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Synthesis and Characterization of Carbon Nanotubes Decorated with Magnesium Ferrite ($MgFe_2O_4$) Nanoparticles by Citrate-Gel Method

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Abstract

In the present work, magnetic nanocomposites of the multi-walled carbon nanotubes (MWCNTs) decorated with magnesium ferrite ($MgFe_2O_4$) nanoparticles were synthesized successfully by citrate-gel method. The shape, structure, size, and properties of the as-synthesized sample were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction pattern (XRD), transmission electron microscope (TEM), vibrating sample magnetometry (VSM), and AC susceptibility measurements. The results showed that MWCNTs and $MgFe_2O_4$ coexisted in the nanocomposite and a large number of the high purity magnesium ferrite $MgFe_2O_4$ nanoparticles were attached on the surface of the MWCNTs. The hysteresis loop of the $MgFe_2O_4$/MWCNTs nanocomposites showed that the nanocomposites were superparamagnetic with the saturated magnetization of 11.79 emu/g, and the coercive of 49 Oe.

Keywords: MWCNTs; $MgFe_2O_4$; Nanocomposite; Citrate-gel

Introduction

Since the discovery by Iijima's [1], carbon nanotubes (CNTs) have attracted considerable attention in the fields of synthesis, and technological applications due to their fascinating one-dimensional tubular structures, electronic, mechanic and chemical properties [2-8]. Modification of CNTs with metals, metal oxides, complex metal oxides and polymers can be improved physical and chemical properties of CNTs. The magnetic modification of CNTs makes them possess unique magnetic nature. Magnetic CNTs have potential applications as magnetic data storage [9], microwave absorbing materials [10], magnetic composites for drug delivery [11], optical transducers for wearable electronics [12], magnetic force microscopes [13], etc.

The spinel ferrite of nanoparticles and composition MFe_2O_4 (M = Co, Ni, Mn, Mg, Fe or Zn) exhibit interesting magnetic, magetoresisitive, and magneto-optical properties that are potentially useful for a broad range of applications [14-16]. Among magnetic ferrites, Magnesium ferrite ($MgFe_2O_4$) has attracted significant research interest based on its fascinating magnetic and electromagnetic properties. It has a cubic structure of normal spinel-type and is a soft magnetic n-type semiconducting material, which finds a number of applications in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies [17]. So far,

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reported nanostructures of $MgFe_2O_4$ are mostly in the form of nanoparticle [18-24].

Liu and Gao prepared $NiFe_2O_4$/CNTs composites by hydrothermal process for the advantages of high purity and uniform particle size [25]. Cao et al. prepared highly coercive carbon nanotube coated with $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocrystals synthesized by chemical precipitation-hydrothermal process [26]. Zhang et al. have synthesized $Mn_{1-x}Zn_xFe_2O_4$/CNTs nanocomposites via solvothermal method [27]. In our recent work [28], have been synthesized $CoFe_2O_4$/CNTs-*g*-PCL nanocomposites via sol-gel method.

Considering the outstanding properties of CNTs as well as $MgFe_2O_4$ nanoparticles, $MgFe_2O_4$/CNTs nanocomposites would be very attractive for practical applications. It can be used in the fabrication of magnetic, heterogeneous catalysis, adsorption, sensors, magnetic technologies [17], and in biotechnology as drug carriers for magnetically guided drug delivery. So far, there are few reports on synthesizing the one-dimensional nanocomposites of $MgFe_2O_4$/CNTs. In this research, we demonstrate a general and efficient synthetic strategy for obtaining $MgFe_2O_4$/CNTs nanocomposites via citrate-gel method. Magnetic measurements show that the $MgFe_2O_4$/MWCNTs nanocomposite display superparamagnetic properties at room temperature.

Materilas and Methods

MWCNTs (formed by CVD process) were provided by Sun Nano Company (China) and the purity was claimed to be 95% by the producer. The outer diameters of CNTs were 10 to 20 nm. Fe $(NO_3)_3$, Mg $(NO_3)_2$ and $C_6H_8O_7$ were purchased from Merck.

