Influence of Surfactant Concentration (carboxymethylcellulose) on Morphology and Particle Sizes of Cobalt Nanoferrites

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Cobalt ferrite nanoparticles were synthesized at different concentration of carboxymethylcellulose (CMC) by coprecipitation route. The influence of CMC concentration on the physical properties of cobalt ferrite nanoparticles has been investigated. All samples, annealed in the furnace at 500§C for 6 h, were characterized through Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Keywords: Nanoparticles, Coprecipitation, X-Ray diffraction, Surfactant

In the last few years an increasing interest in magnetic ferrite nanoparticles is associated with their wide applications in several technological fields including biomedical healthcare. Considerable promise of cobalt ferrite for applications in biomedical and diagnostic fields such as targeted drug delivery, hyperthermia treatment for malignant cell and magnetic resonance imaging (MRI) were intensely investigated [1-3]. Depending on the type of applications magnetic $CoFe_2O_4$ nanoparticles are used such as surface functionalized particles with controllable size ranging from a few nanometers up to tens of nanometers. The key to improve the reproducibility, the biocompatibility and the purity of the resulted nanoparticles is the preparation method [4-7]. A multitude of methods have been proposed to increase the stability of the magnetic nanoferrites in polar or non-polar solvents [8, 9]. These synthetic protocols include co-precipitation method [10], sol-gel method [11], hydrothermal [12], one step citrate–nitrate method [13], combustion method [14] and microemulsion [15].

Among these synthetic protocols, we chose to prepare $CoFe_2O_4$ capped nanoparticles by simple aqueous coprecipitation of cobalt (II) chloride and ferric (III) chloride solutions using NaOH such as alkali and carboxymethylcellulose (CMC) such as surfactant.

This work shows the influence of CMC concentration on synthesis, morphology and particles size of cobalt nanoferrites.

Experimental part

The reagents used, $CoCl_2\cdot 6H_2O$, $FeCl_3\cdot 6H_2O$ and NaOH were of analytical grade and were used without any further purification. In a typical procedure [13] the mixed aqueous solution of 0.2M $CoCl_2\cdot 6H_2O$ and 0.4M $FeCl_3\cdot 6H_2O$ were stirred together for 30min into the reaction vessel of 200 mL. A solution of CMC with 0.1, 0.5, 1.0, 1.5 and 2.0% was added into above solution as a capping agent, followed by the addition of an aqueous solution of 3M NaOH. The *p*H of the solution was continuously monitored and maintained in the range of 11-12. The solution was heated to 80°C and it was constantly stirred for 60 min. The solution was then cooled to the room temperature. A blackish precipitate was magnetically separated and washed several times with distilled water and ethanol. The precipitate was dried for 12h at 110°C and appeared black in color. The samples were heated in the furnace, in air atmosphere, at 500°C for 6h.

Characterization

Fourier transmission infrared (FT-IR) spectra of the powders (as pellets in KBr) were recorded using a Fourier transmission infrared spectrometer (FTIR Spectrometer, Jasco 660 Plus) in the range 4000-400cm^{-1} with a resolution of 4 cm^{-1}. The annealed samples were characterized for crystal phase identification by powder X-ray Diffraction (XRD) using the X-ray diffractometer (LabX XRD-6000) with CuK$_\alpha$ radiation (λ = 0.15406nm). The particle size, chemical composition and external morphology of the fine annealed powders were characterized by scanning electron microscopy, SEM (Tescan, VEGA II LSH).

Results and discussions

FTIR spectroscopy

To understand the absorption mechanism of surfactant molecules on the surface of cobalt nanoferrites FTIR spectra of as-prepared samples synthesized at different concentration of CMC and annealed powders are presented in figure 1 respectively figure 2.

The IR spectra of as-prepared samples (fig. 1) have one broad band in the range 3429.5 - 3437.39cm^{-1}. The characteristic vibrations at 2922.51 - 2924.36cm^{-1} and 2851 - 2858.69cm^{-1} are assigned to the stretching of asymmetric and symmetric vibrations of methylene group ($-CH_2-$) of carboxymethylcellulose. The two distinct vibrations presented in the spectrum in the frequency range 1625.23 - 1634.11cm^{-1} and 1386.46 - 1442.1cm^{-1} are attributed to symmetric and asymmetric vibrations of carboxylic group (COO-). The intense peaks present in the spectra for all as-prepared samples at 581-588.14cm^{-1} corresponds to stretching vibrations of Me-O characteristic cubic spinel structure [14, 15].

