Low-temperature hydrothermal synthesis of multiwall carbon nanotubes

Wenzhong Wang *, J.Y. Huang, D.Z. Wang, Z.F. Ren *

Department of Physics, Boston College, 140 Commonwealth Avenue, Chestnut Hill, MA 02467, USA

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Abstract

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], an endless list of potential applications of CNTs have been proposed. Consequently, a worldwide research interest has been focused on the growth of CNTs to realize their potential applications [2]. Numerous methods for the synthesis of CNTs have been developed [3–11]. Among the variety of methods, chemical vapor deposition (CVD) is the most widely used to synthesize CNTs. Although CVD offers the benefit of significantly lower synthesis temperatures than arc-discharge and laser ablation techniques, it still requires a growth temperature of 600–950 °C. Recently, it has been reported that high-temperature hydrothermal process is an alternative route for the synthesis of CNTs [12,13]. Yoshimura and co-workers synthesized CNTs using polyethylene (PE), ethylene glycol (EG) and other sources with and without catalysts Fe/Co/Ni under hydrothermal conditions at 700–800 °C and 60–100 MPa [12,13]. However, the temperature is comparable with the CVD technique. Hence, it is still a challenge to develop a new approach for the synthesis of CNTs at a low temperature. To date, the lowest-reported temperature for the synthesis of multiwall carbon nanotubes (MWCNTs) is 175 °C, from decomposition of CCl₄ using iron-encapsulated polypropyleneimine dendrimers as a catalyst in supercritical carbon dioxide medium [14]. In this letter, we report the synthesis of MWCNTs by the decomposition of polyethylene glycol (PEG; M₆ 20,000) in a basic aqueous solution with high concentration of NaOH under hydrothermal conditions at a temperature as low as 160 °C, which is the lowest to our knowledge, without the addition of catalyst Fe/Co/Ni. The morphologies and microstructures of the as-prepared MWCNTs were studied with transmission electron microscopy (TEM, JEOL 2010F).

In a typical synthesis, 80 mL ethyl alcohol, 10 mL distilled water, 7 g NaOH and 2 g PEG were added to a 250 mL flask. The mixtures were stirred in a magnetic mixer for 30 min, and then transferred to a Parr reactor (model 4750, Parr Company, Moline, IL) with a capacity of 125 mL. The Parr reactor was sealed and then kept at 160 °C for 20 h in a furnace, and then cooled down to room temperature. The products were washed with alcohol and distilled water for several times, and then dried in a vacuum oven at 60 °C for 10 h.

Fig. 1 shows the TEM images of the as-synthesized MWCNTs at different magnifications. It can be seen that the MWCNTs have outer diameters ranging from 9 to 19 nm and inner diameters ranging from 4 to 8 nm. It is worth pointing out that the diameters of the as-prepared MWCNTs by the current low-temperature hydrothermal route are much smaller than those

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prepared by high-temperature hydrothermal method [12]. The length of the MWCNTs is up to several micrometers. The yield of the as-prepared MWCNTs estimated by TEM observations is about 35% relative to the samples on copper grids.

Fig. 1. TEM images of the as-prepared MWCNTs with different magnifications. (a) ×20,000, (b) ×60,000, and (c) ×120,000.

Fig. 2(a)–(c) show a TEM image, selected area diffraction (SAED) pattern, and a high-resolution TEM (HRTEM) image of a typical MWCNT with an outer diameter of 18 nm, respectively. The SAED pattern, which can be indexed based on the hexagonal graphite
with cell lattice parameter $a = 5.657$ Å, and $c = 6.721$ Å (JCPDS No. 23–64, P63/mmc), exhibits a pair of small but strong arcs for (002), together with a ring for (100) and a pair of weak arcs for (006) diffractions. The appearance of (002) diffractions as a pair of arcs indicates the orientation of the (002) planes in the CNTs [15]. HRTEM image (Fig. 2c) shows that this MWCNT has fairly good graphitization. The interlayer spacing in the multiwalls is about 0.34 nm, corresponding to the (002) plane of graphite carbon [13].

