

A STUDY ON IRON OXIDE NANOPARTICLES COATED WITH DEXTRIN OBTAINED BY COPRECIPITATION

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The iron oxide nanoparticles and iron oxide nanoparticles coated with dextrin have been synthesized using aqueous solution of ferric and ferrous ions and mixtures of dextrin with sodium salt. The size of the iron-oxide nanoparticles is controlled by the concentration of sodium salt in the medium. An average size of iron oxide and iron oxide coated with dextrin was found by transmission electron microscopy (TEM). The iron oxide nanoparticles are nearly spherical with an average diameter of about 8.0 ± 1 nm. The iron oxide nanoparticles coated with dextrin appear as cluster-like aggregates. The average diameter of these nanoparticles is about 5.1 nm. The attachment of the dextrin on the particle surface was confirmed by FTIR spectroscopy and thermogravimetric analyses (TGA).

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1. Introduction

During the recent years, there has been a great deal of interest in biocomposites containing magnetite (Fe_3O_4) nanoparticles dispersed in polymeric, glassy or ceramic matrices. Iron oxide nanoparticles present a great scientific interest in technological applications such as high – density magnetic recording media [1], biosensors [2], ferrofluids [3], magnetic resonance imaging [4], biomedicine [5].

Biomedical applications require iron-oxide nanoparticles with size smaller than 20 nm and a narrow size distribution. The properties of these materials depend strongly on the particle size, the particle-matrix interactions and the disposal of the nanoparticles in the matrix [6-7].

In this work, we report the synthesis of iron-oxide nanoparticles in aqueous solution in the presence of dextrin. Their characteristics were compared with iron-oxide nanoparticles. The samples were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analyses (TGA) and infrared spectroscopy (FT-IR).

2. Experimental

2.1 Materials

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH) and dextrin ($\text{C}_6\text{H}_{10}\text{O}_5$)_n were purchased from Fluca (Merck). These reagents were used directly as received. De-ionized water was used in the synthesis of nanoparticles, and in the rinsing of clusters.

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2.2 Synthesis of iron-oxide nanoparticles

Iron-oxide nanoparticles were prepared according to the following procedure: ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) in 2M HCl and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were mixed at room temperature ($\text{Fe}^{2+}/\text{Fe}^{3+} = 1/2$). The mixture was dropped into 200 ml of 1.5M NaOH solution under vigorous stirring for about 30 min. The resulting precipitate was isolated in the magnetic field added to the precipitate and the solution decanted after centrifugation at 8000 rot/min. By repeating the lost procedure two times, 200 ml of 0.02M HCl solution was added to the precipitate with continuous agitation. The product was separated by centrifugation (8000 rpm) and dried at 40 °C (sample 1).

2.3 Synthesis of iron-oxide - dextrin nanoparticles

Dextrin solution (20 g in 100 ml of water) was heated at 90°C for 1h with continuous agitation (200 rot/min). Then 40 ml of 5M NaOH was added to the solution.

Ferrite solution (30 ml) containing stoichiometric ratio of 1:2 ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was added dropwise to the solution. The suspension was incubated for 1h at 90 °C for 1h with gentle stirring. The 5M NaOH was added dropwise to obtain a pH of 11. The precipitate as centrifuged and washed with deionized water. The product was separated by centrifugation (10000 rpm) and dried at 40 °C (sample 2).

2.4 Sample characterization

The crystallographic analysis of the samples was performed by powder X-ray diffraction (XRD). Diffraction patterns (vs. 2θ) were recorded with a Philips PW 1050 diffractometer. A continuous scan mode was used to collect 2θ data from 10 to 70°.

A transmission electron microscopy (TEM) was carried out on a JEOL 200 CX. The specimen for TEM imaging was prepared from the particles suspension in deionized water. A drop of well-dispersed supernatant was placed on a carbon – coated 200 mesh copper grid, followed by drying the sample at ambient conditions before it is attached to the sample holder on the microscope.

