

Preparation and characterization of cobalt ferrite nanoparticles coated with fucan and oleic acid

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Abstract Cobalt ferrite has attracted considerable attention in recent years due to its unique physical properties such as high Curie temperature, large magnetocrystalline anisotropy, moderate saturation magnetization, large magnetostrictive coefficient,

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excellent chemical stability and mechanical hardness. In this work we present the preparation, of fucan coated cobalt ferrite nanoparticles by a modified coprecipitation method and the study of their structural, microstructural and magnetic characteristics for their application as a solid support for enzymes immobilization and other biotechnology applications. Aqueous suspensions of magnetic particles were prepared by coprecipitation of Fe(III) and Co(II) in the presence of NaOH, acid oleic and fucan polymer. The X-ray diffraction indicates that the functionalization does not degrade the core cobalt ferrite. The infrared (FTIR) bands, indicate the functional characteristics of the coating on the cobalt ferrite. Mössbauer spectra at room temperature indicate the presence of a broadened sextet plus a doublet which is typical of superparamagnetic relaxation. For the Co-ferrite uncoated and coated with fucan the doublets have areas of 36.1 % and 40.3 % respectively, indicating the presence of non-interacting particles and faster relaxation time. The Co-ferrite coated with oleic acid and oleic acid plus fucan have areas around 17.5 % and 17.1 % respectively which indicate a weak superparamagnetic relaxation due to a slow relaxation time. The magnetization measurements of the cobalt ferrite nanoparticles with and without coating confirm that they are superparamagnetic and this behavior is produced by the core nanoparticles rather than the coatings. The cobalt ferrite nanoparticles coated with oleic acid presented the highest magnetization than when coating with fucan.

Keywords Cobalt ferrite · Fucan · Magnetic nanoparticles · Mössbauer spectroscopy · Polysaccharides

1 Introduction

Nanomaterials based on ferrites have already numerous applications, including photocatalysis, adsorption technologies, gas sensor, microwave devices and others [1]. In particular, cobalt ferrite materials have attracted considerable attention in recent years due to their unique physical properties such as, high Curie temperature, moderate saturation magnetization, excellent chemical stability and mechanical hardness [2]. They can be used in a large number of biotechnological applications, such as DNA and RNA purification, cell separation, drug delivery, magnetic resonance imaging [3], magnetic hyperthermia for cancer treatments [4], biosensors [5] and others.

Fucans are highly heterogeneous sulfated polysaccharides composed of different sugar residues, such as fucose, galactose, mannose and uronic acid. It is made up of α -L-fucose units linked by (1–4) and (1–3) glycosidic bands and sulphate at positions 2 and/or 3 and/or 4 depending on the algal species. Fucans and fucoidans are distributed in the intercellular matrix in brown algae and have a wide spectrum of activity in biological systems of potential medicinal value, such as anticoagulant, antitumour, anti-inflammatory, antiviral and antioxidant activities [6, 7].

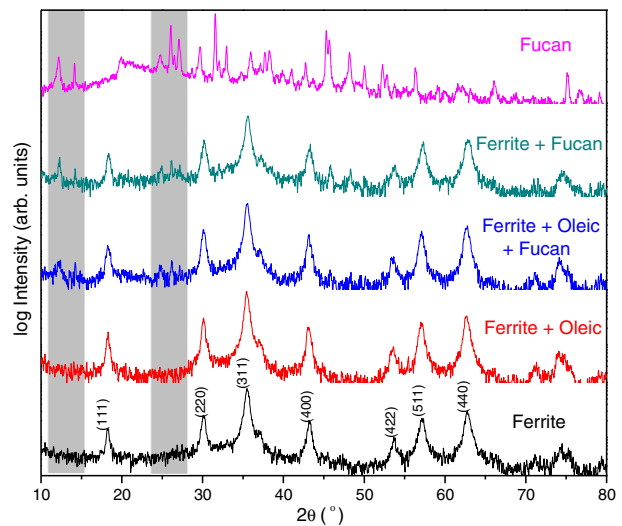
Various preparation techniques, such as sol-gel methods, citrate precursor techniques [8], electrochemical synthesis [9], combustion methods [10], solid state reaction [11], and mechanical alloying [12] are commonly used to produce ferrite

nanoparticles. Among them, the chemical precipitation is an economical way to produce fine powders [13, 14]. This article describes the synthesis of cobalt ferrite (CoFe_2O_4) nanoparticles by the precipitation method, and their coating with oleic acid and fucan polysaccharide. The uncoated and fucan-coated CoFe_2O_4 nanoparticles were characterized structurally, microstructurally and magnetically by X-ray diffractometry, FTIR, Mössbauer spectroscopy and magnetization measurements.

