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SYNTHESIS AND STUDY OF STRUCTURAL AND MAGNETIC PROPERTIES OF DEXTRIN COATED MANGANESE FERRITE NANOPARTICLES

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Magnetic Nanoparticles are so important, on description of their various and charming uses in extensive technical and systematic grounds. Due to their rare optical, microelectronic and magnetic uses metal oxide nanoparticles are the subject to much attention and frequently differ from other nanoparticles. Dextrin coated $MnFe_2O_4$ is a renowned soft magnetic material with large value of coercivity and reasonable value of magnetization. The main purpose of this study was to synthesize the dextrin coated manganese ferrite ($MnFe_2O_4$) nanoparticles and discuss the magnetic and structural properties of these nanoparticles. Co-precipitation method was used for the preparation of dextrin coated manganese ferrite ($MnFe_2O_4$) nanoparticles. Dextrin and metallic chlorides of manganese and iron were used for the synthesis of dextrin-coated $MnFe_2O_4$ nanoparticles. Sodium hydroxide (NaOH) was used as a precipitant agent. At 600°C temperature calcination was done for 5 hrs. The X-ray diffractometer (XRD) and Scanning Electron Microscope (SEM) were used to study structural properties of the prepared sample. We confirmed the single-phase dextrin coated manganese ferrite nanoparticles by XRD. Vibrating sample magnetometer at room temperature was used to study the magnetic properties of dextrin coated $MnFe_2O_4$ nanoparticles. Fourier Transform Infrared Spectroscopy (FTIR) confirms the attachment of dextrin and other alcohol functional group. In this study, we conclude that by increasing the annealing temperature and growth rate, the size of the nanoparticles may increase. The Sherrer formula was used to calculate the crystallite size, which was 24 nm. At the end, we observed that the large field moment is detected to be insignificant for small particles. The field moment is detected to be significant and touches the bulk value for large particles.

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Keywords: Dextrin, Co-precipitation, Vibrating Sample Magnetometer (VSM), X-ray Diffractometer (XRD), Ferrite, Scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR)

1. Introduction

On the description of nanoparticles, their various and charming uses in extensive technical and systematic grounds. More than a few years the production and characterization of nano-size magnetic materials have a significant role. Due to their rare optical, microelectronic and magnetic uses metal oxide nanoparticles are the subject to much attention and frequently differ from other nanoparticles. $MnFe_2O_4$ is a renowned soft magnetic material with a large value of coercivity and reasonable value of magnetization. These things with their excessive physical and chemical permanency, make manganese ferrite nanoparticles appropriate for magnetic soundtrack use, for example, audio and video film and high density recorded CDs etc. [1, 2]. Dextrin coated $MnFe_2O_4$ is also an important member of ferrite group with various

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applications in the up-to-date era of science and technology. The magnetic behavior of this kind of magnetic nanoparticles used in place of recording mass media depends significantly on the sizes, shape and concentration. These magnetic nanoparticles must be a single domain, of pure phase, having a large value of coercivity and medium value of magnetization. The requirement for rising fabrication procedures that are comparatively very easy and yield organized particle sizes.

Conservative methods for synthesis of magnetic nanoparticles include sol-gel method, evaporation- condensation, laser induced vapor phase reactions, matrix isolation, and aerosols. Most categories of nanoparticle synthesized by using these procedures. One drawback of this type of methods is that, it very difficult to control the size and size distribution [1]. In order to overcome these problems, nanometer size reactors for the development of standardized particles of $MnFe_2O_4$ are used. These nanoparticles are frequently covered and isolated in particular mediums likes oleic acid or sodium dodecyl sulfate, this all is done to guard against the corrosion, and to resist nanoparticles from the accumulation, [3, 4].

It is common, to prevent from accumulation some special techniques are used for the synthesis of dextrin coated $MnFe_2O_4$ nanoparticles [5] or microwave assisted synthesis [6]. In the present work, we have discussed the formation of dextrin-coated manganese ferrites ($MnFe_2O_4$) nanoparticle through co-precipitate technique along with heating at 600^{o}C. The size of nanoparticles and size distribution of these particles was organized via directing nucleation and growth rates. Smaller and uniformly disturbed nanoparticles be there attained, when the growing rate is less than the nucleation rate. The benefit of this technique over the others is that the mechanism of manufacture of manganese ferrite nanoparticles is so simple. The size and size distribution is comparatively easy and there is no need of additional mechanical or microwave heat treatments [7].

