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Synthesis and magnetic properties of multiwalled carbon nanotubes decorated with magnetite nanoparticles

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ABSTRACT

Magnetite particles with nanoscale sizes were deposited along multiwalled carbon nanotubes (MWCNT) through a simple, effective and reproducible chemical route. The structure, morphology and magnetic properties of the hybrid materials were characterized by XRD, SEM, TEM, EDX, VSM. The characterization results show that the surface of nanotubes was loaded with iron oxides nanoclusters and each nanocluster is composed by several nanocrystals with a mean diameter of 10 nm. The experimental magnetic hysteretic behavior has been also studied by means of the Preisach model and a good agreement between experimental data and numerical computations was found.

1. Introduction

Multiwall carbon nanotubes (MWCNT) receive great attention because of their outstanding electronic, mechanical, thermal, chemical properties and significant potential applications in nanoscience and nanotechnology [1]. In recent years, more attention has been paid to the modification of carbon nanotubes to expand and/or improve their properties and functions as well as their promising applications and many researches focus on a new type of nanocomposites based on MWCNT coated with inorganic compound exploiting a synergistic effect and charge transfer in MWCNT-hybrids [2,3]. In particular, it has been suggested that MWCNT coated with magnetic elements or compounds are of great importance to magnetic data storage, xerography, nanoprobes in magnetic force microscopy, etc [4]. Carbon nanotubes doped with magnetic nanoparticles are also very interesting as new materials for applications in biomedicine for different human medical treatments including magnetically guided hyperthermia, and as drug delivery/carrier/release in the treatment of tumors [5,6].

In order to combine the advantages of the MWCNT and magnetite nanoparticles, in this paper a very simple, direct, and efficient route to decorate multiwall carbon nanotubes with magnetite nanoparticles is reported. MWCNT/Fe_3O_4 inorganic hybrid material was prepared through deposition–precipitation and wet-impregnation methods and fully characterized by SEM, TEM, EDX, XRD, VSM.

2. Experimental

MWCNT, with average length of 15 μm and average diameter of 10–20 nm, were synthesized by catalytic chemical vapor deposition (CCVD) from isobutane at 600 °C using Fe/Al_2O_3 based catalyst (Fe = 29 wt%) followed by purification treatment with NaOH at 60 °C for 24 h and then with HCl at room temperature for 6 h to remove residual amounts of catalyst particles [7]. Magnetite supported on MWCNT samples, have been prepared by deposition–precipitation and wet-impregnation. Deposition–precipitation samples were prepared by mechanical and ultrasonic stirring.

In the deposition–precipitation synthesis, the appropriate amount of the precursors of iron (III) and iron (II) was added to a MWCNT aqueous dispersion kept at 60 °C, under a constant stream of inert gas and vigorous stirring. An excess of basic agent (NH_4OH) is therefore added drop by drop to precipitate the corresponding iron hydroxides. In the impregnation method, an aqueous solution containing a proper amount of iron (III) and iron (II) was first dispersed onto the MWCNT, then an aqueous solution of NaOH was added. The samples were dried at 323 K overnight.

Table 1 reports the code, the preparation method and the total iron ions loading and Fe_3O_4 content of the investigated samples.

XRD analyses were carried out with an Ital-Structures diffractometer using nickel filtered Cu *Kα* radiation by mounting the powder samples on plexiglas holders. Diffraction peaks were compared with those reported in the JCPDS Data File. TEM analyses were performed on a 200 kV JEOL JEM 2010 analytical electron microscope (LaB_6 electron gun) equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging. A JEOL JSM 5600 LV scanning electron microscope operating at 20 kV and equipped with an

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Oxford Instrument (mod. 6498) was used for SEM/EDX investigations mounting the samples on a double sided adhesive conductive carbon discs. Magnetic hysteresis loops were measured at room temperatures using a vibrating sample magnetometer (VSM) operating in the magnetic field range (H) −10 kOe to 10 kOe. The diamagnetic contribution of sample holder was subtracted from the measured curves. Based on the classical Preisach hysteresis model [8], a numerical model describing the hysteretic behavior of the MWCNT/Fe_3O_4 systems was also validated.

3. Results and discussions

Fig. 1 shows the XRD patterns of the MWCNT/Fe_3O_4 hybrid materials obtained with the different preparation methods at higher (left) and lower (right) iron ions loading. The diffraction peaks at $2\theta = 26.1^\circ$ and 43.2° correspond respectively to reflections of (0 0 2) and (1 0 0) crystallographic planes of MWCNT. Diffraction lines typical of the cubic crystal structures of magnetite (JCPDS 19-0629) are well-defined in the deposition–precipitation samples while the impregnation method gives rise only to very weak peaks of magnetite thus confirming the low magnetite loading calculated by TPR data, as shown in Table 1.

SEM/EDX analysis was performed in order to investigate the overall morphology of MWCNT/Fe_3O_4 composites (Fig. 2). MWCNT/Fe_3O_4 composites appear randomly oriented to form large tangles. The atomic Fe to O ratio, obtained by EDX analyses, very close to a 3:4 ratio, confirmed the presence of Fe_3O_4 nanoparticles on the MWCNT surface.