2 Experimental

An aqueous mixture containing 50 mL of 1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 50 mL of 0.5 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to 0.5 mL of oleic acid [15] and sodium hydroxide to obtain a solution (pH 13). The mixture was heated at 100 ± 3 °C for 1 h with vigorous stirring to obtain in the magnetic particles. The sample was then thoroughly washed with distilled water until it reached a neutral pH following by drying it at 60 °C. The preparation followed the same procedure described by Carneiro Leão et al. [16], except by modifications done during the incubation, which was performed at 85 °C during 30 min, and final pH 13. The nanoparticles were then added to 2 % of fucan polysaccharide solution in distilled water. The final step included drying the sample in an oven and the obtained powder were collected for characterization. The X-ray diffractogram (XRD) of the samples were taken in a Siemens model D5000 diffractometer. The samples were analyzed in the scale of the range $10^\circ < 2\theta < 80^\circ$ using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$ Å), in steps of 0.02° and the counting time of 1 second per step, with acquisition time of three hours. The Scherrer equation: $D = 0.916\lambda / \Gamma \cdot \cos \theta_{\text{hkl}}$ was used to calculate the average grain size; where λ is the wavelength of the X-rays (0.15418 nm), β_{hkl} is the pure diffraction line broadening (in radians), which can be easily found by measuring the full-width-at-half-maximum (FWHM) of the hkl reflection and θ is the Bragg's angle [17]. The latest give a mean grain size of around 20 nm. The Fourier transform infrared (FTIR) was performed by the KBr tablet method in the range $4000\text{--}400$ cm^{-1} , in a BRUKER model IFS 66 instrument. Two milligrams of samples were mixed with 200 mg of KBr and then were pressed at 490 atm and transformed into disks. The magnetization measurements were realized in a SQUID MPMS magnetometer of Quantum Design. The uncoated cobalt ferrite nanoparticles were measured at different temperatures whereas the coated nanoparticles were measured at room temperature. The Mössbauer characterization was performed with a conventional transmission Mössbauer spectrometer, operating with 1024 channels and a Wissel INC. velocity module with a sinusoidal signal. The measurements were taken at room temperature (RT) and the obtained data were adjusted with the help of the program NORMOS [18] which does not present the residual data. In this program, the good fitting is controlled by the value of the χ^2 . The source employed was a ^{57}Co in rhodium matrix with strength 25 mCi. The Isomer shifts and the velocity scale were calibrated with respect to a α -Fe film at RT. The sample holder used has a diameter 1 cm (0.7854 cm^2) and 24 mg mass which permitted to ascertain and quantify the small systematic effects of cosine smearing which usually occur in the folded Mössbauer spectra when relatively large collection solid angles are used.

Fig. 1 X-ray diffraction patterns (in logarithmical scale) of uncoated and coated cobalt ferrite nanoparticles. The grey columns indicate two peak reflections around 14° and three peak reflections around 26° belonging to Fucan, and they are present in all fucan coated samples studied in this work



3 Results and discussion

Figure 1 shows the X-ray diffractogram (XRD), in logarithmical scale, of the cobalt ferrite nanoparticles before and after coating with Fucan and/or oleic acid. The diffractogram of the uncoated nanoparticles (see bottom part of the figure) shows the characteristic of a cubic spinel structure, in accordance with the standard JCPDS card N° 22-1086. The diffractogram does not vary after coating with fucan, oleic acid or combination of them, indicating that the functionalization does not degrade the core cobalt ferrite nanoparticles. However, note that the XRD of the cobalt ferrite nanoparticles coated with fucan shows peaks characteristic of the fucan around 14° and 26° , corroborating the functionalization. No peaks of contaminants were detected in samples.

