TEM/SEM and FT-IR characterization of biocompatible magnetic nanoparticles

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Abstract

Fe-Co-Cr-B(N,C,O,H) nanoparticles were synthesized by chemical reduction in aqueous solutions of cobalt precursor complexes such as (ethylenediamine)dichloro cobalt chloride \([\text{Co(en)}_2\text{Cl}_2\text{Cl}]\) and aqua solutions of \(\text{FeCl}_2\cdot 4\text{H}_2\text{O}\) and \(\text{CrCl}_3\cdot 6\text{H}_2\text{O}\) with sodium borohydride as reducing agent. During the synthesis a reactor insuring hydrodynamic conditions of ideal mixing for solutions at a room temperature and atmospheric pressure was used. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transformation infra red spectroscopy (FT-IR) investigations of nanoparticles obtained were carried out. The influence of the applied d. c. magnetic field during the synthesis on their properties were established. It is visible that a d. c. magnetic field induces a chain arrangement of nanoparticles with higher hydroxide content, possessing higher coercive force and lower transmittance determined by FT-IR.

Keywords: TEM/SEM, FT-IR investigations, nanoparticles, borohydride reduction

1. Introduction

Our work team has a long time experience working on synthesis of nanomaterials using reduction of aqueous salt solutions or complexes with water solutions of sodium borohydride or potassium borohydride [1]. During the synthesis there are possibilities to obtain different in size, structure or shape nanoparticles with specific conductivity/resistivity or ferromagnetic properties.

The obtained from the noble metals gold, silver and platinum nanoparticles contain less than 0.2 wt. % boron included in them by the reducing agent [2]. Nanoparticles are also obtained from non-noble metals such as iron, cobalt or nickel and in these particles, chains or wires the boron content is much higher [3, 4]. The content can be controlled and this element is often used to absorb harmful radiation during cancer treatment.

Recently the biocompatibility of such nanoparticles has been thoroughly investigated for different medical applications [5]. The elements - hydrogen, oxygen, nitrogen and carbon comprise 96.6 wt. % of the human body content [6]. The same atoms bind and form chemical bonds with the surface of the nanomaterials synthesized by the borohydride method (BH). As this case proves too, the formation of cobalt-nitrogen bond and its transfer to the nanoscale ferromagnetic particles is possible [6].

The aim of this work is to investigate, visualize and present with the help of TEM/SEM and FT-IR techniques the processes of nucleation and organization of the chemical bonds between the attached surface atoms. A subsequent task was to synthesize and investigate nanoparticles consisting of iron, cobalt, chromium proportionally to their ratio in the human body.

2. Experimental details

Metallic nanoparticles from \(\text{FeCl}_2\cdot 4\text{H}_2\text{O}\) 7.10^{-2} M salt solution mixing with \(\text{Co[en]}_2\text{Cl}_2\text{Cl}\) and \(\text{CrCl}_3\cdot 6\text{H}_2\text{O}\) 3.10^{-3} M solutions were produced by \((\text{BH})\) method in a reactor of ideal mixing [4]. A d.c. magnetic field (intensity 700 Oe) was applied during the synthesis for some of the prepared samples. After completion of the full reduction for period of two minutes the black precipitate is filtered and washed out many times with distilled water, and acetone. It is dried in a vacuum drier (5.10^{-3} Pa) for about 4 to 24 hours, and the yield is weighted.

The boron weight percentage content of the samples is analytical determined by titrimetric method. Iron, cobalt and chrome weight percentage content are determined by JEOL Superprobe-733 scanning electron microscope/microanalyser and mounted System 5000 (HNU SYSTEMS) EDS X-ray system with Si detector.

The specific surface area (SSA) of the obtained nanoparticles is determined by BET method (AREA meter, Strohlein, nitrogen flow, at temperature 78K).

The obtained nanoparticles morphology is characterized by electron microscope (TEM/SEM JEM 200 CX JEOL – Japan), the image is obtained in a transmission and scanning mode in vacuum 10^{-7} torr and accelerating voltage 100 kV.

Powder X-ray diffraction (XRD) patterns were collected using a TUR-M62 apparatus (Germany) with Co-Kα radiation. Data interpretation was carried out using the JCPDS database. Average crystallite sizes were determined from the XRD peaks using Scherrer’s equation. Moessbauer spectra of the samples were recorded at 295 K on a electromechanical type spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working in a constant acceleration mode. A ^{57}\text{Co/Cr}
(activity $\approx 5$ 0 mCi) source and an $\alpha$-Fe standard were used. The experimental spectra were treated using the least squares method for sextets $S_1$, $S_2$, $S_3$, $S_4$ and doublet (Db).

