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Soluble microcapsules for non-toxic magnetic fluids

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A new preparation technique for stable magnetic fluids containing non-toxic iron oxide nanoparticles in aqueous media originated from salt microcapsules produced by aerosol spray pyrolysis is suggested.

Magnetic iron oxide nanoparticles (MIO) form a base of various 'nanomedicine' magnetic fluids practically applied in hyperthermia,[1] targeted delivery of drugs,[2] protein separation[3] and biological objects labeling.[4] The largest set of MIO preparation techniques is related to a simple 'coprecipitation' reaction resulting in the Fe_3O_4 spinel particles.[5,6] A microemulsion synthesis allows one to prepare MIO with a drastically changed morphology.[7,8] A hydrothermal treatment gives usually well-crystallized particles of a desired shape[9–11] but a few works only can be found on successful preparation of γ-Fe_2O_3 modification.[12] We have developed a scalable and continuous production technique of MIO isolated in water-soluble microspheres.† Such a composite can liberate nanoparticles after long-term storage after contact with water or 'body-simulated-fluid' (BSF) liquids.

Figure 1 represents XRD data‡ of the samples obtained by ASP method at the temperature of furnace hot zone ranged from 550 to 800 °C. Note that, for the samples obtained at 550 and 600 °C, $NaNO_3$ and NaCl phases are present. Increasing the temperature up to 750 °C leads to formation of the hematite phase. Metastable maghemite is formed only at 650–700 °C.

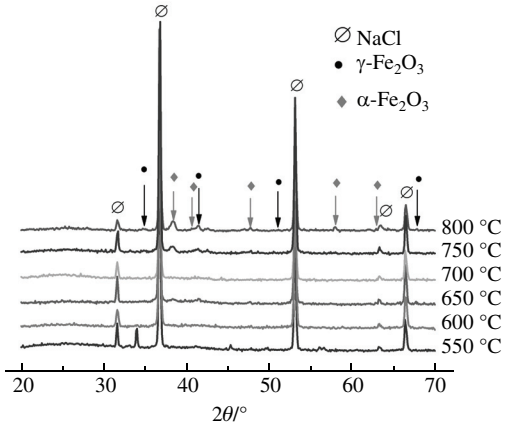

Figure 1 XRD data of the composite of γ-Fe_2O_3 and 10NaCl obtained at different temperatures.

In order to confirm the presence of nanocrystalline γ-Fe_2O_3 in the composites, Mössbauer spectroscopy was applied (Figure 2, Table 1).§ Figure 2 shows low temperature spectra of the sample Fe_2O_3–NaCl obtained by ASP at 650 °C. The spectra correspond to a magnetic oxide with a superparamagnetic behavior. Indeed, lowering temperature gives 'paramagnetic' signals from Fe^{3+} ions (a doublet and a monoline at 300 K), which turn into two sets of hyperfine structure lines (HFS) reflecting the presence of γ-Fe_2O_3 nanoclusters of two characteristic sizes in a magnetically ordered state ($16 < T < 180$ K) denoted in Table 2 as γ-Fe_2O_3(magn.)-1 and γ-Fe_2O_3(magn.)-2, respectively (Table 1).

† Water solution of $Fe(NO_3)_3$ (0.25 M) was used to obtain magnetic iron oxide nanoparticles by aerosol spray pyrolysis (ASP). In a number of samples, urea was added to the solution in order to enhance a combustion procedure in the hot zone of the furnace and yield the formation of a finer fraction of nanoparticles. For incapsulating γ-Fe_2O_3 nanoparticles in a water-soluble salt matrix, sodium chloride was dissolved in a solution containing urea and iron nitrate(III) to achieve the 1 mol γ-Fe_2O_3:10 mol NaCl final ratio. The initial solution was atomized using an ultrasonic nebulizer with a resonant frequency of 1.7 MHz producing 0.5–5 μm solution droplets. The aerosol mist was transferred into a furnace preheated up to 650–900 °C. The inner diameter and the length of a quartz reactor were 20 and 900 mm, respectively. The flow rate of air used as a carrier gas was 10 dm^3 min^{-1}. The final product – water-soluble microspheres containing magnetic nanoparticles – was collected on the furnace outlet at a surface of a microporous glass filter after the mist have been transported and decomposed in the hot zone for 5–7 s. To prepare instantly a stable colloid of magnetic nanoparticles, these microgranules were simply placed in distilled water followed by an ultrasonic treatment for 5–10 min.

