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Magnetic alignment of nickel-coated carbon fibers

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ABSTRACT

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1. Introduction

In recent years, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have attracted much attention because of their fine electromagnetic wave-absorbing properties, high conductivity, corrosion resistance and oxidation resistance [1–4]. CNFs are ideal fillers of structural and functional composites. However, when introduced into a polymeric matrix, CNFs disperse randomly, losing their orientations. The randomly embedded CNFs in bulk samples limited some potential applications of CNFs and exhibited substantially lower electrical and thermal conductivities [5,6] than expected.

Coatings, prepared by the attachment of metals (nickel, iron and cobalt or their alloys) onto CNFs, can overcome these limitations. The fabrication of magnetic CNFs-embedded composites has been extensively investigated. Huang [7] prepared CNFs coated with barium ferrite by sol–gel method and theoretically analyzed their electromagnetic properties. Xu [8] obtained the similar coated CNFs with complete and uniform Fe₃O₄ nanoparticles by annealing in vacuum in the temperature range of 300–550 °C. Yang [9] reported an electrochemical method to fabricate iron-coated CNFs. Recently, Xie [10] employed an electroless deposition route to deposit continuous and uniform Ni–Fe–Co–P coatings on CNFs. The coated CNFs exhibited fine electromagnetic wave-absorbing property in the frequency region of 8–18 GHz. Guzeliya Korneva [11] investigated the magnetic CNTs based on the phenomenon of spontaneous penetration of wetting fluids into capillaries. S.V. Pol

[12] produced fullerene-like Ni–C (graphitic) core–shell nanostructures with a large negative magnetoresistance, of the order of 10%. Xiaosi Qi [13] observed a relatively high magnetization value over carbon nanocoils due to the entrapment of Ni nanoparticles inside the carbon flakes. However, all these methods were complicated and difficult to be processed. There is a need to develop an easier fabrication of magnetic CNFs-embedded

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Magnetic composites of nickel-coated carbon nanofibers have been successfully fabricated by employing

a simple microwave-assisted procedure. The scanning electron microscopy images show that a complete

and uniform nickel coating with mean size of 25 nm could be deposited on carbon fibers. Magnetization

curves demonstrate that the prepared composites are ferromagnetic and that the coercivity is 96 Oe. The

magnetic carbon nanofibers can be aligned as a long-chain structure in an external magnetic field.

composites with better properties.

Herein, we report a simple microwave-assisted procedure for the assembly of a compact layer of magnetic nickel nanoparticles onto CNFs in a water/ethylene glycol system. The CNFs based on the assembly of nickel nanoparticles show an excellent magnetic property. The alignment of CNFs in relatively low magnetic fields could be obtained.

2. Experimental

The CNFs used in this study were synthesized by copper nanoparticles using catalytic chemical vapor deposition at low temperature (300 °C) [14,15]. All of the chemicals used in the experiments were analytical grade without any further purification.

2.1. Preparation of composites

The starting CNFs were subjected to an oxidation treatment in the nitric acid to modify the surface in order to achieve better dispersion. A two-step pretreatment, sensitization and activation, was used to catalyze the CNFs. The sensitizer and activator were stannous chloride/hydrochloric acid (15 g/L SnCl₂·2H₂O and 41 g/L HCl) and palladium chloride/hydrochloric acid (0.5 g/L PdCl₂ and





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Fig. 1. SEM images of nickel-coated coiled CNFs.

12 g/L HCl) solutions, respectively. Ultrasonic vibration was applied during the catalyzation to facilitate uniform activation of the entire surface of the CNFs.

In a typical experiment to prepare the magnetic composites of nickel-coated CNFs, CNFs and 0.15 g NiCl₂·6H₂O were dispersed in 40 mL ethylene glycol by ultrasonic vibration for 0.5 h. 0.12 g N₂H₄·H₂O (80 wt%) solution was added dropwise to the solution, followed by the addition of 2 ml 0.25 M NaOH aqueous solution. 60% (425 W) of the output power of the microwave was used to irradiate the mixture for 5 min. Then, the microwave heating was stopped and the products were collected by centrifugation, washed with distilled water and absolute ethanol repeatedly for three times, and dried at 45 °C under vacuum.

2.2. Characterization

The microwave oven (2.45 GHz, maximum power of 750 W) used for sample preparation was a focused single-mode microwave synthesis system which was equipped with mechanical stirring and a water-cooled condenser. The temperature was controlled by the automatic adjustment of the microwave power. X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/max- γ A X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å) using a 40 kV operation voltage and 70 mA current. Scanning electron microscopy (SEM) images were recorded by JEOL JSM-6700F equipment. Magnetic properties were recorded in a quantum design vibrating sample magnetometer (VSM) at room temperature.