Quantum Design, Vibrating Sample Magnetometer (VSM) is used for all magnetic measurements.

FT-IR spectroscopy study has been carried out with IR spectrophotometer EQUINOX (Bruker) with Fourier transformation in 4000 to 400 cm$^{-1}$ frequency region using KBr matrix and FT-IR spectra of ferromagnetic nanoparticles synthesized have been undertaken. The samples for FT-IR spectroscopy investigations have been prepared mixing nanoscaled materials amounting to 1 mg and KBr (spectral purity) amounting to 200 mg and pressed in a tablet form with a diameter of 13 mm under a press loading of 8 tons/cm$^2$.

3. Results and discussion

Experimental data about the properties of nanoparticles investigated in this article are given in Table 1.

Table 1
Experimental data for the chemical content, the specific surface area (SSA), size and magnetic parameters of the samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th># of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2458 (with m. f.)</td>
</tr>
<tr>
<td>Iron [wt. %]</td>
<td>90.75</td>
</tr>
<tr>
<td>Cobalt [wt. %]</td>
<td>4.06</td>
</tr>
<tr>
<td>Chromium [wt. %]</td>
<td>2.11</td>
</tr>
<tr>
<td>Boron [wt. %]</td>
<td>3.13</td>
</tr>
<tr>
<td>SSA [m$^2$/g]</td>
<td>42.32</td>
</tr>
<tr>
<td>Nanoparticle diameter [nm]</td>
<td></td>
</tr>
<tr>
<td>i) according BET</td>
<td>18</td>
</tr>
<tr>
<td>ii) according TEM</td>
<td>34.2</td>
</tr>
<tr>
<td>iii) for XRD phases:</td>
<td></td>
</tr>
<tr>
<td>- Fe$_3$O$_4$/$\gamma$Fe$_2$O$_3$</td>
<td>11.2</td>
</tr>
<tr>
<td>- Fe, Fe-Co, Fe-B</td>
<td>5.8</td>
</tr>
<tr>
<td>Moessbauer spectra:</td>
<td></td>
</tr>
<tr>
<td>i) $S_{x1,x2,x3,x4}$</td>
<td>67</td>
</tr>
<tr>
<td>ii) Db</td>
<td>33</td>
</tr>
<tr>
<td>Coercive force, $H_c$ [Oe]</td>
<td>207</td>
</tr>
<tr>
<td>Magnetization, $M$ [emu/g]</td>
<td></td>
</tr>
<tr>
<td>i) $M_{saturation}$</td>
<td>65.1</td>
</tr>
<tr>
<td>ii) $M_{remanence}$</td>
<td>13.5</td>
</tr>
<tr>
<td>Aspect ratio $M/M_0$</td>
<td>0.20</td>
</tr>
<tr>
<td>Weight of samples [g]</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The analysis of the two types of samples, obtained with (#2458) and without (#2459) applying d. c. magnetic field displayed a similarity in the chemical content in terms of the elements iron, cobalt and chromium.

Boron content in the samples obtained with applying of magnetic field is smaller, which corresponds to the higher hydrogen content in concordance to some of our previous investigations. Under the influence of the applied magnetic field hydrogen organizes the nanoparticles in chain-like formations.

The higher values of the specific surface area confirm that nanoparticles obtained in magnetic field are smaller in size. The comparative estimations of grain size diameters based on BET and TEM measurements are similar.

3. 1. TEM/SEM investigations of Fe-Co-Cr-B(N,C,O,H) nanoparticles

Figures 1 and 2 present TEM micrographs of nanoparticles obtained with or without applying a d. c. magnetic field during the synthesis.

Fig. 1. TEM micrograph of Fe-Co-Cr-B(N,C,O,H) nanoparticles obtained with applying of a d. c. magnetic field

Fig. 2. TEM micrograph of Fe-Co-Cr-B(N,C,O,H) nanoparticles obtained without applying of a d. c. magnetic field

Figure 1 visualizes the accumulation of iron hydroxides and oxides upon the ferromagnetic chain. The Moessbauer data for the same sample show increase in the doublet part responsible for the oxide phases.

