Synthesis of capped nanosized $Mn_{1-x}Zn_xFe_2O_4$ ($0 \leqslant x \leqslant 0.8$) by microwave refluxing for bio-medical applications

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Abstract

Substituted ferrites [$Mn_{1-x}Zn_xFe_2O_4$ ($0 \leqslant x \leqslant 0.8$)] of nanoscale dimensions have been prepared by a novel microwave refluxing method. The effect of different parameters [such as pH, reflux time, presence of PEG (MW-3350) molecules] on particle morphology and size has been studied. Characterization of the above capped particles was done by XRD, FTIR, TEM and SQUID magnetometry. The as-prepared particles were further used for magnetoliposome preparation.
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1. Introduction

The synthesis of monodispersed magnetic nanoparticles has been an interesting area of study because of its possible applications in a variety of widely diversified areas ranging from information technology to nano-biotechnology. Fe_3O_4 and γ-ferrite are known to be biocompatible within certain threshold limits. Substituted ferrites having attractive temperature-sensitive magnetic properties could be useful and hence may be employed effectively in nano-biotechnology. Different wet chemical methods (e.g. co-precipitation, sol–gel, microemulsion, citrate gel routes, hydrothermal synthesis, etc.) have been used to synthesize spinel ferrites [1–4]. Among the wet chemical methods, hydrothermal synthesis appears to be superior for preparing ultra-fine, well-crystallized ferrite powders [5–7].

The long reaction time at low temperatures (below 200 °C) in conventional hydrothermal process may be accelerated by introducing microwave (MW) heating (called microwave hydrothermal M-H). MW heating reduces the processing

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time and energy cost and has been known in the food industry for over half a century, but its use in chemistry, however, started only from 1986 [8,9]. Its use in the field of inorganic synthesis is therefore relatively recent. During the synthesis of materials, the exact nature of the MW interaction with the reactants is not understood well [10].

In our previous paper, we successfully synthesized ultra-fine Co–Zn ferrite and investigated the influence of different synthesis parameters on microstructure-related properties [11]. We have now investigated the system $Mn_{1-x}Zn_xFe_2O_4$ ($x = 0-0.8$) by varying the refluxing time, pH and volume of polyethylene glycol (PEG) (MW-3350) on the particle size and dispersity.

2. Experimental

$Mn_{1-x}Zn_xFe_2O_4$ ($0 \leqslant x \leqslant 0.8$) has been synthesized by the microwave refluxing technique using a standard 2.45 GHz microwave oven. The experimental arrangement has already been discussed in one of our earlier papers [11]. Analytical grade precursor salts of $MnCl_2 \cdot 4H_2O$, $FeCl_3$ and $ZnCl_2$ were taken in stoichiometric amounts and dissolved in a fixed volume of ethylene glycol. The pH of the solution was varied between 9 and 13, while the refluxing time was varied from 30 min to 3 h. The PEG concentration in the reaction mixture was varied from 0.1 to 0.001 mol. The as-prepared particles were washed several times to bring down the pH to 7. This was followed by washing with methanol for 5–6 times to remove water. These particles give stable dispersion in chloroform ($CHCl_3$) in the presence of phosphatidyl choline (PC).

Thermogravimetric analysis (TGA) was done on the air-dried precursor using a Thermowage L 81 (LINSEIS, Germany) TGA unit. Phase identification of the samples was done by X-ray diffraction (XRD) studies using a Philips powder diffractometer PW1710 with CuK_α radiation. The infrared spectra of the synthesized materials were obtained using a Nicolet spectrometer. The transmission electron microscopy (TEM) of the powder samples was done by a Philips CM 200. For the TEM observation, the powder was first dispersed

in isopropyl alcohol by ultra sonication and then the suspension was deposited dropwise on to a carbon-coated copper grid and dried. The low temperature as well as room temperature magnetization measurement was done using a SQUID magnetometer (quantum design) MPMS-XL7.

