



Original Article

Fabrication and Characterization of $\text{CoFe}_2\text{O}_4/\text{CoFe}_2/\text{SiO}_2$ Nanocomposite Particles

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Abstract: The $\text{CoFe}_2\text{O}_4/\text{CoFe}_2/\text{SiO}_2$ nanocomposite particles were synthesized using a sol-gel method and calcination in hydrogen. The magnetic properties and structure of nanocomposite particles calcinated at 600 °C and 900 °C in range of calcination time from 1 h to 4 h were investigated. The phase composition, surface morphology and magnetic properties of the nanocomposites were investigated using X-ray powder diffraction, scanning electron microscopy and vibrating sample magnetometer. The XRD patterns indicate the existence of both CoFe_2O_4 and CoFe_2 phases in the nanocomposite after reducing at 600 °C for 2 h and 3 h. The single phase CoFe_2 was obtained after reducing at 900 °C. The average particles size was evenly distributed in the range of 20 nm to 120 nm. The magnetization increases significantly with increasing of reduction temperature.

Keywords: Sol-gel synthesis, nanocomposite, core-shell, exchange coupled.

1. Introduction

Nanocomposite particles based on the exchange spring mechanism have become a hot research topic in recent time because of their superior performances [1-3]. According to Kneller and Hawig [4], the composite magnets consisting of a hard magnetic phase and a soft magnetic phase have an inter-phase exchange interaction. The combining of two phases brings about enhancement in the magnetic properties of a magnet. So, the composite magnet has the high magnetization from the soft phase and large coercivity from the hard phase, which makes them suitable for the applications of permanent magnets. For example, magnetic micro electromechanical systems (MEMS) including microactuators, sensors,

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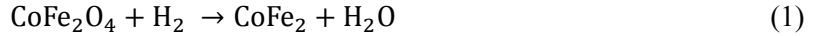
recording heads and micro-motors, spins of electron devices apply in spin- valve read heads [5-7]. Nowadays, nanocomposite particles and core/shell structured nanoparticles having been paid much attention to research. Some kinds of nanocomposite particles have been synthesized, such as $\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ [8], $\text{SrFe}_{12}\text{O}_{19}-\text{CoFe}_2\text{O}_4$ [9, 3], $\text{BaFe}_{12}\text{O}_{19}/\text{Fe}_3\text{O}_4$ [10], $\text{CoFe}_2\text{O}_4-\text{CoFe}_2$ [11]. The saturation magnetization is enhanced markedly with the increase of magnetically soft phase content. For example, in the $\text{BaFe}_{12}\text{O}_{19}/\text{Fe}_3\text{O}_4$ nanocomposite particles, the saturation magnetization increases 22.9 % when the ratio $\text{BaFe}_{12}\text{O}_{19}/\text{Fe}_3\text{O}_4 = 3/1$. A maximum energy product $(\text{BH})_{\text{max}}$ of 1.22 MGOe was achieved at room temperature for $\text{CoFe}_2\text{O}_4/\text{CoFe}_2$ nanocomposites, which is about 115 % higher than the value obtained for CoFe_2O_4 precursor [11]. For the nanocomposite particles, contact area between the aggregated particles is limited so that they could not be sufficiently exchange coupled. In order to make the two phases contacted sufficiently, attempts have been done to synthesize nanocomposite particles with core- shell structure. Although the core/shell structured nanoparticles are less studied, their potential in electromagnetic and magnetic applications is large. In such a system, the intimate contact between, the core and shell leads to effective exchange coupling and therefore cooperative magnetic switching, facilitating the fabrication of nanostructured magnetic materials with tunable properties. In 2004, Hao Zeng et al. researched $\text{FePt}/\text{MFe}_2\text{O}_4$ ($\text{M} = \text{Fe}$ and Co) core/shell nanoparticles synthesized by hydrothermal method [12], the exchange coupling between particles were observed in all of samples. The coercivity of $\text{FePt}/\text{Fe}_3\text{O}_4$ nanoparticle is 2.3 kOe, which is smaller than that of FePt nanoparticles (5.5 kOe), while that of $\text{FePt}/\text{CoFe}_2\text{O}_4$ reached 8 kOe. In 2015, Juan et al. have been studied hard/soft $\text{SrFe}_{12}\text{O}_{19}/\text{Fe}-\text{Co}$ composite nanofibers with core- shell structure are synthesized by reduction process in a hydrogen atmosphere [2]. The core- shell nanofibers show an enhanced saturation magnetization (M_s) of 60.9 emu/g for $\text{SrFe}_{12}\text{O}_{19}/\text{CoFe}_2\text{O}_4$ and 68.8 emu/g for $\text{SrFe}_{12}\text{O}_{19}/\text{FeCo}$ comparing with $\text{SrFe}_{12}\text{O}_{19}$ nanofibers (53.4 emu/g). The coercivities (H_C) for $\text{SrFe}_{12}\text{O}_{19}/\text{CoFe}_2\text{O}_4$ and $\text{SrFe}_{12}\text{O}_{19}/\text{FeCo}$ core- shell nanofibers decrease to 3190 Oe and 1249 Oe, respectively. The hysteresis loop of the core-shell nano fibers shows a single-phase magnetization behavior, implying that the magnetic hard ($\text{SrFe}_{12}\text{O}_{19}$) phase and soft (FeCo alloy) phase are well exchange- coupled.

