Hydrothermal Synthesis of Carbon Nanotube/Nickel Ferrite Nanocomposites

Xudong Jin^{*1}, Qing-Qing Ni^{*2,3}, Yaqin Fu^{*2}, Li Zhang^{*4}, and Toshiaki Natsuki^{*3}

^{*1} Interdisciplinary Graduate School of Science and Technology, Shinshu University, Ueda 386-8567, Japan

^{*2} Key Laboratory of Advanced Textile Materials and Manufacturing Technology Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, P.R. China

^{*3} Department of Functional Machinery and Mechanics, Shinshu University, Ueda 386-8567, Japan

^{*4} Faculty of Engineering, Shinshu University, Japan

Abstract: We report a simple hydrothermal synthesis of carbon nanotube/nickel ferrite (CNT/NiFe₂O₄) nanocomposites. The CNTs used in this work were pretreated with nitric acid. The evolution of the synthesis of the CNT/NiFe₂O₄ nanocomposites was studied using X-ray photoelectron spectroscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy, and transmission electron microscopy. The results suggest that NiFe₂O₄ nanoparticles were synthesized in situ on the CNT surface. Vibrating-sample magnetometer measurements showed that the CNT/NiFe₂O₄ nanocomposites exhibit typical soft ferromagnetic behavior with saturation magnetization (Ms) of about 24 emu/g.

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1. Introduction

Nickel ferrite (NiFe₂O₄) is an important spinel ferrite nanocrystal, and it has been extensively investigated because of its high electrical resistivity, electromagnetic performance, chemical stability, and moderate saturation magnetization (Ms) [1-3]. NiFe₂O₄ nanoparticles have been successfully prepared by a variety of methods such as hydrothermal synthesis [4-7], coprecipitation [8,9], sol-gel methods [10-12], combustion [13], and shock wave methods [14]. Recently, NiFe₂O₄-based magnetic nanocomposites have attracted increasing interest because of their unique properties and potential applications. Much effort has been devoted to this area, and the developed nanocomposites have a wide range of applications, including DNA separation [15], antimicrobial agents [16-19], microwave absorbers [20, 21], and photocatalysts [22-24].

Carbon nanotubes (CNTs) are considered to be suitable candidates for nanocomposite synthesis because of their nanoscale dimensions and excellent properties. Wu et al. [25] synthesized multiwalled CNT/cobalt ferrite magnetic hybrids for drug delivery. A novel glucose biosensor composed of magnetic nanoparticles (Fe₃O₄@SiO₂) and CNTs has been developed by Baby et al. [26]. Deng et al. [27] reported CNTs functionalized with magnetic silica nanoparticles; these CNTs efficiently separate trace aromatic compounds.

The assembly of NiFe₂O₄ nanoparticles on CNTs is

therefore a feasible and interesting method of synthesizing magnetic nanocomposites. However, to our knowledge, there have been few reports of CNT/NiFe₂O₄ nanocomposites. In this work, we synthesized CNT/NiFe₂O₄ nanocomposites in situ using a simple hydrothermal method, and studied the process involved in CNT/NiFe₂O₄ synthesis.

2. Experimental

All reagents were analytical grade and used as received. Multiwalled CNTs of diameter 20-30 nm were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan.

Pristine CNTs (30 mg) were added to 60 mL of 10 M nitric acid and dispersed ultrasonically for 1 h. The CNT suspension was then transferred to a round-bottomed flask equipped with a reflux condenser, and refluxed with constant stirring at 130 °C for 12 h. The obtained CNTs were collected and washed repeatedly with distilled water to remove residual nitric acid and impurities.

A typical synthetic process is as follows. First, 11 mg of treated CNTs were completely dispersed in 50 mL of distilled water by ultrasonication for 1 h. Then 0.1 mmol of Fe(NO₃)₃·9H₂O and 0.05 mmol of Ni(NO₃)₂·6H₂O were dissolved in the CNT suspension. Sodium hydroxide solution was added dropwise, with vigorous stirring, to adjust the pH value to about 12.5.

(The intermediate product formed during precipitation is referred to as CNT/NiFeOH.) The obtained mixture was transferred to a PTFE-lined stainless-steel autoclave, and the hydrothermal reaction was conducted at 170 °C for 12 h. After cooling to room temperature, the as-prepared products were separated by filtration and washed several times with distilled water and ethanol.

The morphologies of the products were examined using transmission electron microscopy (TEM; JEM-2010, JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded using a Rigaku Geigerflex 2028 diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation (1.5406 Å). Energy-dispersive X-ray (EDX) spectroscopy was performed using an instrument attached to a scanning electron microscope (S-3400N, Hitachi, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was performed using an AXIS-ULTRA DLD (Kratos, Hadano, Japan) spectrometer with a standard Mg K α (1256.6 eV) X-ray source (10 mA and 15 kV), and the binding energies were referenced to C1s at 284.3 eV. Magnetic properties were determined using a vibrating-sample magnetometer (VSM) over an applied magnetic field with a maximum strength of ± 10 kOe at room temperature.