‡ Phase analysis was performed by X-ray powder diffraction (XRD) using a DRON-3M diffractometer (CoKα radiation). The size and morphology of magnetic microspheres were observed by transmission electron microscopy (TEM, Hitachi 8100) while dynamic light scattering (DLS, ALV CGS-6010 instrument and a 632.8 nm helium–neon laser as the light source) was used to measure particle size distribution in colloidal solutions. The overall sample morphology was observed using a Leo Supra 50 VP digital scanning microscope.

§ Mössbauer spectra were measured in a temperature range of 16–300 K using a Wissel constant-acceleration spectrometer equipped with a krypton proportional detector, a γ-radiation source of ^{57}Co in a rhodium matrix and a Janis helium cryostat (model CCS-850). Chemical shifts were referred to metallic α-iron. The spectra were fitted using the least square minimization procedure by standard programs. The magnetic properties were analyzed with a vibrating sample magnetometer (VSM, model-155, Digital Measurement System, Inc.).

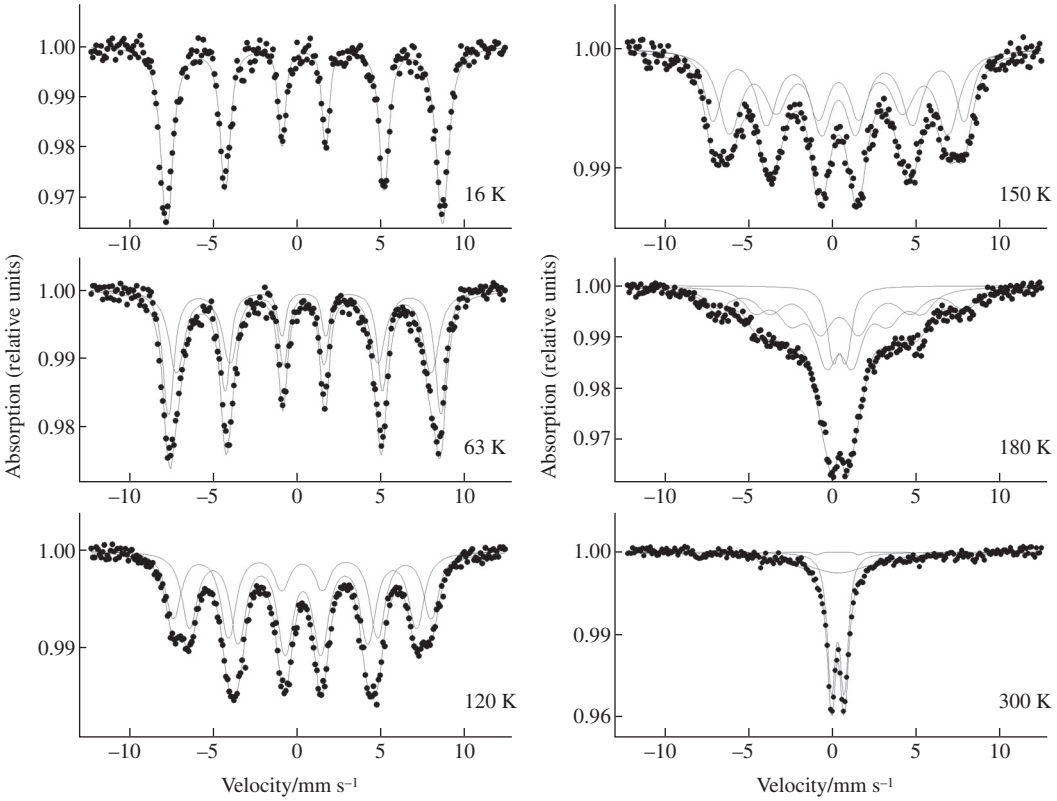

Figure 2 Temperature dependence of Mössbauer spectra of the composite γ-Fe_2O_3–10NaCl obtained by pyrolysis of aerosols at 650 °C.

