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Magnetic Spinel-Type $CoFe_2O_4$ Nanoparticles: Synthesis and Investigation of Structural, Morphological Properties

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Abstract: Spinel-type metal oxide nanoparticles were synthesized via co-precipitation approach. Mono ethylene glycol (MEG) was used as a capping agent to stabilize the particles and prevent them from agglomeration. The structural, morphological and thermal properties of the calcined sample were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), raman spectroscopy and thermal analysis. Energy-dispersive X-ray analysis (EDX) has also proved that the element composition was composed of pure single phase and contained Co, Fe and O elements. The mean crystallite size of the prepared ferrite nanoparticles was determined to be in the range of 30-345 nm based on the SEM images. The magnetic measurements of the $CoFe_2O_4$ nanoparticles were examined with a vibrating sample magnetometer (VSM) at room temperature to determine their magnetic behavior and the magnetic parameters were found.

Manyetik Spinel-Tipi $CoFe_2O_4$ Nanopartiküllerinin Sentezi, Yapısal ve Morfolojik Özelliklerinin İncelenmesi

Anahtar Kelimeler
$CoFe_2O_4$,
Ferrit,
Nanopartiküller,
Raman,
SEM,
Spinel

Özet: Spinel-tipi metal oksit nanopartikülleri birlikte çöktürme yaklaşımı ile sentezlenmiştir. Monoetilen glikol (MEG) parçacıkları stabilize etmek ve aglomerasyonu önlemek için kaplama maddesi olarak kullanılmıştır. Kalsine edilmiş numunenin yapısal, morfolojik ve termal özellikleri, X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM), raman spektroskopisi ve termal analiz ile karakterize edilmiştir. Enerji dağılımlı X-ışını analizi (EDX), aynı zamanda element bileşiminin, saf tek bir fazdan oluştuğunu ve Co, Fe ve O elementlerini içerdiğini kanıtlamıştır. Hazırlanan ferrit nanoparçacıklarının ortalama parçacık boyutunun, SEM görüntülerine dayanılarak 30-345 nm aralığında olduğu belirlenmiştir. $CoFe_2O_4$ nanopartiküllerinin manyetik ölçümleri, manyetik davranışını belirlemek amacıyla oda sıcaklığında titreşimli örnek manyetometre (VSM) ile incelendi ve manyetik parametreleri bulundu.

1. Introduction

Magnetic metal oxide nanocomposites have attracted a great deal of attention as a composite materials on account of their various applications such as lithium ion batteries [1-3], magnetic catalysis [4, 5], magnetic resonance imaging (MRI) [6], sensor and actuators, tissue repairing, microwave devices and biotechnology [7].

Among the various spinel ferrites, $CoFe_2O_4$, as a well-known hard magnetic material, has versatile and technologically important materials owing to its high saturation magnetization [8], high coercivity [9], strong anisotropy [10], thermal stability and mechanical hardness. Therefore, $CoFe_2O_4$, nano composites are the subject of intense research not only for their fundamental scientific interest, but also for their potential applications in magnetic storage media, bio sensing applications [11], catalytic [4, 5, 12, 13], super paramagnetic materials [14, 15] and medical applications. The properties of these nanocomposites mainly depend on their shape, size and structure, which are strongly determined by the preparation methods. Therefore, there are various methods which have been reported previously for the preparation of $CoFe_2O_4$ nanocomposites [16-20].

In present work, we were focused on the synthesized of cobalt ferrites using capping agent (MEG) [21] and were fabricated by co-precipitation method.

We proposed that the use of MEG is highly advantageous for the synthesis in order to reduce

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particle agglomerates as well as to obtain single phase $CoFe_2O_4$ nanoparticles. The synthesized $CoFe_2O_4$ nanocomposites were examined by XRD, SEM, EDX analysis, Raman spectroscopy and TGA/DTA and VSM in order to determine the phase formation, morphology, elemental analysis, vibrational frequencies, thermal stability and magnetic behaviour respectively.

