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Synthesis and magnetic characterization of MCM-41/$CoFe_2O_4$ nano-composite

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ABSTRACT

In this paper, synthesis and magnetic characterization of MCM-41-supported $CoFe_2O_4$ as a magnetic nano-composite has been investigated by incorporating the cobalt ferrite phase in meso-porous MCM-41 matrix by modified impregnation method. MCM-41 channels act as nano-reactor and cobalt ferrite nano-arrays were synthesized in its channels using the polymerizable complex (PC) route. Phase composition, morphology and magnetic properties of the products were investigated by XRD, TEM/EDS and VSM techniques, respectively. TEM image of annealed MCM-41 indicated hexagonally meso-structure with mean pore size of 4 nm. Saturation magnetization and coercivity of $CoFe_2O_4$ dropped from 78.6 emu/g and 0.75 kOe, respectively to 0.6 emu/g and 0.4 kOe for MCM-41-supported $CoFe_2O_4$.

1. Introduction

Recently the study of highly ordered arrays in porous membranes is receiving increasing attraction owing to their application in various fields [1–3]. First manifested interest has been related to information storage by perpendicular magnetic recording employing arrays of magnetic nano-wires. Recently, more realistic applications are related to functionalization of those arrays and of the porous membranes for their use in sensor devices [4–7]. In addition, new opportunities are being opened to prepare novel nano-composites exhibiting long-range ordering of hexagonal symmetry that confer those optimized properties [8].

Highly ordered meso-porous materials like MCM-41 can be used as template to confine conveniently magnetic compounds in a quasi-one-dimensional array because of its particular topology of regular hexagonal parallel channels with usual average diameters of less than 5 nm [9]. Incorporation of precursor species into silica from aqueous solution is often difficult, since the silica surface itself is negatively charged at pH values above approximately 2 [10]. Therefore control of impregnating solution pH value and improving the hydrothermal stability of MCM-41 meso-porous silica are necessary for impregnation by aqueous solution.

Among spinel ferrites, cobalt ferrite, $CoFe_2O_4$ is especially interesting because of its attracting magnetic properties. Also, cobalt ferrite nano-particles show photo-magnetic behavior which is an interesting light-induced coercively change [11,12].

Present work is focused on synthesis and characterization of MCM-41/$CoFe_2O_4$ nano-composite processed by modified impregnation route.

2. Experimental procedure

2.1. Synthesis of cobalt ferrite

Cobalt ferrite powder was synthesized by a polymerizable complex (PC) based on the Pechini-type reaction route [13]. Iron citrate, cobalt nitrate, citric acid, ethylene glycol and benzoic acid all of analytical grade were used as starting materials. A mixed solution with $4.61C_6H_8O_7{:}13.84(CH_2OH)_2{:}0.7C_6H_5COOH{:}2FeC_6H_7O_7{:}1Co(NO_3)\cdot 6H_2O{:}300H_2O$ molar ratio was used to formation of Co–Fe complex solution. First, citric acid was dissolved in water at 60 °C followed by addition of iron citrate and cobalt nitrate to the solution while stirring. Then ethylene glycol and benzoic acid were added to the homogenous solution. The pH of obtained complex solution was 1.6. Further stirring resulted in a gradual gelation of solution. The gel was dried at 150 °C for 24 h and then annealed at 800 °C for 3 h by a heating rate of 10 °C/min.

2.2. Synthesis of MCM-41

MCM-41 powder was synthesized by silylation treatment which was accompanied by pH adjusting to improve the structural stability. The starting materials were solution of sodium silicate in water (26.1%) as silica source, cetyltrimethylammonium bromide (CTAB) as a surfactant and deionized water. Molar ratio of the components in solution was $4SiO_2{:}1CTAB{:}250H_2O$. A solution was heated in a polypropylene bottle under vigorous stirring to achieve a clear solution after which the temperature of solution was increased to 100 °C. The solution was being cooled to room temperature and the solution pH was adjusted to approximately 10 by dropwise acetic acid, pH adjusting and subsequent heating was repeated each 24 h to when no pH changing observed. The resulted precipitate was filtered and washed by deionized water carefully and dried at 100 °C for 24 h. The dried sample was annealed at 800 °C for 3 h in a vacuum furnace with a heating rate of 1 °C/min.

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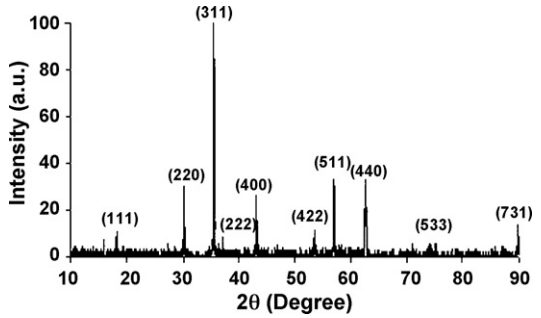

Fig. 1. XRD pattern of cobalt ferrite synthesized under the given experimental conditions.

