RAPID COMMUNICATION

Low temperature one-step synthesis of cobalt nanowires encapsulated in carbon

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Abstract The one-step method of carbon nanotubes filled with continuous cobalt nanowires (CoF-CNT) synthesis is presented. Co/ZSM-5 (8 wt% Co) was used as catalyst for CoF-CNT production by methane decomposition at the temperature of 400 °C and 800 °C at atmospheric pressure in a conventional gas-flow system. The average diameter of the CoF-CNT is about 25 and 40 nm for products obtained at 400 °C and at 800 °C, respectively. The average size of coherently scattering domains along the normal to graphite layers L_c, the interlayer spacing d_{002}, the graphitization degree of carbon, and the relative intensities of the G and D bands in Raman spectroscopy were determined to characterize the quality of carbon. It was proved that cobalt-filled carbon nanotubes can be produced by a simple method. The results of XRD, FE-SEM, and TEM show that CoF-CNT can be obtained even at 400 °C by catalytic decomposition of methane. On the basis of XRD, TEM, Raman spectroscopy was found that at a temperature of 800 °C, a better quality of carbon was produced.

1 Introduction

The initial studies on carbon nanotubes (CNTs) filled with metals were carried out in 1993 by Iijima [1], which demonstrated the successful encapsulation of Pb. In the following years, increasing effort was directed to the preparation of CNTs as template nanowires.

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In order for metal filled CNT synthesis, several methods have been attempted. The CNT can be filled by a physical or chemical method [2]. In the physical method, the nanotubes are filled with melted metal due to the capillarity effect [3, 4]. In the chemical method, the nanotubes are opened by boiling acid, then the inclusion of metal oxide or metal is carried out. One-step methods of metal filled CNT preparation are known as well. Mainly, an arc discharge technique was applied [3, 4], but it requires high temperatures.

Carbon nanotubes filled with continuous cobalt nanorods were synthesized by Liu et al. [5, 6] from $Co(CO)_3NO$. The reaction takes place in an autoclave at a temperature of 900 °C and at autogenic pressure.

Blank et al. [7] described cobalt-filled nanotube synthesis obtained from CO over Co/Y-zeolite catalysts. Despite the applied high temperature (720 °C) and pressure (0.05 GPa) that was applied, TEM analysis showed the presence of some cobalt particles inside the carbon nanotubes. Long cobalt nanowires were not observed.

Some authors reported on methane to carbon nanotubes or nanoparticles decomposition over cobalt contained catalysts [8, 9], but to the best of our knowledge, there is no information on nanotubes filled with continuous cobalt nanowires prepared from methane.

The choice of cobalt as the material encapsulated inside carbon nanotubes (CNTs) is motivated by the interesting magnetic properties of composite cobalt–carbon nanomaterials, which are of great interest for various applications such as magnetic data storage, ferrofluids, or magnetic resonance imaging [10].

In this paper, we show that the Co/ZSM-5 prepared by the impregnation method can be used as catalysts of CNT filled with continuous cobalt nanowires (CoF-CNT) growth from methane decomposition even at the temperature of 400 °C.

This is the one-step method that is simpler and cheaper than the others described up to now.

2 Experimental

2.1 Continuous cobalt nanowires synthesis

Cobalt concentration in the catalyst was equal to 8 wt%. The experimental setup and the catalyst preparation procedures had been reported in detail previously [11–13]. The CoF-CNT growth was carried out at atmospheric pressure in a conventional gas-flow system. The catalyst (1 g) was placed into a veridical tube furnace. When the furnace reached (700 °C) under nitrogen, hydrogen (140 $cm^3 min^{-1}$) was introduced to reduce the catalyst for 1 h. Then the hydrogen flow was stopped, and the reactor was cooled down (under nitrogen) to 650 °C. Methane was introduced into the reactor (140 $cm^3 min^{-1}$) and maintained for 15 min. Then the furnace was switched off and methane was substituted by nitrogen.

