

# Structural and Magnetic Characterization of Functional Surface Coated Maghemite Nanoparticles

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A. Ślawska-Waniewska<sup>1</sup>, P. Dłużewski<sup>1</sup>, M. Bilka<sup>1</sup> and S. Ubizskii<sup>2</sup>

**Abstract.** Nanoparticles composed of magnetic  $\gamma\text{-Fe}_2\text{O}_3$  core and organic shell were synthesized via template synthesis in the presence of functional oligoperoxide surfactants and further graft-polymerization initiated from their surface. X-ray diffraction (XRD), transmission electron microscopy (TEM) and magnetic measurements (PPMS) were used to characterize the obtained magnetic system of core-shell nanoparticles. XRD results confirm the existence of  $\gamma\text{-Fe}_2\text{O}_3$  phase as well as show an average diameter of nanoparticles around 10 nm. The obtained particles are superparamagnetic at the room temperature. Magnetic measurements indicate also sufficiently strong dipolar interparticle interactions at low temperatures.

**Key words:** core-shell  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles, dipolar interparticle interactions.

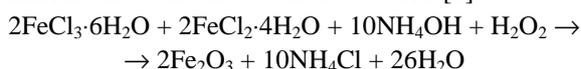
## I. INTRODUCTION

During the last decade superparamagnetic nanoparticles consisting of magnetic core and polymeric shell have been at the focus of a remarkable research interest due to a wide variety of interesting magnetic properties. In addition magnetic nanoparticles based on maghemite or magnetite phases, have a great application potential in the biotechnology and medicine provided by their biocompatibility, in part for biochemical and clinical applications as carriers for drug and gene targeted delivery, enzyme immobilization, and for cancer hyperthermia treatment [1].

In the present paper we report on study of basic structural and magnetic properties of core-shell maghemite nanoparticles synthesized via template synthesis in the presence of functional oligoperoxide surfactants and further graft-polymerization initiated from their surface.

## II. EXPERIMENTAL

Maghemite nanoparticles ( $\gamma\text{-Fe}_2\text{O}_3$ ), were synthesized via mixing the solution of Fe(II) and Fe(III) salts in the presence of ammonia in accordance with the reaction [2]:



Reagent molar ratio  $\text{Fe}^{3+}/\text{Fe}^{2+}$  was 2:3 taking into account  $\text{Fe}^{2+}$  oxidation during solution preparation under aerobic conditions. Water solution of oligoperoxide modifier was

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charged into flask together with ammonia solution [3]. The process was carried out in three-necked flask equipped with the arm stirrer and backflow condenser at 363 K during 1.5 hours. Then 1 M solution of HCl was added to the reaction medium to lower solution pH to neutral and  $\text{Fe}_3\text{O}_4$  present in the system was oxidized to  $\text{Fe}_2\text{O}_3$  using  $\text{H}_2\text{O}_2$  10% solution. Synthesized maghemite was washed with distilled water to constant solution conductivity value and kept as water suspension. In order to obtain the shell of required functionality on magnetic core surface a polymerization of NVP-GMA monomer mixture initiated from oligoperoxide copolymer modified maghemite nanoparticles was carried out. Composite nanoparticles consist of magnetic  $\gamma\text{-Fe}_2\text{O}_3$  core and organic shell containing peroxide and other reactive functional fragments.

XRD was carried out using "DRON-3" system (CuK $\alpha$  irradiation). The typical recorded diffractogram pattern is depicted in Fig. 1. It consists of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) diffraction peaks that are broadened as expected for ultra-fine particles.

The microstructure was studied with a transmission electron microscopy (JEOL JEM 2000-EX). The TEM image (see Fig. 2) shows aggregates of spherical-like grains with diameters from a few up to ~ 20 nm.

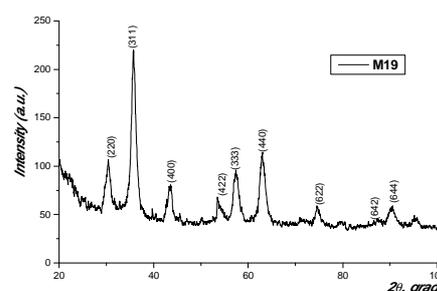


Fig. 1. X-ray powder diffraction pattern of the sample particles.

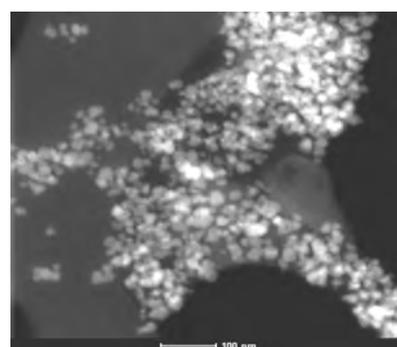


Fig. 2. Transmission electron microscopy image of the sample studied.

