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Preparation and magnetic property of the composite of nitrogen-doped carbon nanotubes decorated with nickel nanoparticles

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ABSTRACT

A magnetic composite of nitrogen-doped carbon nanotubes (CN_x) decorated with nickel nanoparticles was synthesized by a chemical precipitation and deoxidization method. The decorated CN_x were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The XRD pattern showed that CN_x, nickel nanoparticles and little nickel oxides coexisted in the composite, TEM observation indicated that nickel nanoparticles were highly dispersed on the outer walls of CN_x, Magnetic measurements by VSM demonstrated that the saturated magnetization and remanence of CN_x were improved, while the coercivity was lowered after decorating with nickel nanoparticles.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been of great interest because of their unique structural, electrical and mechanical properties. Their potential applications include nanodevices, quantum wires, ultrahigh-strength engineering fibers, sensors and catalyst supports [2–4]. To optimize the uses of nanotubes in many of these applications, it is necessary to decorate the surface of CNTs. Decorating can improve dispersion of CNTs in solvents or impart new optical, electric, magnetic properties [5–7]. Recently, various magnetic materials including iron [8,9], iron oxide [10,11], nickel [12,13], cobalt [14] decorated on CNTs have been prepared. For the nitrogen-doped carbon nanotubes (CN_x), Jiang et al. [15] decorated the activated CN_x with gold nanoparticles. The reactive sites of the activated CN_x allowed a uniform deposition of Au clusters along the nanotubes. Zamudio et al. [16] anchored the CN_x with silver nanoparticles by the reduction of a silver/2-ethylhexanoate complex or $AgNO_3$. Yue [17] and Xavier et al. [18] immobilized CN_x with platinum nanoparticles and investigated their catalytic activity. However, there is no report about magnetic materials of the decorating CN_x. In this work, we synthesized the composite of CN_x decorated with nickel nanoparticles by a chemical precipitation and deoxidization method. Subsequently, the magnetic property of the composite was investigated.

2. Experimental

The CN_x used in this work were prepared by catalytic chemical vapor deposition (CVD) of ethylenediamine using Mg/Fe-layered double hydroxide as catalyst precursor. CN_x were purified by refluxing in a 3 M of HNO_3 solution for about 8 h at 333 K, followed by filtering and washing thoroughly with distilled water. The purified CN_x were dispersed in a concentrated H_2SO_4/HNO_3 mixture (3:1, v/v) and sonicated for 0.5 h at room temperature. The activated CN_x were dispersed in a solution of $Ni(NO_3)_2$ with vigorous stirring, then the ammonia solution (2.5 wt%) was slowly added till the pH value reached 9.5. The solution was filtered with 0.2 μm filter membrane and washed with distilled water repeatedly. Later the product was dried in an oven for 24 h at 333 K. After that the sample was annealed at 773 K for 1.5 h in a stream of Ar, nickel oxides decorated CN_x was obtained. The composite of CN_x decorated with nickel nanoparticles were prepared by reduction of nickel oxides decorated CN_x using H_2 at 673 K for 0.5 h.

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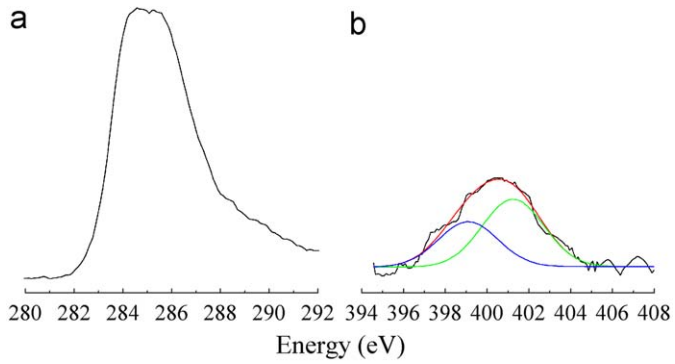

Fig. 1. C1s (a) and N1s (b) XPS spectra of the as-prepared CN_x.

The X-ray photoelectron spectroscopy (XPS) was collected on a Physical electronics PHI 5300 using a vacuum generators XPS system operating with Mg (Kα) radiation. The raw data were corrected for charging using the binding energy of graphite at 284.6 eV. The activated CN_x were characterized by FTIR on a Brucker Vector 22 spectrometer in the wavenumber range 4000–450 cm^{-1}. The X-ray powder diffraction (XRD) of the decorated CN_x were collected on an X' PERT PRO MPD diffractometer operated at 40 kV and 40 mA with Cu Kα radiation. The morphologies of the decorated CN_x were observed through transmission electron microscopy (TEM) with a JEOL JEM-1200EX instrument operated at 100 kV. The magnetic properties of the decorated CN_x were measured using a vibrating sample magnetometer (VSM) with a Lake Shore 7407 instrument. The samples were measured under a magnetic field of 12 kOe at room temperature.

