PREPARATION AND CHARACTERISATION OF MAGHEMITE–CM-DEXTRAN NANOCOMPOSITES

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Introduction

Nanotechnology has, in the past decade, quickly developed and become an important aspect in the field of biomedicine [1]. Among the various magnetic materials, ferromagnetic iron oxides, for example, maghemite and magnetite nanoparticles (MNPs) with a diameter of about 5–10 nm, have attracted great attention. Their applications in biomedicine, such as cellular therapy in cell labeling, separation and purification, protein immobilization, contrast enhancement in magnetic resonance imaging and localized magnetic hyperthermia [2], have become more and more important in recent years. For the application of these MNPs in biomedicine they must possess superparamagnetism, a high saturation magnetization and biocompatibility. Superparamagnetic particles, which do not exhibit any magnetism after the removal of an external magnetic field, are of particular interest to researchers [3]. On the other hand, van der Waals forces and magnetic dipole forces among NMPs lead to an intensive aggregation in ferrofluids (FFs) [4]. Therefore, the surface modification of nanoparticles is very important, and the particle surface should be modified using inorganic or organic coatings. Nevertheless, although the application of MNPs has increased in recent years for both in-vitro and in-vivo diagnostics, studies on the surface modification of MNPs remain important. The coating of MNPs with polymers prevents the particles from aggregating, enhances the compatibility between nanoparticles and the aqueous medium, diminishes the toxicity, etc. Polymers that can be applied for coatings are both natural and synthetic. Among them is CM-dextran polysaharide, with outstanding properties; for instance, it is biodegradable, biocompatible and bioactive, and is therefore commonly used in the stabilization of FFs. In this paper, we describe how superparamagnetic MNPs were prepared by co-precipitation and then surface coated with covalently bounded CM-dextran.

Experimental

To the solution containing Fe^{2+} and Fe^{3+} the ammoniac was added. The solution turns from red brown color to black indicating the formation of magnetite which than oxidizes to maghemite. After that the solution of CM-dextran was added. The suspension was magnetically decanted, the particles re-dispersed in water and centifugated to sediment the agglomerates. Then the suspension was ultra filtrated in order to remove the excess of the CM - dextran. The nanoparticles were characterized using x-ray diffraction analyses and electron microscopy (TEM) (JEOL 2010F). The particle size was established using the Scherer formula. The concentration of CM- dextran adsorbed on the magnetic particles was determined using a thermo-gravimetric analysis, while the magnetizations of the samples were measured using a Quantum Design SQUID magnetometer.

Results and Discussion

Typical TEM images of CM-dextran-coated maghemite nanoparticles are shown in Fig. 1. The particle shape is more or less spherical. The average particle diameter, estimated from the TEM images, is 13.4 nm, in good agreement with the average particle diameter calculated from XRD profile using the Sheerer equation.

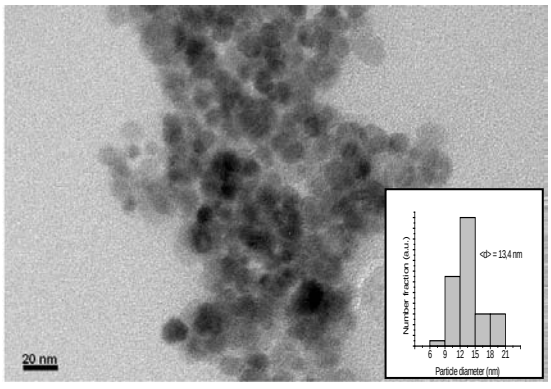

Fig. 1 TEM images of CM-dextran-stabilized maghemite particles and the grain size distribution

The distinctive weight losses established for the magnetic particles covered with CM-dextran can be divided into two temperature regions: 170–460°C and 460–750°C, Fig.2. A total weight loss of 24 % occurred during the thermal heating from room temperature to 1000°C. In the first temperature range, from 170°C to 460°C, the oxidation of t he dextran occurs, as indicated by

an exothermic DTA peak and a weight loss of 19 %. The exothermic peak associated with this mass loss is the result of the oxidation of the dextran molecules due to the temperature, which is consistent with the literature data on free polysaharides at 230–400^{o}C [5]. The last step is associated with an endothermic peak at 800^{0}C and a weight loss of 5%. This endothermic peak is associated with the removal of the CM-dextran covalently bound to the particle surface, i.e., the very first covalent bound layer of CM-dextran to the particle surface. An exothermic reaction takes place when oxidation occurs, while the endothermic peak reaction appears when the decomposition occurs.