It is well known that Cobalt ferrite CoFe_2O_4 is a popular hard magnetic because of high magnetocrystalline anisotropy, low cost and high chemical stability. Therefore it is a candidate of the hard magnetic for researching the exchange coupling behavior in the nanocomposites. The recent researchs show that the $\text{CoFe}_2\text{O}_4/\text{CoFe}_2$ with core- shell structure can be easily prepared by reducing CoFe_2O_4 [11, 13]. Otherwise, magnetic particles tend to agglomerate. So, in this paper, we chose non-magnetic SiO_2 to coat on $\text{CoFe}_2\text{O}_4/\text{CoFe}_2$ nanoparticles by reducing $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanoparticles in hydrogen at different temperatures. The effects of the reduction time (t_r) and calcination temperature (T_c) on structural and magnetic properties of samples are investigated.

2. Experiment

$\text{CoFe}_2\text{O}_4/\text{SiO}_2$ powders with the mass ratio of $(\text{Co}^{2+} + \text{Fe}^{3+})$ and SiO_2 of 3:1 were synthesized by a sol- gel method. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2$ were dissolved in deionized water to form aqueous 1M solution and then citric acid was added. The molar ratio of solutes in the solution was $\text{Co}^{2+} : \text{Fe}^{3+} : \text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 = 1 : 2 : 3$. We use NH_4OH to adjust the pH of the solution 1. After the pH had stabilized, tetraethyl orthosilicate SiO_2 (TEOS) was added into the solution with the ratio of $[\text{Co}^{2+} + \text{Fe}^{3+} + \text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3] : \text{SiO}_2 = 3:1$. The solution was stirred at 1000 rpm and gradually evaporated at 70 °C. After the water evaporated, the remainder became highly viscous gel with red- brown color as a result of the chelation process. The gel was dried at 80 °C for 24 h and then heated at 300 °C for 2 h to eliminate the remaining residual water and other organic impurities (aerogel was formed). To form the

CoFe₂O₄/CoFe₂/SiO₂ nanocomposite particles, the gels were reduced in hydrogen at 600 °C and 900 °C temperatures for different times, promoting the following chemical reduction:



The crystal structure and phases of the obtained samples were identified via X-ray powder diffraction (XRD) using a Siemens D5000 diffractometer (CuK α radiation, $\lambda = 1.54056 \text{ \AA}$). Morphological features and particle size were observed by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). The magnetic properties were measured using a vibrating sample magnetometer (VSM, Lakeshore 7410) with applied magnetic fields up to 10 kOe. Thermogravimetric analyses (TGA) were employed to study thermal behavior using a Universal V2960T with a heating rate of 10 °C/min in air, whereas pure alumina powder was used as the reference specimen. The synthesis and characterization of the samples are shown in Figure 1.

