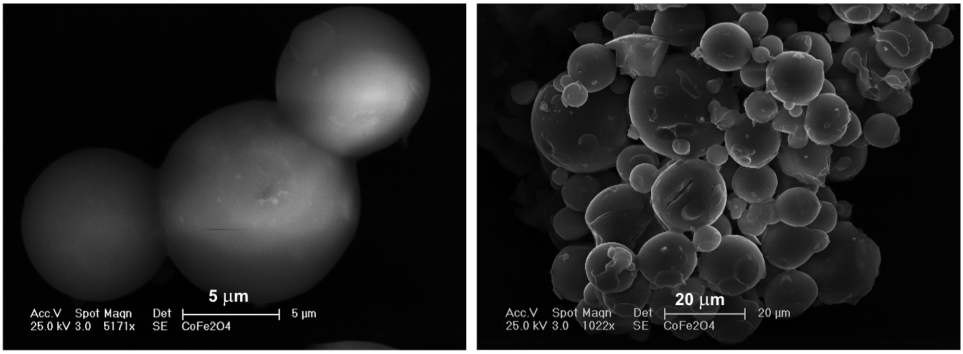

Fig. 3. SEM of the final $CoFe_2O_4/SiO_2$ composite morphology at various magnifications

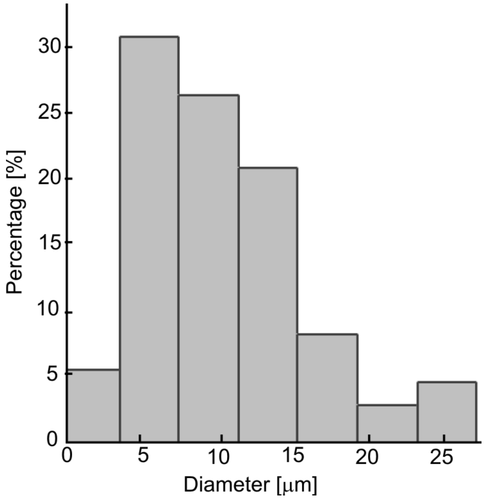

Fig. 4. Size distribution of $CoFe_2O_4$ doped silica spheres
(calculated from SEM micrographs)

The size distribution calculated from the SEM measurements is shown in Fig. 4. The average diameter of the particles of the silica/ferrite composite was determined as 11.04 ± 7.7 μm. The size of the silica spheres is determined by the volume of the hydrophilic microdroplets of the microemulsion at ca. 60 °C, where silicon dioxide gel is formed from the pre-hydrolyzed TMOS.

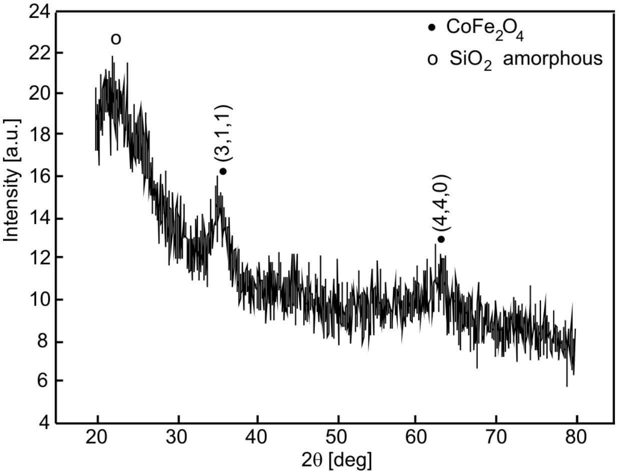

Fig. 5. Powder X-ray diffraction pattern of the final product. The two reflections above 30°
are attributed to the Co ferrite nanoparticles, the broad maximum at around 25°
corresponds to the contribution of the amorphous silica microspheres

The powder XRD measurements, shown in Fig. 5 proved the presence of the $CoFe_2O_4$ with the spinel structure, as demonstrated by the two strongest reflections in the XRD pattern (PDF 22-1086), and amorphous silica, which contribute as a broad maximum at around 25°. The Co-ferrite related reflections are very broad and of low intensity, which points to a very small particle size.

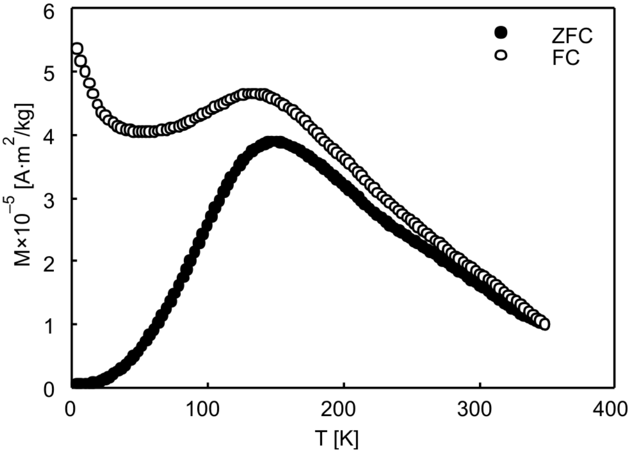

Fig. 6. Temperature dependence of the zero field cooled (ZFC) and field-cooled (FC) magnetization of SiO_2 microspheres doped with $CoFe_2O_4$measured at 10 mT