2. Experimental

2.1. Material and methods

$FeCl_3.6H_2O$, $CoCl_2.6H_2O$, Mono ethylene glycol (MEG) (capping agent) and NaOH were purchased from Merck and used without further purification. In addition, ethanol and distilled water as a solvent were used.

The synthesized $CoFe_2O_4$ nanocomposites were subjected to X-ray diffraction studies [using a Panalytical diffractometer and a Cu Kα radiation source] to determine the crystal phase composition. The formation and elemental compositions of $CoFe_2O_4$ nanoparticles were confirmed by scanning electron microscopy combined with an energy dispersed X-ray analysis which was carried out using FEI Quanta FEG 250. Raman spectra were recorded using a Renishaw Invia model Raman Spectrophotometer. Thermogravimetric analysis (TGA) and differential analysis (DTA) were performed by using a Schimadzu DTG-60H instrument under nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The heating rate was 10 °C/min. Magnetic measurements were investigated using Lakeshore 7407 model VSM analyzer at room temperature.

2.2. Preparation of $CoFe_2O_4$ nanocomposite

0.02 mmol of $FeCl_3.6H_2O$ and 0.01 mmol $CoCl_2.6H_2O$ were individually dissolved in the 20 mL of MEG and then two solutions were mixed on magnetic stirrer at 70 °C to achieve a homogeneous solution. Then sodium hydroxide solution were added slowly into the solution under magnetic stirring and the mixture immediately turned into a dark brown. The obtained precipitation was filtered, washed several times with distilled water and ethanol to afford the pure product and dried in air. Subsequently, the dried product was calcined in furnace at 700 °C for 6 h in order to remove the organic compounds such as MEG, ethanol leading to the formation of pure cobalt ferrites nanocomposites, as indicated in Figure 1.

3. Results

3.1. Phase identification by XRD

The phases and crystallinity of the calcined specimen were identified by X-ray powder diffraction. As shown in Figure 2, the X-ray pattern of the synthesized $CoFe_2O_4$ nanoparticles was depicted.

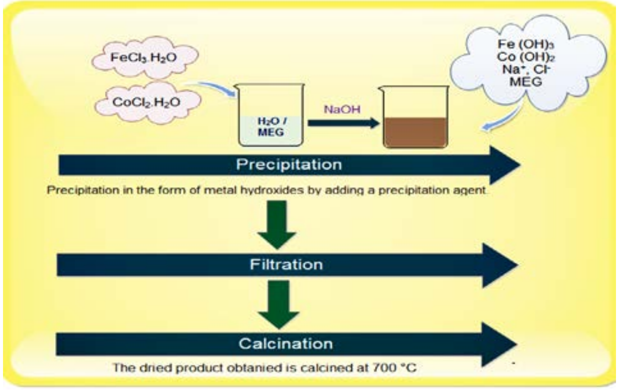

Figure 1. Schematic representation of the formation of $CoFe_2O_4$ nanoparticles by a co-precipitation process.

It can be seen from the relative intensities and positions of all the peaks that the crystalline structure of the product was confirm the presence of single-phase $CoFe_2O_4$ with a face-centered cubic structure, which was according to JCPDS card no 22-1086. No other characteristic peaks were detected except for $CoFe_2O_4$ nanoparticles in XRD patterns.

3.2. Morphological characterization

The morphology of the nanoparticles was determined using SEM analysis. It is clear from Figure 3 and 4 that $CoFe_2O_4$ have non-uniform morphology with the individual particles have a particles size from 30 to 345 nm but there is agglomeration of particles. We conclude from SEM analysis that non-uniform, heterogeneous morphology and grown $CoFe_2O_4$ particles have agglomeration due to magnetic force.

The composition of structure was analyzed by EDX as illustrated in Figure 5. The nanocomposite which consisted of only three kinds of elements, Co, Fe and O were observed as indicated in Table 1.