3. Results and discussions

Fig. 1a and b shows the typical TGA curve of the as-prepared air-dried $MnFe_2O_4$ sample prepared at different pH and refluxing time, respectively. All the TGA curves show the same pattern of decomposition, but the percentage of weight losses at different temperatures is different. The weight loss at ~150 °C is attributed to the physically and chemically adsorbed water, or surface –OH groups. The weight losses at ~250 °C for different samples are different, which may be attributed to decomposition of capped organic molecules (ethylene glycol or its polymer) [12]. In the co-precipitation method, the formation of ferrite phase (Mn-ferrite) increases with increasing pH up to 12. A further increase in pH results in the formation of paramagnetic hydro-hausmanite $Mn_3O_4 \cdot nH_2O$ [13]. As the reflux time increases, the weight loss at around 100 °C is found to decrease. At this temperature, the weight losses for the three different refluxing times (90, 120 and 180 min) are 10%, 2% and 1.25%, respectively, which account for the associated water and –OH group. An interesting observation is that the percentage weight gain at around 400 °C gradually increases with refluxing time. This weight gain could be ascribed to the formation of surface carbonate, as the capped magnetic particles interact with oxygen at temperatures above 200 °C [12]. The weight gain at around 400 °C increases from 0.3% to 1.2% when the refluxing time increases from 90 to 180 min. This is due to the fact that with more refluxing, the dispersity of the particles increases (observed from TEM micrographs), which would suggest better capping of particles by EG/PEG molecules on the particle surface. Fig. 1b shows the % weight losses of the sample prepared at two different values of pH = 9 and 12.5. The weight loss for the samples with pH = 9
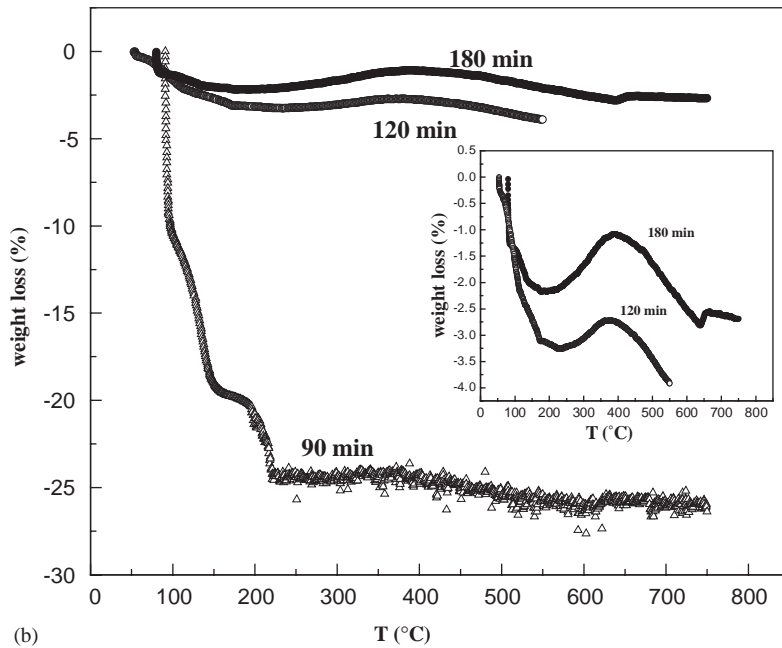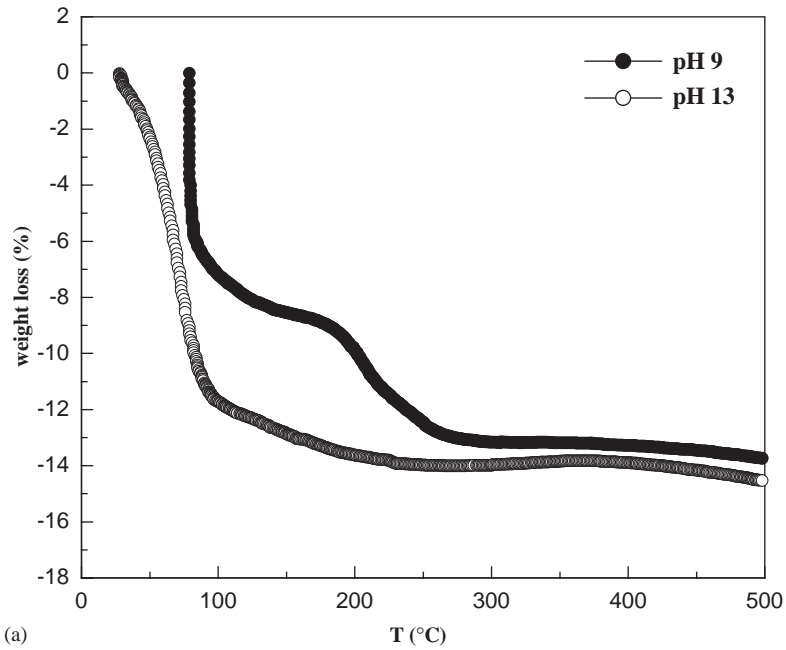
Fig. 1. (a) TGA plot of air-dried Mn-ferrite prepared at different pH (9 and 13) with a fixed refluxing time of 30 min. (b) TGA plot of Mn-ferrite prepared at different refluxing times at fixed pH 11. The inset is a magnified TGA plot of the samples with refluxing times of 120 and 180 min.