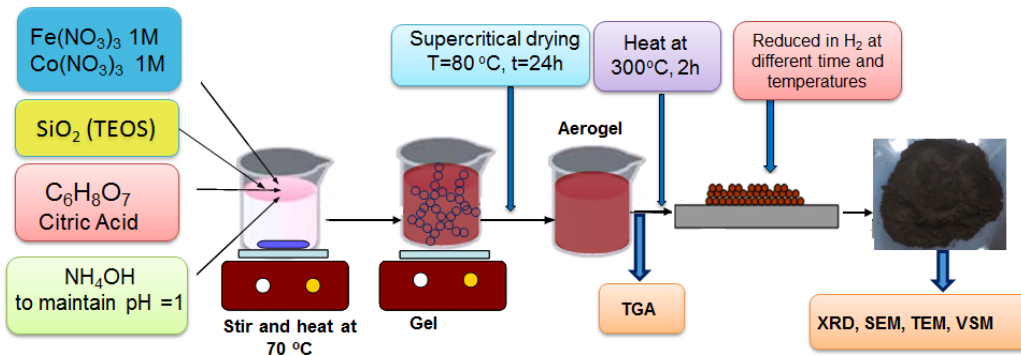


Figure 1. Flowchart for preparation of CoFe₂O₄/CoFe₂/SiO₂ nanocomposite particles.

3. Results and Discussion

The TGA of gel precursor CoFe₂O₄/SiO₂ is shown in figure 2. The experiment was performed using 36.746 mg of gel precursor and a heating of 10 °C/ min in static air. At approximately 136 °C of temperature, the weight loss of 20%. It was attributed to the decomposition of NH₄NO₃ to liberate NO, O₂, and H₂O. The exothermic peak at approximately 225 °C showed the decomposition of the remaining unreactive organic material induced by excess citric and weight loss of 85.05%. At the approximately 306 °C, the weight loss about 86.47% and the crystallization process of the main phase may be obtained at higher temperature (306 °C) following equation 1. Based on the results obtained from the thermal analysis of the precursor (figure 2), we choose 300 °C of temperature for heating gels and eliminating the remaining residual water and other organic impurities.

To investigate the monitor phase development with reducing time (t_r), the obtained xerogel was reduced in hydrogen at 600 °C and 900 °C. Figure. 3 shows the XRD patterns of the samples reduced at 600 °C and 900 °C with different time t_r (1 hour, 2 hours, 3 hours and 4 hours). The XRD results indicate that the samples which reduced at 600 °C for 1 h CoFe₂O₄ phase is formed. The samples reduced at 600 °C in 2 h and 3 h compose two phases: main phase CoFe₂ and a little of CoFe₂O₄ phase which appear at about 35.4° and 62.5°. When increasing reduction temperature and time, all the samples only compose CoFe₂ phase. The peaks of CoFe₂ phase appear at about 45° and 65°. The strength of the peaks

of CoFe_2 phase increases obviously with increasing reduction temperature and time. There is not a characteristic of amorphous SiO_2 for all the sample. The average crystallite size is calculated using Debays' Scherrer equation. The lattice constant (a), volume of the unit cell (V) are calculated from the expression $a = d\sqrt{h^2 + l^2 + k^2}$. The lattice constant a , average crystallite size D and volume of the unit cell $V(a^3)$ of CoFe_2O_4 and CoFe_2 nanoparticles in the nanoparticles are listed in table 1. The average crystallite size D increase with increasing of reduction temperature and time.

