Chemical preparation of core-shell nanoparticles

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Abstract. Nanoparticles obtained during layer-by-layer chemical deposition have been obtained. The particles diameter varied between 5 nm and 9 nm and can be tuned by changing molarity of the synthesis ingredients. The intention was the creation of copper or iron oxide layer during the process. Layer composition were changed using Cu rich or Fe rich ingredients. Magnetic properties of the particles strongly depend on the composition of covered material, indicating for their core-shell structure.

Key words: core-shell nanoparticles • magnetic nanoparticles • Mössbauer spectroscopy

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Introduction

The growing interest in nanotechnology causes the development of a big variety of nanoscale particles with different shapes. Magnetic dots, cylinders, wires and more sophisticated objects are subjected to study due to fundamental and technological interest [3]. The important application target is a medicine where nano-materials can play variety of roles from drug delivery media to structural material in biological composites and sensors [4, 5, 7]. Magnetic materials opens a new avenue to develop support material for carrying of numerous labels (enzymes, proteins, vitamins). Magnetic properties utilize an additional manipulation method of fabricated nanostructures. Many efforts have been made to achieve multifunctional materials with simple synthetic procedure and easy processing for subsequent application.

It was reported that Ag_{core}-Co_{shell} particles were obtained using colloid chemistry methods. Core-shell structure without additional CoO outer layer was demonstrated by electron energy-loss spectroscopy [10].

The nanostructures presented in the paper were obtained by wet chemical methods. Nanoparticles were synthesized by decomposition of $Fe(acac)_3$ or $Cu(acac)_3$ at elevated temperature [11] in a step-by-step manner. Nanostructures were examined by transmission electron microscopy, X-ray diffraction, differential scanning calorimetry, infra-red spectroscopy. The magnetic properties were studied by Mössbauer spectroscopy.

Experimental

Materials and used apparatus

In the synthesis, the following pure chemicals were used: $Fe(acac)_3$ (Aldrich), $Cu(acac)_2$ (Aldrich), phenyl ether (Aldrich) oleic acid (POCH), oleylamine (Fluka), 1,2-hexadecanetiol (Aldrich), 1-octadecanol (Fluka), acetone (POCH). To collect IR spectra a Nicolet 6700 infrared spectrometer was used. Cleaning and particles separation were performed with the use of a sonification bath and permanent magnet. Quality of nanopowders was imaged by a transmission electron microscope (TEM) Tecnai G2 X-TWIN. Temperature stability of nanomaterial was tested by a differential scanning calorimeter STAR system (DSC). Crystal structure was checked with an X-ray diffractometer Agilent technologies SuperNova with a Mo micro source (XRD). Mössbauer spectra were obtained using the spectrometer working in constant acceleration mode with a CoRh radioactive source.

Synthesis of nanoparticles

The nanoparticles were synthesized using the Sun recipe [11]. During the first step of preparation phenyl ether, 1,2-hexadecanethiol, oleylamine, oleic acid and $Fe(acac)_3$ were stirred in an argon atmosphere at temperature of 230°C for about 30 minutes.

In the second step, modifications of a seed-mediated growth method [11] were applied:
– addition of 1-octadecanol, oleylamine, oleic acid and $Fe(acac)_3$;
– addition of 1-octadecanol, oleylamine, oleic acid and $Cu(acac)_3$;
– addition of 1-octadecanol, oleylamine, oleic acid and $Cu(acac)_3$, next, the mixture was stirred at a temperature of 200°C for 30 minutes, and than, 1-octadecanol, oleylamine, oleic acid and $Fe(acac)_3$ were added;
– addition of 1-octadecanol, oleylamine, oleic acid and $Fe(acac)_3$, next, the mixture was stirred at a temperature for 200°C by 30 minutes, and last, the 1-octadecanol, oleylamine, oleic acid and $Cu(acac)_3$ were added.

After every step of the described modification, the components were stirred and heated at a temperature of 200°C, in an argon atmosphere for 30 minutes. Obtained mixtures were cooled down to room temperature and the resultant dark solution was separated with the use of a permanent magnet. Obtained particles of black color were washed three times with deoxygenated acetone. In the last step, the nanoparticles were dried to powder form in an evaporator.