3. Results and discussion

Multiwalled CNTs can be considered to be “rolled-up” sheets of graphite [28]. The structure of CNTs gives them some excellent properties, but it also leads to poor solubility and chemical inertness, and these significantly limit further extension of CNT applications. In this work, to overcome these limitations, concentrated aqueous nitric acid was used to functionalize the CNTs.

XPS measurements were performed to determine the elemental composition at the CNT surface; the survey scan spectra are presented in Fig. 1(a). In the spectrum of the treated CNTs, in addition to the intense C1s peak, an O1s peak, significantly more intense than the corresponding peak in the spectrum of the pristine CNTs, is observed. This could be attributed to the presence of oxygen-containing functional groups on the CNT surface after oxidative treatment. The high-resolution spectra for C1s from pristine and treated CNTs are presented in Fig. 1(b). It can be observed that the shoulder of the spectrum of the treated CNTs is higher than that of the pristine CNTs. Furthermore, the C1s peaks from pristine and treated CNTs were fitted by a superposition of five peaks, giving a detailed description of the oxidation states of the carbons. As well as the peaks corresponding to

-C-C- (sp^2 , sp^3) at 284.3 eV and 284.7 eV, there were three other peaks, which could be indexed to -C-O- (286.2 eV), -C=O (287.5 eV), and -COO- (289.2 eV). According to the peak areas from treated CNT, the percentages of the corresponding functional groups were as follows: -C-O-, 5.7%; -C=O, 4.4%; and -COO-, 10.4%. The XPS results therefore indicated that oxygen-containing functional groups were introduced on the surface of pristine CNTs through the nitric acid treatment; this agrees with previously reported results [29].

The oxidative treatment is considered to play a critical role in the whole synthetic process. The created oxygen-containing functional groups improve the hydrophilicity of the CNTs, enabling them to be well dispersed in water, which could favor uniform distribution of synthesized nanoparticles on the CNTs.

Fig. 1 XPS spectra of CNTs before and after treatment with nitric acid: (a) wide-scan spectra and (b) high-resolution spectra for C1s.

Fig. 2 Schematic diagram of the proposed process for CNT/NiFe₂O₄ synthesis.

These functional groups could also adsorb metal ions in solution [30, 31] by electrostatic interactions. The synthesis of CNT/NiFe₂O₄ could therefore involve the following three steps, shown in Fig. 2.

First, as mentioned above, pristine CNTs were oxidized by nitric acid, and functional groups (carbonyl, carboxyl, and hydroxy) were introduced. Secondly, the Fe³⁺ and Ni²⁺ in the solution were self-adsorbed on the CNT surface, where the functional groups were grafted. In step 3, NiFe₂O₄ nanoparticles were hydrothermally synthesized in situ on the CNT surface in an alkaline medium; the reaction is as follows :

Corresponding to this process (Fig. 2), TEM images of the CNTs before and after hydrothermal synthesis are presented in Fig. 3. The image in Fig. 3(a) shows well-distributed oxidized CNTs; the good distribution could be attributed to improved hydrophilicity. Although oxidative treatments always induce significant etching of CNTs, no obvious fractures or shortening phenomena are observed in Fig. 3(a). The image of CNT/NiFe₂O₄ sample hydrothermally synthesized at 170 °C is shown in Fig. 3(b). Many nanoscale particles are observed supported on the surface of the CNTs. This indicates that the CNT/NiFe₂O₄ nanocomposites were successfully synthesized at 170 °C. The loading of NiFe₂O₄ nanoparticles on CNT was measured by removing CNT at a high temperature, and the result showed a weight percentage (NiFe₂O₄ : CNT/NiFe₂O₄) of 50.6 wt.%, which approximately agrees with the value calculated based on initial amount of the CNTs and metallic salts.

The XRD patterns were used to determine the evolution of the crystal structures of the CNT/NiFe₂O₄ nanocomposites. For the intermediate product CNT/NiFeOH, as shown in Fig. 4(a), except for the peak at around $\theta = 26^\circ$, no diffraction peaks are observed; the peak at $\theta = 26^\circ$ could be assigned to the (002) planes of the CNTs, corresponding to the stacked graphene layers of the CNTs. The results show that an NiFe₂O₄ crystal

Fig. 3 TEM images of (a) treated CNTs, (b) CNT/NiFe₂O₄ synthesized at 170 °C.

Fig. 4 XRD patterns of (a) CNT/NiFe₂O₄ and CNT/NiFeOH and (b) NiFe₂O₄.

structure was not formed when the metal ions were precipitated, before the hydrothermal reaction. However, for the sample hydrothermally synthesized at 170 °C, as well as the peak at around $\theta = 26^\circ$, the pattern also shows several other obvious diffraction peaks that could be indexed to the (220), (311), (222), (400), (422), (511), and (440) crystal planes, matching the spinel structure of NiFe₂O₄ (JCPDS 54-0964) well. This confirmed that the CNT/NiFe₂O₄ nanocomposites were successfully produced. Moreover, Fig. 4(a) illustrates that the NiFe₂O₄ crystal structure was formed during the hydrothermal

process.