2.3. Preparation of MCM-41/$CoFe_2O_4$ nano-composite

Annealed MCM-41 was incorporated by modified impregnation in Co–Fe complex solution under reduced pressure achieved via water aspiration for several times. The incorporated MCM-41 was filtered, washed with deionized water, and dried at 150 °C for 1 h. Finally the dried powder was re-annealed at 800 °C for 3 h by a heating rate of 1 °C/min.

Phase composition, morphology and magnetic properties of the products were characterized by XRD using Cu Kα radiation, TEM/EDS and VSM techniques, respectively.

3. Results and discussion

Fig. 1 shows the XRD pattern of single phase cobalt ferrite synthesized under the given experimental conditions. The annealed MCM-41 was characterized by low-angle XRD analysis which exhibited characteristic reflections of high quality ordered hexagonal meso-structure (Fig. 2). XRD pattern of MCM-41/$CoFe_2O_4$ is represented in Fig. 3. Low-angle region analysis ($2\theta = 1–10^\circ$) confirms that the ordered hexagonal structure of MCM-41 is still intact and remained unchanged. In high-angle region ($2\theta = 10–70^\circ$) the tiny reflections of the $CoFe_2O_4$ ($2\theta = 30.1^\circ$, 35.5°, 43.1°, 57.1° and 62.6°) are observed and indicate the formation of $CoFe_2O_4$ phase inside MCM-41 channels. Trifling intensities related $CoFe_2O_4$ phase implies the low amount of impregnated cobalt ferrite on high surface area of MCM-41 or its very small crystallite size [14].

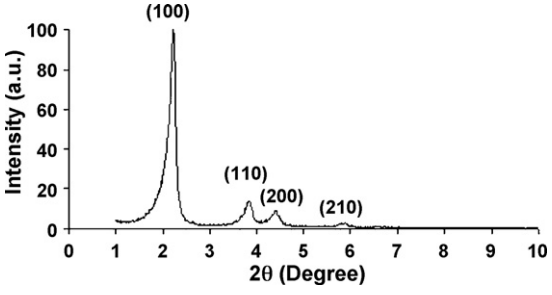

Fig. 2. Low-angle XRD pattern of processed MCM-41.

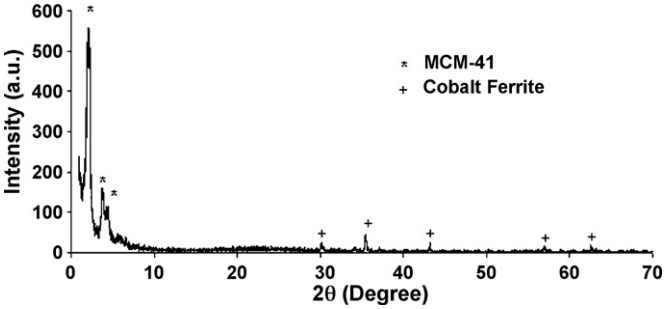

Fig. 3. XRD pattern of MCM-41/$CoFe_2O_4$ nano-composite.