Size of nanoparticles and size distribution of the nanoparticles synthesized via this technique was calculated by SEM in addition to XRD. The dependence of the size of nanoparticle on the annealing temperature and annealing time was also discussed [8].

In the current effort, ultra-fine and nano-sized dextrin coated $MnFe_2O_4$ particles synthesized by co-precipitation method by means of dextrin and metallic chlorides of iron and Manganese as precursors. The structural and magnetic properties of these nanoparticles studies by XRD ($\lambda = 1.5304$ A^o), SEM, FTIR and VSM.

2. Experimental procedure

Nano-sized precipitate of dextrin-coated manganese ferrite ($MnFe_2O_4$) was synthesized by co-precipitation technique. The separate metal chlorides in suitable stoichiometric quantities were mixed in a diluted hydrochloric acid (0.1mol/liter Hcl) solution, and heated up to 70^{o}C.

A mixed solution (4mol/ liter) of sodium hydroxide and 12.5 grams dextrin was arranged independently and heated up to 70^{o}C. These hot solutions at that time were quickly mixed up by using magnetic stirring (ending pH 12). The high temperature was then raised up to hundred degree Celsius (100^{o}C) and magnetic stirrer was continuously kept on for an hour. This period is required for crystallization of the dextrin coated manganese ferrite samples. Later on, the mixture was cooled at room temperature by covering jar. Then these the precipitate were collected by a permanent magnet and washed down numerous times by means of distilled water to neutralize the precipitates. The dextrin coated manganese ferrite samples were dried out at room temperature. [9].

The concluding dextrin-coated manganese ferrite precipitates were characterized by SEM (The Philips XL30) operated at 25 Kilovolts and 50 Kilovolts, XRD (X' Pert Pro, PAN alytical, Netherlands), and VSM (BHV-50, Richen Denish Company, Japan). The particles size was determined by Sherrer's method. This size was calculated from the full width at half maximum of the X-ray diffractometer pattern for the plane (311) of the spinel ferrite structure.

$$t = 0.9 \lambda / B \cos \Theta_B$$

Here
"t" is the average crystallite size.
"B" is full width of the relevant diffraction peak.
"λ" is the wavelength and θ is the angle of deflection [10].
The broadening (B) of the diffraction peak matches to the size of the crystal.

3. Results and discussion

X-ray Diffractometer (XRD)

The XRD pattern recorded for dextrin coated manganese ferrite obtained by co-precipitation and calcined at 600 ° C illustrated in Fig. 1. The powder pattern exhibited all the main peaks related to the structure of the single-phase cubic spinel dextrin coated manganese ferrite ($MnFe_2O_{4)}$ [11]. No external peak was noticed in the synthesized sample. The lattice parameter calculated from the XRD information is 8.492Å. The size of the nanoparticles was calculated by Scherrer formula using first two strongest peaks. The average sizes of the particles calcined at 600^{o}C were found to be 19nm and 21±3 nm with variation in sizes being introduced by controlling the rate of mixing of NaOH with the salt solution. Slow rates of mixing resulted in larger size particles as the growth rate begins to exceed the nucleation rate. By further annealing 19 nm particles at 800, 850, 900 and 1000^{o}C respectively for 10 hours, particle sizes of 24, 25, 26 and 27± 3nm were obtained. Finally, on further annealing of the 21 nm particles, at 1000^{o}C for 10 hrs 29 ± 3 nm nanoparticles were obtained. Thus the size variation and control has been achieved by both the rate of reaction and the annealing conditions. Slow mixing rates have led to larger particles when the growth rate starts to go beyond the nucleation rate. The values of the lattice constant and the particle size are in line with the previously published results of manganese ferrite prepared by co-precipitation, as well as other methods.

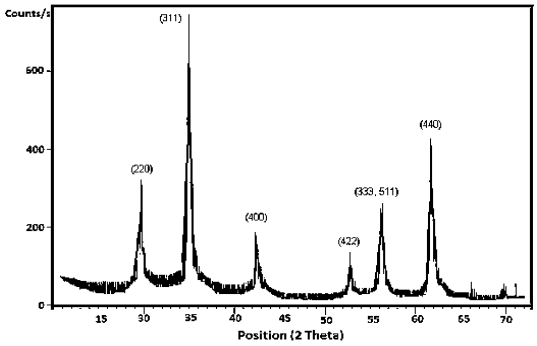

Fig. 1. XRD pattern of dextrin coated manganese ferrite powder.