Results and discussion

The procedure described by Sun [11] allows to produce magnetite nanoparticles. In the first step of our synthesis seed particles were obtained. In the second step growth of the particles was performed with the intention to build the Fe or Cu oxide layer and we expected to obtain the following types of multilayered nanostruc-
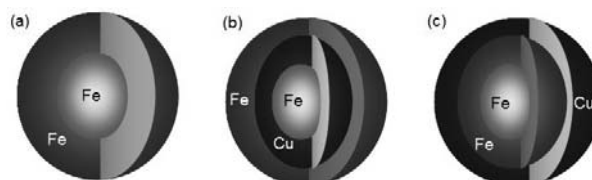

Fig. 1. Schematic drawing of core-shell nanoparticles: (a) Fe/Fe, (b) Fe/Cu/Fe, (c) Fe/Fe/Cu. Fe stands for Fe reach, Cu stands for Cu reach part of the particle.

tures: Fe/Fe, Fe/Cu/Fe, Fe/Fe/Cu, what is schematically drawn in Fig. 1.

The structures of the obtained nanoparticles were characterized by XRD and TEM. Seeds particles are presented in Fig. 2a (diameter around 4 nm). The modified particles images are also depicted in Fig. 2, where (b) stands for the double-layered particles Fe/Fe and (c–d) presents the triple-layered Fe/Cu/Fe and Fe/Fe/ Cu, respectively. High resolution images (e–f) presents crystalline structure of single particle both double- and triple-layered, respectively. It can be seen that the double-layered nanoparticles have a mean diameter around 5–6 nm, where the triple-layered structures are a couple of nanometres larger (8–9 nm). From high resolution images neither polycrystalline nor layered structures were detected indicating for a continuous growth of the subsequent layers, as suggested by Sun [11].

XRD data is also the proof that nanoparticle adopt rather magnetite structures because only typical (220),
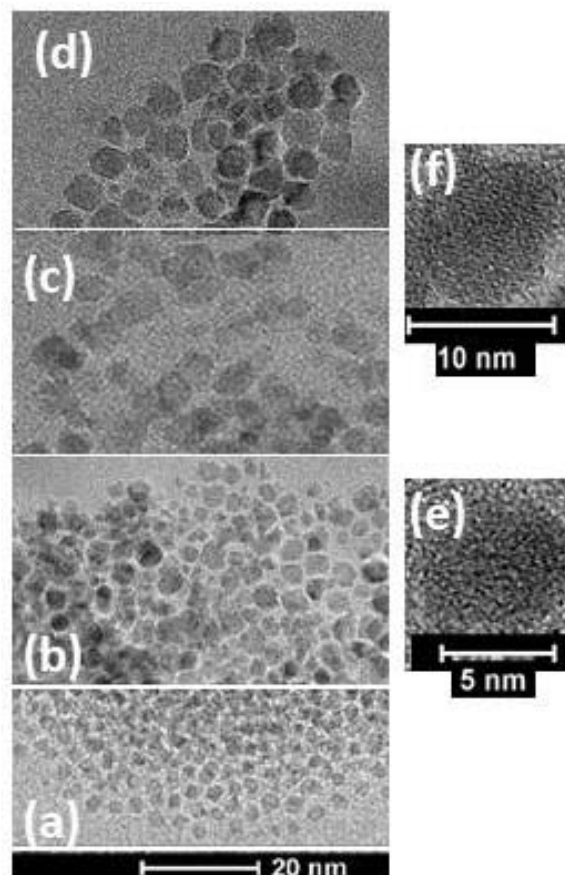