and 12.5 are 8% and 12%, respectively, up to 100 °C, which corresponds to associated water. The weight loss between 100 and 250 °C is 4.5% and 2%, respectively. The weight gain above 250 °C for the sample prepared at pH = 13 is more than the sample with pH = 9. This would suggest that the formation of carbonate at the surface due to decomposition of organic molecules (EG/PEG) is more for the sample prepared at higher pH. This result implies that at higher pH, the adsorbed molecules are bonded on to the particle's surface such that it will not decompose around 250 °C but at 400–500 °C. A higher pH gives a better capping which leads to smaller particle size.

The formation mechanism of nanoparticles in glycothermal reaction may be similar to that of hydrothermal reaction [14,15]. Ethylene glycol acts as solvent and complexing agent, and also aids in capping molecules during the growth of nuclei. It may form complexes with metal ions and become polymerized through ethylene glycol intermediates, which give rise to nanosize particles. The water required for hydrolysis is obtained from the reaction between ethylene glycol and KOH [16]. Solution chemistry plays a significant role in the nucleation, growth, dispersion and morphology of nanoparticles thus prepared.

Fig. 2 shows the FTIR spectra of pure PEG and Mn ferrite. The adsorbed water is featured by bands at 3420 and 1620–1630 cm^{-1}, which are assigned to O–H stretching and H–O–H bending modes of vibration [12,17]. These bands are observed in all the PEG coated and as well as in blank PEG. But the intensity of these bands is different. A band around 580 cm^{-1} is possibly caused by the stretching vibration due to the interactions produced between the oxygen and the cation occupying the octahedral and tetrahedral sites [18]. But for pure PEG and coated magnetic particles, clear bands are observed at around 3400–3450 cm^{-1} (v_{O-H}) and 1000–1030 cm^{-1} (v_{C-O}), which are attributed to the presence of –OH, and C–O group vibration modes. Spectra of the as-prepared nanoparticles consist of bands at 2878 and 2948 cm^{-1} and are attributed to symmetric and asymmetric methylene (–CH$_2$–) and methyl (–CH$_3$) vibrations [19]. The bands observed between 1405 and 1460 cm^{-1} are due to the bending vibration of the –CH$_2$– group. It is important to note that all these peaks may be either due to ethylene glycol molecules or PEG.
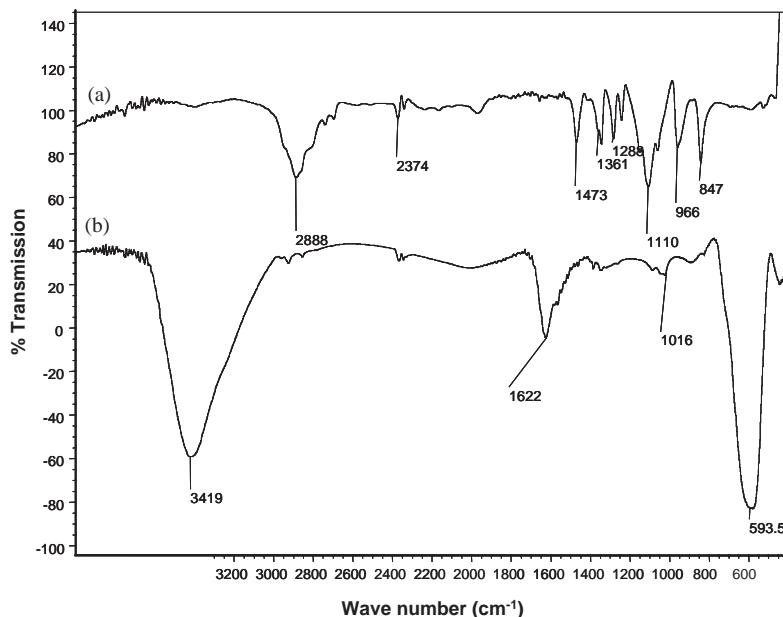

Fig. 2. FTIR spectra of (a) pure PEG and (b) Mn-ferrite prepared in the presence of 0.01 M PEG solution.