MWCNTs were first opened according to the procedure reported in literature [29,30]. Briefly, MWCNTs was milled and dispersed in a 3/1 mixture of H_2SO_4/ HNO_3 by an ultrasonic shaker. The mixture was refluxed for 17 h at 120 °C. Then it was cooled, filtered and washed by distilled water adjusted at pH 6. Finally, the oxidized carbon nanotubes (*o*-MWCNTs) were dried at 100 °C for 12 h before use. An insitu chemical citrate-gel method was developed to obtain the $MgFe_2O_4$-MWCNTs precursor. A proper amount of *o*-MWCNTs was first added to a solution of citric acid ($C_6H_8O_7.H_2O$) and ultrasonicated in distilled water for 10 min. Afterward, this suspension was mixed with an aqueous solution of $Mg(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$, in which the Mg:Fe molar ratio was maintained at 1:2. In order to reach the PH of the solution to 9, ammonia solution was drop wisely added to the mixture with vigorous stirring. The mixture was also stirred at 30 °C for 48 h and dried in an oven at 100°C for 12 h, followed by calcination at temperature 475°C and 600 °C for 2h in an Argon atmosphere. Also we synthesized magnesium ferrite ($MgFe_2O_4$) nanoparticles by citrate-gel method. To synthesize nanoparticle, $Fe(NO_3)_3$ and $Mg(NO_3)_2$ mixed solution was added to citric acid dissolved in distilled water. The solution was stirred and then was concentrated until a viscous liquid was obtained. The liquid was dried in an oven at 120 °C and calcined at temperature 600 °C for 2h in an Argon atmosphere.

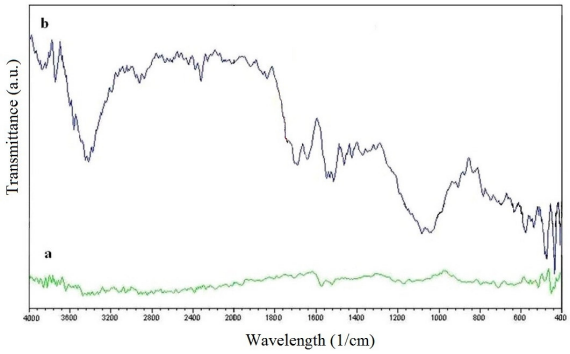

Figure 1. FT-IR spectra of (a) Pristine MWCNTs (b) opened MWCNs.

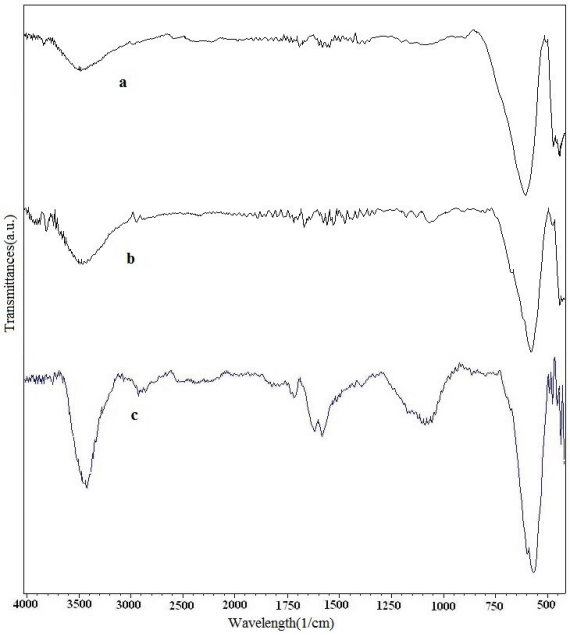

Figure 2. FT-IR spectrum of (a) the $MgFe_2O_4$ nanoparticles calcined in Ar at 600 °C/2h. The $MgFe_2O_4$/MWCNTs nanocomposites calcined in Ar at (b) 475°/2hC and (c) 600 °C/2h.

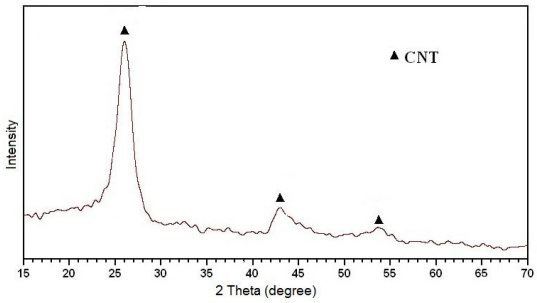

Figure 3. XRD pattern of the opened MWCNT.

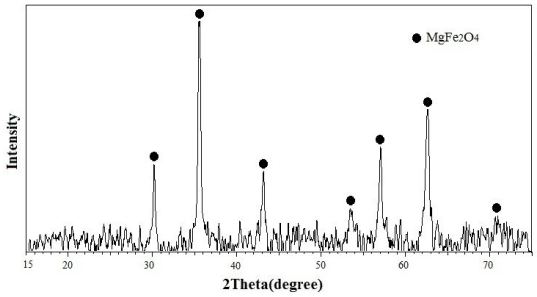

Figure 4. XRD pattern of the $MgFe_2O_4$ nanoparticles calcined in Ar at 600 °C/2h.

