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One-step synthesis of carbon nanotubes with Ni nanoparticles as a catalyst by the microwave-assisted polyol method

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ABSTRACT

Carbon nanotubes (CNTs) were firstly synthesized by the microwave-assisted polyol method and magnetic Ni nanoparticles were employed as a catalyst in the process. The structures, morphologies and magnetic properties of the as-synthesized samples were investigated by using X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM), respectively. Our results indicated that CNTs can be synthesized after the observation of a small electric spark with Ni particles used as a catalyst. TEM showed that the length of the hollow carbon nanotubes was of the order of micron. VSM demonstrated that Ni/CNTs composite was ferromagnetic characteristic with hysteretic behavior at room temperature.

1. Introduction

Since the original report by Iijima in 1991 [1], a considerable amount of work has been done on carbon nanotubes (CNTs). The applications of CNTs and related materials have attracted great interest over the last decade [2–4]. Owing to their outstanding and unique physical properties derived from a combination of unique dimensional, structural and topological features [5–7], such as high flexibility, large aspect ratio, electronic conductive or semi-conductive behavior, excellent mechanical strength and high thermal conductivity, CNTs have a wide range of applications such as hydrogen reservoirs [8], nanoelectrodes [9], mechanical actuators [10], catalysis [11], sensors [12], electromagnetic characteristics [13], field emission displays [14] and human therapy [15].

CNTs can be produced by diverse techniques such as chemical vapor deposition [16–18], arc discharge [19] and laser evaporation [20]. Up to now, CNTs can be also synthesized by a wide variety of other routes such as heat treating the polymer [21], flame [22,23], ion-beam irradiation [24], electrolytic formation [25], in situ synthesis [26], solar synthesis [27] and microwave irradiation heating method [28]. It is well known that the methods of CNTs synthesis mostly require metallic particles as a catalyst, and magnetic Fe, Co, Ni nanoparticles are the best catalyst for CNTs growth. In the present work, the microwave-assisted polyol method was firstly utilized to prepare CNTs, and nano-sized nickel particles were used as a catalyst in the process. Compared with other approaches, this method is simple and economical of time. Furthermore, it does not require any complex or expensive equipments. In this paper, the effects of surfactant concentration and temperature were discussed. The magnetism of the nickel nanoparticles was also investigated. In the case of encapsulated ferromagnetic Ni nanoparticles within carbon nanotubes or any other special components and structures, it may provide possibilities to develop magnetic composite materials and find many new applications.

2. Experimental

The materials used in this study were nickel (II) acetate tetrahydrate (99.99%) and ethylene glycol (>99%). Following our previous work [29–31], before the reaction, 50 ml of a solution of 0.125 M (or 0.250 M) $Ni(Ac)_2$ in ethylene glycol was prepared in a 100 ml glass flask. Considering that nickel nanoparticles agglomerate easily while heating [32] and greatly decrease their catalytic efficiency, so-called surfactants or dispersants with polyvinylpyrrolidone (PVP, average molecular weight 40,000) had to be added to solve the dispersibility of nickel nanoparticles. During our experiments, 2–4 g PVP was added. After the solution was ready, the flask was placed in the center of a microwave oven (Spectra, 900 W), connected to a condenser, purged by argon for about 20 min, and then the microwave oven was turned on at the power level of 50% (or 60%, or 70%, or 80%) with a continued flow of the gas. The argon flowing rate was 80 ml/min. After reacting for about 20 min, the black suspension appeared. If the inner wall of the glass flask was plated with metal nickel, a small electric spark was observed. One or two minutes later, the microwave oven was turned off and the gas valve was closed. Then the flask was taken out and corked up, cooled in ice water immediately. The resulting solid product was washed thoroughly with ethanol and centrifuged. All these processes were repeated five times. The products were dried under vacuum and kept in a glove box.

The powder X-ray diffraction (XRD) data were collected on a Bruker AXSD* Advanced Powder X-ray diffractometer by using Cu-Kα radiation (λ = 0.15418 nm).

