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SYNTHESIS OF COBALT FERRITE NANOPARTICLES VIA A SOL-GEL COMBUSTION METHOD

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ABSTRACT. This paper presents the synthesis of $CoFe_2O_4$ nanoparticles via a sol-gel combustion method. Nanoparticles with the grain size in the range of 20-70 nm were synthesized using hydrated nitrates of cobalt and iron, sucrose and pectin. Sucrose was used as a polycondensation agent for the formation of the gel. The reaction mechanism for the gel formation is discussed in the paper. The addition of pectin facilitated the formation of a hard gel through the drying of the precursor solution at 200°C. Through a thermogravimetric analysis on the gel, the temperature at which the entire organic part has decomposed is concluded. The fine black nanopowder was obtained after a thermal treatment of the gel at a temperature of 700°C. Infrared spectroscopy (FT-IR) highlighted the presence, respectively the absence of organic compounds before and after the thermal treatment. Structural, morphological and magnetic measurements were conducted using X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM).

Keywords: *$CoFe_2O_4$, Sol-gel, nanoparticles, magnetic, ferrite*

INTRODUCTION

Given the various applications of $CoFe_2O_4$ spinel ferrite, in areas such as magnetic recording, magnetic fluids and micro wave devices [1,2], this paper explores the possibility of synthesizing said particles through a cost-effective, environmentally safe, sol-gel combustion method.

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Adapting a technique proven successful in synthesizing other oxide nanoparticles such as NiO, ZrO_2, La_2O_3, $BaFe_{12}O_{19}$ [3,4] a $CoFe_2O_4$ single phase fine powder was obtained.

Recent studies have reported the successful synthesis of spinel cobalt ferrite through various other methods such as the precipitation method [5], the solvothermal method [6], the co-precipitation method [5], the hydrothermal method [7], and the sol-gel PVA method [8].

The reason behind studying and opting for this sol-gel route is that the reactants used for the process are cost effective, and the polycondensation and gelation agents (sucrose and pectin, respectively) are safe and environmentally friendly.

Sucrose was utilized in the synthesis of nanopowders for various purposes: as a source of C for obtaining composites [9-11], as fuel for obtaining nanomaterials through the combustion method [12-22], and as a chelation agent for the sol-gel method [23-32].

Adapting the sucrose-pectin sol-gel method for obtaining $CoFe_2O_4$ following the drying of the precursor solution, a hard porous gel was obtained. For a thorough understanding of the calcination process that followed, a thermogravimetric analysis was conducted. Results from this analysis gave information regarding the quantitative and qualitative composition of the gel, and the temperatures at which the combustion reactions (organic decompositions) occur.

X-ray diffraction and FT-IR techniques were used in order to characterize the structural properties and purity of the obtained powder and TEM imaging was used for the morphological characterization.

By using these characterization methods, the study concludes that the sucrose-pectin sol-gel combustion method is viable in obtaining $CoFe_2O_4$ nanoparticles with the grain size of 20-70 nm.

RESULTS AND DISCUSSIONS

The following mechanism was proposed for the formation of $CoFe_2O_4$ nanoparticles:

Global reaction:

$$Co(NO_3)_2{\cdot}4H_2O + 2Fe(NO_3)_3{\cdot}9H_2O + nC_{12}H_{22}O_{11} + (12n-2)O_2 \rightarrow CoFe_2O_4 + 8NO_2 + 12nCO_2 + 11(n+2)H_2O$$

Thermal analysis of the gel decomposition

The thermal analysis (Figure 1) describes the decomposition process of the gel. Correlating the TG curve with the process at hand, we attribute the different stages of weight loss as follows:

In the interval of 20-150°C, a 5.89 % weight loss is experienced, attributed to the evaporation of water present in the gel.

The combustion of the gel takes place in the 150-471°C temperature range, in two stages. The first process, between 150-395 °C, is slightly exothermic and has a mass loss of approximately 51.17%. The second process, between 395-471°C, is strongly exothermic and has a mass loss of 40.6%.

Above 471°C, no weight loss was recorded.