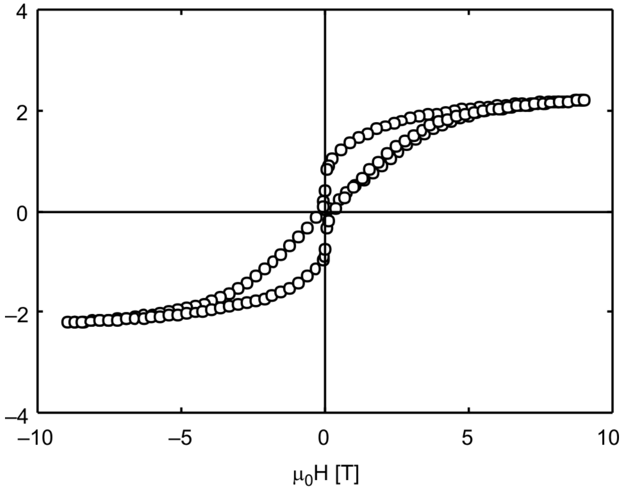

Fig. 7. Hysteresis loop of silica microspeheres doped with $CoFe_2O_4$ recorded at 2 K

Comprehensive investigations by means of magnetization and ac susceptibility measurements were performed in the temperature range 2–350 K. The temperature dependence of the ZFC and FC magnetization is shown in Fig. 6. The ZFC curve exhibits a broad maximum at ca. 150 K, which can be attributed to the blocking temperature, TB, of small Co-ferrite nanocrystals. The FC curve shows a similar maximum at a slightly lower temperature, and indicates an additional paramagnetic-like contribution at lower temperatures. The enhanced values on FC curve can be caused by the presence of particles below 2 nm, which do not interact with each other and follow the pure SPM trend. On the other hand, both curves correspond to slightly higher values than the proposed T_B level, which can be explained either by particle size distribution or rather by weak interparticle interactions between the majority particles of larger size, mediated by dipolar forces [13, 14].

The Co-ferrite particle diameter (R) of the majority fraction was estimated from the blocking temperature using the formula derived for a pure SPM system of non-interacting superspins: $V = 25k_BT_B/K_1$ and $R = (3V/4\pi)^{1/3}$, where V is the volume of one particle, K_1 is the first order anisotropy constant of the bulk Co-ferrite, k_B is the Boltzman constant and T_B is the blocking temperature. The estimated particle diameter was $R = (3.4 \pm 0.2)$ nm.

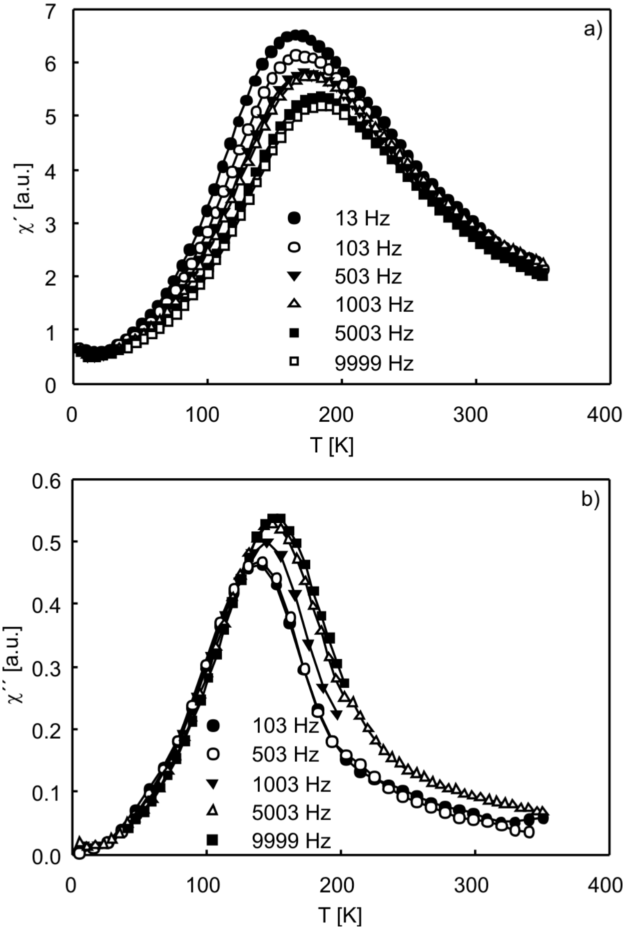

Fig. 8. Temperature dependence of the real χ' and imaginary χ'' parts of the ac susceptibility of silica microspeheres doped with $CoFe_2O_4$

The presence of hysteresis and remanence below the TB level was investigated by taking hysteresis loop measurements at 2 K (Fig. 7). The tapering of the loop in a magnetic field close to zero can be explained by the presence of a small proportion of small particles, as already suggested in the discussion of the temperature dependence of the ZFC/FC magnetization, which does not cause any hysteresis. The saturated magnetization at 2 K reaches ca. $2\cdot10^{-3}$ $\mathrm{A\cdot m^2/kg}$ calculated relative to the total mass of the composite).