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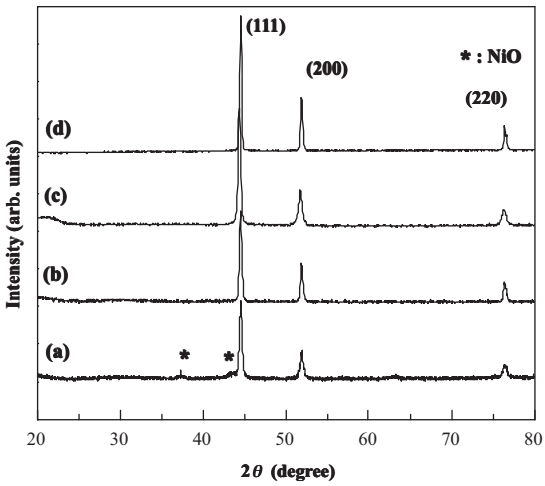

Fig. 1. X-ray powder diffraction pattern of the samples generated using different power levels of the microwave oven: (a) 50%; (b) 60%; (c) 70%; (d) 80%.

The patterns were recorded in the 2-theta (2θ) range from 20° to 80°. Transmission electron microscopy (TEM) investigations were carried out using a JEOL-JEM 100 SX microscope operating at 100 kV. Samples for TEM observation were prepared by sonicating in absolute ethanol for 1–2 min, followed by placing a drop of the sample suspension on a copper grid (400 meshes, Electron Microscopy Sciences) coated with carbon film. The magnetic measurements were carried out using a BHV-55 type vibrating sample magnetometer (VSM) at room temperature with an applied magnetic field up to 1 T to reach saturation values.

3. Results and discussion

The XRD patterns of the catalyst after the black suspension appeared but before a small electric spark can be observed at various conditions are shown in Fig. 1. The positions of the diffraction peaks are in good accordance with the reported JCPDS 04-0850 data. As we can see, when the power level employed was 50% of the microwave oven, besides the phase of Ni, a phase of NiO (JCPDS 78-0643) was found by XRD simultaneously (Fig. 1a). This can be explained by the fact that the power level of 50% was not enough to obtain nickel particles by reducing reaction. It was also observed that when the microwave oven was turned on at above the power level of 50%, a single phase of Ni with face-centered cubic (fcc) structure was formed in the process of CNTs synthesis and no other impurity was detected in the XRD patterns (Fig. 1b–d). Moreover, with increasing the power level, the relative intensity of the diffraction peak was stronger and stronger. All the peaks at different angles correspond to fcc Ni (1 1 1), (2 0 0) and (2 2 0). The grain size of nickel particle was calculated according to the Scherrer formula [33]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the particle size, λ is wavelength of X-ray, β is full width at half maximum measured in radians and θ is the Bragg angle of the (1 1 1) plane. The values obtained are 26.8, 30.6 and 38.2 nm, respectively. This clearly indicates that Ni particles used as a catalyst in this experiment are nano-sized with enough power level of the microwave oven, these nanoparticles are very advantageous for CNTs growth.

In order to reveal the morphology and structure of the catalyst after reduction, the TEM experiment was performed for the catalyst formed under a solution of 0.250 M $Ni(Ac)_2$ in ethylene glycol. During the current experiments, some of PVP were added (3 g PVP) and the microwave oven was turned on at a power level of 60–70%. Two TEM images of the catalyst after the black suspension appeared but before a small electric spark can be observed are shown in Fig. 2, which demonstrates Ni particles with the particle sizes in the range of 20–30 nm. It demonstrated that a suitable amount of PVP as surfactant was needed during the microwave-assisted reaction and prevented the agglomeration. It can be thought that on the one hand the nucleation of Ni was accelerated with microwave irradiation [34], on the other hand, PVP as surfactant could absorb and decrease the surface tension. Therefore the single particle was prevented from growing, and several particles were prevented from coming together with adding a suitable amount of PVP [31]. Thus it indicates that this technique is an effective and convenient method to obtain dispersed and active Ni nanoparticles.

In order to provide a direct evidence for carbon nanotubes formation and to investigate the morphology, the as-synthesized samples were examined by transmission electron microscopy (TEM). As a typical example, two magnified TEM images of CNTs synthesized are shown in Fig. 3. Carbon nanotubes synthesized in our experiment have a tubular structure with smooth and uniform walls. We can see that the length of hollow carbon nanotubes is of the order of micron. The diameters of most of the CNTs are about 20 nm. Especially, in our experiment a very large carbon nanotube with a diameter of 40 nm can be also clearly observed. Carbon nanotubes can be distinguished from their solid fibre counterparts by their wall characteristics. The former typically have smooth and uniform walls, whereas the latter tends to have bumpy sides and rarely grows straight [35]. By comparison with earlier report [4], single-walled nanotubes have diameters in the range 0.4–2 nm. Typical multi-walled nanotubes diameters grown by the arc-discharge method are about 20 nm in diameter, while CVD grown nanotubes can have much larger diameters of up to 100 nm.

