



SHORT COMMUNICATION

Synthesis of normal spinel magnetite/MWNT nanocomposite

Mahdi, Ghazanfari^{a*}; Ahmad Yazdani^a

Department of Basic Sciences, Tarbiat Modares University (TMU), P.O. Box 14115-175, Tehran, Iran

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ABSTRACT

Fe₃O₄/MWNT magnetic nanocomposites were synthesized by a facile solvothermal route. Distribution of Ferrous and Ferric cations among the two interstitial (tetrahedral and octahedral) sites has been estimated by applying the full pattern fitting of the Rietveld refinement method. This analysis indicated that Ferrous cations occupy tetrahedral sites. Raman spectroscopy (RS), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR) confirmed the formation of the ferrite structure on the external surfaces of the CNTs. Vibrating sample magnetometer (VSM) measurement indicated that this nanocomposite at room temperature was treated as superparamagnetic material with high saturation magnetization.

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1. Introduction

CNTs have unique electronic, chemical, and mechanical properties that make them constructive nanomaterials for significant potential applications in materials science, nanotechnology and magnetically guided drug delivery systems [1, 2]. To optimize the potential applications of CNTs, it is essential to modify them with functional groups, in order to enhance their attached property. Decoration of CNTs with magnetic nanoparticles

can improve new optical, magnetic and electrochemical properties of CNTs. Diverse wet-chemistry methods have been reported for synthesizing Fe₃O₄/CNTs nanocomposites. Correa-Duarte et al. used polymer wrapping and layer-by-layer assembly method to cover CNTs with iron oxide nanoparticles and aligned the magnetic CNTs under low magnetic fields [3]. Jia et al. achieved the magnetic functionalization of CNTs by coating with Fe₃O₄ nanoparticles via a simple hydrothermal process, in which the Fe₃O₄ beads orderly self-assembled along CNTs and form necklace-like nanostructures [4].

*Corresponding Author Email: m.ghazanfari@modares.ac.ir

Tel.: +98 21 82883439

In this paper, Fe₃O₄/MWNT nanocomposites have (PVP) as in situ polymer wrapping agent in a polyol medium. The resulting Nanohybrid demonstrated superparamagnetic-like behaviour at room temperature and they could alignment under relatively low magnetic fields.

2. xperimental Procedure

In this study, multi-walled carbon nanotubes (length 3000nm; o.d. 10–20 nm; MWCNTs content >95%) were provided by the Neutrino Corporation of Iran. The other chemical reagents used in this work are Ferric chloride six hydrate (FeCl₃•6H₂O), Polyvinylpyrrolidone (PVP, average MW: 40000), sodium acetate, ethylene glycol, and polyethylene glycol (MW ~3000 Da). All reagents were of analytical grade from Merck and were used without further purification.

The pristine MWCNTs were first annealed in air at 350°C for 2h and then dispersed into concentrated nitric acid and refluxed at 140°C with constant stirring for 8hr. Finally, the product was diluted with distilled water and rinsed several times until the pH value was neutralized. The resulting MWCNTs were separated from the substance, product, and outcome by filtration and dried in vacuum at 80°C for further use.

The typical preparation procedure of Fe₃O₄/CNTs magnetic nanocomposites was as follows: Initially, 20 mg of purified MWCNTs fully dispersed in 30 ml of EG in an ultrasonic bath for half an hour to form a clear solution. After that 3mmol FeCl₃•6H₂O (0.811g) was dissolved in the resulting MWCNTs dispersion. The substance had an acidic PH. By adding sodium acetate (2.5g, 30 mmol) and polyethylene glycol (0.6 g, 0.03 mmol) and 6mg of polyvinylpyrrolidone to the resulting solution, a homogeneous mixture was yielded under vigorous stirring for 1 h. Then the acquired precursor was transferred to a Teflon-lined autoclave of 50ml capacity, and the sealed autoclave was maintained at 200°C for 16 hours. After being cooled to ambient temperature, the black products were collected by magnet and rinsed several times with deionized water and ethanol and subsequently dried at 80°C for 8 h.