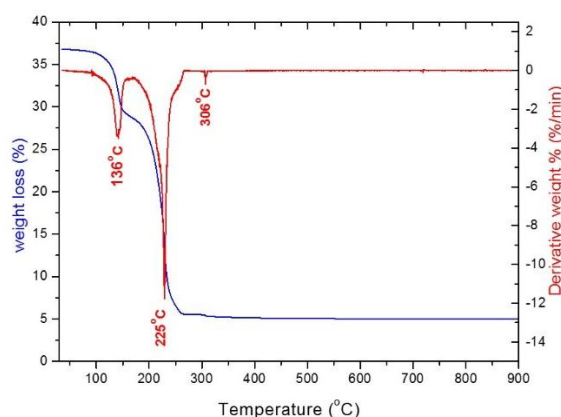


Figure 2. Thermogravimetric (TGA) curve of the gel precursor $\text{CoFe}_2\text{O}_4/\text{SiO}_2$.

Table 1. XRD refinement results: lattice parameters (a), average size of coherent scattering region (D) and volume unit (V) in the samples.

Characteristic parameter/ reduction temperature	a (Å)	D (nm)	V (Å) ³
600°C 1h	8.345	10.0	581.14
600°C 2h	2.862	20.12	23.44
600°C 3h	2.871	21.34	23.66
600°C 4h	2.869	20.31	23.62
900°C 1h	2.875	30.02	23.76
900°C 2h	2.867	31.24	23.59
900°C 3h	2.870	30.94	23.64
900°C 3h	2.873	31.32	23.71

Scanning electron micrographs of samples are shown in figure 4. We can see clearly from the micrographs that samples reduced at 600 °C show agglomeration to certain amount. The particles size distribute from 10 nm to 20 nm and the samples exhibits nearly spherical morphology. For samples reduced at 900 °C, the particles size is larger and distribute from 80 nm to 120 nm. The particles exhibit cubic morphology for the sample reduced in 1 h. When increase the reduction time (3 h), sample consisted of triangle morphology particles. This phenomenon can be understood via the development of grain size and breaking of grains with increase in the reduction time. Figure 5 shows the transmission electron micrographs of the samples reduced at 600 °C for 1 h and 900 °C for 1 h. The samples show non uniform morphology and the particles are virtually spherical morphology. The micrographs have the formation of large agglomerates of nanoscale particles.