3. Results and discussion

Fig. 1 shows SEM images of nickel-coated CNFs. The nickel nanoparticles were synthesized by redox in microwave. CNFs were coated directly by the prepared nickel nanoparticles in one-step. As the low magnification SEM image shows in Fig. 1a, the CNFs have been coated by a uniform layer of nickel particles. The CNFs are 50–200 nm in diameter. The dense layer of nickel homogeneously covers the CNFs. Fig. 1b shows part of the CNFs which are coated by nickel nanoparticles. It can be observed that the nickel nanoparticles are spheres and 25 nm in diameter. No aggregation exists around the CNFs.

The XRD pattern of as-synthesized samples is shown in Fig. 2. The diffraction peaks at $2\theta = 44.49^{\circ}$ and 51.83° can be assigned to (1 1 1) and (2 0 0) planes of nickel, respectively. The diameter of nanoparticles characterized from Scherrer formula is 21.5 nm, which is slightly lower than that observed in Fig. 1. A scattered peak at $20-40^{\circ}$ is considered to be the carbon peak. No other



Fig. 2. XRD pattern of nickel-coated coiled CNFs.

diffraction peaks can be found, indicating that the coating consists only of nickel nanoparticles.

The magnetic properties of nickel nanoparticles and the nickelcoated CNFs were determined using a vibrating sample magnetometer. Fig. 3 shows the magnetization curves and the enlarged hysteresis loops of the products. It is clear to be seen from Fig. 3a that the nickel nanoparticles and the nickel-coated CNFs are all ferromagnetic. The saturation magnetization (Ms) of nickel nanoparticles and magnetic composites are 29.0 emu/g and 6.0 emu/g, respectively, considerably smaller than that of bulk nickel (Ms = 54.39 emu/g) [16]. The curve of the composites, as assumed, mainly displays the magnetic contribution of nickel nanoparticles deposited on the CNFs. Thus, the nickel-coated CNFs are ferromagnetic with sizes beyond the super paramagnetic limit, which is 15 nm for spherical nickel nanoparticles [17]. As can be seen in Fig. 3b, the nickel nanoparticles and magnetic composites have different coercivities. After the nickel nanoparticles coated CNFs, the coercivity decreases from 209 Oe to 96 Oe. The magnetic composite tends to transform to paramagnetism.

Fig. 4 shows illustration of the process and the SEM images of nickel-coated CNFs in the absence (c) and presence (d, e) of an external magnetic field. The specimens were obtained when ethanol solution containing magnetic carbon nanofibers was drying. Fig. 4b shows the histogram of the chain length. It is clear that the nanofibers are mostly 50–80 μ m long. As no magnetic field was applied in Fig. 4c, the CNFs randomly deposit on a silicon



Fig. 3. Magnetization curves (a) and the enlarged hysteresis loops (b) of nickel nanoparticles and the nickel-coated CNFs.



Fig. 4. (a) Illustration of the process; (b) histogram of the chain length; (c) SEM image of nickel-coated CNFs in the absence of an external magnetic field; (d and e) SEM images of nickel-coated CNFs with an external magnetic field (0.5 T).

substrate which agrees with reported observations [18]. In order to visualize the magnetic response of these magnetic CNFs, a small parallel magnetic field (magnetic flux density = 0.5 T) was applied when the CNFs dried on a silicon wafer. It is interesting that the coated CNFs were aligned as a long-chain structure under magnetic field (see Fig. 4d and e). The arrows indicated the direction of the magnetic field.

In zero field, the magnetic moments of the nickel nanoparticles randomly point in different directions, resulting in a vanishing net magnetization. However, after a sufficiently large homogeneous magnetic field was applied, the magnetic moments of the nanoparticles aligned in parallel. And the resulting dipolar interactions are sufficiently large to overcome thermal motion and to reorient the magnetic CNFs favoring the formation of chains of CNFs [19]. As shown in Fig. 4d and e, these chain-like structures are formed by connecting the magnetic CNFs in line, touching each other in a head-to-tail fashion. This can be explained by capillary and Van der Waals forces. The magnetic chains form double or triple structures which are parallel and close to each other but are offset to each other along the long axis.

4. Conclusions

Our experimental results demonstrate the readiness of a method by which CNFs can be uniformly coated with nickel nanoparticles, following a two-step treatment of sensitization and activation. The prepared composites are ferromagnetic and with a small value of coercivity. Upon such functionalization, the CNFs can be aligned in a relatively small external magnetic field. These coated CNFs could be incorporated into metal matrixes to produce new composites with novel properties.

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