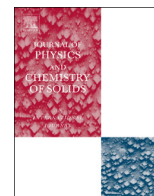




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Size-dependent magnetic properties of iron oxide nanoparticles

Vitalii Patsula^a, Maksym Moskvina^a, Silvio Dutz^{b,c}, Daniel Horák^{a,*}^a Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic^b Institute of Biomedical Engineering and Informatics (BMTI), Technische Universität Ilmenau, Gustav-Kirchhoff-Straße 2, 98693 Ilmenau, Germany^c Department of Nano Biophotonics, Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Straße 9, 07745 Jena, Germany

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ABSTRACT

Uniform iron oxide nanoparticles in the size range from 10 to 24 nm and polydisperse 14 nm iron oxide particles were prepared by thermal decomposition of Fe(III) carboxylates in the presence of oleic acid and co-precipitation of Fe(II) and Fe(III) chlorides by ammonium hydroxide followed by oxidation, respectively. While the first method produced hydrophobic oleic acid coated particles, the second one formed hydrophilic, but uncoated, nanoparticles. To make the iron oxide particles water dispersible and colloidally stable, their surface was modified with poly(ethylene glycol) and sucrose, respectively. Size and size distribution of the nanoparticles was determined by transmission electron microscopy, dynamic light scattering and X-ray diffraction. Surface of the PEG-functionalized and sucrose-modified iron oxide particles was characterized by Fourier transform infrared (FT-IR) and Raman spectroscopy and thermogravimetric analysis (TGA). Magnetic properties were measured by means of vibration sample magnetometry and specific absorption rate in alternating magnetic fields was determined calorimetrically. It was found, that larger ferrimagnetic particles showed higher heating performance than smaller superparamagnetic ones. In the transition range between superparamagnetism and ferrimagnetism, samples with a broader size distribution provided higher heating power than narrow size distributed particles of comparable mean size. Here presented particles showed promising properties for a possible application in magnetic hyperthermia.

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1. Introduction

In the last two decades, huge effort was devoted to the development and characterization of new nanomaterials with unique optical, magnetic, electrical, or other properties. Such materials have the potential to be used in electronics, optics, aerospace, medicine, fuel cells, as well as energy generation and storage [1,2]. Biomedicine and biotechnology take advantage of nanomaterials due to their small size that allows them to interact with biological systems at the molecular level [3]. Among a variety of nanomaterials investigated for biomedical applications, magnetic nanoparticles play a prominent role in areas such as magnetic separation [4], biosensors [5], contrast agents for magnetic resonance imaging [6–8] and magnetic particle imaging, drug delivery [9,10], tissue repair [11] and hyperthermia [12,13].

Hyperthermia is a minimally invasive procedure which destroys cancer cells by heat generated in alternating magnetic fields due to magnetization reversal losses of magnetic nanoparticles applied to a tumor. Different thermotolerance between tumor and

healthy tissue cells enhances sensitivity of the cancer cells to a simultaneous chemotherapy or radiotherapy [4]. The first application of magnetic iron oxide nanoparticles (20–100 nm) in hyperthermia was described already five decades ago [14]. Since that time many metal [15] and metal oxide [16,17] particles were suggested for hyperthermia using different magnetic field strengths and frequencies. However, iron oxide particles (magnetite $\gamma\text{-Fe}_2\text{O}_3$ and magnetite Fe_3O_4) are still considered as the best candidates for the biomedical applications since they exhibit minimum toxic effects [18]. Nevertheless, the mechanism of heat generation by the nanoparticles is still not fully understood [19] since the heat can be affected by viscosity, susceptibility and hysteresis losses, etc. [20]. In the superparamagnetic particles, the heat is induced by susceptibility losses having two relaxation times, i.e., Néel relaxation (τ_N) and Brownian rotation (τ_B) [4]. Both relaxation times differ in their dependence on the nanoparticle size. The susceptibility loss of particles of the identical size induced by the Brownian rotation is higher at low frequencies of alternating magnetic field than that due to Néel relaxation. The second mechanism addresses magnetic hysteresis losses which occurs for larger ferrimagnetic particles with a magnetic anisotropy [21].