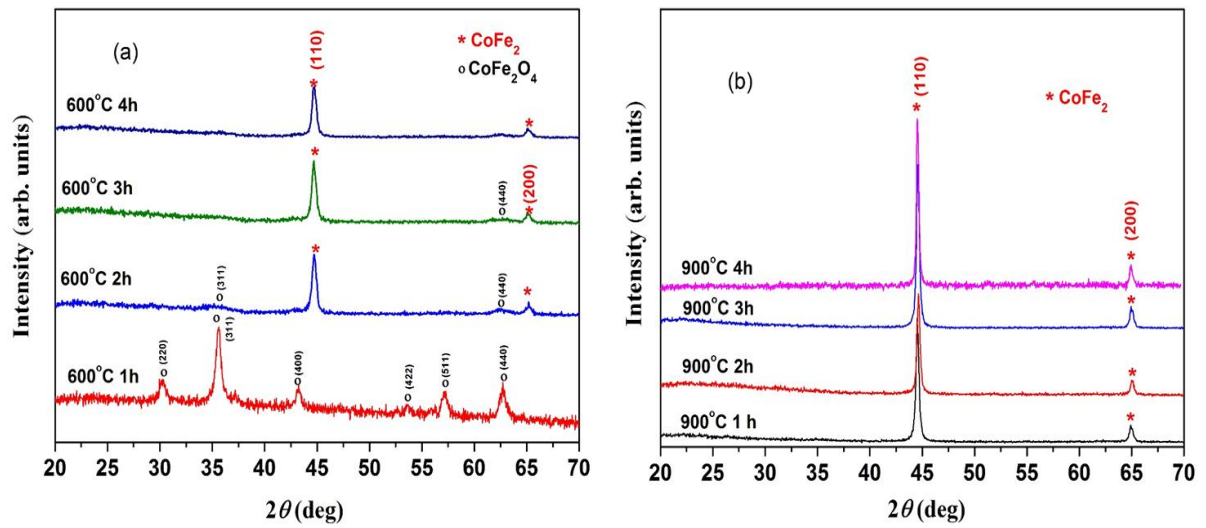


Figure 3. XRD patterns of CoFe₂O₄/CoFe₂/SiO₂ nanocomposite samples: (a) reduced at 600 °C for different times; (b) reduced at 900 °C for different times

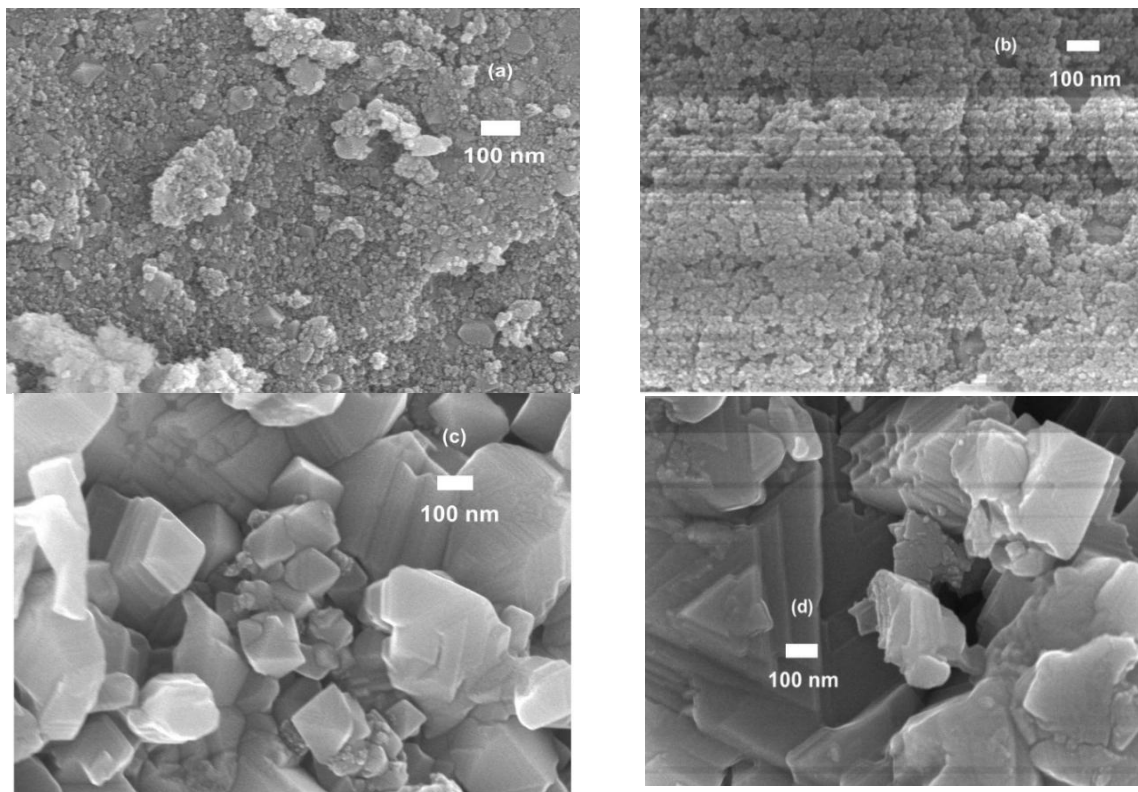


Figure 4. SEM micrographs of samples reduced at: a) 600 °C for 1h; b) 600 °C for 3h; c) 900 °C for 1h and d) 900 °C for 3h.