A further investigation on the microstructures of the as-prepared MWCNTs was performed by HRTEM. Fig. 3a shows a typical HRTEM image of a bundle of MWCNTs, indicating that the MWCNTs have clear graphite layers with defects aligned to the tube axis. The HRTEM observations also show that the MWCNTs have open- and closed-end structures. Fig. 3b and c show the HRTEM images of closed- and open-end MWCNTs, respectively.

In the absence of PEG, no CNTs were observed, indicating that the CNTs were formed by the decomposition of PEG. Our experiments also indicated that a NaOH aqueous solution with high concentration was essential for the formation of the MWCNTs. There were no CNTs detected by the TEM observations when the reactions were conducted in aqueous solutions with low NaOH concentration. We propose that the role of high concentration NaOH during the formation of MWCNTs is most likely as a chemical activation agent to activate PEG. At the present hydrothermal conditions, the activated PEG becomes easy to decompose into element carbon and other products. The C with active surfaces is probably preferential for the growth of CNTs under the hydrothermal conditions. However, the true role of NaOH for the formation of MWCNTs is not clear. A detailed study is required to understand the growth mechanism of the MWCNTs.

In summary, a low-temperature hydrothermal route has been successfully developed to synthesize MWCNTs at 160 °C without catalysts Fe/Co/Ni by using PEG as the carbon source. To our knowledge, the synthesis temperature is the lowest ever reported. The diameters of the as-prepared MWCNTs are much smaller than those prepared by high-temperature hydrothermal method.

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References

Optical and scanning electron microscopies cross-fertilization: Application to worn carbon/carbon composite surface studies

B. Rousseau a, H. Estrade-Szwarckopf a,*, S. Bonnamy a, M. Gouider b, Y. Berthier b, P. Jacquemard c

a Centre de Recherche sur la Matière Divisée, UMR 6619 CNRS-Université d’Orléans 1B, rue de la Ferollière, 45071 Orléans Cedex 2, France
b Laboratoire de Mécanique des Contacts Solides, UMR 5514, CNRS-INSA de Lyon, 20, Avenue Albert Einstein, 69621 Villeurbanne Cedex, France
c Messier-Bugatti, Division Carbone Industrie, 7, Avenue du Bel Air, 69627 Villeurbanne Cedex, France

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Optical microscopy (OM) as well as scanning electron microscopy (SEM) are classical techniques for carbon surface studies [1–3]. However few studies have compared images obtained from them in spite of the rich new information, not attainable if using only one of them [3]. This letter will show how such comparison is useful for the study of wear mechanism during friction between carbon/carbon composites.

The surface imaging techniques were used in following conditions:

1/OM (Leica DM IRM)-Lateral resolution: 0.5 μ; depth of focus: 20 to 1 μ depending on magnification (≈50 to 1000); the penetration depth δ in carbon of the visible wavelength is smaller than 60 nm. In the case of carbon, observations between crossed polarizers are made with addition of a retarder plate (λ = 551 nm) to investigate the aromatic layer average directions and misorientations. Indeed, due to interference phenomena resulting in color extinction, edge-on aromatic layer sections appear magenta when parallel to the analyzer plane, dark when perpendicular and either blue/green or yellow when oblique. When the aromatic layers are parallel to the observation plane or when they are randomly oriented in the material (isotropic texture), they always appear magenta [4]. In C/C composites, the texture of the pyrocarbon matrix is oriented concentrically to the fibres. In transverse fibre sections, opposite quadrants of the pyrocarbon appear blue or yellow/orange depending on their preferential aromatic layer orientation relative to the polarizers and the retarder plate. PAN-fibres in which the aromatic layers are almost aligned parallel to the fibre axis but misoriented at nanometric scale appear magenta.