Synthesis and Characterization of Carbon Nanotubes Decorated with Magnesium Ferrite (MgFe₂O₄) Nanoparticles by Citrate-Gel Method

R. Sepahvand* and R. Mohamadzade

Department of Physics, Faculty of Science, Lorestan University, Khoramabad, Islamic Republic of Iran

Received: 14 February 2011 / Revised: 21 May 2011 / Accepted: 31 July 2011

Abstract

In the present work, magnetic nanocomposites of the multi-walled carbon nanotubes (MWCNTs) decorated with magnesium ferrite (MgFe₂O₄) 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 MgFe₂O₄ coexisted in the nanocomposite and a large number of the high purity magnesium ferrite MgFe₂O₄ nanoparticles were attached on the surface of the MWCNTs. The hysteresis loop of the MgFe₂O₄/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; MgFe₂O₄; 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 MFe₂O₄ (M = Co, Ni, Mn, Mg, Fe or Zn) exhibit interesting magnetic, magnetoresistive, and magneto-optical properties that are potentially useful for a broad range of applications [14-16]. Among magnetic ferrites, Magnesium ferrite (MgFe₂O₄) 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,
reported nanostructures of MgFe$_2$O$_4$ are mostly in the form of nanoparticle [18-24].

Liu and Gao prepared NiFe$_2$O$_4$/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$_2$O$_4$ nanocrystals synthesized by chemical precipitation-hydrothermal process [26]. Zhang et al. have synthesized Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$/CNTs nanocomposites via solvothermal method [27]. In our recent work [28], have been synthesized CoFe$_2$O$_4$/CNTs-g-PCL nanocomposites via sol-gel method.

Considering the outstanding properties of CNTs as well as MgFe$_2$O$_4$ nanoparticles, MgFe$_2$O$_4$/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$_2$O$_4$/CNTs. In this research, we demonstrate a general and efficient synthetic strategy for obtaining MgFe$_2$O$_4$/CNTs nanocomposites via citrate-gel method. Magnetic measurements show that the MgFe$_2$O$_4$/MWCNTs nanocomposite display superparamagnetic properties at room temperature.

Materials 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$_6$H$_8$O$_7$ 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$_2$SO$_4$/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$_2$O$_4$/MWCNTs precursor. A proper amount of o-MWCNTs was first added to a solution of citric acid (C$_6$H$_8$O$_7$).6H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O, 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$_2$O$_4$) 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 MWCNTs.

Figure 2. FT-IR spectrum of (a) the MgFe$_2$O$_4$ nanoparticles calcined in Ar at 600 °C/2h. The MgFe$_2$O$_4$/MWCNTs nanocomposites calcined in Ar at (b) 475 °C/2h and (c) 600 °C/2h.
Archive of SID

Synthesis and Characterization of Carbon Nanotubes Decorated with...

The XRD of the synthesized composites were obtained by an X-ray powder diffractometer (XRD, D8ADVANCE, Bruker, Germany) with Cu Kα 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, LaB6 –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 MgFe₂O₄/MWCNTs nanocomposites and MgFe₂O₄ 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 MgFe₂O₄/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 MgFe₂O₄/MWCNTs nanocomposites calcined in Ar at (a) 475°C/2h and (b) 600°C/2h. The XRD peaks correspond with the reported values of MgFe₂O₄ (PDF card: 36-0398), CNTs (PDF card: 01-0640) and α-Fe₂O₃ (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$_2$O$_4$/MWCNTs nanocomposites calcined in Ar at 600 °C/2h and (d) MgFe$_2$O$_4$ nanoparticles calcined in Ar at 600 °C/2h.

Figure 6. TEM images of (a) the pristine, (b) opened, (c) decorated MWCNTs and (d) MgFe$_2$O$_4$ nanoparticles, respectively. In (Fig. 6c) the MgFe$_2$O$_4$ 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$_2$O$_4$ 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 (Ms), retentivity (Mr) and coercivity (Hc) of MgFe$_2$O$_4$/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$_2$O$_4$ nanoparticles and decorated MWCNTs. Also, the values of Ms, Hc and Mh of specimens obtained from the VSM data were compared in (Table 1). Pradeep et al. [18] reported magnetic parameters Ms, Mh and Hc for nanoparticle of MgFe$_2$O$_4$ 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
the existence of MWCNTs which it is caused to be synthesized the smaller size of MgFe₂O₄ nanoparticles. As, shown in the inset of (Fig. 7), the coercive force (Hc) 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 MgFe₂O₄/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 MgFe₂O₄/MWCNTs is 195 K.

The synthesized superparamagnetic MgFe₂O₄/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 MgFe₂O₄ nanoparticles and MgFe₂O₄/MWCNTs nanocomposites calcined in Ar at 600 °C/2h

<table>
<thead>
<tr>
<th>Specimen</th>
<th>M_s (mueg⁻¹)</th>
<th>H_c (Oe)</th>
<th>M_r (mueg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe₂O₄</td>
<td>21</td>
<td>69</td>
<td>5.3</td>
</tr>
<tr>
<td>MgFe₂O₄[18]</td>
<td>21.89</td>
<td>202.55</td>
<td>4.48</td>
</tr>
<tr>
<td>MgFe₂O₄/MWCNTs</td>
<td>11.79</td>
<td>49</td>
<td>1.58</td>
</tr>
</tbody>
</table>

References

6. Bakalis E., Zerbetto F., Double-wall carbon nanotubes: The outer shell may pattern the structure of the inner one.