Note that the state of magnetic saturation for both nanocluster systems 1 and 2 is reached at $T = 16$ K where we can see only a unique HFS pattern. As shown in Figure 2, a magnetic disorder–order transition proceeds *via* intermediate states characterized by line broadening and triangle-like spectra typical of superparamagnetic materials (see, for example, the spectrum at $T = 180$ K). A blocking temperature for the studied systems might be estimated as $T \sim 140$–150 K.

Very small quadrupole shift values in the Mössbauer spectra taken at $16 < T \leq 180$ K (Table 1) are indicative of iron ions occupying highly symmetric sites typical of the γ-Fe_2O_3 spinel structure, which is in a good agreement with the observed XRD data. When analyzing the spectrum at $T = 300$ K, we suppose that the doublet is related to smaller γ-Fe_2O_3 nanoclusters being in a paramagnetic state while the monoline, most likely, answers larger γ-Fe_2O_3 nanoclusters in a state close to magnetic disorder.

Table 1 Mössbauer parameters of the samples Fe_2O_3–10NaCl obtained by ASP at 650 °C [δ is the isomer shift relative to α-Fe, Δ is the quadruple splitting or shift and H_{in} is the internal magnetic field (T)].

Temperature/K	Components	δ	Δ	H_{in}, ±0.5 T	Relative content (%) ±0.05 %
		±0.03 mm s^{-1}			
300	Fe^{3+} (monoline)	0.34	—	—	0.43
	Fe^{3+} (paramagn.)	0.32	0.76	—	0.53
	α-Fe_2O_3 (magn.)	0.30	0.20	51.0	0.04
180	Fe^{3+} (paramagn.)	0.36	0.72	—	0.13
	γ-Fe_2O_3 (magn.)-1	0.36	0.04	44.8	0.45
	γ-Fe_2O_3 (magn.)-2	0.35	0.05	30.6	0.42
150	γ-Fe_2O_3 (magn.)-1	0.37	0.06	46.3	0.46
	γ-Fe_2O_3 (magn.)-2	0.37	0.07	40.2	0.54
120	γ-Fe_2O_3 (magn.)-1	0.38	0.01	47.4	0.42
	γ-Fe_2O_3 (magn.)-2	0.38	0.00	41.6	0.58
90	γ-Fe_2O_3 (magn.)-1	0.41	0.04	48.3	0.42
	γ-Fe_2O_3 (magn.)-2	0.40	0.08	43.0	0.58
63	γ-Fe_2O_3 (magn.)-1	0.42	0.04	50.0	0.45
	γ-Fe_2O_3 (magn.)-2	0.43	–0.02	46.6	0.55
16	γ-Fe_2O_3 (magn.)	0.46	0.04	50.7	1.00

The small sextet observed at $T = 300$ K corresponds most likely to an admixture of magnetically ordered α-Fe_2O_3 clusters. Room temperature Mössbauer spectra of Fe_2O_3–10NaCl samples, obtained by pyrolysis at 650 and 700 °C are very similar and correspond to superparamagnetic γ-Fe_2O_3 above its blocking temperature. Thus, within the applied pyrolysis temperature range of 650–700 °C, the local structure of the samples suffers no significant changes.