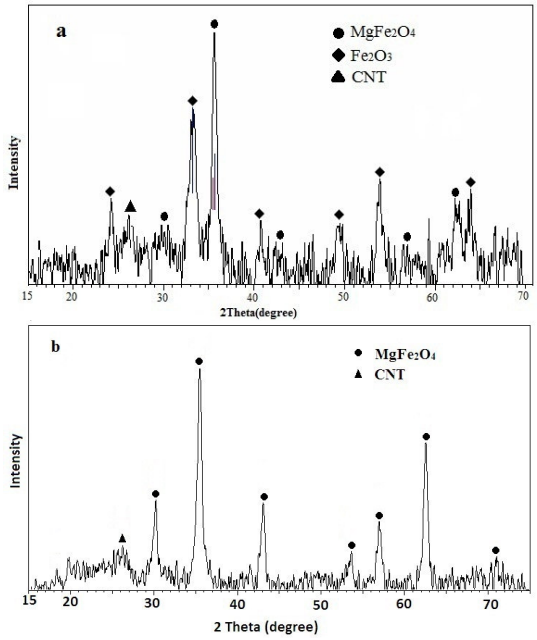

Figure 5. XRD patterns of the $MgFe_2O_4$/MWCNTs nano-composites calcined in Ar at (a) 475°C/2h and (b) 600 °C/2h.

The XRD of the synthesized composites were obtained by an X-ray powder diffractometer (XRD, D8ADVANCE, Bruker, Germany) with Cu K_α radiation (λ= 1. 5406 Å) and a Ni-filter. IR spectra were recorded on an FT-IR, Nicolet 320. The morphologies of the samples were observed through transmission electron microscopy (TEM, Philips CH 200, LaB_6 –Cathode160 kv). Magnetic properties of the samples were measured by vibrating sample magnetometers (VSM) with a maximal applied field of 10 kOe.

Results and Discussion

FTIR Study

The FT-IR spectrum of the pristine, opened MWCNTs, the $MgFe_2O_4$/MWCNTs nanocomposites and $MgFe_2O_4$ nanoparticles in the range of 4000-400 cm^{-1} are shown in (Fig. 1) and (Fig. 2) respectively. As it can be seen, the IR spectra of the pristine CNTs (Fig. 1a) show no obvious absorbance bands due to the symmetrical structure of carbon nanotube. Treatment of the carbon nanotubes with acid in order to open their tips causes the formation of functional groups on their surface. In the IR spectra of the opened MWCNTs (Fig. 1b) and the $MgFe_2O_4$/MWCNTs nanocomposites (Fig. 2b) and (Fig. 2c) the absorbance band at 3600-3100 is assigned to the O-H bond of the carboxyl functional groups created on their surface. Absorbance bands around at 1700, 1620 and 1500 cm^{-1} could be attributed to the stretching frequencies of the C=O and C=C bonds, respectively. The absorption bands around 1100 cm^{-1} could be attributed to the stretching vibration of C–C–C group. In addition (Fig. 2a, b, c) show two persistent absorption bands corresponding to the vibration of tetrahedral and octahedral complexes at 567 and 435 cm^{-1}, respectively, which are indicative of formation of spinel ferrite structure [31]. As is seen from (Fig. 2), the normal mode of vibration of tetrahedral cluster (567 cm^{-1}) is higher than that of octahedral cluster (435 cm^{-1}).

XRD Study

Figure 3 shows the XRD pattern of the opened MWCNTs. (Fig. 4), show $MgFe_2O_4$/MWCNTs nano-composites calcined in Ar at (a) 475°C/2h and (b) 600°C/2h. The XRD peaks correspond with the reported values of $MgFe_2O_4$ (PDF card: 36–0398), CNTs (PDF card: 01-0640) and α-Fe_2O_3 (PDF card: 33-0664). The diffraction peaks at 2θ= 26.4°, 43.08° and 53.8° in (Fig. 3) and (Fig. 5) are the typical Bragg peak of pristine CNTs and can be indexed to the (002), (101) and (004)