In figure 2 is shown the spectra for annealed at 500°C of CMC capped cobalt nanoparticles prepared at different concentration of CMC solution. Observing peaks around 580cm^{-1} confirm the formation, in all samples, of the cubic spinel phase. Additionally, as it can be observed, all samples

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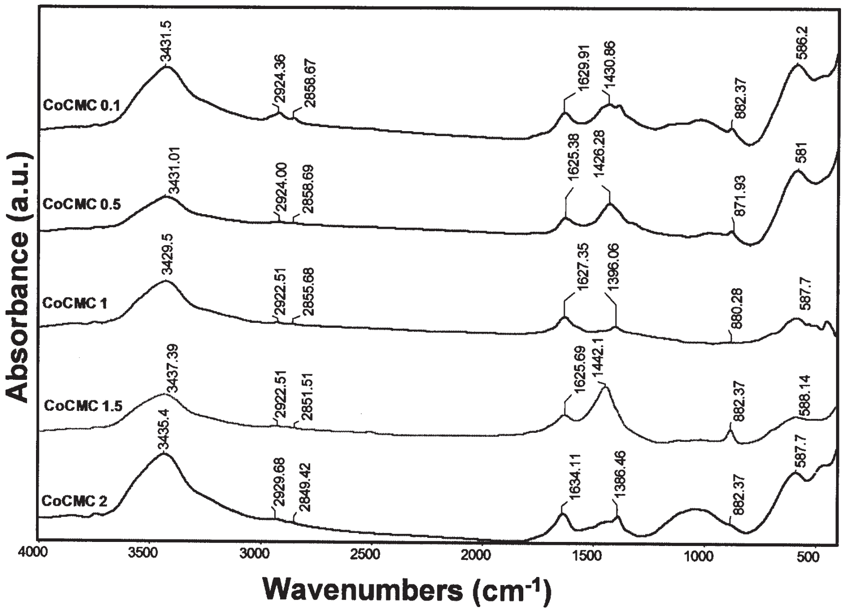

Fig. 1. FT-IR spectra of as-prepared cobalt nanoferrites

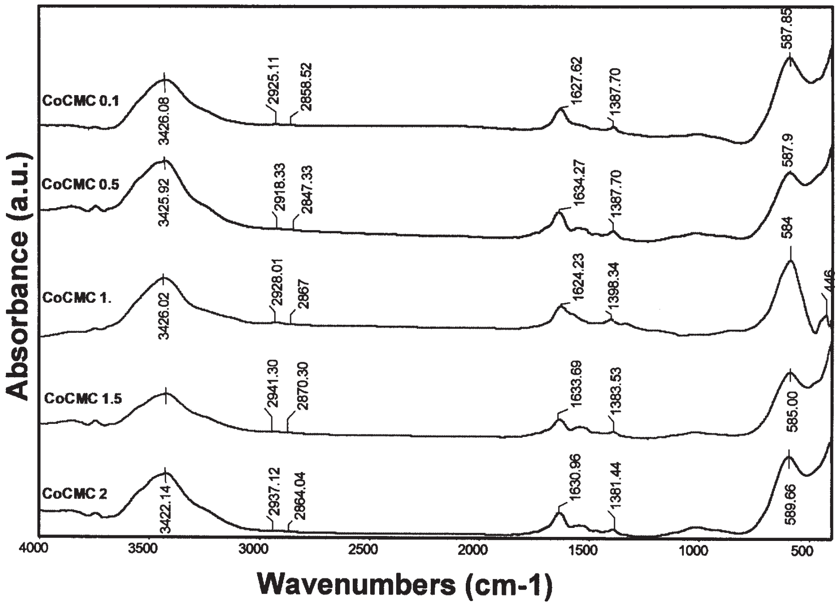

Fig. 2. FT-IR spectra of annealed cobalt nanoferrites at 500 °C / 6 h

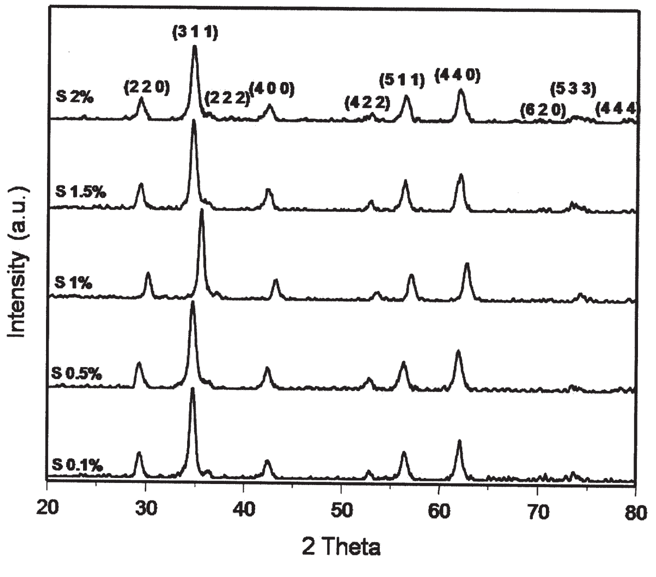

Fig. 3. Powder X-Ray diffraction patterns of $CoFe_2O_4$ prepared with different concentration of CMC and annealed at 500°C for 6 h

present the peaks like in the case of as-prepared powders but the positions are moved to the lower values and the intensity is increased. Because the functional group of surfactant molecules exhibit absorption vibrations bands even for this samples annealed at 500°C, that suggest the nonexistence of physically absorbed CMC and the formation of monolayer of CMC on the surface of $CoFe_2O_4$ nanoparticles.