Scanning Electron Microscopy (SEM)

The morphological model of the prepared dextrin coated manganese ferrite powder taken by scanning electron microscopy is shown in Fig. 2 with different magnification. The SEM visibly indicates that nanostructure of the particles in the sample is ultra-small. There is a very large amount of grains that contain many small atoms in Nano-size, with an average particle size of 24 (±5, n=200) nm. The size distribution is extraordinarily narrow also, there are some larger nano-size particles that also have normal growth.

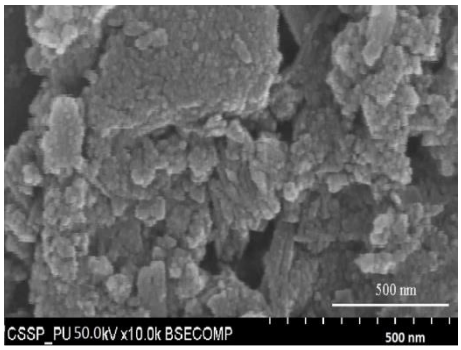

Fig. 2. SEM of $MnFe_2O_4$ sample coated with dextrin.

Size distribution

Figure 3 shows the distribution of the size of these nano-size particles as acquired by the XRD data. The distribution appears to be symmetrical around 24 nm, with nanoparticles of size 19-29 nanometers for the sample. The highest number is in the middle of 23 and 25 nm, reaching a maximum of 24 nm, in accordance with the size of the crystalline materials in XRD, which was 24 nm. Most of the particles have a spherical shape, though some lengthened nanoparticles are also existed as shown in SEM image. Some agglomerated nanoparticles, along with separated nanoparticles are existing in the images [12].

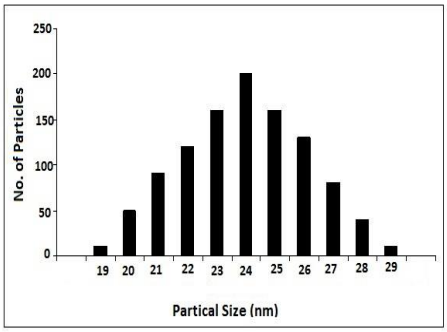

Fig. 3. Distribution of the size (histogram) of $MnFe_2O_4$ nanoparticles coated with dextrin.

Particle size and annealing temperature

Fig. 4 demonstrates the correlation among the particle size and annealing temperature. This shows that the size of particles increases by increasing linearly with the annealing temperature. It appears that that increase in size with temperature becomes rapid between 900-1000^{o}C and appears to be slowing down above 1000^{o}C. While annealing generally decreases the lattice defects and strains, however it can also cause coalescence of crystallites that results in increasing the average size of the nanoparticles [13]. The particle size appears to increase almost linearly with annealing temperature, most likely due to the fact that longer annealing temperature enhances the mobility of atoms that increases coalescence process resulting in an increase in the particle size. Thus it appears that particle size may be controlled by annealing temperature [14].

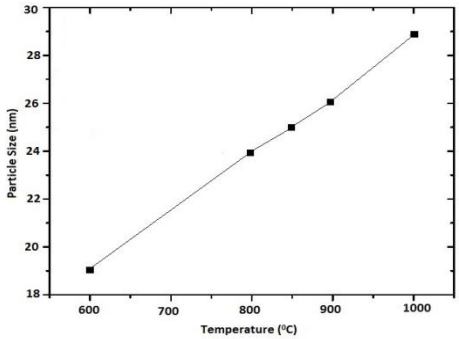

Fig. 4. Correlation b/w the particle size and annealing temperature.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra recorded for synthesized dextrin coated of $MnFe_2O_4$ powder is shown in Fig. 5. The IR spectra indicated that two main metal–oxygen bands due to vibrations of the Fe–O and Mn–O at the tetrahedral site appear in the frequency range 500–660 cm^{-1} and also their vibrations at the octahedral site in the frequency range 400–480 cm^{-1} [15,16]. Also, the adsorption broad band at the range of 3200–3450 cm^{-1} represents a stretching mode of –OH groups and H2O molecules. In the case of as-synthesized powders, weak adsorption bands appeared at 1000–1255 cm^{-1} and 2315–2720 cm^{-1}which can be attributed to the formation of symmetrical and asymmetrical stretching vibration of the O–H mode, C–O mode, C=H stretching-mode and CH2 groups as organic sources in the magnetic nanoparticles. However, these organic functional groups does not exist in this type of samples which annealed at high temperature. The strength of dextrin coated manganese ferrite nanoparticles was also investigated by recording FTIR spectra. It was establish that coating of the nanoparticles was stable for no less than four months.