In the EDX pattern, the presence of Fe, Co and O elements in proper proportions suggested that the expected stoichiometry was maintained in the prepared samples. These results indicated that had spinel form of calcined $CoFe_2O_4$ nanoparticles and neither sodium nor carbon signals were detected so, it means that product was pure and had not any impurities.

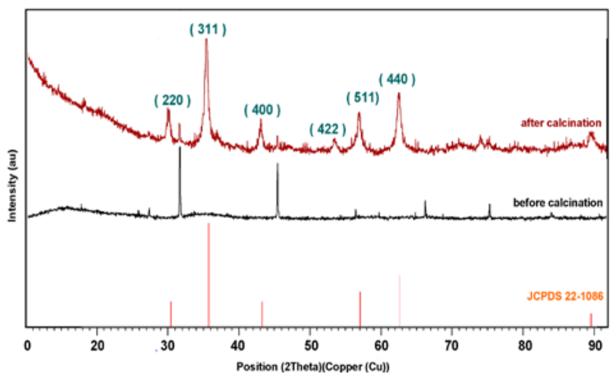

Figure 2. The XRD diffraction patterns of as prepared $CoFe_2O_4$ nanoparticles after calcination, before calcination and reference pattern, respectively.

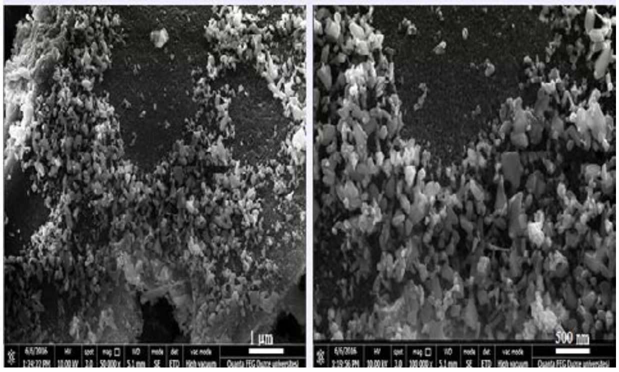

Figure 3. SEM images of calcined $CoFe_2O_4$ nanoparticles.

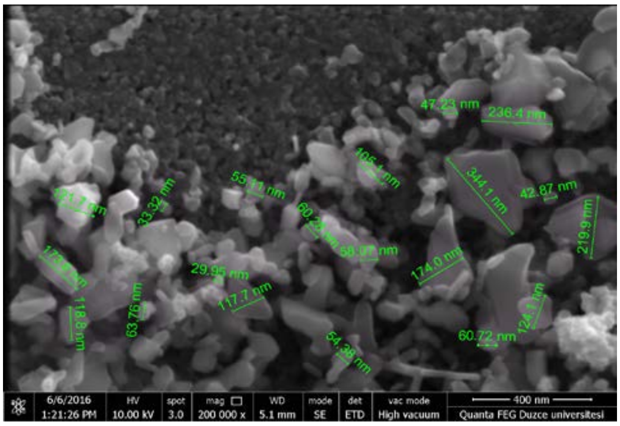

Figure 4. SEM images of calcined $CoFe_2O_4$ nanoparticles.

Table 1. The elemental composition of $CoFe_2O_4$ nanoparticles according to EDX spectrum.

Element	(wt. %)			
	I.	II.	III.	Average
CoK	17.78	17.68	16.50	17.32
FeK	49.54	54.71	52.40	52.21
O K	32.68	27.61	31.10	30.46

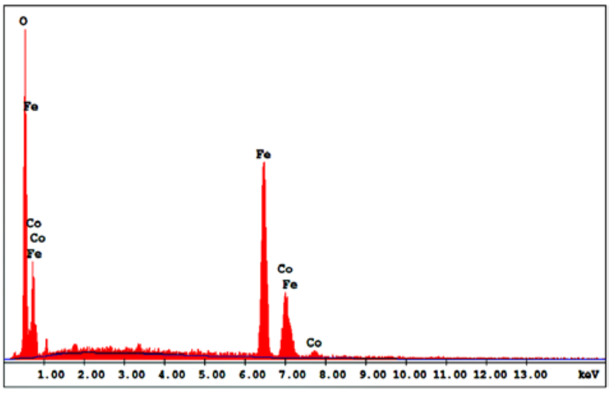

Figure 5. EDX image of calcined $CoFe_2O_4$ nanoparticles.