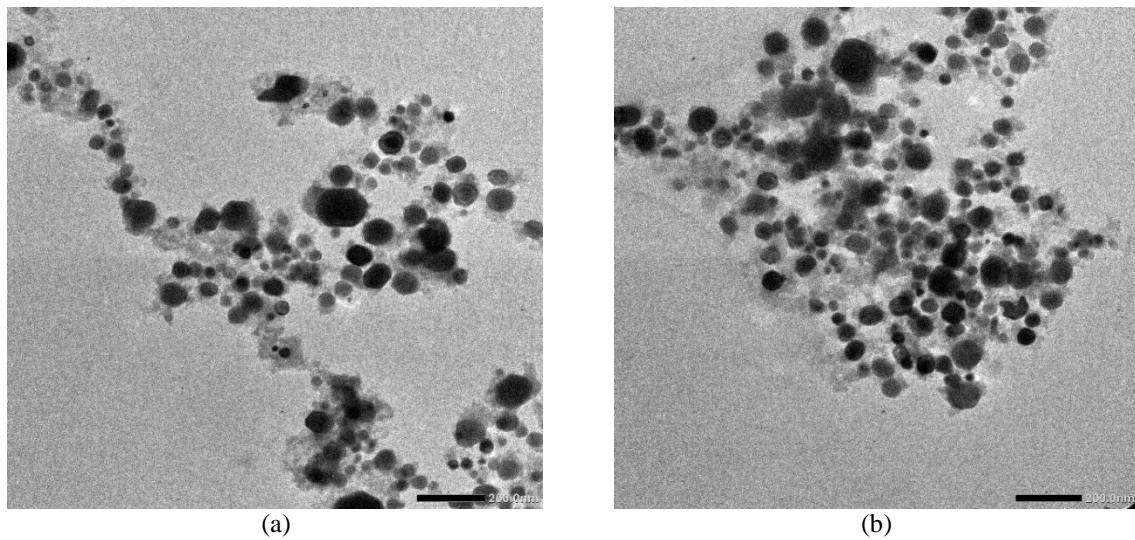


Figure 5. TEM of the samples reduced at (a) 600 °C for 1 h and (b) 900 °C for 1 h

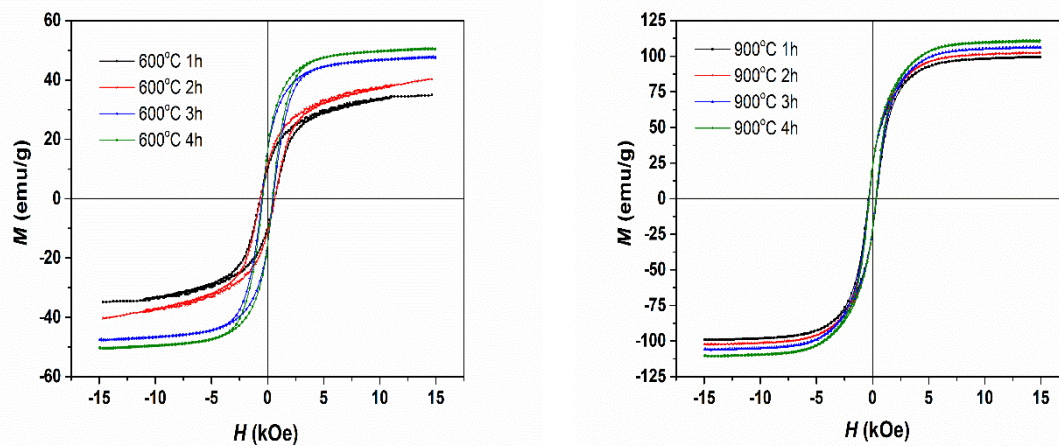


Figure 6. Hysteresis loops of $\text{CoFe}_2\text{O}_4/\text{CoFe}_2/\text{SiO}_2$ nanocomposite samples.