The mean diameter of particles estimated from an image processing is about 10 nm. The TEM image reveals also that the particles in agglomerates are mostly separated confirming existence of polymeric surface shells.

Magnetic behaviour of the particles was studied with a commercial Physical Property Measurement System (PPMS, Quantum Design). The magnetization curve  $M(H)$  recorded at 300 K is shown in Fig. 3. The presented loop displays negligible coercivity indicating that the superparamagnetic behaviour dominates in the sample.

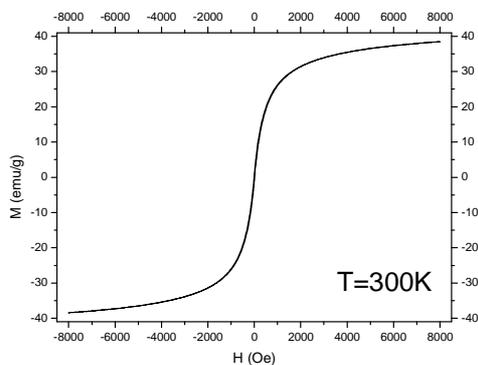


Fig. 3. Field dependence of the magnetization at 300 K.

The  $M(T)$  curves were measured under both zero-field-cooled (ZFC) and field-cooled (FC) conditions [4]. The ZFC cycle was performed after cooling the sample down from 300 K to 2 K in zero field and then by measuring the magnetization in the applied field of 50 Oe with increasing temperature. The FC measurements were performed after cooling the sample in the same external field. The obtained  $M(T)$  results for ZFC-FC dependences are shown in Fig. 4 by circles and triangles, respectively. The ZFC curve exhibits a broad peak at 170 K whereas the FC magnetization decreases with increasing temperature. When the random assembly of particles is cooled down in ZFC conditions, the magnetic moments of particles become frozen with random orientations. If the magnetization is measured versus an increased temperature in a low applied field, the magnetic moments tend initially to align along the field and the magnetization will increase as long as the relaxation phenomena are not significant. At higher temperatures, the relaxation becomes more and more activated. The consequence is that the magnetization reaches a maximum at a certain temperature – the so called blocking temperature, and then progressively decreases. In turn when particles are cooled down in the applied field (FC cycle), the magnetic moments tend to become frozen in the field direction and when the temperature is re-increased the magnetization decreases continuously due to magnetic relaxations and finally overlaps with ZFC curve above blocking temperature when all particles are in the superparamagnetic state. For the sample studied the average blocking temperature is 170 K but the broad maximum observed in ZFC curve, the relatively slow initial decay of magnetization in FC process as well as the split of ZFC-FC curves maintained at temperatures much higher than the blocking temperature point indicate the important role of interparticle interaction. Since the particles are separated one

from each other with the polymer shell thus the exchange interactions between particles can be excluded. However due to small interparticle distance the magnetodipole interaction between particles can be significant. The long-range dipolar interactions increase the effective anisotropy energy barrier for magnetization reversal, cause the broadening of the ZFC curve and delay the transition to the superparamagnetic state. At room temperature these interactions are not strongly enough to prevent superparamagnetic relaxation. However at lower temperatures the magnetic properties of the core-shell particles studied are governed by collective effects; they cannot be described by a single-particle approximation but resemble rather a spin-glass like state characteristic of strongly interacting nanoparticle systems.

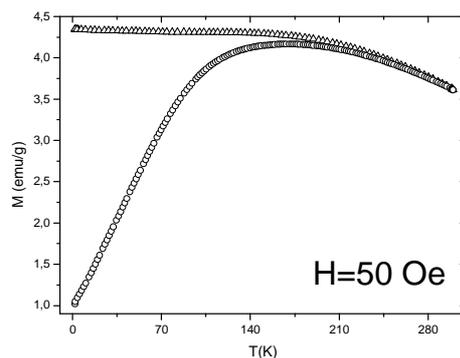


Fig. 4. Temperature dependencies of ZFC (circles) – FC (triangles) magnetization measured in the applied field of 50 Oe.

### III. CONCLUSIONS

Magnetic properties of novel core-shell maghemite nanoparticles synthesized via template synthesis in the presence of oligoperoxide surfactants were studied. XRD and TEM results confirm existence of  $\gamma$ - $\text{Fe}_2\text{O}_3$  phase and formation of spherical-like grains with an average diameter of about 10 nm separated by a organic surface shell. Magnetization measurements indicated superparamagnetic properties of the system at the room temperature. However at lower temperatures the magnetic behaviour cannot be considered as a blocking process of independent particles but rather as a spin-glass like system. It results from strong dipolar interactions combined with randomness in the particle positions and orientations of anisotropy axes in the aggregated structure of maghemite particles separated by the organic interfacial layer.

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