In order to study the functional groups formed in the coated cobalt ferrite sample, FTIR measurements were performed (Fig. 2). In the figure, the presence of the OH band (3500 cm^{-1}) in all the spectra indicates the presence of water, which is reasonable since the functionalization was performed in aqueous solutions as mentioned in the experimental section. However, in the case of the presence of water in the cobalt ferrite case, it should indicate that the powder were not dry enough. Moreover, the characteristic absorption band of Co (Fe)-O can be seen at 583 cm^{-1} . In the case of the cobalt ferrite coated with fucan, the bands at 2921 and 2851 cm^{-1} are related to the vibration of C-H. The band Co-OH is indicated by the vibration at 430 cm^{-1} . The band at 1626 cm^{-1} corresponds to H-O-H absorption, and that at 904 cm^{-1} is characteristic of the FeOOH (goethite) [19]. These results clearly indicate the functionalization of the cobalt ferrite nanoparticles with fucan and/or oleic acid.

Figure 3 shows the magnetic hysteresis loops of the cobalt ferrite nanoparticles without coating at three different temperatures (173 , 243 and 300 K). No saturation is observed under the maximum applied magnetic field (75 kOe). In addition, from the inset in the figure, it is observed that the remanence and coercivity slightly increase when the temperature is decreased. Despite the ratio of increment is not linear

Fig. 2 FTIR of uncoated and coated cobalt ferrite nanoparticles

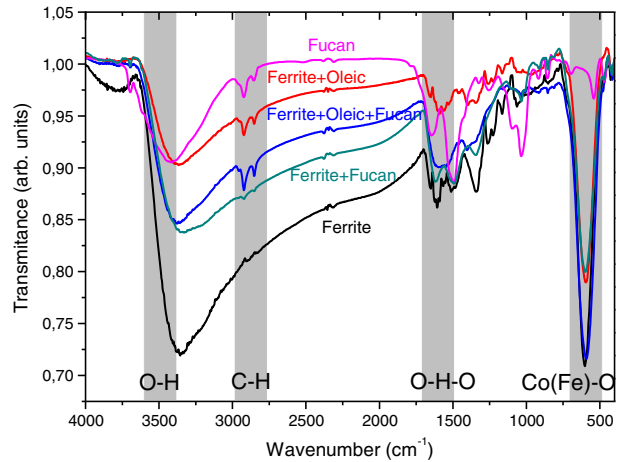
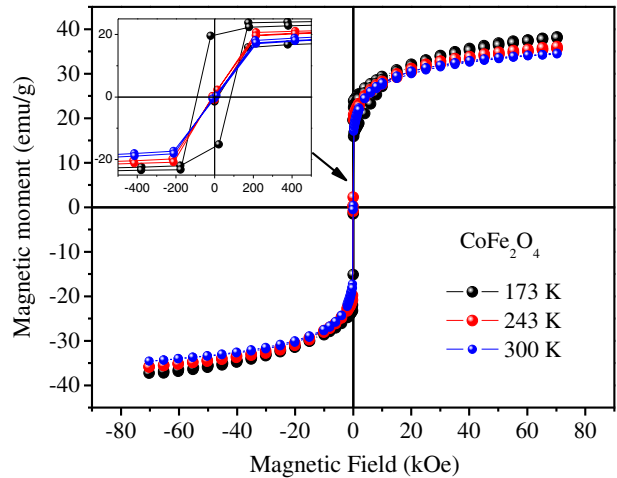


Fig. 3 Hysteresis loops of the cobalt ferrite nanoparticles at different temperatures



(especially in the case of the coercivity), we can infer from the last observations that the sample is superparamagnetic, which is typical for iron oxide based nanoparticles. The hysteresis shows remanence and coercive field at 173 K and not at 243 K and 300 K, indicating that the blocking temperature (T_B) should fall between 173 and 243 K. At temperatures above the T_B , the thermal effects allow rotation of the single domains to the easiest magnetization directions by getting over the energy barriers in zero field and consequently there is no coercivity. Recent studies also demonstrate the lack of coercivity in ferromagnetic microspheres in liquid suspension [20]. In that case the effect is originated by physical rotation of the magnetic spheres under applying a magnetic field.