IR spectroscopic studies were performed in the range 1800-400 cm^{-1} using a FTIR Spectrum BX spectrometer. Samples dehydrated at room temperature were pelleted with dried KBr. On the powders. The differential thermogravimetric analysis (TGA, DTG) and differential thermal analysis (DTA) of these samples were carried out on a Perkin Elmer Diamond thermal analyzer in the presence of static air at a linear heating rate of 10° from 25 °C to 800 °C.

3. Results and discussion

X-Ray Diffraction (XRD) patterns (Fig. 1) are typical of the spinel phase.

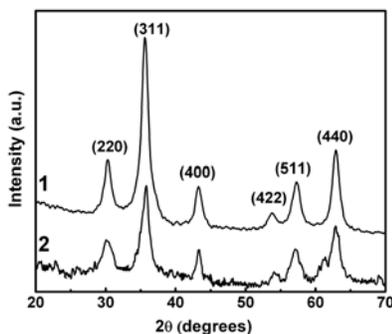


Fig. 1. The X-ray diffraction patterns of samples prepared: (1) iron oxide and (2) iron oxide coated with dextrin.

The line positions are the same for all samples, indicating no significant structural variations between the samples. Figure 2 shows TEM images of the sample 1 and samples 2. Electron micrographs show spheroidal particles whatever the synthesis conditions, but with different mine sizes.

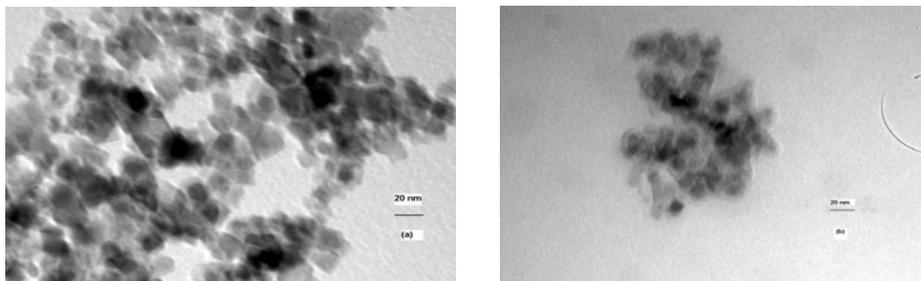


Fig. 2. Transmission electron microscopy images of sample 1 (a) and sample 2 (b).

The attachment of the dextrin on the particle surface was confirmed by FTIR spectroscopy. Fig. 3 shows the IR transmission spectra of iron oxide, iron oxide nanoparticles coated with dextrin and pure dextrin. Correspondingly, the assignments of the absorption bands in the spectra were listed in Table 2. The spectrum of the latter colloidal iron oxide contains characteristic OH stretching (ν OH) and HOH bending (δ OH) vibrational bands at 3400 cm^{-1} and 1600 cm^{-1} due to the adsorbed water in the sample [8]. The band observed at 620 cm^{-1} - 580 cm^{-1} corresponds to the stretching vibration $M_{\text{Th}}\text{-O-M}_{\text{Oh}}$, and $M_{\text{Th}}\text{-M}_{\text{Oh}}$ ($\nu_3 \approx 350\text{-}400\text{ cm}^{-1}$), where M_{Th} and M_{Oh} correspond to the metal occupying tetrahedral and octahedral positions, respectively [9-10]. The stretching vibration $\nu(\text{Fe-O})$ corresponds to tetrahedral iron atoms.

