

Functionalization of Cobalt Ferrite Nanoparticles with Alginate Coating for Biocompatible Applications

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ABSTRACT

The soft magnetic materials have potential applications in the field of bioengineering as carriers for targeted drug delivery. The magnetic properties, particle size after coating, Curie temperature and its biocompatibility are important parameters for the synthesis of materials. In the present communication cobalt ferrite nanoparticles have been synthesized using co-precipitation method and coated with sodium alginate. The X-ray diffraction and infrared spectroscopic measurements have been used to confirm the ferrite structure formation and coating of the samples with alginate. The SEM micrographs have been used to confirm the particle size which is found to be 45 nm before coating and 78 nm after coating. The saturation magnetization obtained using the hysteresis data for the uncoated cobalt ferrite sample is 19.8 emu/gm while for the coated sample it reduces to 10.2 emu/gm. The AC susceptibility measurements indicate SP structure for the uncoated samples with Curie temperature less than 100 °C. The thermo gravimetric measurements have been used to estimate the amount of alginate coating on the sample and it has been correlated with retention of magnetic properties after coating. The value of saturation magnetization reduces after coating due to mass reduction of magnetic material in the sample in accordance with the TGA measurements.

Keywords: Nanomagnetic Materials, Biocompatible Coating, Co-Precipitation Method

1. Introduction

The soft magnetic materials have potential applications as carriers for targeted drug delivery but there are limitations due to their toxicity [1-8]. The switching property is advantages for the hyperthermia and drug release mechanism. Coating these nanoparticles with biocompatible polymeric material is the area of research. Some critical parameters in the synthesis include the size of the magnetic nanoparticles. Different methods have been used by researchers to synthesize uniform sized nanoparticles one of them is the co-precipitation method. The biological applications of these particles require the size to be in the range of 30 to 50 nm and the coating thickness to increase the size to 70 to 80 nm [9]. At the same time there should be retention of ambient magnetic property so that they can be used for switching applications [10]

For targeted drug delivery the external magnetic field gradients can be used to direct the functionalized magnetic particles to the specific site, retain and subsequently

remove them. The in vivo route inherently has certain limitations which can be overcome by modifications in techniques and materials used in the process [11-15]. The coated magnetic nano particles are required to exhibit magnetic properties, remain stable, well dispersed and not aggregate to inhibit the blood flow. Once injected, they are opsonized [16] and the reticulo-endothelial system of the body, mainly sets the macrophage cells of the liver into phagocytic activity, where these nanoparticles are taken up due to hydrophobic surface of the cells. Thus the surface of the magnetic nanoparticles for its in vivo usage require surface modifications to ensure they are non toxic, biocompatible and stable to the reticulo-endothelial system of the body. Considering the hydrophobic and hydrophilic interaction during opsonization the coating of polymer materials such as dextran, polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyethylene oxide (PEO), oleic acid has been reported [7].

In the present communication the cobalt ferrite nanoparticles have been coated with alginate. The choice of

alginate is because alginic acid is composed of residue of D-Mannuronic acid, L-Glucuronic acid. The molecule consists of chains of D-Glucuronic acid units joined by B-14 Glycosidic linkages. The chain length is long and varies with the method of preparation. The molecular weight and viscosity measurement suggest molecules of from 220 to 860 units. The alginate absorbable haemostatic dressing is reported to be non toxic and non irritant. They have advantage over oxidized Cellulose, which include selective rate of absorption, Sterilization by auto cleaning or dry heat and compatibility with antibiotics such as penicillin. They may be used internally in neurosurgery, dental surgery to be subsequently absorbed. Externally they may be used (e.g. for burns or sites from which skin graft have been taken) to arrest bleeding and form a protective dressing which may be left or later washed away with sodium citrate solution. Protective films of calcium alginates may also be used by painting the insured surfaced with sodium alginate solution and then spraying it with calcium chloride solution. Alginate is insoluble in water and most of the organic solvents [17-22].

Considering the above applications of alginate the coating of magnetic nanoparticles has been carried out and analyzed using the XRD and IR. The SEM micrographs have been used to confirm the particle size while the thermo gravimetric measurements (TGA) have been used to estimate the amount of alginate coating on the sample and it has been correlated with retention of magnetic properties after coating.

