Full Length Article

Modified ferrite core-shell nanoparticles magneto-structural characterization

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ABSTRACT

In this study, ferrite nanoparticles with core-shell structures and different chemical compositions of both the core and shell were prepared with success. Proposed nanoparticles have in the first and second series magnetite core, and the shell is composed of a mixture of ferrites with Fe^{3+}, Fe^{2+} and M ions (where M = Co^{2+}, Mn^{2+} or Ni^{2+}) with a general composition of $M_{0.5}Fe_{2.5}O_4$. In the third series, the composition is inverted, the core is composed of a mixture of ferrites and as a shell magnetite is placed. Morphology and structural characterization of nanoparticles were done using Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), and Infrared spectroscopy (IR). While room temperature magnetic properties were measured using Mössbauer spectroscopy (MS). It is seen from Mössbauer measurements that Co always increases hyperfine magnetic field on Fe atoms at RT, while Ni and Mn have opposite influences in comparison to pure Fe ferrite, regardless of the nanoparticles structure.

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1. Introduction

Recently, core-shell nanoparticles on the basis of spinel-MFe_2O_4 compounds (where M is the bivalent transition metal, e.g. Co, Mn, Ni, Zn, Cu) are of interest because such morphology can influence the nanoparticles' properties differently in comparison to playing with the individual compounds (Fe_3O_4, $CoFe_2O_4$). For example, core-shell nanoparticles with structure $Fe_3O_4/CoFe_2O_4$ causes an increase in specific loss power [1]. Therefore it suggests that other dopants will also influence it somehow. The main advantage of core-shell structures is their properties, which are not synergic as it can be expected for individual compounds of the core and shell. Novel properties allow for the application of core/shell systems in magnetic recording devices [2], microwave absorption devices [1], and for biomedical use [3]. Observed behavior suggests that these kinds of particles can be foreseen as useful heating centers for hyperthermia treatment [4].

Most of the studied ferrite nanoparticles are prepared from iron oxides (e.g. magnetite, maghemite, hematite) [5–7]. Another interesting, from the application point of view, the group of ferrites are these, which are doped by bivalent transition metals: Co, Mn, or Ni [8–10]. Such materials possess a number of advantages among which most important are: tuneable magnetic properties, good

biocompatibility [11], and easy surface functionalization [12]. Presence of other than Fe element in the structure does not exclude the possibility of the particles manipulation by an external magnetic field which is an important benefit of this system. Substitution of one transition metal by another causes not only changes in chemical composition but also variation in particles interaction on the fast-changing external magnetic field which is closely related to hyperthermia application [13,14] and thermal induced drug release [15,16]. The variable chemical composition, on the other hand, modifies the chemical activity and influences oxidation capability. Most of the applications of general systems depend on structure, morphology, and magnetic properties of studied structures.

Nanoparticles in which the core and shell are prepared from different substances are a new group of nanomaterials in comparison to a single phase. Such nanostructures allow for combining properties which are typical for both core and shell and develop unique one, which is only specific for one particular system [17]. When magnetite or other ferrites are used as a part of the particle (core or shell) adding chemically different layer may influence its magnetic and/or surface properties. For example, superparamagnetic blocking temperature [18], specific loss power [1] or specific reactivity. Some of these phenomena were observed and reported in our previous papers. Only a few more studies where core-shell nanostructures with different oxides were reported and therefore, its properties are not described very well, while potential in the

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application is huge if adequate characteristic will be achieved. There, core and shell varied between magnetite, maghemite, and hematite [19] or metallic elements. Here in addition, into the structure in layered manner different 3d elements were added into the pristine Fe ferrite structure which influenced the composition and occupation of the crystallographic position of Fe. Such modification reflected significant changes in the overall magnetic behavior of the resultant particles and allowed to tune RT magnetic response of the particles.

Magnetite measured by Mössbauer spectroscopy show two well-resolved magnetically split patterns, connected with Fe atoms located in tetrahedral (A) and octahedral (B) crystallographic positions [20]. For low concentrations of elements like Co, Mn Ni, relative intensities of sextets seen by Mössbauer spectroscopy, cause changes that depend on the type of metal [1]. When sextet related to iron B position decreases, it means that the tested atoms are preferentially located in the B-site of the magnetite structure. A-site is seen in an analogical manner. In the case of nanoparticles, qualitative analysis of the spectra, suggests that Mn and Ni are located both in A and B sites, while Co is only located in the A-site especially in low concentration. With increased concentration of the dopant metal, broadening of the magnetically split part of the Mössbauer spectra is observed and a superparamagnetic doublet appears in the central part [21]. Such results were observed for one-pot synthesis. Therefore, it is interesting to study the influence of the core-shell morphology and composition on the nanoparticles magnetic properties and what determines the potential applications. Such studies are missing in the literature.

In this work, synthesis based on the decomposition of Fe(acac)$_3$ in presence of phenyl ether as a solvent, as well as alcohol, carboxylic acid, and amine as surfactants are used. This method leans on layered growth on seeds with the size of about 4 nm in accordance with precursor concentration. Such grains play as a growth precursor of final nanoparticles with the sizes range from 7 to 14 nm. Controlled subsequent layers origin on primary seeds, allow for the obtainment of purposely designed core-shell nanoparticles [22].

2. Experimental

2.1. Materials and apparatus

To fabricate core-shell nanoparticles, the following chemicals were purchased: Fe(acac)$_3$, Fe(acac)$_2$, Mn(acac)$_3$, Ni(acac)$_2$, Co (acac)$_2$, 1,2-hexadecanediol, phenyl ether. 1-octadecanol and oleyl amine were obtained from Sigma Aldrich and oleic acid from POCH. Nanoparticles were finally purified and dried with use of acetone, sonication bath, and a permanent magnet.