Table 1
Total iron ions and magnetite content of MWCNT/Fe_3O_4 composites synthesized by deposition–precipitation, ultrasonicated deposition–precipitation and wet-impregnation methods.

Sample code	Preparation method	Total Fe ions (wt%)[a]	Fe_3O_4 (wt%)[b]
FDH	Deposition–precipitation under mechanical stirring	21.5	18
FDL	Deposition–precipitation under mechanical stirring	12.3	5.6
FIH	Wet impregnation	25.9	5.2
FIL	Wet impregnation	16.6	4.9
FDUH	Deposition–precipitation under ultrasonic stirring	29	12
FDUL	Deposition–precipitation under ultrasonic stirring	13.4	7.1

[a] Calculated by atomic adsorption spectroscopy.
[b] Calculated by temperature programmed reduction.

Representative TEM images of MWCNT/Fe_3O_4 composites prepared by deposition–precipitation methods, in Fig. 3 (upper, left), clearly shows that MWCNT have been coated with large aggregates of iron oxide particles with spherical shape. Instead, MWCNT/Fe_3O_4 composites prepared by impregnation method show an homogenous distribution of iron oxide particles along the MWCNT surface, as shown in Fig. 3 (upper, right). High Resolution TEM images of FDH sample, in Fig. 3 (bottom), revealed that the surface of MWCNT was loaded with nanoclusters and each nanocluster is composed by several nanocrystals. HRTEM analyses demonstrated good crystallinity and clear lattice fringes of the nanocrystals with a mean diameter of 10 nm, (see Fig. 3, bottom). The experimental lattice spacing of 0.25 nm is consistent with the d value of the (3 1 1) planes of Fe_3O_4, while the 0.34 nm was corresponding to the graphitic interlayer distance of the MWCNT.

Room-temperature hysteresis loops have been measured by exploiting a high sensitivity Vibrating Sample Magnetometer (maximum applied field 10^4 A/m). Table 2 reports the main magnetic characterization results of the investigated samples. Fig. 4 shows a representative hysteresis curve of the MWCNT/Fe_3O_4 systems; a typical superparamagnetic behaviour marked by a slow approach to saturation is observed. However, an ideal superparamagnetic system is also characterised by the absence of coercive field. In the curve shown in Fig. 4, a faint, non-zero value of the coercivity is found (around 200 A/m). The inset of Fig. 4 shows a zoom of the hysteresis loop. This behaviour can be ascribed to the existence of magnetic interaction among the magnetic nanoparticles due to aggregation effects. Such an hypothesis is confirmed by the HRTEM images shown in Fig. 3, where nanoparticles aggregation is evident resulting in higher magnetic volume with respect to the single nanoparticle [8].

The experimental magnetic hysteretic behavior has been studied by means of the Preisach model. The reversible and irreversible part of the hysteresis loop have been identified from the experimental data directly. To describe the irreversible part, we consider the Gaussian approximation for the Preisach Function $P(U,V)$ being U and V the switching fields of the hysteron. By considering the hypothesis that the probability distribution functions of the switching fields are statistically independent $P(U,V) = P_S(U)P_S(-V)$ being

$$P_S(U) = A\exp\left[-\left(\frac{U-hc}{\sigma}\right)^2\right] \quad (1)$$

where the parameters hc and σ have been identified by using a generalization of the procedure developed in Refs. [9] and [10] for the Lorentzian approximation, A is a normalization constant. The reversible part has been modeled as a state independent (depend on the external field H only) function $M_r = a\tan[kH]$ being k a proportionality constant (for more details see Refs. [9] and [10]).

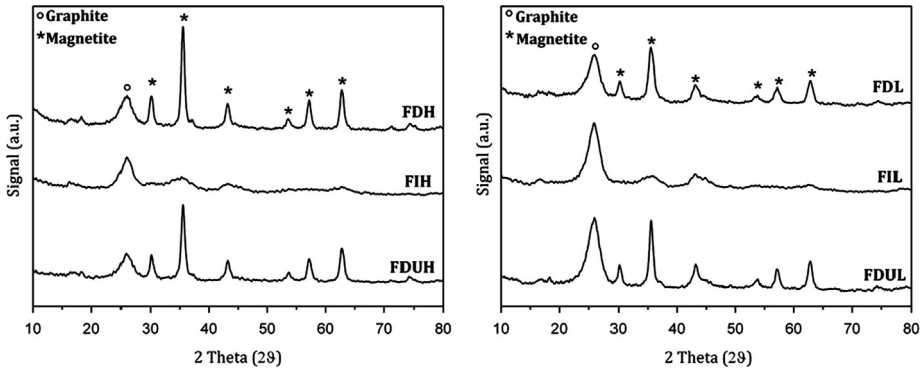

Fig. 1. XRD patterns of MWCNT/Fe_3O_4 hybrid materials.