Powder X-Ray diffraction analysis

The X-Ray diffraction patterns at room temperature of the calcined powders synthesized at different concentration values of CMC solution are given in figure 3. The calcined samples contain only a phase, which have a cubic spinel structure (*Fd-3m*) with $CoFe_2O_4$ phase (JCPDS no. 22-1086). The analysis of XRD patterns of all synthesized samples reveal the presence of spinel phase without any XRD peak corresponding to the other phases such as Fe_2O_3, CoO or Co_3O_4.

The diffraction patterns for all samples have been analyzed by the refinement method using FULLPROF program [16] and the refined data are listed in table 1.

SEM analysis

Figure 5 shows the SEM micrographs of the cobalt nanoferrites synthesized by varying the concentration of carboxymethylcellulose in the range 0.1-2.0%. It can be seen from this SEM images that the preparation protocols and conditions reactions (different concentration of CMC) have a significant influence on the texture and morphologies of the obtained products.

Sample	Cell parameter (nm)	Cell volume (nm^3)	D_{XRD} (nm)
CMC 0.1%	0.8371	0.5867	10.5
CMC 0.5%	0.8380	0.5885	10.1
CMC 1%	0.8374	0.5873	12.5
CMC 1.5%	0.8386	0.5898	10.2
CMC 2%	0.8375	0.5875	8.9

Table 1
CELL PARAMETER, CELL VOLUME AND CRYSTALLITE SIZE OF $CoFe_2O_4$ AT DIFFERENT CONCENTRATION OF CMC, ANNEALED AT 500 °C.