3. Results and discussion

XPS analysis was carried out on the CN_x to look for the N-doped level and structure. The C1s and N1s XPS spectra of CN_x are displayed in Fig. 1(a) and (b). All XPS spectra show that the tubes consist of C accompanied by traces of N. The N-doped level, which is defined as the N/(N+C) atomic ratio%, was estimated by the area ration of the C1s and N1s peaks, taking into consideration of their relative sensitivities. The N-doped level is 6.3 at% in our tubes. The asymmetric C1s band and N1s band can be observed centered at 284.6 and 400.6 eV. From the curve fitting, the N1s band can be deconvoluted into two bands at around 399.4 eV (PN1) and 401.6 eV (PN2), which correspond to pyridine-like and graphitic-like N [19], respectively. The pyridine-like N is referred to the N atoms that contribute to the system with a pair of pi electrons, whereas graphitic-like N corresponds to the coordinated N atoms substituting for C atoms in the graphite layers [20]. The distribution of PN1and PN2 in CN_x is 38% and 62%.

Fig. 2 shows FTIR spectra of the as-prepared and activated CN_x. The peaks in Fig. 2(b) at 1710 and 1385 cm^{-1} are assigned to carboxyl groups and sulfate groups [15], which are not found in as-prepared CN_x (Fig. 2(a)). These functional groups are hydrophilic, which makes CN_x disperse easily in water.

Fig. 3 shows the XRD patterns of the activated and decorated CN_x. The diffraction peak at about $2\theta = 26^\circ$ is assigned to the (0 0 2) plane of CN_x. After being decorated with nickel, the new diffraction peaks at $2\theta = 44.4^\circ$, 51.8° and 76.4° correspond to the (1 1 1), (2 0 0) and (2 2 0) reflections of Ni (JCPDS, no. 04-0850). The other two weak diffraction peaks at $2\theta = 37.3^\circ$ and 62.9° are assigned to the (1 1 1) and (2 2 0) plane of NiO (JCPDS, no. 78-0643). The remaining little NiO is not reduced due to the lower

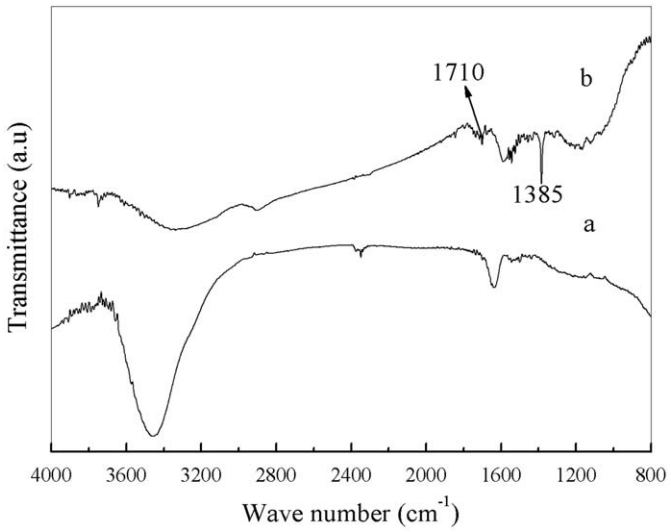

Fig. 2. FTIR spectra of the as-prepared (a) and activated CN_x (b).

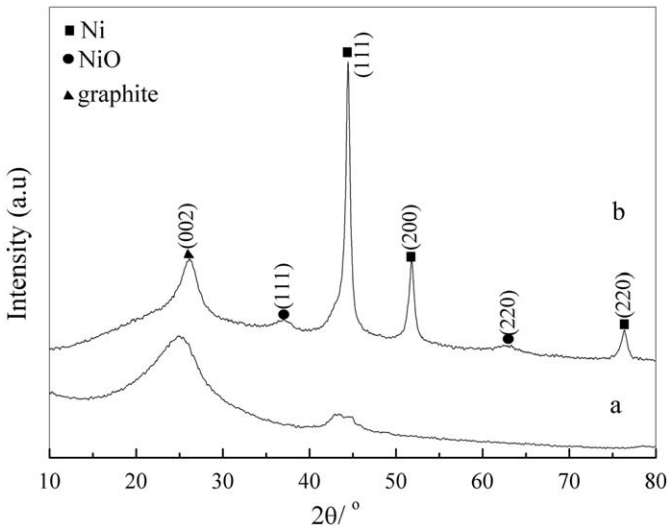

Fig. 3. XRD patterns of the activated (a) and decorated CN_x (b).

temperature. These results identify that CN_x, Ni and little NiO coexist in the composite.

The morphologies of the decorated CN_x are examined by TEM, and some typical images are shown in Fig. 4. After being activated, the typical "bamboo-like" structure of CN_x has not changed (Fig. 4(a)). It can be seen from Fig. 4(b) and (c) that the decorated CN_x show rough surface, indicating the deposition of nanoparticles. The highly dispersed spherical nickel nanoparticles are mainly deposited on the outer walls of CN_x, and the size of most particles is from 5 to 15 nm, which is consistent with the result calculated using the Scherrer equation. The length of the decorated nanotubes is decreased sharply. The similar route was used to decorate CNTs with iron or cobalt oxides, but the length of CNTs was not decreased [10,11,14]. In our work, the decreased length may attribute to the high reactive activity of CN_x, which leads to the destroyed structure of CN_x during the decoration [16,21].

The magnetic properties of the activated and decorated CN_x were measured in fields between ± 12 kOe at room temperature.