2. Experimental

Ferrite nanoparticles were synthesized using controlled co-precipitation method in which AR Grade metal chlorides were used as starting agents, taken in proper molar proportions, in aqueous medium and alkalinized using strong alkali 1.5 M NaOH, adding it drop by drop with constant stirring on mechanical stirrer till the reaction is complete at constant temperature of 25°C to obtain the required size of the particles. The obtained precipitate was filtered through filter paper and washed several times with deionised water and dried in oven at 80°C for 2 hours to obtain fine ferrite powder.

For coating of the ferrite powder the 0.1M solution of Sodium Alginate CaCl₂ was prepared in deionised water. Then 2gms of ferrite powder was mixed with sodium Alginate and CaCl₂ solution in 1:1 proportion stored over night and filtered to obtain precipitate which was dried for 2 hours at 80°C in oven.

The characterization was carried out using PHILIPS (PW3710) X-ray diffractometer with Cu K α radiation ($\lambda = 1.5424$ A.U.). The parameters chosen for measurement were 2θ of 0.5° and 2θ range from 20° to 90°. Approxi-

mately 20mg of the sample was sprinkled onto a low background quartz XRD holder coated with a thin layer of silicone grease to retain the sample. The IR spectrographs were carried out on SHIMADZU (FTIR – 8400 s) spectrometer in the wavelength range 400 cm⁻¹ to 2000 cm⁻¹. Each spectrum was obtained by averaging 30 interferograms with resolution of 2 cm⁻¹. Pellets for FT-IR analysis were prepared by mixing the samples with spectroscopic grade KBr powder. The SEM micrographs were taken on JEOL-JEM-6360 microscope. The TGA/DTA measurements were carried out using UNIVERSAL V2 4F TA instrument in the Nitrogen atmosphere at the rate 10°C/min. The magnetization measurements were carried out on Magnets make hysteresis loop tracer using magnetic field of 100 Gauss.

3. Results and Discussion

Figure 1(a) and **(b)** show the XRD patterns for uncoated and alginate coated cobalt ferrite. The peaks on the XRD patterns were indexed in the light of natural spinal structure MgAl₂O₄. According to spinal structure the planes that diffract x-rays are (220), (311), (400), (422), (511) and (440). For spinel ferrite the (311) plane line is intense line. The observed reflections in the present case are also similar to these. The sample exhibits cubic spinal structure, the absence of extra-lines in the present patterns confirms single phase formation of the ferrites by completion of solid state reaction at much lower temperature than the conventional sintering method. The broadening of the line at half height, δ , was related to the average diameter DRX of the particles according to the law $DRX = 0.9 \lambda / \delta(\theta) \cos \theta$, where λ is the wavelength of the beam and θ is the Bragg angle. The average crystallite size was calculated on the main peak, *i.e.*, the (311) reflection peak. The lattice parameters and the particle sized estimated using the XRD data were found to be 8.325 Å and 46 nm respectively. The values of lattice parameter are found to be in agreement with the reported values for the uncoated ferrites [23]. The particle size is mainly dependent on the method of preparation and the co-precipitation method used for the synthesis is found to be useful to obtain ferrite particles in the required size range. The XRD pattern retains peak pattern after coating indicating that the ferrite structure is retained after coating.

Figures 2(a) and **(b)** depict the IR spectrographs for the cobalt ferrite and alginate coated cobalt ferrite respectively. The IR spectra for uncoated cobalt ferrite shows two characteristic peaks ν_1 at 430 cm⁻¹ and ν_2 at 525 cm⁻¹, which have been attributed to the intrinsic vibrations of the tetrahedral (T_d) and octahedral (O_h) coordination compounds and lattice vibrations of E-symmetry [24,25]. The IR spectra for the coated sample shows peak