3.3. Spectroscopic characterization

As shown in Figure 6, Raman spectra of the $CoFe_2O_4$ nanoparticles (a) were showed six peak maxima at 188, 300, 473, 564, 616 and 689 cm^{-1} , respectively. Five Raman active modes of cobalt ferrite $3T_{2g}$, E_g and A_{1g} were tabulated in Table 2. E_g and T_{2g} (3) modes correspond to the symmetric and anti-symmetric bending of oxygen atom in M-O bond at octahedral void. A_{1g} mode were related to the motion of oxygen atom around metal ions (Co^{2+}-O, Fe^{3+}-O) in the tetrahedral sites at 619 and 689 cm^{-1}[22].

But, two peaks at 506 and 601 were observed in the raman spectrum taken without calcination. The medium band around 1250 cm^{-1} was correspond to stretching of oxygen-carbon vibration associated with the MEG as shown in Figure 6.

The thermal behaviours of the as-prepared $CoFe_2O_4$ nanoparticles were determined by using TGA/DTA with flow rate N_2 of 50 mL per minute as shown in Figure 7.

Table 2. Observed Raman modes for after calcination (a) and before calcination (b) of $CoFe_2O_4$ nanoparticles

Entry	Assigned Raman modes	(a)	(b)
1	$T_{2g}(3)$	188	-
2	E_g	300	-
3	$T_{2g}(2)$	473	-
4	$T_{2g}(1)$	564	-
5	$A_{1g}(1)$	689	-

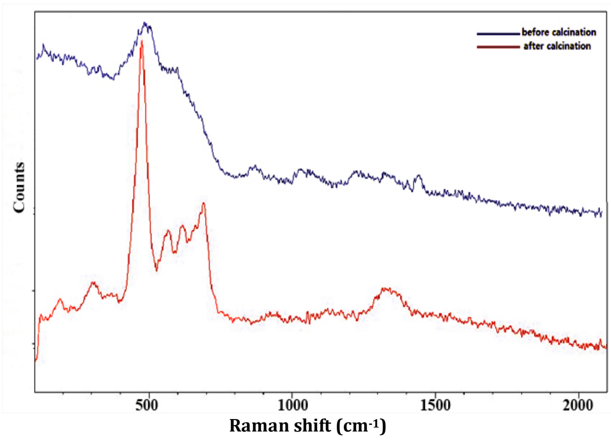

Figure 6. The Raman spectra of $CoFe_2O_4$ nanocomposites: after calcination (a) before calcination (b).

From the TG curve of the calcinated sample no appreciable weight loss to 790 °C was observed. The DTA graph showed an exothermic reaction between 790 and 990 °C, which corresponded, on the TGA graph, to a 10.95 % weight loss. The reason for this weight loss was the presence of hydroxyl groups in the structure and this similar behavior was supported by literatures [23, 24].

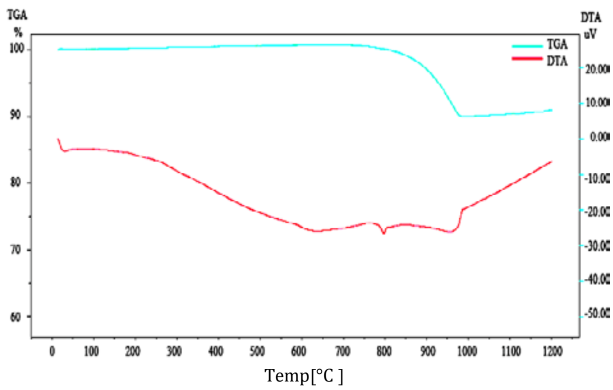

Figure 7. The TGA / DTA curve of the calcined $CoFe_2O_4$ nanoparticles at 700 °C.