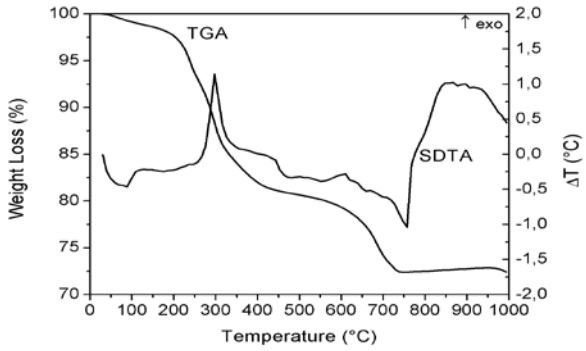

Fig 2 Thermal analysis (TGA) of maghemite nanoparticles coated with CM-dextran and the corresponding (SDTA).

It is well known that dextran dissolved in water is in equilibrium with that attached physically to the magnetic particles. Namely, after the very first layer of the dextran, which is covalently bound to the particle surface, further, subsequent layers are attached by physical bonds, where hydrogen bonding prevails. In the water suspension this dextran is in equilibrium with that in the suspension [5]. From the amount of the CM-dextran deposited on the particles determined from TGA one can estimate the dextran layer thickness of 5.7 nm. Here, the average particle size of the particles was taken as 13.4 nm and the density of the dextran as 1.5 g/cm^3 [6]. The magnetizations vs the magnetic field for the as-synthesized and CM-dextran-covered maghemite particles are shown in fig. 3. Both samples show no hysteresis with no coercivity and behave as super-paramagnets Fig.4. The uncoated particles exhibit a saturation magnetization of 64 emu/g. This value is smaller than that for the bulk materials M_{bulk} = 88 emu/g. The reduction of the magnetization of the magnetic particles with the decreasing particle size is usually caused by the incomplete coordination of the atoms on the particle surface, leading to a non-collinear

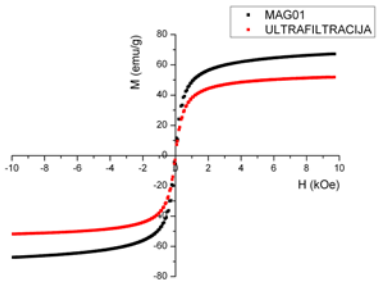

Fig. 3 Hysteresis of as–synthesized maghemite samples (Mag01) and CM-dextran-coated particles (ULTR.FILTR.) at 300K

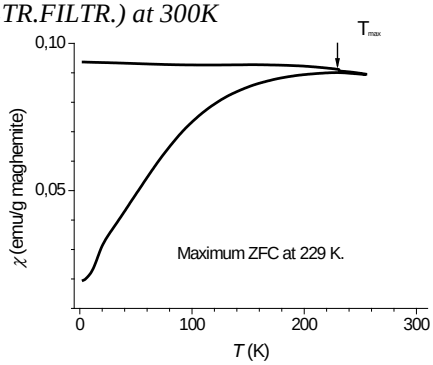

Fig.4 ZFC and FC magnetization of coated maghemite particles in the FF, T_B = 220 K

spin configuration, which causes the formation of a surface spin canting nonmagnetic layer, i.e., a "dead" layer, which might reduce the particle's magnetization. The results of the investigation revealed that the synthesized NMPs exhibit all the required magnetic properties necessary for the application of magnetic particles for in-vitro applications in biomedicine. Of particular importance is the fact that a part of the dextran is bound to the maghemite surface by a covalent bond and so could be not removed by rinsing in water media.

References

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