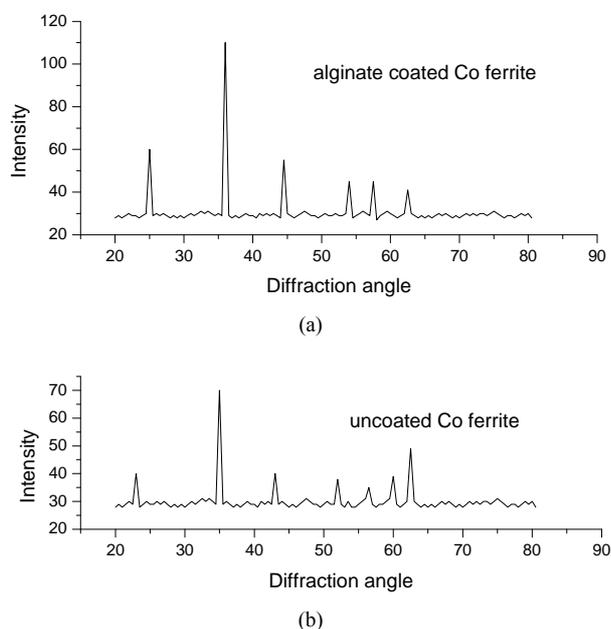


Figure 1. X-ray diffractograms for uncoated and alginate coated cobalt ferrites.

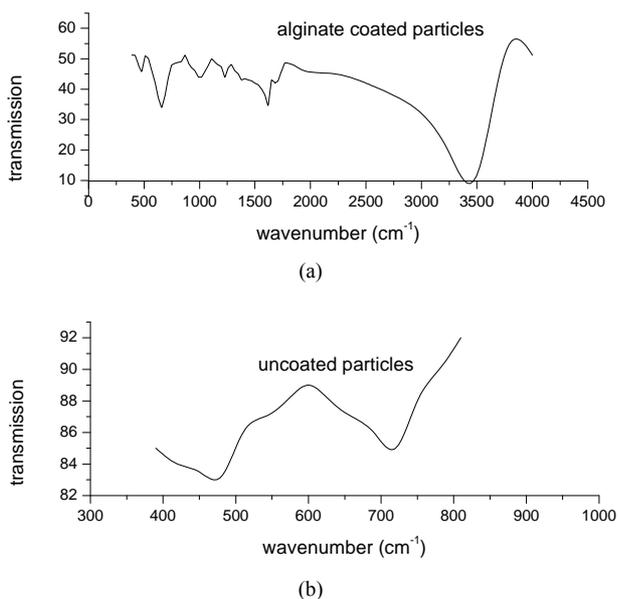
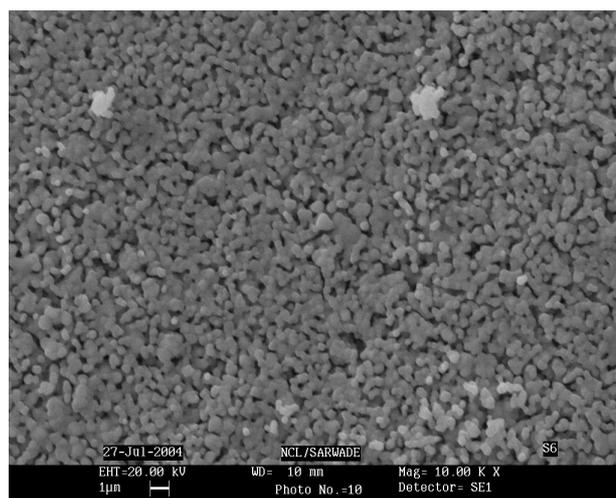


Figure 2. IR spectrograph for uncoated and alginate coated cobalt ferrite.

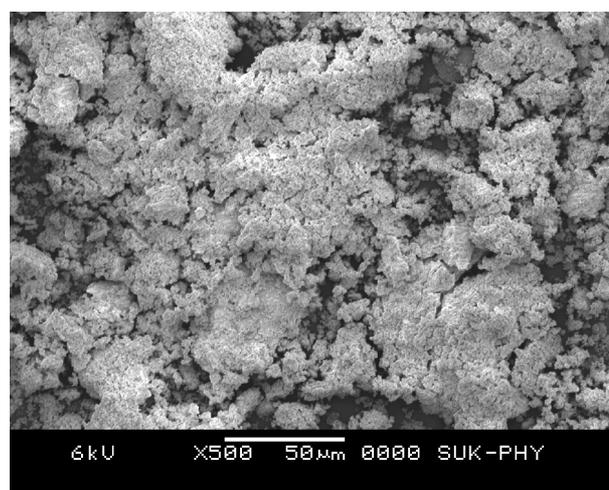
at 3410 cm^{-1} which is attributed to the O-H Stretching vibrations while at 3000 cm^{-1} to the Symmetric C-H Stretching vibrations. The peak at 1697 cm^{-1} and 1622 cm^{-1} may be attributed to the C=O and H-O-H bending vibrations respectively. The peak at 1251 cm^{-1} is attributed to the C-O weak bond due to surfactants while 870 cm^{-1} to the CH_2 rocking vibrations. The peaks at 570 cm^{-1} and 480 cm^{-1} to the Tetrahedral Metal & Oxygen