Fig. 2. TEM images of core-shell nanoparticles (a) seeds particles, (b) Fe/Fe, (c) Fe/Cu/Fe, (d) Fe/Fe/Cu, high magnification: (e) of Fe/Fe single particle, (f) of Fe/Cu/Fe single particle.
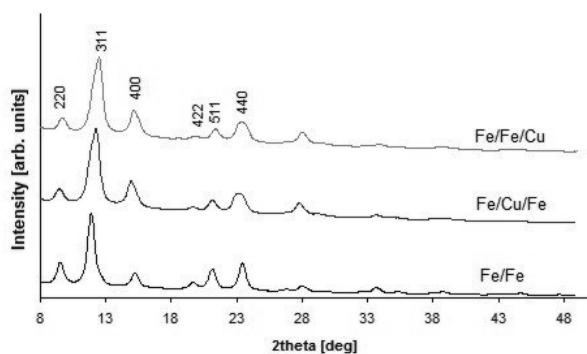
Fig. 3. XRD data of obtained nanostructures.

(311), (400), (422), (511) and (440) signals are detected. However, especially in the case of triple layered particles the diffraction peaks are broadened (see Fig. 3). One of the possible reason is distortion of the crystal structure by a Cu-rich layer.

Mössbauer spectra of Fe/Fe, Fe/Fe/Cu and Fe/Cu/Fe particles measured at room temperature are shown in Fig. 4. The spectra have six-line pattern contribution typical of the presence of magnetite/maghemite [6]. Broadening of the lines and presence of a component located at close to zero velocities, indicates clearly that superparamagnetic behavior [12, 13] of the Fe/Fe particles occurs. Shapes of the measured spectra are consistent with a core-shell structure shown schematically in Fig. 1. Indeed, the Fe/Fe particles with an average diameter between 5 and 6 nm (Fig. 4) show clear superparamagnetic behavior at room temperature because of the most intense zero-velocity component. Additional Cu-oxide layer results in 8 to 9 nm in diameter Fe/Fe/Cu particles (Fig. 4) and shows a clear decrease of superparamagnetic relaxation processes of the hyperfine
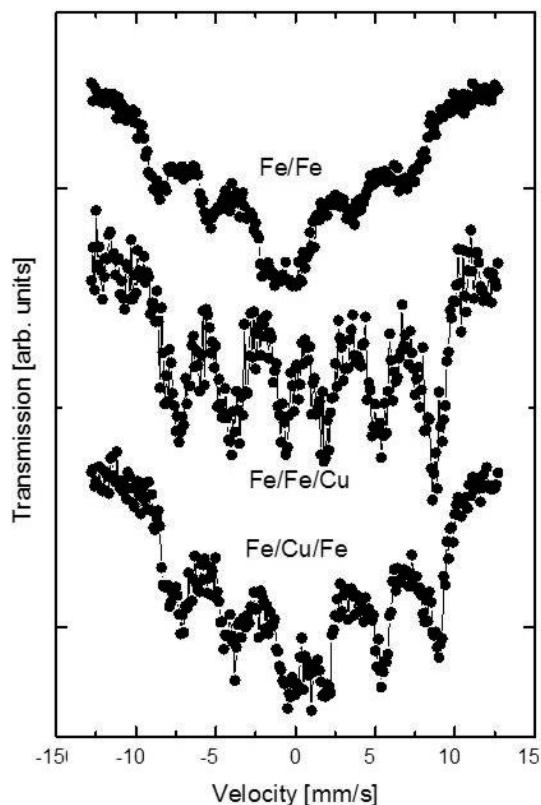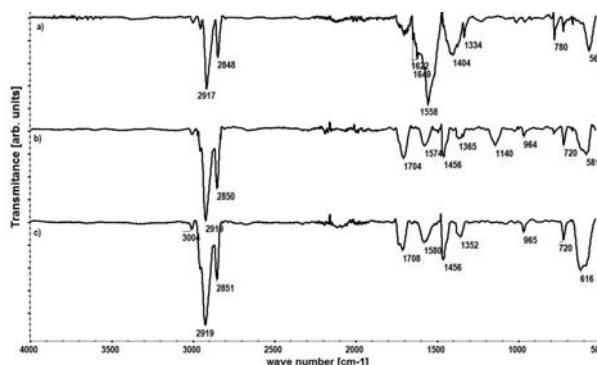

Fig. 5. IR spectra of obtained nanostructures: (a) Fe/Fe (b) Fe/Cu/Fe, (c) Fe/Fe/Cu.

magnetic field detected by ^{57}Fe nuclear probe. Particles of the same size but with different sequence of layers, Fe/Cu/Fe, show again an increase of the superparamagnetic relaxation (Fig. 4). This is consistent with the picture of nonmagnetic Cu-O layer separating Fe-O layers as shown schematically in Fig. 1.