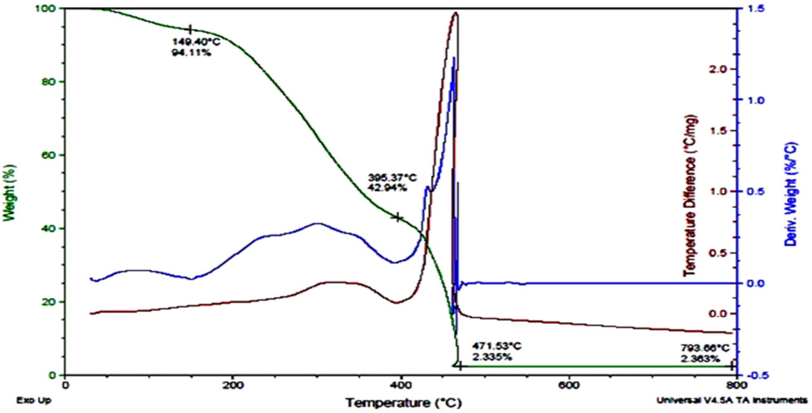

Figure 1. Thermal analysis of the dried gel

X-ray diffraction

The structural characterization was carried out at room temperature by powder X-ray diffraction using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation in the 2θ region 20°-70°. The crystallite sizes were calculated using the Debye-Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where β is the peak full width at half maximum (in radians) at the observed peak angle θ, k is the crystallite shape factor (was considered 0.94) and λ is the X-ray wavelength.

The X-ray diffraction pattern (Figure 2) shows that the $CoFe_2O_4$ powder is in a single phase and well crystallized in the cubic spinel structure, with the lattice parameter of 8.382(3) A, obtained from Rietveld analysis. The broadened XRD maxima indicates that the crystallite size is in the nanometer range. The crystallite size calculated using the Debye-Scherrer formula is about 65 nm.

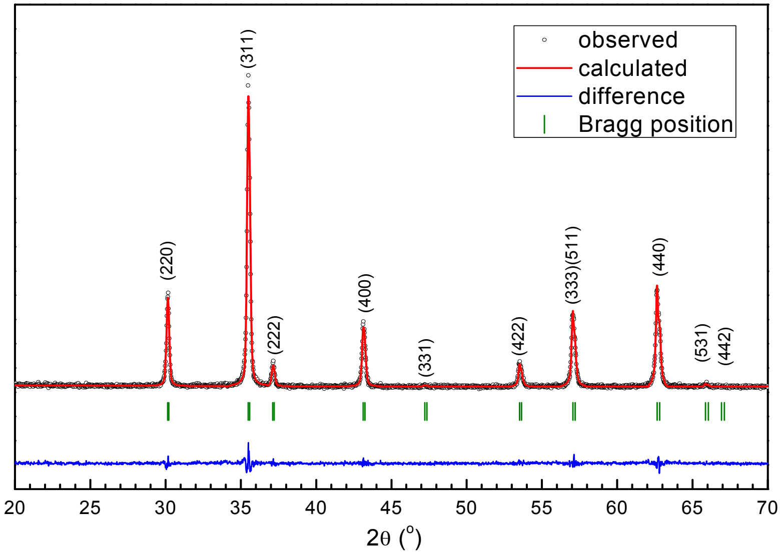

Figure 2. XRD pattern of the $CoFe_2O_4$ nanopowder

FT-IR spectroscopy

The FTIR spectra of the precursor and the thermally-treated samples have been presented in Figure 3. The peaks from the precursor spectra can be assigned to the main chemical groups of the starting reagents. The large band observed at approximately 3290 cm^{-1} is attributed to the stretching vibration - $\nu(OH)$ of water. The asymmetric $\nu_{asym}(CH_2)$ and the symmetric $\nu_{sym}(CH_2)$ stretching modes can be observed at 2932 and 2865 and are in good agreement with the literature [33,34]. The interaction between pectin and metal salts is shown by presence of the asymmetric $\nu_{asym}(COO^-)$ and the symmetric $\nu_{sym}(COO^-)$ stretching modes observed at 1630 and 1340 cm^{-1} that correspond to the carboxylic anions coordinated by the metal ions. The difference in their frequencies $\Delta\nu(COO^-)=\nu_{asym}(COO^-)-\nu_{sym}(COO^-)$ is around 290 cm^{-1} suggesting a bidentate coordination between the carboxylate and metal ions. [35] The band at 1539 cm^{-1} is attributed to the stretching vibration of NO^{2-} group, while the CH_2 wagging mode is observed at 1447 cm^{-1}. In the 1100-600 cm^{-1} domain the precursor spectrum presents bands corresponding to symmetric stretching mode of C-O-C group (1037 cm^{-1}) and to the wagging mode of C-O bond (778 cm^{-1}). The high intensity band observed in the 600-350 cm^{-1} domain is assigned to the stretching modes of metal-oxygen bonds. The FTIR spectrum of the thermally treated sample confirms the decomposition of the organic part and the stretching vibrations corresponding to the metal – oxygen bonds increase in intensities.