Stretching and Octahedral Metal Oxygen Stretching vibrations respectively [7]. The shift in characteristic peak towards higher wave number after coating may be attributed to the Doppler shift due to coating material on the ferrite material. The peaks correspond to the alginate structure, confirming the coating of the ferrite powder.

Figures 3(a) and **(b)** depict the microstructure of the uncoated and coated cobalt ferrite samples respectively. The micrographs have been taken on the powder samples and the particle size determined using line intercept method which is 42 nm for uncoated ferrite powder and 78 nm after alginate coating. The XRD analysis also shows the value in the same range. The smaller particle size may be attributed to the method of preparation of the samples. The increase in particle size for coated samples is as expected. The particle size obtained is suitable from



(a)



(b)

Figure 3. (a) SEM micrograph of cobalt ferrite; (b) SEM micrograph of alginate coated cobalt ferrite.

the intended application point of view.

Figure 4 depicts the TGA/DTA plot of alginate coated cobalt ferrite sample. The plot has been used for estimation of percentage of coating material on the magnetic material. It has been used to estimate the amount of magnetic material per unit mass of the coated sample and correlated with the saturation magnetization of the coated sample. The values of saturation magnetization for uncoated and coated samples are 94.4 emu/gm and 32.8 emu/gm respectively [26]. The lower values for the coated samples may be attributed to the percentage reduction of ferrite material in the sample after coating and the surface bonding of coating material with free oxygen ions at the surface in the ferrite material. The amount of magnetic property retained per unit Volume in the coated sample is in the range which may be used in biocompatible applications. Since below which it behaves as a hard magnet making it unsuitable for switching applications [9]. Additionally there is particle size at which stabilizing magnetic energy of the particle is equal to thermal energy of the environment making it unsuitable for such applications. Therefore the size of magnetic nanoparticles is of prime importance from the point of view of application.

4. Conclusions

Uniform sized magnetic nanoparticles can be synthesized using the co-precipitation method and coated with alginate. The retention of requisite amount of magnetization after coating ensures its possible applicability in biologi-

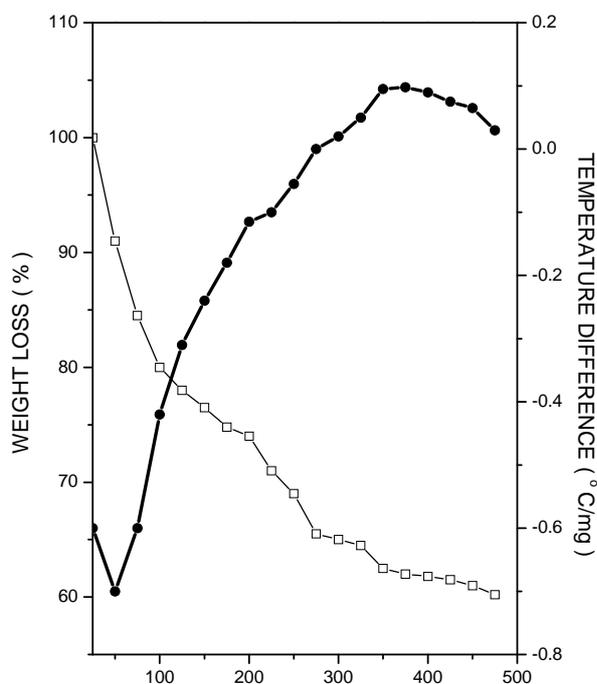


Figure 4. TGA/DTA plot for alginate coated cobalt ferrite.

cal and in vivo applications.

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