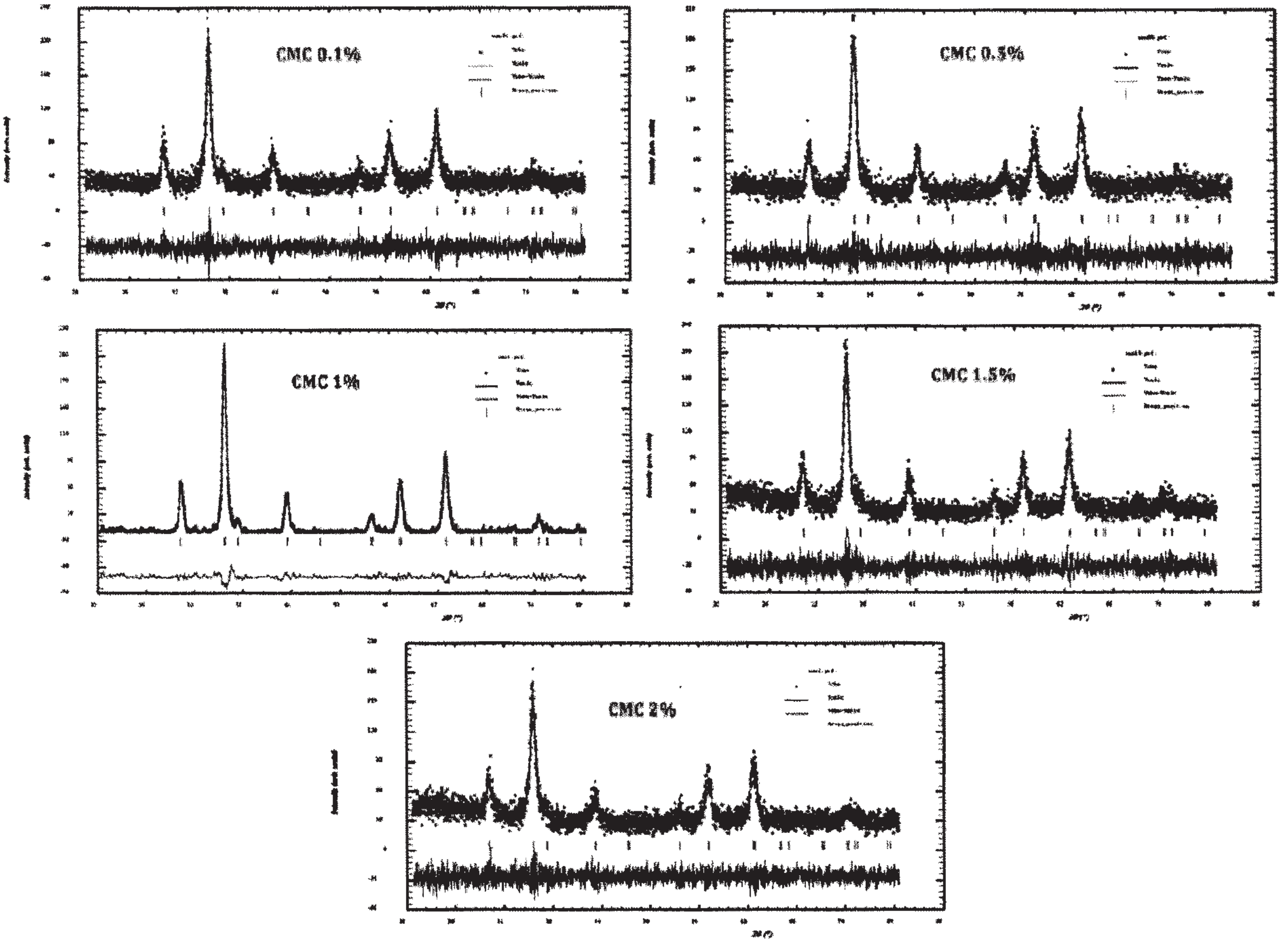

Fig. 4. XRD patterns of $CoFe_2O_4$ prepared at various concentration of CMC and calcined at 500°C (observed and calculated)

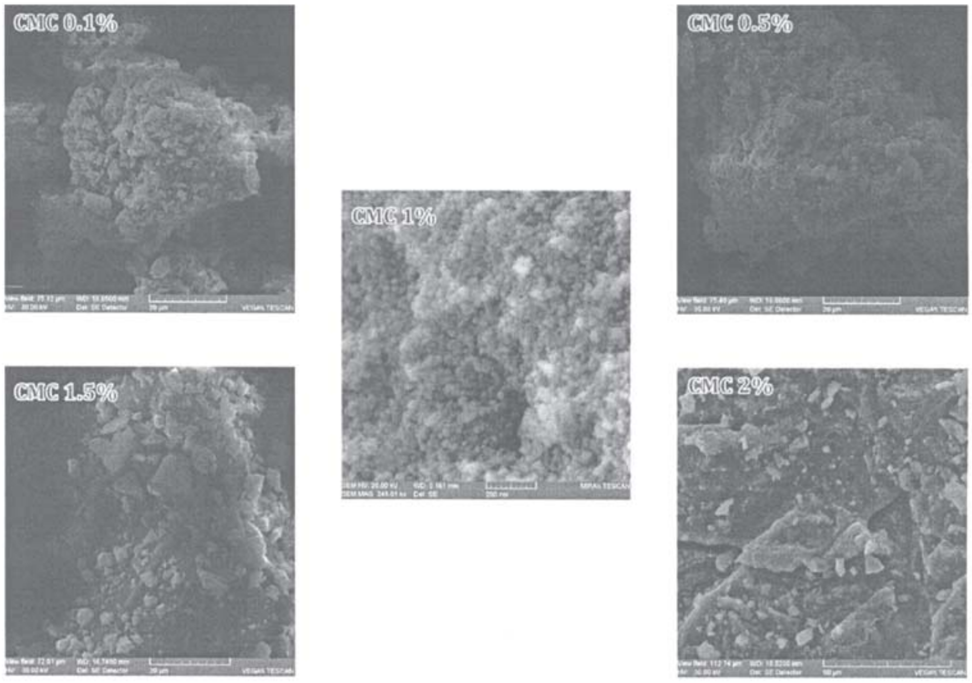

Fig. 5. SEM micrographes of cobalt nanoferrite prepared at various concetration of CMC (0.1, 0.5, 1.0, 1.5 and 2.0%)

The micrographs (CMC 0.1% and CMC 0.5%) show irregular size of the particles with high degree of agglomeration. In whatever manner, the nanoparticles of cobalt ferrite synthesized with concentration of CMC 1.0% are spherical and well-separated [13]. For the nanoparticles prepared at concentration of CMC 1.5% exhibit more agglomerations in comparison to the nanoparticles synthesized at CMC 1.0% and the particles display some type morphologies. Irregular type morphologies can be also observed when the cobalt ferrite was done at CMC concentration 2%.

Conclusions

In conclusion, nanocrystalline cobalt ferrite was successfully synthesized by coprecipitation method changing the condition reactions by varying the concentration of surfactant. The cubic spinel phase was confirmed by XRD measurements. The bonding of functional groups from CMC on the surface of nanoparticles was also confirmed by FTIR analysis. The influence of different concentration of CMC on the size and on the morphologies was also investigated to find the appropriate parameters of the synthesis. The variations of concentration during the synthesis method are found to be crucial on the structural morphologies of the nanoparticles. The optimum concentration of CMC to obtain spherical nanoparticles is 1%.

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