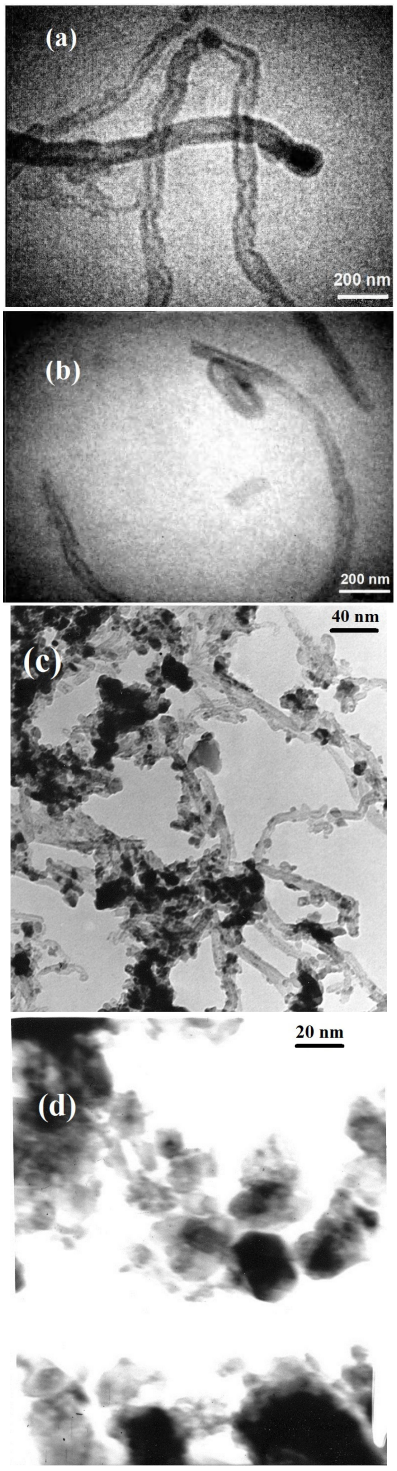

Figure 6. TEM images of (a) the pristine MWCNTs, (b) MWCNTs after acid treatment , (c) the $MgFe_2O_4$/MWCNTs nanocomposites calcined in Ar at 600 °C/2h and (d) $MgFe_2O_4$ nanoparticles calcined in Ar at 600 °C/2h.

reflection of CNTs, respectively. In (Fig. 4) and (Fig. 5) well-resolved diffraction peaks revealed the good crystallinity of the $MgFe_2O_4$ specimens, located at 2θ of 30.27°, 35.49°, 43.27°, 53.45°, 57.21°, 62.59° and 71.04°, respectively. These diffraction peaks corresponding to planes (111), (311), (400), (422), (333), (440) and (620) provide a clear evidence for the formation of spinel structure of the ferrite. This observation matches well with those of earlier reporters [18,32]. In (Fig. 5a), diffraction peaks at 2θ=24.40°, 33.3°, 41°, 49.75°, 54.1° and 64.2° correspond to the (012), (104), (113), (024), (116) and (300) planes of hematite (α-Fe2O3), respectively. Also, This observation matches well with those of earlier reporters [34].

It is clear from (Fig. 5a) that the calcined powder in Ar at 475°C/2h is a mixture of α-Fe_2O_3 and CNTs, with very small quantities of $MgFe_2O_4$ formed during calcination. On increasing the calcination temperature to 600 °C, it can be seen (Fig. 5b) that the formation reaction of $MgFe_2O_4$ is complete and that Fe_2O_3 phase present previously has vanished. Prolonged calcination at 600 °C for 2h result in an increase in the average particle size. The grain size of $MgFe_2O_4$ at 600 °C is obtained using Scherrer's formula as 13.5 nm.

TEM Study

Figure 6 shows the TEM images of (a) the pristine, (b) opened, (c) decorated MWCNTs and (d) $MgFe_2O_4$ nanoparticles, respectively. In (Fig. 6c) the $MgFe_2O_4$ nanoparticles can be seen clearly on the surface of the MWCNTs. The sizes of the nanoparticles ranges from 10 to 20 nm, which is consistent with the result calculated from the Scherrer equation.

VSM and AC-Susceptibility Study

The magnetic properties of the $MgFe_2O_4$ nanoparticles and decorated MWCNTs were measured in magnetic fields of ±10 kOe at room temperature. The hysteresis loop of the decorated MWCNTs is presented in (Fig. 7). The values of the saturation magnetization (M_S), retentivity (M_R) and coercivity (H_C) of $MgFe_2O_4$/MWCNTs, obtained from the VSM data, were obtained as 11.79, 1.58 emu/g, and 49 Oe, respectively. In Fig. 8, the Hysteresis loops were compared for the $MgFe_2O_4$ nanoparticles and decorated MWCNTs. Also, the values of M_S, H_C and M_R of specimens obtained from the VSM data were compared in (Table 1). Pradeep et al. [18] reported magnetic parameters M_S, M_R and H_C for nanoparticle of $MgFe_2O_4$ as 21.89, 4.48 emu/g and 202.55 Oe, respectively. The decrease in all values of magnetic parameters is due to the method and