Biomedical applications of the magnetic nanoparticles require

* Corresponding author.

E-mail address: horak@imc.cas.cz (D. Horák).

tailored particle morphology and size, narrow particle size distribution, specific surface chemistry and high saturation magnetization. This primarily depends on the selection of a proper synthesis method, which can include co-precipitation [22], spray pyrolysis [23], thermal decomposition, and hydrothermal [24] or sol-gel [25] approaches. Moreover, selection of appropriate coating of the particles is crucial, because it ensures colloidal stability and targeting, prolongs circulation in blood stream, determines interactions with different cells, and influences nanoparticle distribution in the living tissues. The particle surface can be modified by physical adsorption or chemical immobilization of various substances, e.g., dopamine [26], ascorbic acid [27], peptides [28] and others [29,30].

Aim of present study was to compare magnetic properties of differently sized poly(ethylene glycol)-coated iron oxide (PEG-IO) particles obtained by thermal decomposition with those of sucrose-coated nanoparticles (SC-IO) synthesized by co-precipitation in terms of their prospective application as heat mediators for hyperthermia.

2. Experimental

2.1. Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (95%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (98%), sodium hydroxide (98.9%), octadec-1-ene (OD; 99%), icosane (IS; 99%), trioctylamine (TOA; 98%), trimethyl phosphite (99%), mandelic acid (99%), and sodium oleate were purchased from Sigma-Aldrich and used as received. Ethanol (95%) and oleic acid (OA; 95%) were from Lachema. Hydrochloric acid (37%), ammonium hydroxide (25%) and hydrogen peroxide (35%), as well as crystalline sucrose (SC), were obtained from Lach-Ner. α -Methyl- ω -bromo poly(ethylene glycol) (Br-PEG, $M_w = 750$ Da) was from Rapp Polymere. All other reagent grade chemicals were purchased from Sigma-Aldrich and used as received. Ultrapure Q-water ultrafiltered from a Millipore-Q Gradient A10 system was used throughout the experiments.

Phosphonic acid-terminated methyl-PEG (PA-PEG) was synthesized according to the following procedure. Trimethyl phosphite (0.47 ml; 4 mmol) was added to Br-PEG (1 g; 1.33 mmol) at 80 °C under magnetic stirring, the reaction mixture was heated at 130 °C for 10 h and the residual trimethyl phosphite was removed at 90 °C by vacuum distillation (3 kPa). Dimethyl ester of PA-PEG was hydrolyzed in 10% HCl (10 ml) for 4 h under reflux. Finally, NaHCO_3 (5 wt%) aqueous solution was added to the reaction mixture to reach pH 4 and the resulting PA-PEG was extracted three times with dichloromethane (8 ml each). Volume of the organic phase was reduced to 20% using a vacuum evaporator and added to petroleum ether at 0 °C to precipitate PA-PEG. The product was filtered-off and vacuum-dried for 6 h over phosphorus pentoxide.

Fe(III) oleate and mandelate were prepared following a standard procedure [31]. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10.8 g; 40 mmol) and sodium oleate (36.5 g; 120 mmol) were dissolved in an ethanol/water/hexane (80/60/140 v/v/v) mixture (280 ml), which was heated at 70 °C for 4 h under magnetic stirring. Organic layer was separated and washed three times with water (30 ml each). Volatile substances were removed using a rotary evaporator under formation of waxy-like Fe(III) oleate. Alternatively, mandelic acid (18.54 g; 122 mmol) was added to a solution of sodium hydroxide (4.88 g; 122 mmol) in methanol (120 ml), the mixture was stirred for 15 min, a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (11 g; 40.7 mmol) in methanol (50 ml) was added, and the mixture refluxed for 4 h. After completion of the reaction, the mixture was filtered and methanol was removed at 60 °C using a rotary evaporator. The resulting Fe(III) mandelate was dissolved in acetone (100 ml), NaCl was

filtered off and the product vacuum-dried at room temperature for 6 h.