The magnetic properties of the samples were measured at room temperature via VSM. The hysteresis loops are illustrated in figure 6. The samples exhibited a magnetically soft behavior. As seen in the figure 6, all samples exhibit a smooth hysteresis loop and show a single-phase magnetization behavior. The magnetization at 15 kOe increased from 34.6 emu/g to 50.51 emu/g and from 99.39 emu/g to 140.37 emu/g when the reduction time increased from 1 h to 4 h at 600 °C and 900 °C, respectively. As expected, the magnetic properties of nanocomposite particles can be enhanced with a strong exchange coupling. For the samples reduced at 600 °C for 2 h and 3 h, although their crystallographically compose of two phases, the hysteresis loop exhibits a single-phase magnetization behavior. It indicates two magnetic phases are switching individually due to the incomplete exchange-coupling [3, 11, 14]. The dependence of magnetization M (at 15 kOe) and coercivity H_C on reduction time is shown in figure 7. The reducing H_C of these samples with increasing reduction time may be due to the growth of particles size and the

dense presence of CoFe_2 phase. Otherwise, as concentration of the soft phase increases, the role of dipolar interactions among the soft grains becomes more important [3] and the reverse domains in soft phase with low nucleation field nucleate readily. Thus, the value of H_C decreases. When increasing the reduction time, the H_C of samples reduced at 900°C are almost unchanged. It is due to the competition between the growth particle size and a strong exchange coupling spring in these samples.

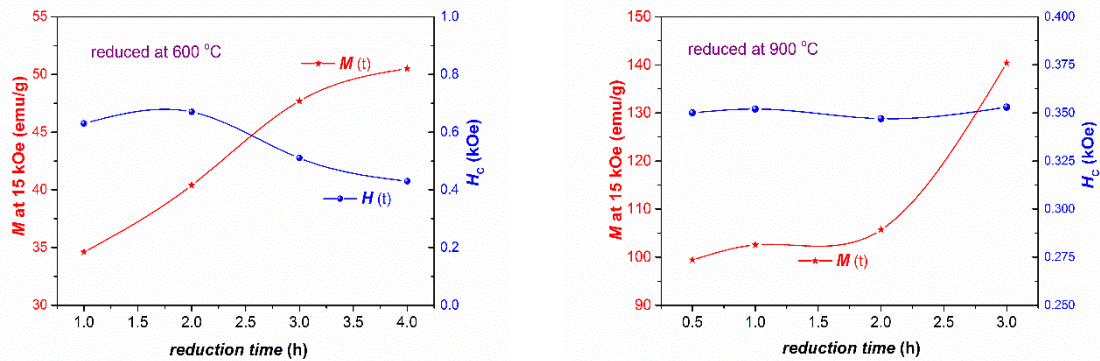


Figure 7. The variation in magnetization M (at 15 kOe) and coercive force (H_C) with increasing of reduction time.

4. Conclusion

The $\text{CoFe}_2\text{O}_4/\text{CoFe}_2/\text{SiO}_2$ nanocomposites particles are prepared by sol–gel method. The particles displayed a spherical shape with particle size distribute from 10 nm to 20 nm and from 80 nm to 120 nm after reducing at 600°C and 900°C , respectively. The XRD patterns confirmed the coexistence of CoFe_2O_4 and CoFe_2 phases after reducing at 600°C in 2 h and 3 h. When increasing reduction temperature and time, samples only compose CoFe_2 phase. The magnetizations at 15 kOe increase from 34.6 emu/g to 50.51 emu/g and from 99.39 emu/g to 140.37 emu/g when the reduction time increased from 1 h to 4 h at 600°C and 900°C , respectively. The homogeneity of phases, grain size, and exchange coupling between the two phases among others may result in variations in coercivity and saturation magnetization of the nanocomposite samples.

Acknowledgments

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