On Figures 3 and 4 SEM micrographs of the same nanoparticles are presented. The coercive force of this type of nanoparticles (chain) is higher and reaches up to 207 Oe, while in nanoparticles obtained without magnetic field hydroxide shells lack (Figure 2). They have a smaller doublet and much lower coercive force – 32 Oe. The values of magnetization and aspect ratio follow the general rules for ferromagnetic particles self-organization.
Fig. 3. SEM micrograph of Fe-Co-Cr-B(N,C,O,H) nanoparticles obtained with applying of a d. c. magnetic field

Fig. 4. SEM micrograph of Fe-Co-Cr-B(N,C,O,H) nanoparticles obtained without applying of a d. c. magnetic field

The d. c. magnetic field applied during the synthesis induces a chain arrangement of nanoparticles. This phenomenon was observed earlier at the synthesis of nanoparticles obtained by the borohydride reduction method [7, 8].

These nanoparticle chains hold on the surface quantities of OH groups. The OH groups have been observed in TEM micrographs and in FT-IR spectra [9].

The yield of obtained samples as a weight by using identical concentrations of initial solutions undoubtedly shows the inclusion of oxygen and the formation of greater quantity of oxides/hydroxides upon the formed nanoparticle chains. The smaller particles forming nanoparticle chains allow obtaining a higher yield (1.31g) after filtration, while the loss of bigger nanoparticles obtained without applying of d. c. magnetic field during the synthesis is higher (up to 30%).

The determined via XRD data diameters of the crystallites of the Fe₃O₄/γFe₂O₃ phases and of Fe/Fe-Co/Fe-B - phases are close in values. They not allow precise evaluation of the influence of the applied magnetic field on grain size.

3. 2. FT-IR study Fe-Co-Cr-B(N,C,O,H) nanoparticles

Figure 5 present FT-IR spectra of nanoparticles obtained by chemical reduction with NaBH₄ in aqueous solutions of Co (en)₂ complexes [Co(en)₂Cl₂]Cl and aqua solutions of FeCl₂·4H₂O and CrCl₃·6H₂O respectively applying and not applying a magnetic field during the synthesis.

FT-IR spectra of Fe-Co-Cr-B(N,C,O,H) nanoparticles in Figure 5 prove the creation of chemical bonds between N-H, C-N, B-O, H-O atoms in different attached to surface atom groups and molecules and give information about the synthesis conditions. FT-IR spectrum of nanoparticles obtained in the presence of magnetic field during the synthesis differ from FT-IR spectrum of nanoparticles obtained without the presence of a magnetic field during the synthesis.

The absorption bands observed in 3500-4000 cm⁻¹ frequency range characterize stretching vibrations ν(NH₂) mode of N-H bonds in NH₂ groups (at 1339.2 ÷ 1338.0 cm⁻¹) and stretching vibrations ν(CN) mode of C-N bonds (at 1020.7 ÷ 1006.8 cm⁻¹), as well as stretching symmetric νₛ(BO₄) mode of vibrations of B-O bonds in BO₄ groups (at 686.5 ÷ 685.5 cm⁻¹), respectively deformation δ(BO₄) mode vibrations of B-O-B bonds in the same BO₄ groups (489.6 ÷ 485.5 cm⁻¹).

Absorption bands characteristic for stretching and deformation vibrations of O-H bonds in OH groups and H₂O molecules have appear at
3398.7 ± 3387.4 cm⁻¹, and 1648.9 ± 1634.9 cm⁻¹ respectively.

FT-IR spectra undertaken catch the change in the synthesis technological conditions such as a magnetic field applied or not during the synthesis and show the influence of the magnetic field on the nanoparticles absorption. They prove the formation of different atom groups such as NH₂, CN, BO₄, respectively the adsorption of OH free groups and H₂O molecules on the nanomaterials surface.

4. Conclusion

The d. c. magnetic field applied during the chemical reduction synthesis of Fe-Co-Cr-B(N,C,O,H) nanoparticles influences on the magnetic parameters, as well as on the chain formation phenomenon from the smaller particles holding OH groups on their surface.

FT-IR spectroscopy study of the obtained nanoparticles proves the influence of the synthesis conditions and the d. c. magnetic field application on the creation of chemical bonds in different atom groups attached to the surface, respectively on the nanoparticles absorption/transmittance in the mid-IR range. The synthesized nanoparticles in the presence of a d. c. magnetic field decreasing significantly their transmittance.

Acknowledgments:

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References