It is unlikely that for applied magnetic fields above 75 kOe, the magnetization turns higher than 40 emu/g ($3.25 \mu_B$ / formula unit). Moreover, considering that cobalt ferrites generally form an inverse spinel with the ion Co^{2+} replacing the Fe^{2+} in

Fig. 4 M(H) loops of the ferrite (F), ferrite with oleic acid (FAO) and ferrite with fucan (FF)

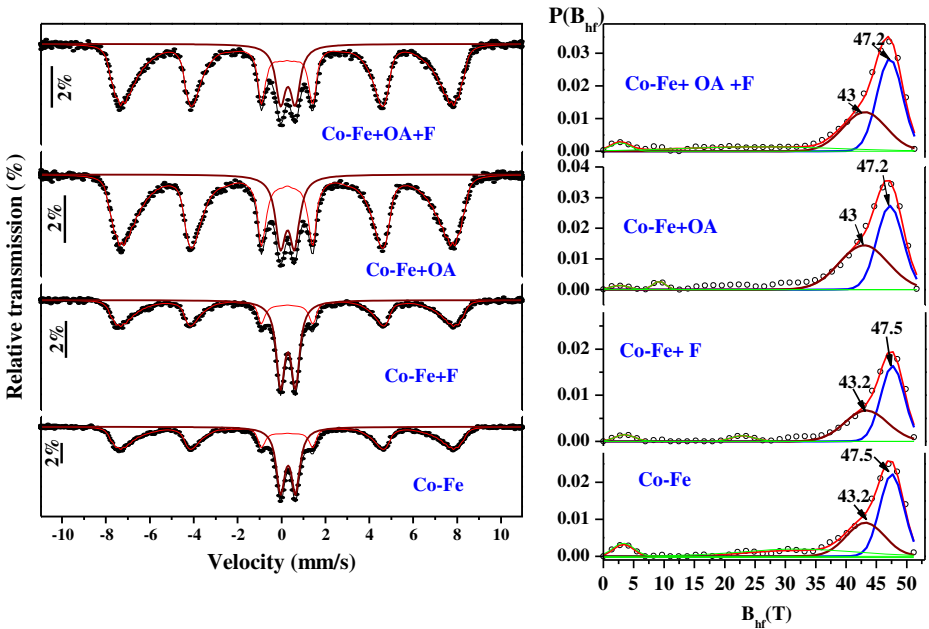
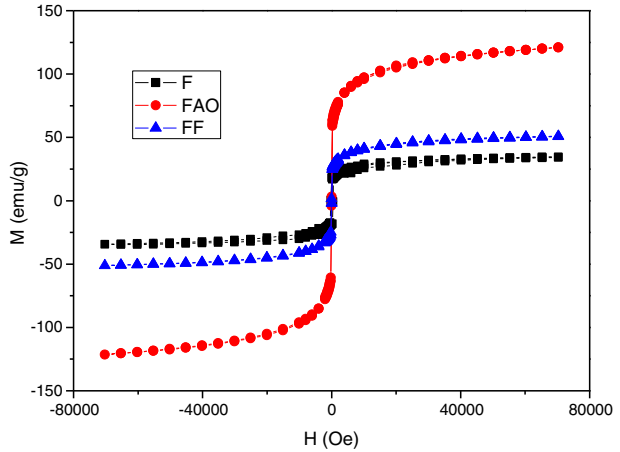


Fig. 5 MS of the cobalt ferrite with oleic acid and fucan (Co–Fe+OA+F), cobalt ferrite with oleic acid (Co–Fe+OA), ferrite with fucan (Co–Fe+F) and cobalt ferrite (Co–Fe). The corresponding hyperfine field distributions $P(B_{hf})$ and two average magnetic fields are shown on the right hand size

the site B of an octahedral structure and that this structure produces a theoretical magnetic moment of $3.0 \mu_B/f.u.$ (at 0K), then our result ($3.25 \mu_B$) is consistent with the theoretical value of $3.6 \mu_B/f.u.$ calculated by Slonczewski [21] and Tachiki [22] in which they assumed that the structure of cobalt ferrite is not completely inverse spinel and the degree of the reversal depends on the heat treatment. Figure 4 shows the magnetic hysteresis loops of the coated cobalt ferrite nanoparticles measured at