Figure 3 shows the TEM images of hollow 0.5–2.0 μm salt microgranules formed at 650 °C from initial submicron solution droplets and loaded with magnetic nanoparticles. The microspheres are nanostructured and consist of ~20–50 nm nanoparticles building their shells. It should be noted that the morphology of the composite is dependent on the concentration of initial spray solution, flow velocity and furnace temperature.[13,14]

Magnetization curves of the samples at 8 and 300 K are shown in Figure 4. The samples demonstrate clearly a behavior typical of superparamagnetic nanoparticles and this agrees well with the above Mössbauer data. At the lowest temperatures, the total magnetic moment is small due to freezing the separate nanoparticle moments in random directions. An increase of temperature leads to a growth of the total magnetic moment due to the alignment of moments in the field direction.

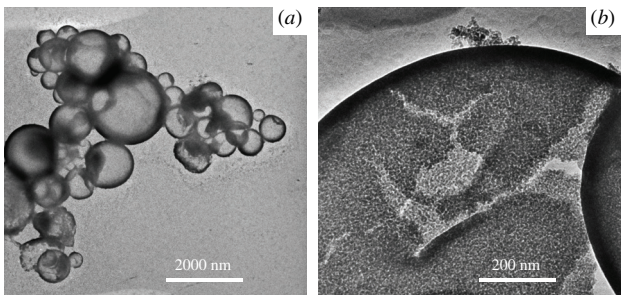

Figure 3 TEM images of the composite obtained by ASP method at 650 °C, (*a*) general and (*b*) magnified views.

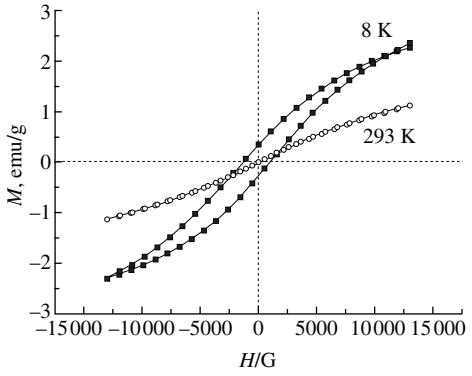

Figure 4 Field dependence of magnetization at 8 and 293 K for the sample γ-Fe_2O_3–10NaCl, obtained at 650 °C.

Dissolution of the nanocomposite in water leads to formation of a stable water suspension of magnetic nanoparticles especially enhanced with an ultrasonic treatment for disaggregation of the nanocomposite microspheres after their storage in a dry state. It gives nanoparticles of ~40 nm in diameter, as seen in Figure 5, together with a larger fraction that could be simply filtered. The observed size of the nanoparticles is close to that found by TEM (Figure 3). The obtained colloidal solution of magnetic nanoparticles is stable at least for 10 h.

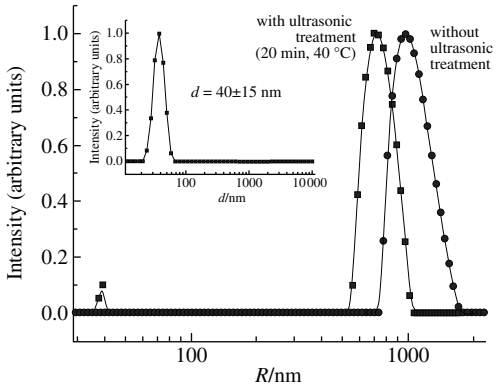

Figure 5 DLS data for the sample Fe_2O_3–10NaCl obtained by the ASP method at 650 °C and then dissolved in distilled water. Inset shows DLS data of a fraction of 40 nm particles obtained after filtering the dissolved nanocomposite using a 200 nm filter.

In conclusion, the application of ultrasonic aerosol spray pyrolysis allowed us to obtain incapsulated magnetic nanoparticles of γ-Fe_2O_3. The obtained brownish dust consisted of hollow water-soluble microspheres of 0.1–2 μm in diameter containing 20–50 nm nanoparticles of γ-Fe_2O_3 formed in a narrow hot zone temperature range around 650 °C. The method suggested could be considered as a suitable way of preparation and storage of magnetic nanoparticles for medical applications.

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