The absorption band at $1100\,cm^{-1}$ is created by the C–O–C stretching that indicates the presence of linkage in the absorbed molecules due to PEG. FTIR studies revealed that the PEG molecules are on the surface of as-prepared particles. Since the PEG has large chain length, it imparts a higher repulsive steric hindrance, resulting in better dispersity of the as-prepared particles.

Fig. 3 shows the XRD patterns of the as-prepared $MnFe_2O_4$ sample, which corresponds to single-phase cubic ferrite lattice. The crystallite size is measured from XRD line broadening using Scherer's formula:

$$D = 0.9\lambda/\beta\cos\theta,$$

where D is average crystallite size, λ is the X-ray wavelength used, β is the angular line width of half maximum intensity and θ is Bragg's angle in degrees. It has been observed that with pH increasing from 9 to 13, the crystallite size decreases from nearly 8 to 6 nm.

Fig. 4 shows the magnetization (M) vs. field (H) curve at 300 K for samples prepared at two different values of pH (pH = 13 (TSH4) and 9 (TSH5). From the curve it is observed that the sample prepared at higher pH has lower magnetization compared to that of the sample prepared at lower pH. It is also observed from the TGA curve that the weight loss for TSH4 is higher (14%) than for TSH5 (12%). This presumably corresponds to the percentage of non-magnetic components present in the system.

The blocking temperature (T_B) is determined from the branching of the ZFC and FC curves or from the maxima in the ZFC data. As is well
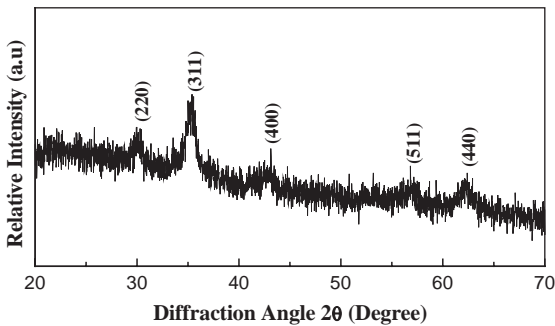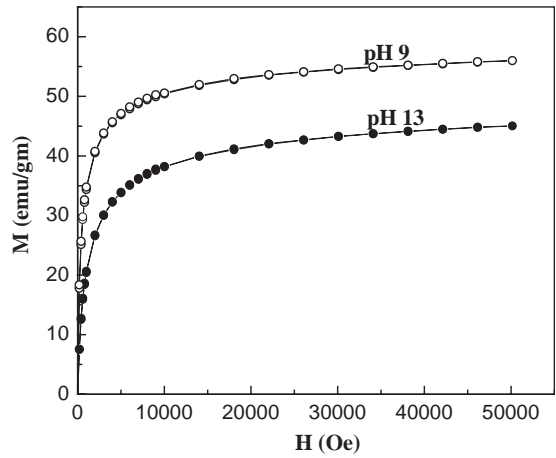

Fig. 4. Magnetization vs. field plots of sample prepared at different pH with a fixed refluxing time of 30 min.
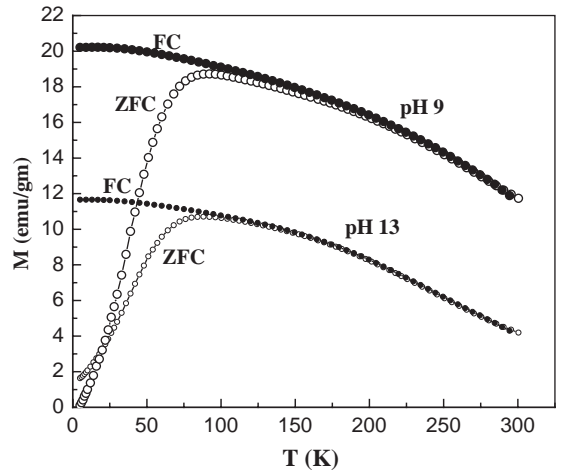

Fig. 5. Magnetization vs. temperature plots (ZFC and FC) of sample prepared at pH 9 (TSH5) and pH 13 (TSH4).

known, above T_B, superparamagnetic particles become thermally unstable and magnetization exponentially decreases as KV/kT is less than 1 where the symbols K, V, k and T have their own significance.