Table 1 Mössbauer hyperfine parameters obtained at RT

| Samples | δ (mm/s) \pm 0.03 | Δ (mm/s) \pm 0.02 ^a | B_{hf} (T) ^b | Area (%) \pm 2 |
|--|----------------------------|---|----------------------------------|------------------|
| Cobalt ferrite | 0.413 | 0.68 | 47.5–43.2 | 36.1 |
| | 0.370 | | | 63.9 |
| Cobalt ferrite with fucan | 0.408 | 0.68 | 47.5–43.2 | 40.3 |
| | 0.370 | | | 59.7 |
| Cobalt ferrite with oleic acid | 0.388 | 0.64 | 47.23–43.0 | 17.5 |
| | 0.370 | | | 82.6 |
| Cobalt ferrite with oleic acid and fucan | 0.405 | 0.67 | 47.2–43.0 | 17.1 |
| | 0.369 | | | 82.9 |

^aRepresenting the superparamagnetic doublet

^bAverage magnetic fields are shown in the right side of Fig. 5

δ is the isomer shift relative to α iron, Δ is the quadrupole splitting and A is the spectral fraction as obtained from the fit. B_{hf} is the hyperfine field in Tesla

room temperature. It is observed that the saturation magnetization of cobalt ferrite nanoparticles coated with oleic acid is far higher than the uncoated cobalt ferrite. This also occurs with the nanoparticles coated with fucan. This effect should be caused by magnetic disorder on the surface due to the effect of external media interactions (i.e. interaction between particles). It is almost sure that fucan and oleic acid coatings weaken the interaction between particles, which in turn reduces the disorder of the spins on the surface, thus resulting in the increase of the magnetization.

The uncoated cobalt ferrite and fucan cobalt ferrite nanoparticles (with average size of 20 nm) have similar Mössbauer spectra at RT (Fig. 5). In the Mössbauer spectra of the coated with fucan polysaccharides, the coating minimizes the interactions between particles which are reflected in a diminution of the hyperfine field and showing one sextet with broadened linewidth and one doublet. The fitting was made using an hyperfine field distribution $P(B_{\text{hf}})$ and one doublet. The spectrum is typical for magnetic relaxation of ferrites nanoparticles. In this case, the magnetic moment of an individual particle fluctuates through the easiest axis of magnetization during a time $\tau = \tau_0 \exp(KV/k_B T)$ where K is the magnetic anisotropy constant, V is the volume of the particle, k_B is the Boltzmann constant, T is the temperature and τ_0 is a constant characteristic of material. Therefore, for a fluctuation time longer than the characteristic Mössbauer time (10^{-8} s). A magnetically splitted spectra can be measured due to slow relaxation. Their Mössbauer hyperfine parameters are similar and they are listed in Table 1. The presence of the cobalt ferrite cores in each sample are confirmed by the sextets with hyperfine fields < 47.7 T (two representative values are 47.5 and 43.2 T) with areas 63.9 % and 59.7 % for the uncoated and the coated particles, respectively. The doublets, which denote the superparamagnetic effect, have slightly different peak areas, 36.1 % for the uncoated and 40.3 % for the coated.

The Mössbauer spectra of the cobalt ferrite nanoparticles coated with oleic acid and oleic plus fucan, are very similar and the effect of oleic acid to produce a decrease in particle size, which on average are 16 nm and a decrease of the dipole-dipole interaction that is reflected in a slight decrease in magnetic field hyperfine giving a relaxation time more slow, manifested through a superparamagnetic doublet of lower intensity. What is striking is that the peak area or the superparamagnetism of the samples are reduced to half, with areas of 17.5 % ferrite with oleic acid and 17.1 % ferrite with oleic acid and fucan compared to the previous two samples.

4 Conclusions

Oleic acid prevents agglomeration of the cobalt ferrite nanoparticles with and without fucan coating. The presence of polysaccharides in the fucan coated cobalt ferrite nanoparticles was confirmed by X-ray diffractogram. The crystallinity of the cobalt ferrite nanoparticles are not affected by any of the types of coatings used in this work. Magnetization measurements of the cobalt ferrite nanoparticles with and without coating reveal superparamagnetism and this behavior is produced by the core nanoparticles rather than the coatings. The cobalt ferrite nanoparticles coated with oleic acid presented the highest magnetization than when coating with fucan. This might cause by the reordering of the spins located in the surface of the nanoparticles caused by their functionalization with oleic acid. Mössbauer spectroscopy confirms that the cobalt ferrite nanoparticles with and without coating have superparamagnetic relaxation. The nanoparticles covered with fucan has a faster relaxation time than those covered with oleic acid.

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