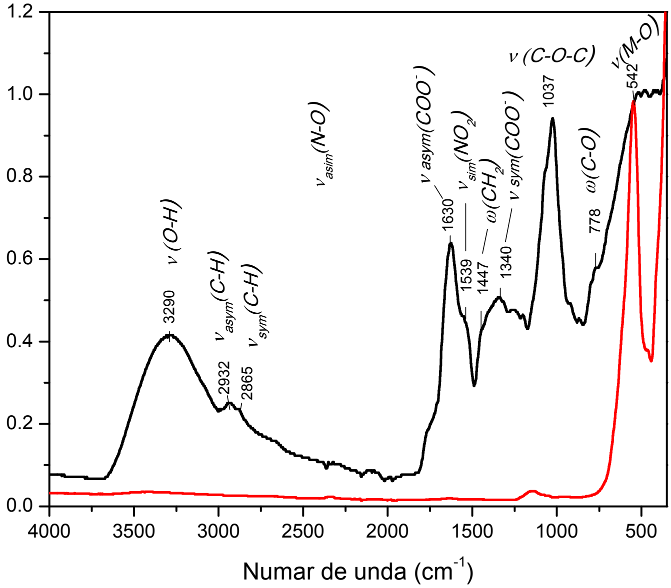

Figure 3. FT-IR spectra of the dried gel (black) and the $CoFe_2O_4$ powder (red).

Transmission electron microscopy

The TEM analysis presented in Figure 4 reveals mildly agglomerate pseudo-spherical particles with a grain size ranging between 20 – 75 nm.

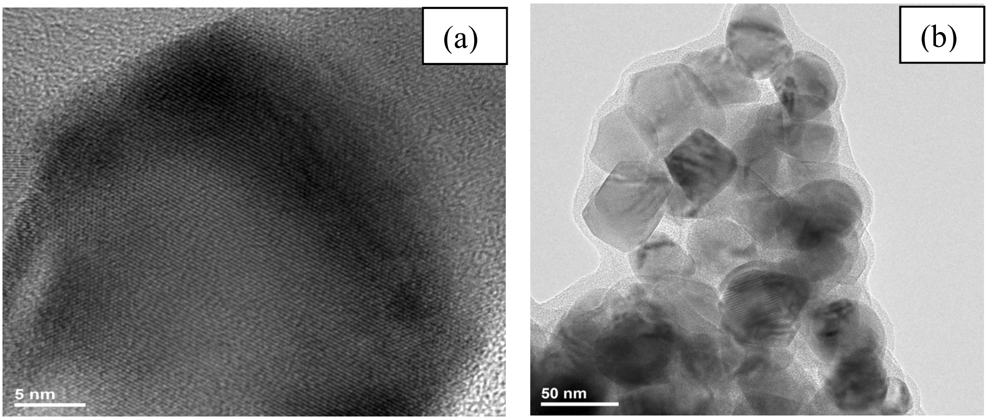

Figure 4. TEM images of the $CoFe_2O_4$ nanoparticles at a scale of 5 nm (a), and 50 nm (b)

Vibrating sample magnetometer

Figure 5 shows the field dependence of magnetization for $CoFe_2O_4$ nanoparticles at room temperature. For the $CoFe_2O_4$ nanoparticles the value of the saturation magnetization (Ms) and coercivity (Hc) are found as ~1.2 emu/g and ~55 Oe respectively. The small value of the coercivity of $CoFe_2O_4$ nanoparticles indicates that these nanoparticles are near the superparamagnetic limit. The M(H) curve also contains a linear part at higher fields indicating a very significant paramagnetic contribution to the magnetization.