3.4. Magnetic properties

Magnetic measurements of the $CoFe_2O_4$ nanoparticles were studied by vibrating sample magnetometer (VSM) at room temperature in order to identify the magnetic states and envisage their behavior. The VSM measurements were recorded in the +20 kOe applied magnetic field. From the obtained hysteresis loops, the saturation magnetization (Ms), remanent magnetization (Mr), Coercivity (Hc) and squareness were determined. The measured values were: Ms=61.05 emu/g, Mr= 25.73 emu/g, Hc= 812.47 Oe and Mr/Ms=0.42. According to the results obtained from the magnetic hysteresis loops as shown in Figure 8, as-prepared cobalt ferrite nanoparticles were exhibited ferromagnetic behaviors. Especially with hard magnetic feature observed in $CoFe_2O_4$, due to large Hc value.

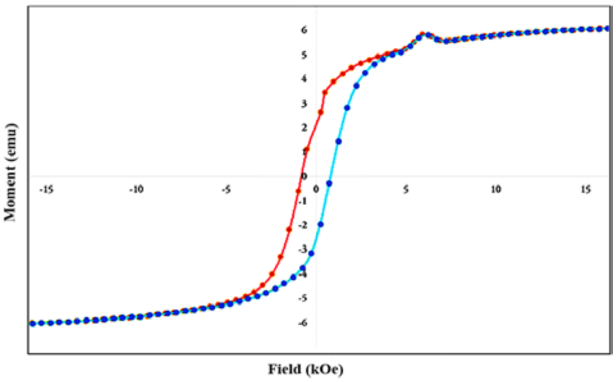

Figure 8. Room temperature hysteresis loops of $CoFe_2O_4$ nanoparticles annealed at 700 °C.

It was observed that if we do not implement calcination process, $CoFe_2O_4$ nanoparticles were not attracted by the magnet.
In case of implementing calcination process, it was observed that the nanoparticles were attracted by the magnet. The interaction of the as-synthesized $CoFe_2O_4$ nanoparticles with magnet were clearly depicted in Figure 9.

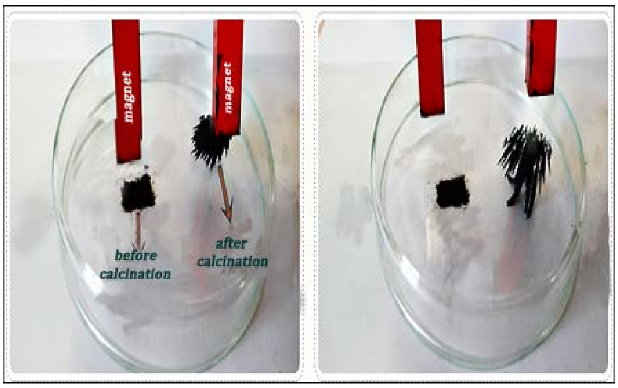

Figure 9. The interaction of cobalt ferrite nanoparticles with magnet before and after calcination.

4. Discussion and Conclusion

$CoFe_2O_4$ nanoparticles were synthesized successfully via co-precipitation methods assisted to MEG. These method was provided the short reaction times to produce well crystallized nanoparticles and reduce the agglomerations. High purity of the as-prepared nanocrystalline sample was proved by XRD and EDX analyses. SEM image results revealed that calcined sample was showed irregular shape and heterogeneous structure morphology. The $CoFe_2O_4$ nanoparticles size were obtained from the analysis of SEM images and were found to be about 30–345 nm. Consequently, when the calcination process was performed, $CoFe_2O_4$ nanoparticles were attracted by the magnet and exhibited ferromagnetic behaviors.

Acknowledgments

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