To perform structural and morphology characterization, transmission electron microscope (TEM) – 200 kV Tecnai G2 X-TWIN was used. Verification of crystal structures was done by X-ray diffractometer Agilent Technologies SuperNova equipped with a Mo (K$_\alpha$ = 0.7136 Å) micro-focused source (XRD). Room temperature Mössbauer spectra (MS) were obtained using the spectrometer working in constant acceleration mode with a ^{57}CoCr radioactive source. The α-Fe foil was used as a reference.

2.2. Nanoparticles preparation

All three series of presented below core-shell nanoparticles were fabricated by the same base method which was lean on the modification of seed-mediated synthesis of magnetite [23–25]. It is a two-step procedure, performed in the inert gas atmosphere, where the proper amount of metal acetylacetonate salt is decomposed at 260 °C in phenyl ether environment and 1,2-hexadecanediol, oleic acid, and oleylamine which play a role of surfactants. In the primary routine origins for next steps are obtained. Repeating described above process on pristine seeds, core-shell nanoparticles fabrication protocol is received. However, by variation relative ratio between precursors and other synthesis constituents miscellaneous particles can be fulfilled. In this paper, the composition of the nanoparticles was changed as follows: the core in first and second series (MNP-1 and MNP-2) was nominally the same and was expected to be magnetite, as it is claimed by Sun [25]. Here, however, morphology will be changed due to the usage of different amount of Fe(acac)$_3$ precursor (see Fig. 1). The shell, whereas, contained 2 (Fe^{2+}, Fe^{3+}) or 3 types of ions (Fe^{2+}, Fe^{3+}, and Co^{2+}, Ni^{2+}, or Mn^{2+}) in the various molar ratio (for details see Table 1). In the third case (MNP-3), the composition of nanoparticles was inversed, so as a core mixture of Fe^{2+}, Fe^{3+}, as well as Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, or Mn^{2+} was used. On the surface of such cores, magnetite shell from Fe(acac)$_3$ was made. Schematic presentation of the types of prepared nanoparticles and each sample proportion of ions are presented in Fig. 1 and Table 1. At the end of the procedure, nanoparticles were washed three times with deoxygenated acetone and dried in the vacuum evaporator to obtain a dark magnetic powder.

It is important to highlight that magnetite obtained only from the Fe^{3+} salt is not the same as the one obtained from the stoichiometric mixture of Fe^{2+} and Fe^{3+}. Therefore, its usually called nonstoichiometric magnetite, and studies on this was already published [23].
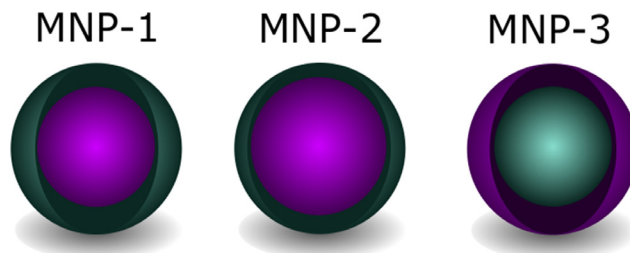

Fig. 1. Schematic presentation of the types of prepared core-shell nanoparticles with different core and shell composition.

Table 1
The composition of the nanoparticles: column (1) – samples abbreviation, (2) – molar ratio, (3) – core composition, (4) – shell composition. In column (2) first number describes the molar ratio of the core, and second after a colon in the bracket is the molar ratio of the shell ions. For example, 1:[2:1], means that the core is obtained from Fe^{3+} acetylacetonate complex with a molar ratio of 1 and the shell is a mixture of Fe^{3+} and Fe^{2+} complexes in the molar ratio 2:1, or Fe^{3+}, Fe^{2+} and Co^{2+} complexes in the molar ratio 2:0.5:0.5, etc. The last series has the opposite meaning of the brackets, the core is a mixture of different 3d elements, and the shell is always the same (Fe (acac)$_3$).

Name (1)	Molar ratio (2)	Core (3)	Shell (4)
MNP-1	1:[2:1]	Fe$_3$O$_4$	Fe$_3$O$_4$
MNP-1Co	1:[2:0.5:0.5]	Fe$_3$O$_4$	Co$_{0.5}$Fe$_{2.5}$O$_4$
MNP-1Mn	1:[2:0.5:0.5]	Fe$_3$O$_4$	Mn$_{0.5}$Fe$_{2.5}$O$_4$
MNP-1Ni	1:[2:0.5:0.5]	Fe$_3$O$_4$	Ni$_{0.5}$Fe$_{2.5}$O$_4$
MNP-2	4:[2:1]	Fe$_3$O$_4$	Fe$_3$O$_4$
MNP-2Co	4:[2:0.5:0.5]	Fe$_3$O$_4$	Co$_{0.5}$Fe$_{2.5}$O$_4$
MNP-2Mn	4:[2:0.5:0.5]	Fe$_3$O$_4$	Mn$_{0.5}$Fe$_{2.5}$O$_4$
MNP-2Ni	4:[2:0.5:0.5]	Fe$_3$O$_4$	Ni$_{0.5}$Fe$_{2.5}$O$_4$
MNP-3	[2:1]:4	Fe$_3$O$_4$	Fe$_3$O$_4$
MNP-3Co	[2:0.5:0.5]:4	Co$_{0.5}$Fe$_{2.5}$O$_4$	Fe$_3$O$_4$
MNP-3Mn	[2:0.5:0.5]:4	Mn$_{0.5}$Fe$_{2.5}$O$_4$	Fe$_3$O$_4$
MNP-3Ni	[2:0.5:0.5]:4	Ni$_{0.5}$Fe$_{2.5}$O$_4$	Fe$_3$O$_4$