The results of IR measurements of Fe/Fe particles are shown in Fig. 5. There are typical signal of Fe-O bonds in magnetite situated around 580 cm^{-1} [1]. Absorption peaks around 2900 cm^{-1} are most probably results of asymmetric stretching oscillations of the methylene group –CH$_2$- of the oleic amine used during preparation process. In the range of 1700 cm^{-1} vibrations of bonds in carboxylic groups are expected, while at 1400 cm^{-1} CH$_3$-CH=O gives characteristic IR signals [2]. In the spectra of Fe/Fe/Cu and Fe/Cu/Fe particles (Fig. 5b,c) new bands at 950 cm^{-1}, 1450 cm^{-1} and 1330 cm^{-1} from the carboxylic groups of oleic acid appear, respectively for bending and stretching oscillations. At 720 cm^{-1}, signals form –CH$_2$ and at 1570 cm^{-1}, the deformation of symmetric vibrations of –CH- group [9] is present. Around 1140 cm^{-1} -C-N- bounds from oleic amine can be detected. We observe that for particles with outer Cu the layers absorption peak characteristic of Fe-O bonds is shifted to about 620 cm^{-1} (Fig. 5c), while for Fe at the surface this peak appears at 580 cm^{-1} (Fig. 5a,b). The reason of this behaviors is still unclear and show apparent interactions of Fe-rich and Cu-rich layers. IR peaks characteristic of Cu-O bonds are located below 500 cm^{-1} [8] and could not be observed in the current experiments.

In Figure 6 DSC curves for the tested series are depicted. Fe covered particles show a very smooth temperature run and only very weak and wide thermal processes can be observed. On the contrary, samples covered by Cu outer layer show much more intensive
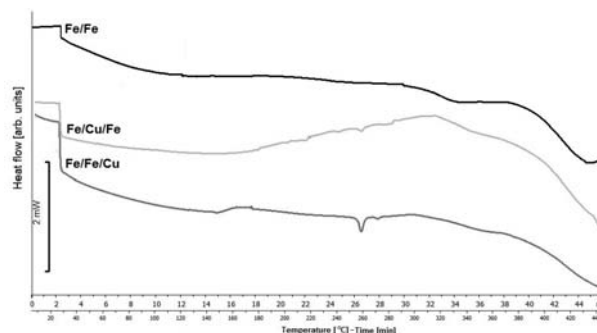

Fig. 4. Mössbauer spectra of obtained nanostructures.

Fig. 6. DSC curves of obtained nanostructures.

thermal processes. Physical origin of the process is not recognized yet. DSC temperature scans show clearly that particles with outer Cu layer are less stable than the particles with Fe outer layer (Fe/Fe and Fe/Cu/Fe).

Summary and conclusions

The nanoparticles were synthesized by the Fe-O seed--mediated growth using Fe-based or Cu-based precursors. TEM results indicated an increase of the diameter after each growth process and coherent structure of all the synthetized particles. XRD show the presence of single magnetite/maghemite crystal structure. Mössbauer results show a strong dependence of superparamagnetic behavior on the sequence of the synthetized layers. Therefore, although we have no direct evidence of the layered structure, our results indicate that indeed seed-mediated growth with Fe or Cu precursors results in coherent magnetite/maghemite crystal structure and layered chemical composition. DSC measurement indicated that the outer Cu-O layer is much less stable than the Fe-O outer layer. By IR spectroscopy we have shown that the Cu layer modifies vibrations of the Fe-O bonds. Further experiments are planned with selective ^{57}Fe and ^{56}Fe oxide layers and with electron energy-loss spectroscopy.

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