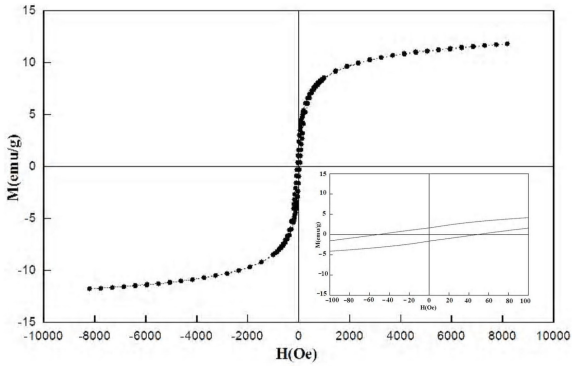

Figure 7. Hysteresis loop of the $MgFe_2O_4$/MWCNTs nanocomposites calcined in Ar at calcined in Ar at 600 °C/2h.

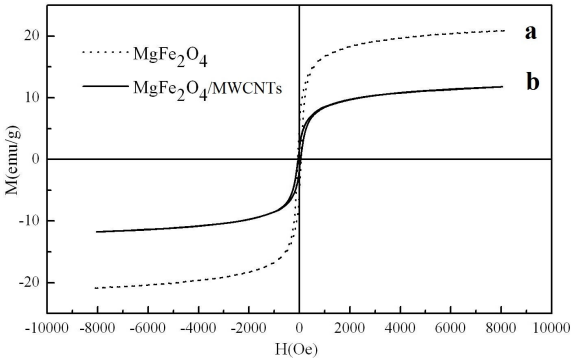

Figure 8. Hysteresis loops of (a) $MgFe_2O_4$ nanoparticeles and (b) the $MgFe_2O_4$/MWCNTs nanocomposites calcined in Ar at 600 °C/2h.

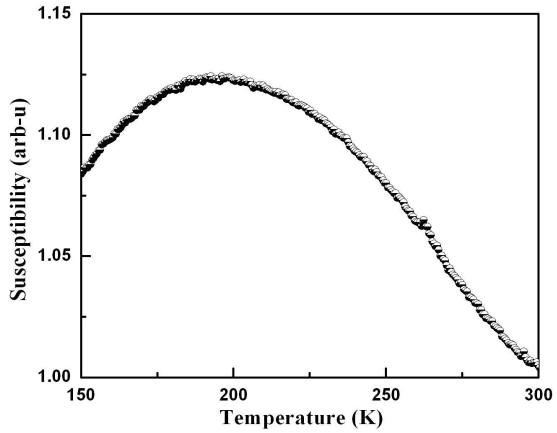

Figure 9. Temperature dependence of the real part of AC susceptibility for the $MgFe_2O_4$/MWCNTs nanocomposites calcined in Ar at 600 °C/2h. The applied field is 800 A/m.

the existence of MWCNTs which it is coused to be synthesized the smaller size of $MgFe_2O_4$ nanoparticles. As, shown in the inset of (Fig. 7), the coercive force (H_C) of the magnetic nanocomposites is only 49 Oe, which can reflect a typical characteristic of super-paramagnetic materials [33]. With this unique property, it can be used as a promising vehicle for magnetic field-directed drug delivery systems.

The AC susceptibility measurement of the $MgFe_2O_4$/MWCNTs as a function of temperature is shown in (Fig. 9). At first, we cooled the sample at 150 K without any external magnetic field and then, a magnetic field of 800 A/m was applied and the magnetization was recorded as the temperature slowly raises. Initially, the magnetic susceptibility increases upon reaching a certain temperature, then it starts to decrease with increasing temperature. The temperature at which the magnetic susceptibility starts to decrease is called the blocking temperature T_B. The measurement results show that the blocking temperature of the synthesized $MgFe_2O_4$/MWCNTs is 195 K.

The synthesised superparamagnetic $MgFe_2O_4$/MWCNTs nanocomposites can be used in the fabrication of magnetic, heterogeneous catalysis, magnetic technologies, and in biotechnology as promising vehicle for magnetic field-directed drug delivery systems.

Table 1. Comparison of the Magnetic properties of $MgFe_2O_4$ nanoparticeles and $MgFe_2O_4$/MWCNTs nanocomposites calcined in Ar at 600 °C/2h

Specimen	M_S(mueg^{-1})	H_C(Oe)	M_R(mueg^{-1})
$MgFe_2O_4$	21	69	5.3
$MgFe_2O_4$[18]	21.89	202.55	4.48
$MgFe_2O_4$/MWCNTs	11.79	49	1.58

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