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Water based suspensions of iron oxide obtained by laser target evaporation for biomedical applications

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ABSTRACT

In this work spherical magnetic nanoparticles (MNPs) of iron oxide were obtained by laser target evaporation technique (LTE). Water based suspensions were prepared on the basis of obtained MNPs and their properties were also studied including inductive heat capacity. Their structure and properties were studied by a number of techniques including magnetometry and heat capacity measurements. Magnetic induction heating experiment show the specific loss power (SLP) value in the narrow range from 1.30 to 1.45 W/g for all samples under consideration when using alternating magnetic field of 1.7 kA/m and frequency of 210 kHz. These parameters insure that LTE MNPs are interesting materials promising for magnetic fluid hyperthermia.

1. Introduction

Recently magnetic nanoparticles (MNPs) become a subject of special interest because some of them exhibit unique and advantageous properties suitable for a large variety of applications including biomedicine area [1,2]. Magnetite (Fe_3O_4) and maghemite (Fe_2O_3) are among the most versatile magnetic materials suitable for very different applications. Slightly lower bulk saturation magnetization of maghemite is compensated by its longer term stability comparing with magnetite MNPs. Even so Fe_3O_4 is one of the most studied ferromagnetic materials relatively stable under ambient conditions, having a high saturation magnetization and Curie temperature well above the room temperature. It has a relatively weak magneto-crystalline anisotropy and shows characteristic superparamagnetic behavior in the nanoscale [3,4]. The attraction of magnetite is based firstly on its officially approved biocompatibility [1]. MNPs of the iron oxides are employed in biosensing, magnetic separation, medical screening and therapies, bio-assays, magnetic resonance imaging, magnetically addressed drug delivery and hyperthermia [5–7]. Hyperthermia is a form of cancer therapy based on the property of tumor cells to have higher temperature sensitivity in the range of 42–45 °C than normal cells. The base of such a difference is the distinction of the functions of many cell proteins which can be altered in cells [8]. Hyperthermia performed in the range of 41–46 °C to stimulate the immune response for non-specific immunotherapy and thermoablation using the temperature range of 46–56 °C for tumor destruction are currently distinguished. The characteristic temperature of tumor cell thermoablation is very close to that of normal cell, i.e. temperature control is very important. MNPs in hyperthermia play a role of mediators converting the electromagnetic energy into heat under application of electric/magnetic field. Inductive hyperthermia with MNPs injection seems currently most useful option because body tissues susceptibility is very low [9].

There are different aspects related to MNPs for hyperthermia applications: big size of the batch is very important, the ability to form water based stable ferrofluids and others [3,6,9]. Electrophysical methods such as electric explosion of wire and laser target evaporation (LTE) are highly productive techniques providing enhanced batch sizes [6,10]. For LTE iron oxide MNPs high production rate of about 50 g/h can be achieved [6].

In many studies devoted to the hyperthermia development the working frequencies were selected in the MHz range. The lowering of the operational frequency is desired. Therefore, study of the features of the high frequency magnetization of iron oxide MNPs for the kHz frequency range of alternating magnetic field and verification of the ability to heat up the ferrofluid is an important task.

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In this work, magnetic LTE nanoparticles and ferrofluids on their basis were fabricated and carefully characterized including induction heating in relatively weak alternating magnetic field of the 210 kHz in order to estimate the perspectives of their possible applications for hyperthermia.

2. Experimental methods

Series of the MNPs were prepared by LTE method using different parameters: type of the working gas, pressure in the preparation chamber, laser pulse frequency. The laboratory setup provided synthesis of iron oxide MNPs with the production rate of about 50 g/h [6]. The target pellet pressed from Fe_3O_4 micron-sized magnetite powder purchased from Alfa Aesar manufacturer was used. Laser beam (optical system Optoscand d25 f60/200) was focused onto the target, positioned in the hermetic chamber. A driving mechanism rotated the target to ensure a uniform wear-out of the pellet surface and scan rate on the target surface of 20 cm/s. Different stoichiometry of obtained iron oxide MNPs was obtained as a result of variation of the pressure of the working gas (either air or argon) and the pulse duration (more technological details is given in Refs. [10,11]). Following conditions were used: S1–540 mm Hg, 100 μs, S2–730 mm Hg, 50 μs and S3–540 mm Hg, 50 μs. Structure of obtained MNPs was studied by X-ray diffraction (XRD) with DISCOVER D8 Bruker apparatus using Cu-Kα radiation. TOPAS program provided accurate fit for the full profile, identification of the Miller indices of the peaks and determination of the MNPs phase composition. The average size of coherent diffraction domains was estimated using the Scherrer approach [12].

Ferrofluids (FF), i.e. stable de-aggregated suspensions of iron oxide MNPs were prepared on the basis of a distilled water. MNPs were electrostatically stabilized by adsorbed sodium citrate ions with 5 mM concentration and de-aggregated by ultrasonic treatment on Cole Parmer CPX-750 ultrasound processor at 300 W average power output levels. Activator diameter of 13 mm was immersed in a container with a suspension, which was equipped with a cooling water flow. Ultrasound treatment was carried out up to stable numbers of the measured parameters. Average hydrodynamic diameter of aggregates in suspension was monitored by the dynamic light scattering (DSL) and electrokinetic zeta potential was measured by electrophoretic light scattering (ELS) on Brookhaven Zeta Plus analyzer. Particle size distribution was calculated from transmission electron microscopy (TEM) images using a set of about 2000 particles. TEM was performed by a JEOL JEM 2100 microscope operating at 200 kV.