The dynamic properties of the system were examined by taking ac susceptibility measurements, and they are shown in Fig. 8. The character of the real and imaginary part of the ac susceptibility reflects the expected SPM behaviour, demonstrated by the frequency-dependent maximum at T_B at the corresponding frequency (T_f).

A useful criterion for classifying the observed freezing process is the empirical parameter Φ, which represents the relative shift of the blocking temperature per the frequency decade: $\Phi = \Delta T_f/[T_f \Delta \log 10(f)]$, where ΔT_f is the difference between the blocking temperature measured in the $\Delta\log 10 f$. We obtained the value $\Phi = 0.04$, which is slightly lower than the 0.1 value expected for a superparamagnetic (SPM) system. Smaller values of Φ are usually caused by the spin-glass-like behaviour of the nanoparticle surface, or are simply due to non-negligible interparticle interactions, which corroborate the interpretation of the magnetization measurements. The Arrhenius plot of the ac susceptibility data, namely $\ln(1/f)$ vs. $1/T_B$, revealed an almost linear dependence, however, the obtained values are unrealistic fit, probably due to the dipolar phenomena proposed above.

4. Conclusion

We reported an easy route for the preparation of silica microspheres doped with cobalt ferrite magnetic nanocrystals. The synthesis was based on the acid-catalyzed sol -gel process in microemulsion. The final product consists of microspheres with average diameter of 11 μm, and very small Co-ferrite nanocrystals, as proved by SEM, HR TEM and XRD analyses. We have further demonstrated a full magnetic characterization of the resulting powder, which revealed that the size of the Co-ferrite nanocrystals is about 3.4 nm and suggested SPM behaviour, disturbed weak interparticle interaction of dipolar origin. Embedded magnetic particles in silica microspheres show different behaviour than pure co-particles 12]. Thanks to the limited concentration of the ferrofluid inside the microemulsion, the magnetic properties seem to be weaker. The composite may be used in the case when magnetic crystals have to be protected by a chemically inert matrix (SiO_2), which can be further functionalized, and simultaneously when manipulation in the micro-scale is required.

Acknowledgements

This work was supported by the project: *New preparation methods of magnetic nanocomposites (spinel ferrites) and study of their physical properties* by the Grant Agency of Czech Republic, GA106/07/0949.

References

[1] MASSART R., IEEE Trans. Magn., 17 (1981), 1247.

[2] POPE E.J.A., MACKENZIE J.D., J. Non-Cryst. Solids, 87 (1986), 185.

[3] CHEN K.C., TSUCHIYA T., MACKENZIE J.D., J. Non-Cryst. Solids, 81 (1986), 227.

[4] ARTAKI I., ZERDA T.W., JONAS J., J. Non-Cryst. Solids, 81 (1986), 381.

[5] MORNET S., GRASSET F., PORTIER J., DUGUET E., Europ. Cells Mater. Vol. 3., Supll. 2 (2002), 110.

[6] MORITAK S.E., TAIRA S., ICHIYANAGI Y., MORONE N., SONG S.-Y., HATANAKA T., YUASA S., SETOU M., J. Nanosci. Nanotechn., 7 (2007), 937.

[7] BORAK B., LASKOWSKI S., HECZKO O., AALTONEN A., BASZCZUK A., JASIORSKI M., SÖDERBERG O., MAZUREK B., OJA M., HANNULA S.-P., MARUZSZEWSKI K., Mater. Sci.-Poland, 25 (2007), 167.

[8] CHENG J., NI X., ZHENG H., LI B., ZHANG X., ZHANG D., Mater. Res. Bull., 41 (2006), 1424.

[9] TAGO T., HATSUTA T., MIYAJIMA K., KISHIDA M., TASHIRO S., WAKABAYASHI K., J. Am. Ceram. Soc., 85 (2002) 2188.

[10] NOUMEN M., PILENI M.P., J. Phys. Chem., 100 (1996), 1867.

[11] FELTIN M., PILENI M.P., Langmuir, 13(1997), 3927.

[12] JOLIVET J.-P., TRONC E., CHANEAC C., Chimie 5 (2002), 1.

[13] DJURBERG C., SVENDLINH P., NORDBLAD P., HANSEN M.F., BØDKER F., MØRUP S., Phys. Rev. Lett., 79 (1997), 51.

[14] DORMANN J.L. , FIORANI D., CHERKAOUI R., TRONC E., LUCARI F., D'ORAZIO F., SPINU L., NOGUES M., KACHKACHI H., JOLIVET J.-P., J. Magn. Magn. Mater., 203 (1999), 23.

Received 2 December 2008
Revised 2 July 2009