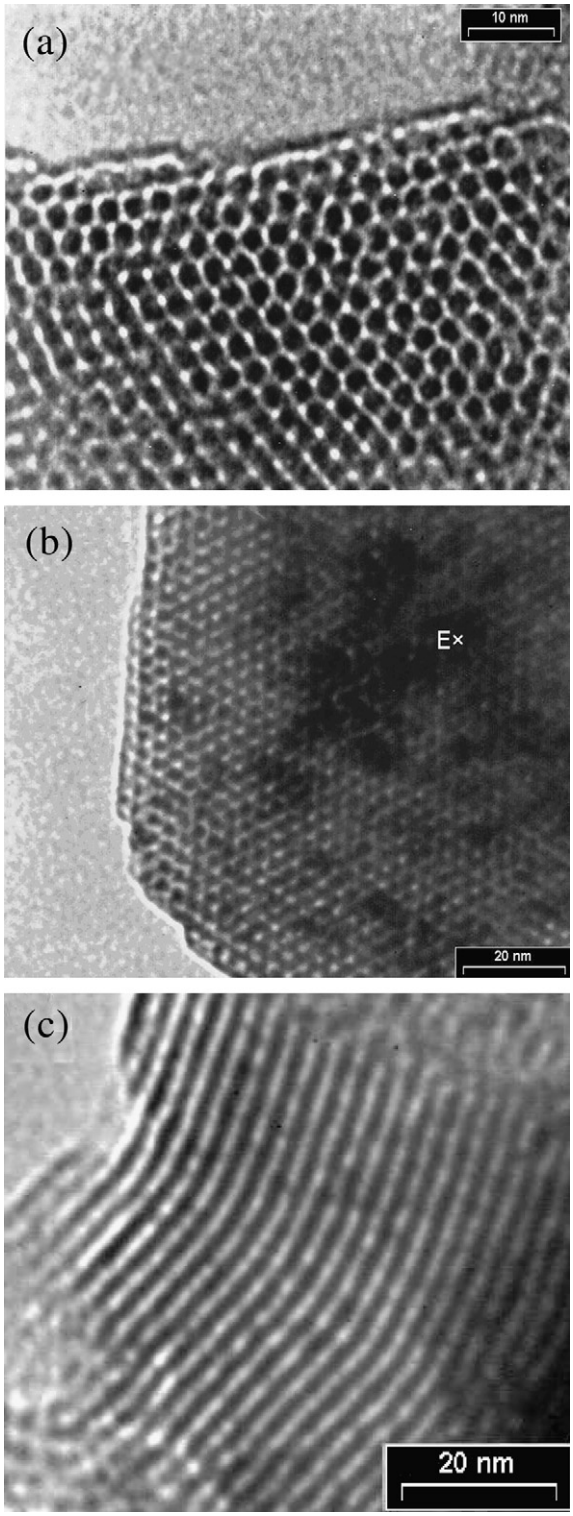

Fig. 4. TEM images of annealed MCM-41 (a), MCM-41/$CoFe_2O_4$ nano-composite through the pore axis (b) and along the channels (c).

TEM image of the annealed MCM-41 (Fig. 4a) exhibits the constitution of high quality hexagonally ordered meso-structure with a mean pore size of about 3 nm which are arranged beside themselves with honeycomb arrangement and a thick wall about 50 Å. TEM images of MCM-41/$CoFe_2O_4$ nano-composite have been shown through the pore axis and along the channels in Fig. 4b and c,

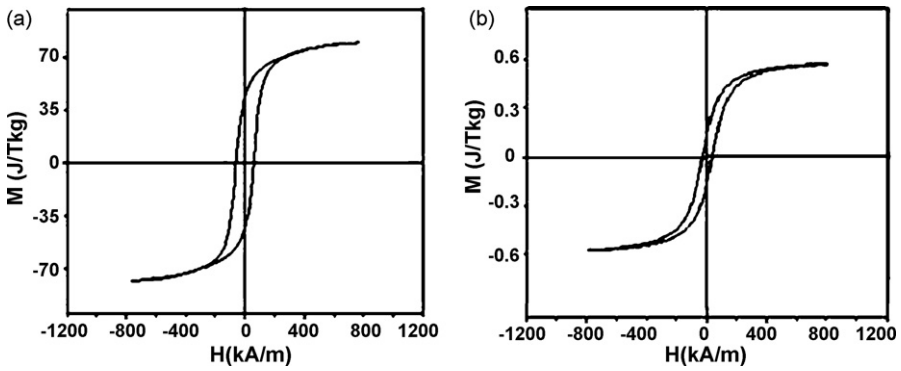

Fig. 5. Magnetization curves of (a) cobalt ferrite and (b) MCM-41/$CoFe_2O_4$ nano-composite.

Table 1
EDS analysis of the region marked in Fig. 4b.

	Element			
	O K	Si K	Fe K	Co K
Weight%	55.47	40.24	2.81	1.48
Atomic%	69.68	28.80	1.01	0.50

respectively. Comparison of Fig. 4a and b demonstrates the intactness of MCM-41 host material and the formation of second phase inside the MCM-41. Although nano-crystalline phase has formed within the meso-porous silica channels, it can be observed that incorporating of cobalt ferrite is done inhomogeneous in channels that are ascribed to vacuum power during the incorporation and impregnation periods. Fig. 4c clearly shows the formation of second phase nano-arrays within silica matrix which are arranged orderly.

EDS analysis of the region marked in Fig. 4b proves the existence of a component consisted of Co and Fe with an atomic percent ratio satisfactory close to cobalt ferrite stoichiometry (Table 1).

Magnetization curves of cobalt ferrite and MCM-41/$CoFe_2O_4$ nano-composite are shown in Fig. 5. Saturation magnetization and coercivity of $CoFe_2O_4$ dropped from 78.6 emu/g and 0.75 kOe, respectively to 0.6 emu/g and 0.4 kOe for MCM-41/$CoFe_2O_4$ nano-composite. MCM-41-supported $CoFe_2O_4$ is a composite system from which cobalt ferrite nano-arrays are isolated by silica matrix and have narrow size distribution (3–5 nm). The magnetization pattern of MCM-41-supported is determined by a competition between dipole–dipole interactions and alignment of the moments along the easy axes of magnetization. Note that the magneto-crystalline anisotropy energy of cobalt-ferrite is considerable and introduces energy barriers in the individual nano-arrays [15].

4. Conclusions

$CoFe_2O_4$ powder with interesting magnetic properties was synthesized by a polymerizable complex route, under natural strongly acidic condition and based on polyesterification reaction between citric acid and ethylene glycol.

The MCM-41/$CoFe_2O_4$ nano-composite was also prepared by incorporating the cobalt ferrite in MCM-41 meso-porous silica by modified impregnation in Co–Fe complex solution. Magnetic saturation and coercivity of cobalt ferrite were measured 78.6 emu/g and 0.75 kOe, respectively while these values dropped to 0.6 emu/g and 0.4 kOe for MCM-41/$CoFe_2O_4$ nano-composite.

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