2.2 Characterization

The morphology of as prepared cobalt nanorods was characterized by a Field Emission Scanning Electron Microscope (FE-SEM) equipped with a secondary electron (SE) and backscattered electron (BSE) detectors—Hitachi SU 8200 and Transmission Electron Microscope (TEM)—TEM-FEI Tecnai F20. The samples for FE-SEM were dispersed onto carbon tape without any metal coating. Specimens for the TEM measurements were prepared via drop casting a droplet of acetone suspension onto a copper grid, and dried at 200 °C for 5 minutes. Raman measurements were performed in a Renishaw InVia spectrometer using the 514.5 nm line of an Ar^+ laser. The X-ray diffraction patterns (XRD) of the products were recorded with a Philips X-pert Diffraction System using a CuK_α source ($\lambda = 0.154178$ nm) in the range of $5 \leq 2\theta \leq 100$ at room temperature. Before the XRD analysis, the catalyst was removed by a HF solution.

The average size of coherently scattering domains along the normal to graphite layers L_c, was determined from the full width at half-maximum of the reflection 002, after correcting for the instrumental broadening (β_{002}) by the Scherrer equation [14]. The interlayer spacing d_{002} was determined by using the Bragg law [12]. The graphitization degree of carbon was calculated by the Maire and Mering formula [15]. For ideal graphite with $d_{002} = 0.3354$ nm, $g = 1$; and for amorphous carbon with $d_{002} = 0.344$ nm, $g = 0$. In this definition, a d_{002} spacing of 0.344 nm distinguishes a carbon with random orientation of layer planes (turbostratic) with no notable three-dimensional ordering [16].
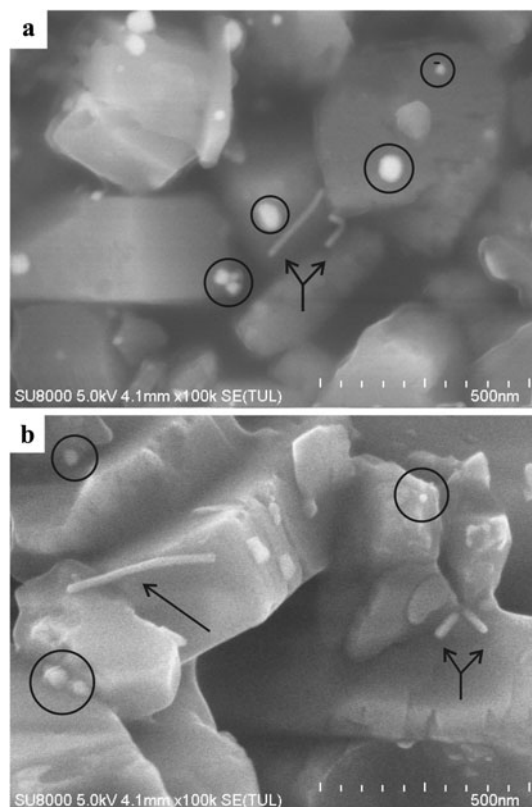

Fig. 1 FE-SEM images of CoF-CNT produced at 400 °C (**a**) and at 800 °C (**b**), magnitude 100 000, SE & BSE detectors; *arrows* show cobalt nanowires, *circles* show metal particles

3 Results and discussion

The SEM images of the catalyst and CoF-CNT obtained at 400 and 800 °C are presented in Fig. 1. Since the BSE detector was applied, heavy elements backscatter electrons more strongly than light elements, and thus appear brighter in the image. Figure 1a shows a few cobalt particles (bright particles with a spherical morphology) and two cobalt nanowires (bright oblong shape). In Fig. 1b, the cobalt nanowire is observed.

TEM analysis of CoF-CNT obtained at 400 and 800 °C showed the presence of cobalt nanorods encapsulated inside the carbon tubes. The carbon produced at 400 °C seems to be amorphous whereas the graphitic lattice of a carbon nanotube can be clearly resolved, confirming the multiwalled nature of the carbon nanotube. The interplanar distance for the (002) planes of carbon layers measured from TEM micrographs (Fig. 2e) and was equal to 0.34 nm. The average diameter of the CoF-CNT is about 25 and 40 nm for products obtained at 400 °C and at 800 °C, respectively. On the basis of TEM micrographs at the lower magnification, one can conclude that at the temperature of 400 °C only cobalt nanorods encapsulated inside the carbon tubes are produced (Fig. 2c), whereas at 800 °C amorphous carbon and carbon nanotubes were produced as well (Fig. 2f).