3. Results and Discussion

Figure 1 shows the FTIR spectrum of CNT/Fe₃O₄. Infrared studies indicated the presence of a strong absorption line located at 563 cm⁻¹ which was

been synthesized by using Polyvinylpyrrolidone attributed to the stretching vibration of Fe-O intetrahedral sites in Fe₃O₄. The band at 1633 cm⁻¹ can be assigned to the C=O stretch of a bound quinine.

The formation of Fe₃O₄ in CNT was confirmed by X-ray diffraction (XRD) which is shown in Figure 2. The X-ray diffraction pattern corresponds to a spinel cubic structure Fd3m-Oh7 space group (no. 227). The weak diffraction peak at 2θ =26° could be ascribed to the reflection of the MWCNTs. The average grain size, D_{hkl}, was determined by applying Scherrer formula to the most intense (311) diffraction:

$$D_{hkl} = \frac{k \lambda}{\beta \cos \theta_{hkl}} \quad (1)$$

where k is a shape factor which normally ranges between 0.89 and 1.0 (in our case, k = 0.9); λ is the Co Kα₁ wavelength; θ_{hkl} is the Bragg angle; and β is the difference of the full-width-at-half-maximum (FWHM) of XRD peaks and natural width of XRD spectrometer, generally replaced by full width at

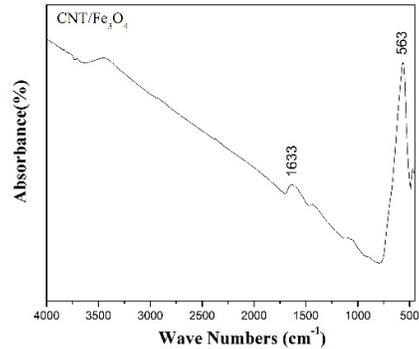


Fig.1. FTIR spectrum of CNT/Fe₃O₄

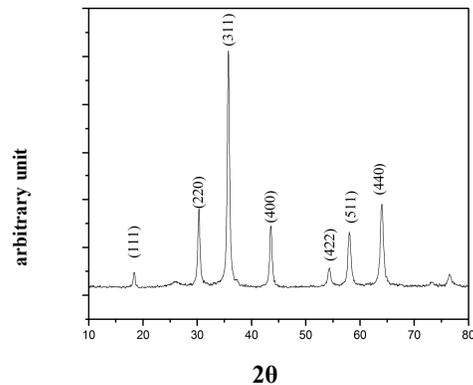


Fig.2. X-ray diffraction patterns for CNT/Fe₃O₄

half height of standard sample, in radians: $\beta_{\text{actual}} = \beta_{\text{sample}} - \beta_{\text{standard}}$. The average grain size for magnetite was determined 22nm.

The lattice constant of the cubic crystal was computed 0.837nm by using the d-spacing values and the respective (hkl).

The cations distributions are estimated by Rietveld refinement using diffraction (MAUD) program. In spinel ferrite the cations are distributed with the general formula $(M^{2+}_{1-x}Fe^{3+}_x)[M^{2+}_xFe^{3+}_{2-x}]O_4$ where the round and square brackets indicate tetrahedral sites (Td or A sites) and octahedral sites (Oh or B sites), respectively, and x represents the degree of inversion (defined as the fraction of tetrahedral site occupied by Fe^{3+} cations) which depends on the synthesis method and thermal treatment. The site occupancies of the cations in the two interstitial sites are constrained as $(Fe^{2+}_{1-x}Fe^{3+}_x)[Fe^{2+}_xFe^{3+}_{2-x}]O_4$ to preserve electrical neutrality. The ideal magnetite has an inverse spinel structure (x=1). So the initial cation distribution is assumed as $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$. The resulted cations distributions indicated the migration of ferrous ions to A site occurred in magnetite. This consequence was used in interpretation of magnetic properties.

Figure 3 shows the Raman spectra of the CNT and CNT/ Fe_3O_4 in the spectral region 1000–3000 cm^{-1} . Tangential modes of CNT were observed at 1593 cm^{-1} (G mode peak) and at 1354 cm^{-1} (D mode peak). Intensity of these modes was diminished by capping CNT with magnetite.

The SEM image is shown in figure 4 which indicates the good quality of magnetite coating onto CNT.