In Fig. 5, the sample TSH5 shows the splitting of the ZFC and FC curve at 181 K, whereas for the sample TSH4, the splitting is at around 100 K. Considering that T_B is the temperature where the branching takes place, TSH4 has lower blocking

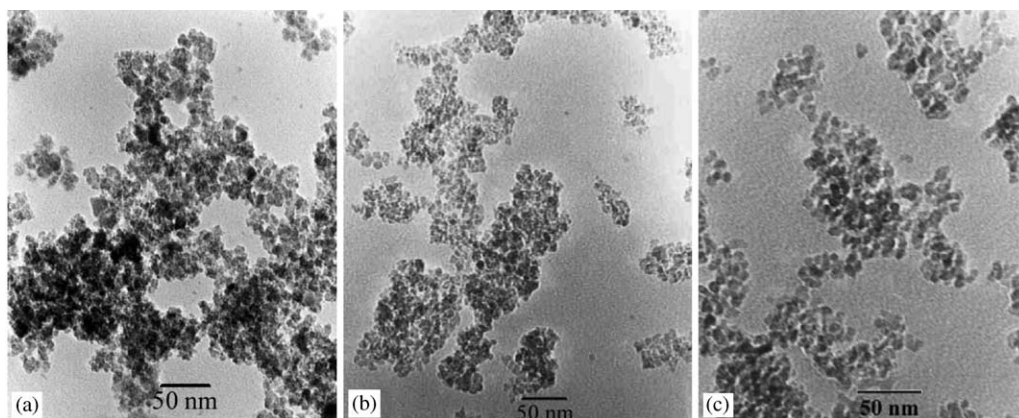Fig. 3. XRD pattern of as-prepared air-dried Mn-ferrite.

Fig. 6. Transmission electron microscopy picture of capped magnetic particles ($MnFe_2O_4$) prepared at (a) pH 9 refluxed for 30 min, (b) pH 13 refluxed for 30 min, and (c) pH 11 refluxed for 160 min.

temperature than TSH5. The peak magnetization of the ZFC curve is also different for different samples. For TSH5 it is 92 K, whereas for TSH4 it is 88 K. T_B depends on the interaction between particles as well as particle size. It is noteworthy that the difference between T_B and T_{peak} is much higher for TSH5 (181 vs. 92 K) compared to TSH4, which is relatively smaller (100 vs. 88 K). These have been discussed in terms of particle size distribution and inter-particle dipole–dipole interaction [20]. If the distance between the particles is more, then the inter-particle dipole–dipole interaction is less, thereby shifting T_B to a lower temperature. A similar trend is observed for small particle sizes. As the particles are smaller, T_B shifts to lower temperature.

When the particles are chemically coated with EG/PEG, i.e. capped, the blocking temperature is suppressed to a lower temperature. In the case of TSH5, there is a tendency towards agglomeration as is observed from the TEM micrographs. These agglomerated particles act as a cluster, resulting in an increase in the blocking temperature. For TSH4, which appears to be capped, the total magnetic moment decreases due to the contribution of the volume of the diamagnetic mass (coating/non-magnetic materials) to the total sample.

Fig. 6(a)–(c) shows the TEM micrograph of $MnFe_2O_4$ particles prepared under different pro-

cess conditions. In Fig. 6a, the particles are in an agglomerated state, which is formed at pH = 9 whereas relatively less agglomeration is seen for the sample prepared at pH = 13 (Fig. 6b). This may be attributed to better capping of ethylene glycol molecules on the particles. Fig. 6(c) shows that the particles are relatively separated (dispersed) and are spherical. It has been observed that the dispersity increases with refluxing time. From the magnetization, TGA and XRD data, it is clear that with increasing pH and refluxing time the capping of EG/PEG molecules is also increased, resulting in smaller relatively dispersed particle formation.

4. Conclusions

Ultra-fine Mn–Zn ferrites have been successfully synthesized by a microwave refluxing method. The particle morphology and size depend on different parameters such as pH, refluxing time, and the presence of long chain molecules (PEG). PEG improves the water dispersity of the as-prepared particles. The extent of capping on magnetic particles increases with refluxing times and pH, leading to lower particle sizes. This method of microwave refluxing provides an edge over other chemical methods in terms of energy conservation efficiency and particle size distribution.

Acknowledgements

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