2.2. Synthesis of PEG-IO nanoparticles

Monodisperse iron oxide nanoparticles (10 or 14 nm) were prepared at 320 °C in OD or at 345 °C in IS (both 25 ml) by thermal decomposition of Fe(III) oleate (8 mmol) in the presence of OA (0.3 mmol/ml). The 24 nm particles were obtained at 365 °C by the decomposition of Fe(III) mandelate in a solution of OA (0.3 mmol/ml) in TOA (25 ml). After cooling to room temperature, ethanol (100 ml) was added to the reaction mixture and the particles were separated using a magnet. The nanoparticles were ten times washed with ethanol (100 ml each) to remove any residual solvent and OA, and, finally, dispersed in toluene and stored.

Surface of the hydrophobic iron oxide nanoparticles was functionalized with PEG via a ligand exchange. To a dispersion of the nanoparticles (10 mg) in tetrachloromethane/toluene (1:1 v/v; 10 ml), PA-PEG (70 mg) was added, the mixture sonicated at 100 W (UP200S Hielscher Ultrasound Technology; Teltow, Germany) for 5 min and then stirred (400 rpm) at 70 °C for 48 h. The resulting PEG-IO particles were three times washed with diethyl ether (50 ml each), three times with petroleum ether (50 ml each), vacuum-dried (150 Pa) for 6 h, and, finally, redispersed in water to reach concentration 4.4 mg/ml.

2.3. Synthesis of SC-IO nanoparticles

Aqueous solutions of 0.3 M FeCl_3 (135.5 ml) and 1 M FeCl_2 (20.33 ml) were charged in a 500-ml glass reactor equipped with a mechanical turbine impeller and the mixture was heated to 70 °C with stirring (600 rpm). 25% NH_4OH solution (30.66 ml) was added, iron oxide precipitated and the reaction mixture heated to 90 °C for 1 h with stirring. After cooling to room temperature, pH of the reaction medium was adjusted from 10–11 to 5–6 by addition of 37% HCl (20 ml). To obtain chemically stable samples, the particles were oxidized (to transform possibly formed Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$) by adding 35% H_2O_2 (5 ml) under slow heating from 20 to 90 °C for 1 h with stirring (550 rpm) since maghemite is the magnetic iron oxide with the highest thermodynamic stability. The nanoparticles were then three times washed with water (100 ml each) via magnetic separation. Finally, the resulting particles were dispersed in water (100 ml) under sonication (240 W; Bandeline Electronics; Berlin, Germany) for 10 min. Concentration of the particles was 45 mg/ml.

Coating of the iron oxide particles with sucrose was performed by adsorption. For this, aqueous iron oxide colloid (2.22 ml; 45 mg iron oxide/ml) was diluted with water to 15 ml, charged in a 25-ml glass reactor equipped with a mechanical turbine impeller and the mixture was heated to 50 °C with stirring (670 rpm). After dropwise addition of aqueous sucrose solution (5 ml; 20 mg/ml), the reaction proceeded for 2 h with stirring (500 rpm). The resulting SC-IO nanoparticles were washed three times with water (50 ml each), magnetically separated and redispersed in water (20 ml) under sonication at 190 W for 2 min to reach concentration 4.5 mg/ml.

2.4. Nanoparticle characterization

Dispersion of magnetic iron oxide nanoparticles in water was investigated in a Tecnai Spirit G^2 transmission electron microscope (TEM; FEI). Number-average diameter ($D_n = \sum D_i / N$, D_i is diameter of i -th particle and N is total number of the particles), weight-average diameter ($D_w = \sum D_i^4 / \sum D_i^3$) and polydispersity index ($\text{PDI} = D_w / D_n$) were calculated from the micrographs by counting minimum 900 individual particles using Atlas software (Tescan

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