Magnetic properties of nano composite were characterized using VSM with a maximal applied field of 10 kOe. Figure 5 shows the magnetic hysteresis loops of the nanoparticles at room temperature. Saturation magnetization (M_s), coercive field (H_c) and reduced remanent magnetization (M_r/M_s) are 64 emu/g, 40Oe and 0.07 respectively. The Saturation magnetization of mere magnetite can be obtained from the following formula:

$$MS_{Fe_3O_4} = \frac{MS_T}{1 - \frac{M_{MWNT}}{M_{Fe_3O_4}}} \quad (2)$$

Magnetic moment in units of Bohr magnetons n_B at room temperature can be calculated as,

$$n_B = \frac{M}{N_A \cdot \mu_B} \cdot MS = \frac{M}{5585} \cdot MS \quad (3)$$

where M is the molecular weight of the Fe_3O_4 (231.6g), $N = 6.02 \times 10^{23} \text{ mol}^{-1}$ represents Avogadro's number, μ_B the Bohr magneton, and M_s is Saturation magnetization of mere magnetite. So $M_{sFe_3O_4}$ and n_{Bexp} became 66 emu/g and 2.74 μ_B .

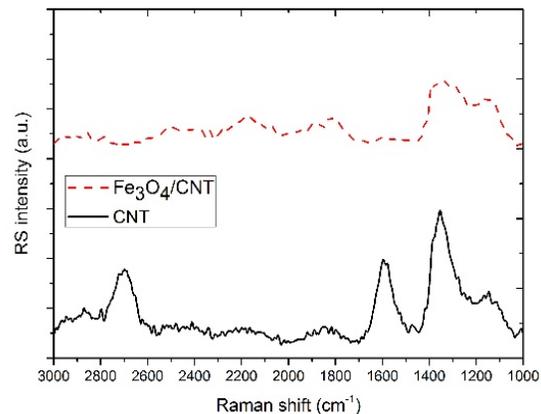


Fig.3. Raman scattering spectra of the CNT and CNT/ Fe_3O_4

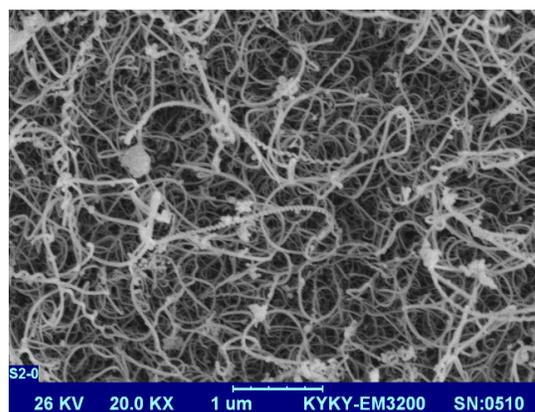


Fig.4. SEM image of CNT/ Fe_3O_4

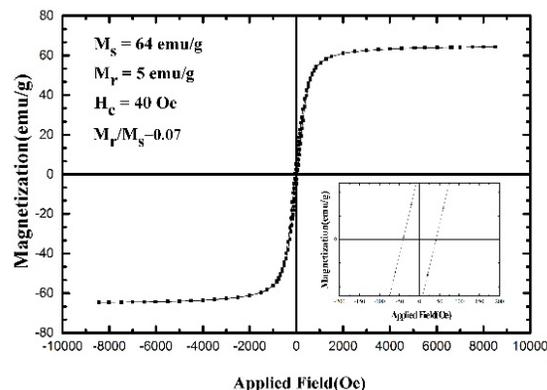


Fig.5. Hysteresis loop of CNT/ Fe_3O_4

4. Conclusion

In summary, the facile solvothermal technique has been used to yield CNT/Fe₃O₄ nano composite with the high saturation magnetization. The presence of magnetite nanoparticles in the single-domain region agglomerate which are separate by poly ethylene glycol, can be the reason of enhancement in the stability of magnetic properties. Since the PVP molecules have pyrrolidone functional groups, they can easily arrest crystals of Fe₃O₄ nanoparticles that can help to form ultrasmall magnetic particles and stop the aggregation of the nanoparticles. The resulting nanohybrid might be useful in catalysis, new functional device assemblies, and magnetic resonance imaging.

Acknowledgements

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