We also see a small diffraction peak between the (220) and (311) planes. This peak is believed to correspond to the Fe_2O_3 phase [32, 33], which means that there is a small amount of Fe_2O_3 impurities in the CNT/ NiFe_2O_4 nanocomposites. As a reference, pure NiFe_2O_4 nanoparticles were synthesized under the same conditions, and the XRD pattern is shown in Fig. 4(b). For the NiFe_2O_4 synthesized at 170 °C, the diffraction peaks match the standard spinel structure of NiFe_2O_4 well, and no other impurity peaks are observed.

It could therefore be concluded that the CNTs interfered with the synthesis of NiFe_2O_4 . We think that the adsorption of metal ions on the CNTs hinders free movement of these ions; this means that the synthesis cannot completely follow the initial stoichiometric ratios of the metal ions, which were added in a molar ratio of 2 : 1 ($\text{Fe}^{3+} : \text{Ni}^{2+}$).

EDX spectrometry was used to further analyze the chemical compositions of the product, and a typical EDX spectrum of a CNT/ NiFe_2O_4 nanocomposite is shown in Fig. 5. Ni, Fe, and C were obviously detected. A few small peaks corresponding to Si and Ca were also observed in the spectrum; these impurities could be imported from the glass tube used for holding the CNT/ NiFe_2O_4 sample; hence we could still consider that the as-prepared CNT/ NiFe_2O_4 sample contained only the desired elements (Ni, Fe, and C), and no other impurities. The strong C peak in the spectrum could be attributed to the CNTs. In addition, the atomic ratio of Fe to Ni (as shown in the inset) is 2.07, which is very close to the stoichiometric composition of NiFe_2O_4 .

The XPS spectra shown in Fig. 6 were used to further investigate the evolution of the CNT surface. The

Fig. 5 EDX pattern for CNT/ NiFe_2O_4 .

wide-scan spectra of treated CNTs and CNT/ NiFe_2O_4 are shown in Fig. 6(a). In addition to the strong peaks corresponding to O1s and C1s (seen in Fig. 1), peaks assigned to Ni2p and Fe2p are also clearly observed in the spectrum of CNT/ NiFe_2O_4 . This indicates that Fe and Ni are present on the CNT surface of the sample obtained by hydrothermal synthesis, and it also agrees with the EDX results (Fig. 5).

As shown in Fig. 6(b), the high-resolution spectra of Ni2p provide further detailed descriptions of the

Fig. 6 (a) XPS wide-scan spectra of CNT/ NiFe_2O_4 and treated CNTs; (b) high-resolution Ni2p spectra of CNT/ NiFe_2O_4 and CNT/ NiFeOH ; and (c) high-resolution Fe2p spectrum of CNT/ NiFe_2O_4 .

evolution before and after hydrothermal synthesis. For CNT/NiFeOH, the main peak, assigned to Ni2p3/2, appeared at 855.8 eV, accompanied by a satellite at 861.9 eV; it was speculated that Ni(OH)₂ was formed on the CNT surface. [34] Compared with CNT/NiFeOH, there is a slight shift of Ni2p for CNT/NiFe₂O₄, and the peak assigned to Ni2p is located at 855.2 eV. [35] This shift could be attributed to the influence of NiFe₂O₄ formation after hydrothermal synthesis. The presence of Ni on the CNT surface for CNT/NiFeOH, even after washing several times, also supported the suggestion that Ni²⁺ was adsorbed on the CNT surface.

The formation of NiFe₂O₄ was also proved by the Fe 2p spectrum, as shown in Fig. 6(c). The high-resolution spectrum shows an Fe2p3/2 peak at 711 eV. This result is consistent with others reported in the literature [35, 36]. As indicated by a dotted line in Fig. 6(c), a small satellite peak appearing at about 8 eV above the main Fe2p3/2 peak suggested the presence of Fe³⁺ in CNT/NiFe₂O₄ [36, 37].

The magnetic properties of the as-prepared CNT/NiFe₂O₄ nanocomposites were determined by VSM at room temperature, and the field-dependent magnetization of as-prepared CNT/NiFe₂O₄ nanocomposites was obtained with a maximum applied field up to 10 kOe. The corresponding curve is presented in Fig. 7, and the typical hysteresis loop indicates soft ferromagnetic behavior. It is observed that the CNT/NiFe₂O₄ nanocomposites synthesized at 170 °C exhibit a saturation magnetization (M_s) of about 24 emu/g. The results of the magnetic measurements therefore suggested that CNT/NiFe₂O₄ nanocomposites with soft ferromagnetic behavior were obtained in this work.

Fig. 7 Magnetization curve of CNT/NiFe₂O₄ at room temperature.

4. Conclusion

In this work, CNT/NiFe₂O₄ nanocomposites were synthesized using a simple hydrothermal method. A process for the synthesis of CNT/NiFe₂O₄ nanocomposites was proposed and confirmed by characterization using XPS, XRD, and EDX. The results suggested that NiFe₂O₄ was synthesized in situ on the CNT surface. The TEM image showed NiFe₂O₄ nanoparticles supported on the CNTs. Magnetic measurements illustrated that the CNT/NiFe₂O₄ nanocomposites are typical soft ferromagnetic materials with an M_s of about 24 emu/g.

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