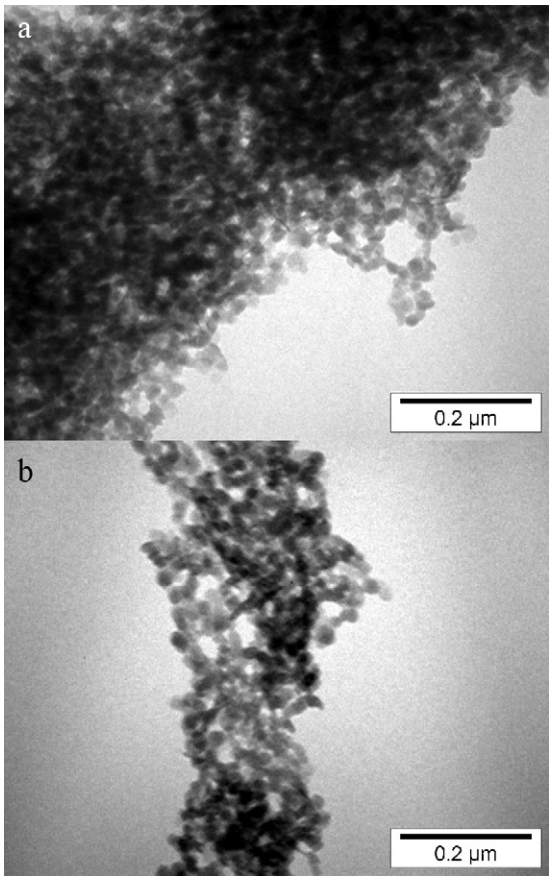

Fig. 2. TEM images of Ni catalyst nanoparticles after the black suspension appeared but before the small electric spark observed: (a) at the power level of 60% of the microwave oven; (b) at the power level of 70% of the microwave oven.

The combined results of the thickness of the walls and the relatively large diameters of the nanotubes demonstrate that these nanotubes are possibly multi-walled. The possible carbon source may be the ethylene glycol, or acetate ions, or PVP. We are inclined to think that carbon nanotubes are made from the ethylene glycol. This is in agreement with previous results using a similar carbon source with alcohol [36]. During our experiments for synthesizing carbon nanotubes, it was very key factor that an electric spark was excited under the microwave owing to the inner wall of the glass flask plated with metal nickel.

For deep insight into the nature of the as-synthesized samples, the magnetic properties of the samples have been measured by VSM at room temperature. The static hysteresis loops of the samples are shown in Fig. 4. During the experiment, the amount of nickel was normalized. The magnetic hysteresis loop of Ni nanoparticles obtained after the black suspension appeared but before the small electric spark, was given with the coercivity H_C = 89.9 Oe and saturation magnetization σ_s = 38.1 A m^2/kg (Fig. 4a). For Ni/CNTs composites obtained by reacting for 1 min after the small electric spark was measured. The values obtained are with H_C = 119.9 Oe and σ_s = 32.4 A m^2/kg (Fig. 4b). The result corresponding to Ni/CNTs sample reacting for 2 min after the electric spark is shown in Fig. 4c, which has a larger hysteresis loop with coercivity (H_C = 162.4 Oe) and saturation magnetization (σ_s = 23.4 A m^2/kg). The hysteresis loop of all the samples shows ferromagnetic characteristic. The saturation magnetization value for Ni/CNTs composites is lower than those of Ni nanoparticles without the small electric spark under the same measurement conditions. The coercivity is larger for Ni/CNTs composites regarding Ni nanoparticles and bulk Ni (H_C = 0.7 Oe)