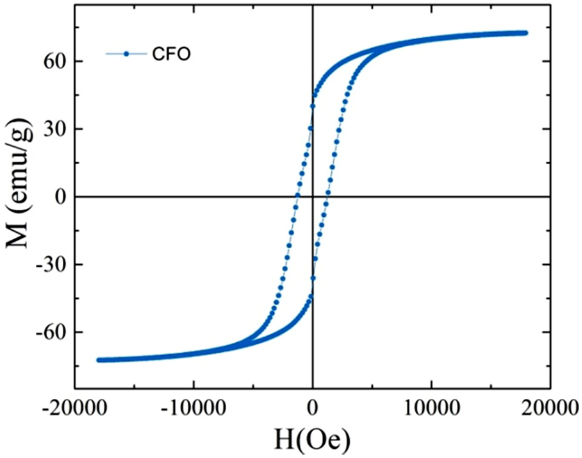

Figure 5. Magnetic hysteresis loops for $CoFe_2O_4$ nanoparticles at room temperature.

CONCLUSIONS

Through this endeavor it has been proven that $CoFe_2O_4$ nanoparticles can be synthesized via the sol-gel, pectin-sucrose route. This method has potential value considering these organic compounds are non-toxic, cheap and available at an industrial scale. Also it is worth mentioning that by proving that $CoFe_2O_4$ can be synthesized through this method, it has again been validated that the sol-gel method has immense applicability, is versatile and could be used for synthesizing various other systems.

Following the information in this paper the process could be easily adapted at a large scale.

The thermogravimetric analysis, besides giving information about the decomposition of the gel can prove useful in devising calcination diagrams for this kind of products.

Using X-ray diffraction and FT-IR spectroscopy it has been proved that the obtained powder is a single phase spinel $CoFe_2O_4$ ferrite.

TEM imaging has permitted the precise view regarding the size and shape of the obtained particles. The results showed mildly agglomerate particles with a grain size of 20-75 nm.

The small value of coercivity of $CoFe_2O_4$ nanoparticles indicates that these nanoparticles are near the superparamagnetic limit.

EXPERIMENTAL SECTION

Synthesis of $CoFe_2O_4$ ferrite nanoparticles

The $CoFe_2O_4$ nanoparticles, were obtained via the sol-gel method, using sucrose as a poly-condensation agent and pectin as a gelation agent. In order to synthesize 2 mmols of $CoFe_2O_4$, 2 mmols of $Co(NO_3)_2{\cdot}4H_2O$ and 4 mmols of $Fe(NO_3)_3{\cdot}9H_2O$, respectively, were separately dissolved in Milli-Q water. The solutions were heated to 60°C and vigorously stirred. The quantity of water needed was deduced by slowly adding droplets to the solutions until the full dissolution of the precursor salts. As the pre-mentioned solutions were getting thoroughly homogenized, 14.6 mmols of sucrose were dissolved in 50 ml Milli-Q water. The obtained sucrose solution was halved, and each half was mixed with the precursor solutions under strong magnetic stirring, lowering the temperature to 40°C. After 30 minutes the two solutions were mixed, continuing the strong magnetic stirring. Following the homogenization of the solution, pectin was added in a quantity of 1:5 weight ratio - pectin: sucrose. After 20 minutes of stirring, using a 1 M solution of nitric acid, the pH was fixed to be in the range of 1.5-3. This final solution was poured in a ceramic capsule and subjected to drying at 80 °C for 24 hours and at 200 °C for another 24 hours. After the annealing of the gel at 700°C for 2 hours, a fine black powder was obtained.

Analysis Techniques

Thermogravimetry and differential thermal analysis (TG/DTA) curves were recorded with a thermal analyzer TA Instruments SDT Q600 up to 800°C, in air, at a heating rate of 10°C/min, using Al_2O_3 as a reference.

The structural characterization has been carried out at room temperature by powder X-ray diffraction using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation in the 2θ region 20°-70°.

FT-IR spectral analysis was conducted using a Nicolet 6700 FT-IR Spectrometer.

The high-resolution images were obtained using a Tecnai G2 F30 S TWIN transmission electron microscope, TEM, (FEI, Nederlands), equipped with a STEM/HAADF detector. The microscope operates at an acceleration voltage of 300 kV (Schottky field emitter) with a TEM point resolution of 2 Å nm and a TEM line resolution of 1 Å.

The magnetization properties were studied using a vibrating sample magnetometer (VSM Lake Shore).

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