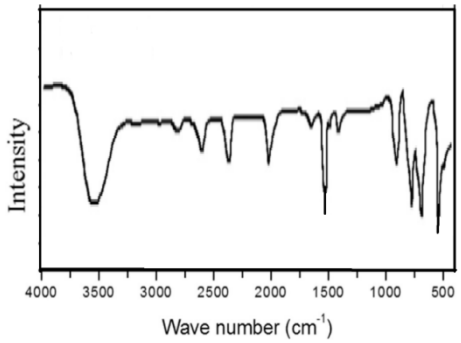

Fig. 5. FTIR spectrum of dextrin-coated of $MnFe_2O_4$ Nanoparticles.

Vibrating Sample Magnetometer (VSM)

Fig. 6 demonstrates the hysteresis loop of $MnFe_2O_4$ sample coated with dextrin taken from the VSM at room temperature. Instead of having a smaller size, the sample showed a clear hysteresis curve that showed a typical magnetic behavior with a non-zero coercivity and remanence. The value of the magnetic saturation 16.47 emu /g for the value of B is equal to 6.5 KOe. The hysteresis loop of the low area shows that the formed material is of soft magnetic material which have much repute in magnetic memory purposes and as well as a MRI contrast agents [17].

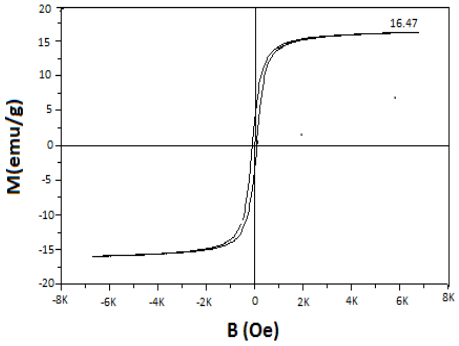

Fig. 6. Magnetic hysteresis curve of $MnFe_2O_4$ sample coated with dextrin measured at room temperature via VSM.

From the above whole discussion, it is clear that, which nanoparticles we have synthesized are nano-sized and their structure is ultra-fine. We also coated these nanoparticles with dextrin, which makes them water suspendable and avoid these nanoparticles from agglutination. We have discussed in detail that agglomeration increases with the increase in annealing temperature. We have also seen the magnetic behavior of these nanoparticles which is exactly in our favor, magnetization increases with increase in annealing temperature [18]. We have compared these all results with other published research work, but we have some advantages over them. Our synthesized nanoparticles are nano-sized, ultra-fine, water suspendable and these nanoparticles are non-agglutinate.

4. Conclusion

In this research work, we present the synthesis of dextrin-coated $MnFe_2O_4$ nano-size particles having size in the range of 24 nm. The size of these nano-size particles was calculated by means of XRD and SEM. They coincided wonderfully, indicating that there was no agglomeration and that the size distribution of the prepared nanoparticles was a little bit small. The size of the nano-size particles seemed to increase linearly with annealing temperature and time most probably due to coalescence that increases with increasing temperature of anneal [13]. It is obvious that the size of nano-size particle and their size distribution can be organized by monitoring the reaction rate, annealing temperature and the interval of reaction. Instead of having a smaller size, the sample showed a clear. Hysteresis curve that showed a typical magnetic behavior with a non-zero coercivity and remanence. We find that for smaller particles the saturation magnetization had a value that was significantly lower than the bulk value while the larger size particles have values approaching those of the bulk

In this work, an effort is made possible to synthesize the dextrin coated manganese ferrite nanoparticles by a very simple co-precipitation process that has achieved reasonably incredible success, resulting in small particle size and good magnetic properties as shown by the curve of hysteresis taken by VSM. It was also found that the magnetic properties of dextrin coated manganese ferrite nanoparticles increased with increasing the annealing temperature. In addition, we needs to perform further studies on the synthesis of dextrin coated bismuth doped manganese ferrite nanoparticles for MRI, CT scan and X-Rays contrast agents.

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