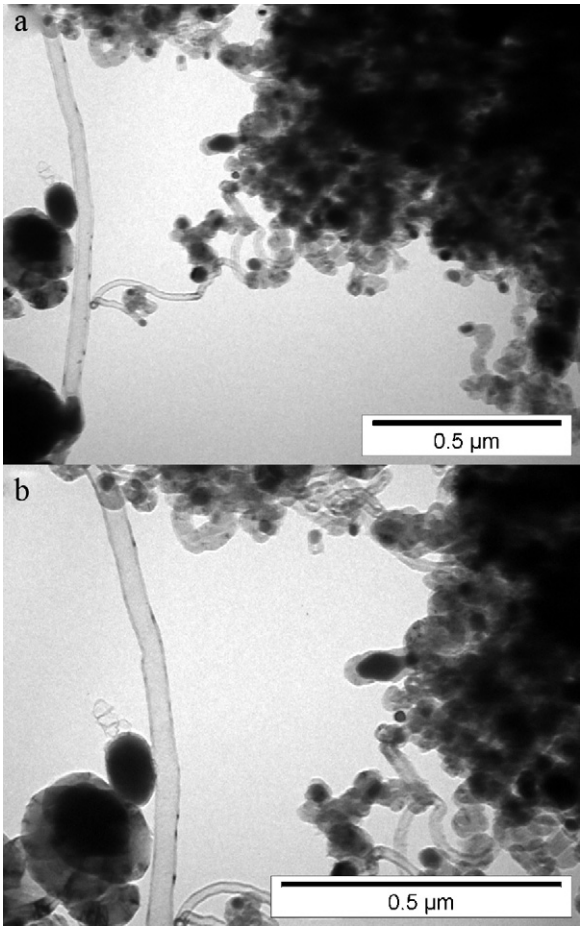

Fig. 3. Magnified TEM images of CNTs synthesized at the power level of 80% of the microwave oven.

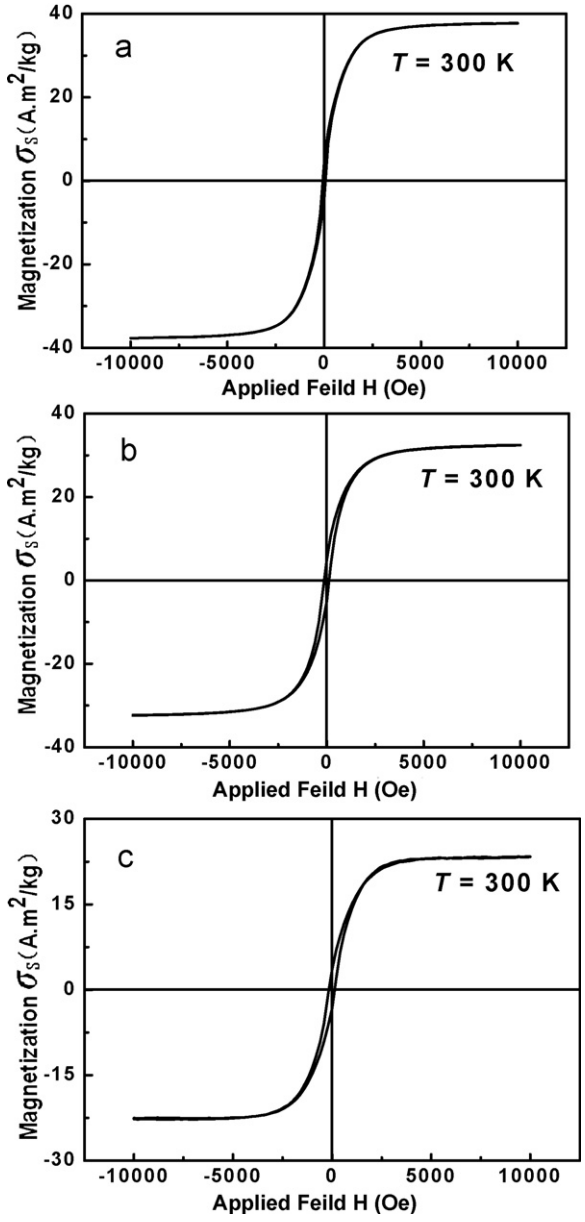

Fig. 4. The magnetic hysteresis loops of (a) Ni nanoparticles obtained after the black suspension appeared but before the small electric spark observed; (b) Ni/CNTs composites obtained by reacting for 1 min after the small electric spark observed; (c) Ni/CNTs composites obtained by reacting for 2 min after the electric spark.

[37], which is similar to those found in the literature [38]. It can be thought that CNTs may have a great impact on the magnetic properties of Ni particles. The reason of this phenomenon is not fully clear now and the further work is underway.

4. Conclusions

In this study, CNTs of diameter about 20 nm were successfully synthesized by the microwave-assisted polyol method and magnetic Ni nanoparticles were employed as a catalyst. As the microwave eddy current effect excited an electric spark on the inner wall of a glass flask which was plated metal nickel in the glass flask, metal Ni nanoparticles can induce CNTs' formation in the further reaction. CNTs can be observed after the observation of the small electric spark, and the length of hollow carbon nanotubes is of the order of micron. The further experimental results indicated that the as-synthesized samples were ferromagnetic. Ni/CNTs compos-

ites exhibited some different ferromagnetic behaviors compared with Ni nanoparticles and bulk Ni.

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