Fig. 2 TEM images of CoF-CNT produced at 400 °C (**a**), (**b**), (**c**) and at 800 °C (**d**), (**e**), (**f**)
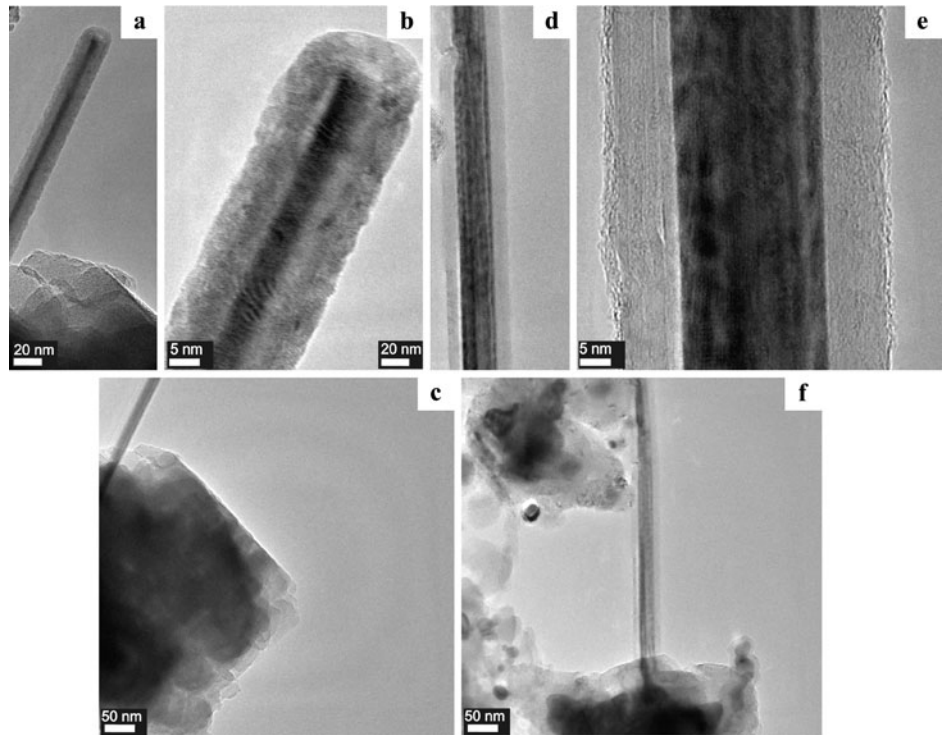

Fig. 3 The XRD pattern of CoF-CNT produced at 400 °C and at 800 °C
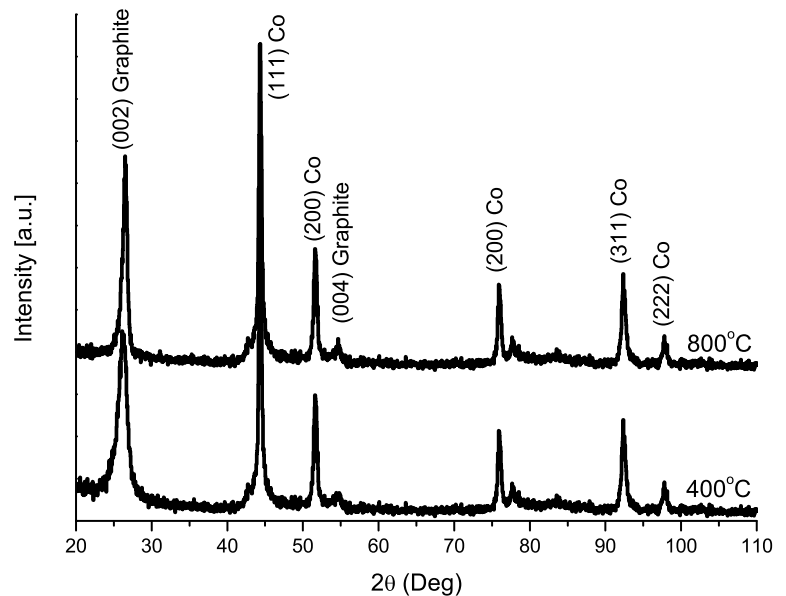
The XRD patterns of cobalt nanorods are shown in Fig. 3. For cobalt, all the five peaks ($2\theta = 44.26°$, $51.57°$, $75.93°$, $92.33°$, $97.77°$) according to JCDPS, card no. 15-0806 are observed. The peaks can be indexed as (111), (200), (220), (311), and (222) and crystal planes indicate the formation of the face-centered cubic (fcc) structure.