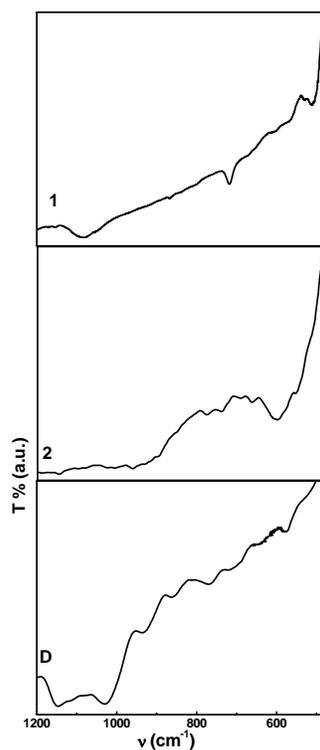


Fig. 3. The FT-IR spectra of samples: (1) iron oxide; (2) iron oxide nanoparticles coated with dextrin and pure dextrin (D).

A typical IR spectrum of the dextrin presents bands at 3365 cm^{-1} (O-H), $2851\text{-}2940\text{ cm}^{-1}$ (C-H), $1040\text{-}1110\text{ cm}^{-1}$ (C-O) [11].

The spectra of the iron oxide nanoparticles coated with dextrin exhibit few differences if compared to the ones of pure dextrin, which indicates that the interactions between dextrin and iron oxide nanoparticles are intermolecular interactions.

Table 1. Assignment of the absorption bands in the IR spectra.

Dextrin	Iron oxide nanoparticles coated with dextrin (cm^{-1})	Iron-oxide nanoparticles (cm^{-1})	Assignments
3500-3200	3500	3500	$\nu^* \text{H-O} \dots \text{H}$
2925	2917		$\nu_{\text{as}}^* \text{C-H of } -\text{CH}_2$
1455; 1370	1460; 1350	1600	$\delta^* \text{H-C-OH}$
1277	1273		$\delta^* \text{H-C-OH}$
1152	1160		$\nu_s^* \text{C-O-C}$
800-1200	800-1200		C-C
	590	590	Fe-O

Notations used:

ν^* : stretching vibration

ν_{as}^* : asymmetrical stretching vibration

ν_s^* : symmetrical stretching vibration

δ^* : deformation

The attachment of the dextrin on the surface of the magnetite particle was further confirmed by TGA. The TGA curves of samples 1, 2 and pure dextrin (D) are shown in Fig. 4.

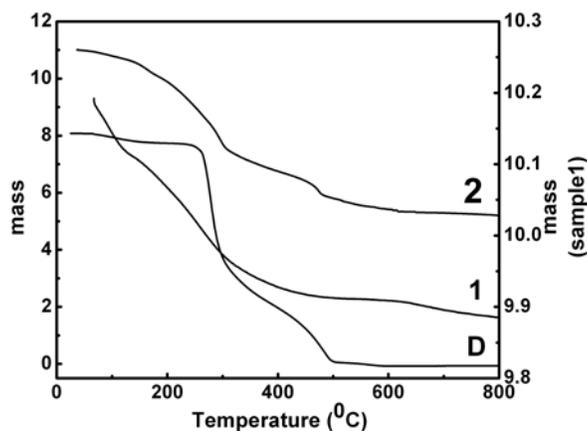


Fig. 4. The TGA curves of samples 1, 2 and pure dextrin (D).

In our samples it was observed that the percentage of weight loss is more important when the magnetite nanoparticles are coated with dextrin (52.68%) compared to that of iron oxide (3.04%). The TGA thermogram of sample 2 shows a continuous weight loss in the range of decomposition temperature for dextrin (compare parts D and 2 in the Fig. 4).

5. Conclusions

Iron oxide nanoparticles coated with the dextrin were synthesized by coprecipitation of two main solutions $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a stoichiometric ratio 1:2 in dextrin solution, by adding 5M NaOH. The iron oxide phase was described to be a ferrite with properties of the magnetite. The TEM images suggest that the use of dextrin in the material synthesis limits the particle size. The iron oxide-dextrin preparation generates particles that are significantly smaller than the iron oxide preparation in which dextrin is not present. Moreover the adsorption of dextrin on iron oxide nanoparticles was evidenced by FTIR spectroscopy and was confirmed by TG analysis.

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