Magnetic measurements – dependencies of magnetization on the magnetic field strength $M(H)$ and thermomagnetic curves zero field cooled – field cooled (ZFC-FC) [6] were done by MPMS XL7 SQUID measurement system at the temperature range 5–300 K, field range $H = \pm 5.12 \times 10^6$ A/m for $M(H)$ and 5–300 K, $H = 8$ kA/m for ZFC-FC curves. Samples for magnetic measurements were fixed in polycarbonate capsule. Ferrofluids were dried prior to the sample preparation for all types of magnetic measurements.

Investigations of magnetic losses were carried out by direct calorimetric method using laboratory setup based on Calvet calorimeter with a solenoid incorporated inside the working cell which produced an alternating magnetic field of 1.7 kA/m strength and frequency of 210 kHz. The specific loss power (SLP) of magnetic material as a result of the induction heating was calculated by the formula:

$$\mathrm{SLP}=\frac{k\cdot\Delta}{m},$$

where k is calorimeter constant, Δ is calorimeter signal (mV), m is mass of the sample.

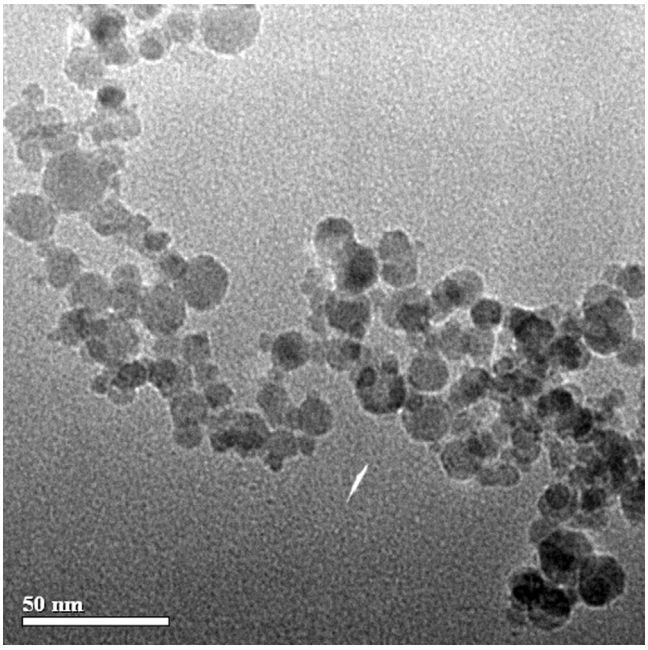

Fig. 1. Transmission electron microscopy (TEM) image of S1 MNPs.

3. Results and discussion

Fig. 1 shows TEM image of MNPs evidencing spherical shape. MNPs are not agglomerated, the size distribution is not wide and it obeys lognormal function (Fig. 2). Sample description and some selected parameters for MNPs and FF based on them are shown in Table 1.

Comparison of the values of weighted average diameters obtained by TEM (D_{TEM}) [10] and by XRD (D_{XRD}) [11] showed that they were reasonably close to each other. The experimental XRD data were well fitted by the magnetite database but exact chemical composition of MNPs was determined by the combination of redox titration and the lattice period analysis provided by XRD [6]. The lattice period (a) of LTE MNPs was substantially lower that of stoichiometric magnetite but higher that the lattice period of γ-Fe_2O_3: $a = 8.358(5)$ Å. It is lower than typical value for the magnetite $a = 8.396$ Å. Data in the Table 1 for chemical composition are reasonably close to the stoichiometric maghemite. MNPs demonstrated good ability to form a stable suspension when

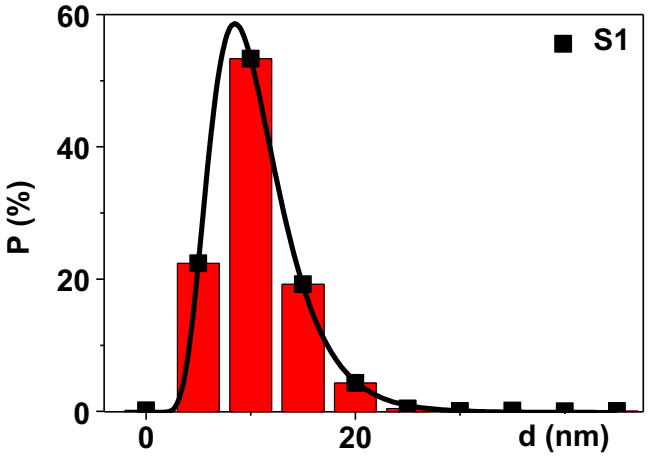

Fig. 2. Square points-S1 MNPs size distribution calculated from TEM images (set 2000 NP), black line-fitting curve with lognormal function, red columns – histogram of size distribution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)