Additionally, the two peaks at 2θ of 26.45 and 54.56 indexed as (002) and (004) indicate the presence of graphite-like carbon (JCPDS 08-0415).

The interplanar distance between the graphitic layers was determined on the basis of the accurate position of the prominent peak about $2\theta = 26°$, which can be attributed to the (002) reflection of graphite. The interplanar distance was equal to 0.3518 nm and 0.3991 nm for carbon layers obtained at 800 °C and at 400 °C, respectively. The graphitization degree of carbon obtained at 800 °C (0.91) was considerably higher than obtained at 400 °C (0.47). Statistically, the degree of graphitization is the probability of parallel orientation for two consecutive graphite layers.

Fig. 4 Raman spectra of CoF-CNT produced at 400 °C (*dashed line*) and at 800 °C (*solid line*)
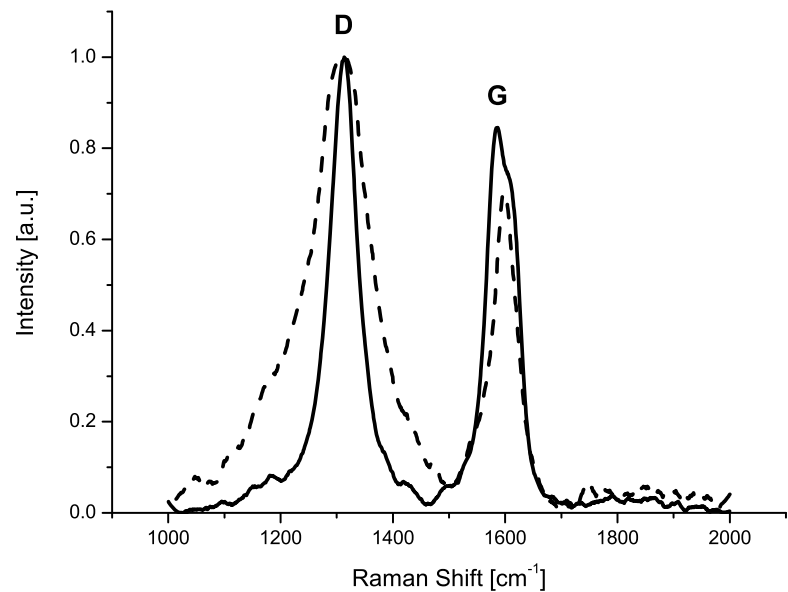
Raman spectra of CoF-CNT produced at 400 °C and at 800 °C are presented in Fig. 4. Two bands were observed: at ca. 1310 cm^{-1} (D band) and at ca. 1600 cm^{-1} (G band). The G band can be attributed to the in-plane carbon–carbon stretching vibrations of graphite layers and the D band was thought to arise from structural imperfection of graphite. The relative intensities of the G and D bands, IG/ID are a measure of the degree of perfection of carbon nanomaterials. IG/ID was equal to 0.84 for CoF-CNT obtained at 800 °C and 0.69 for obtained at 400 °C ones.

4 Conclusion

In conclusion, cobalt-filled carbon nanotubes can be produced by the simple method. The results of XRD, FE-SEM, and TEM indicate that carbon nanotubes filled with cobalt nanowires can be prepared even at 400 °C by catalytic decomposition of methane. The results of XRD, TEM, and Raman spectroscopy show that at a temperature 800 °C a better quality of carbon was obtained.

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