Available online at www.sciencedirect.com
SCIENCE DIRECT®
Diamond & Related Materials 15 (2006) 164 – 170
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

High-pressure pyrolysis of melamine route to nitrogen-doped conical hollow and bamboo-like carbon nanotubes

Xingcai Wu [a,c,1], Yourong Tao [a,*], Yinong Lu [b], Lin Dong [a,1], Zheng Hu [a,1]

[a] Key Laboratory of Mesoscopic Chemistry (Ministry of Education), Department of Chemistry, Nanjing University, Nanjing 210093, P. R. China
[b] College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China
[c] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

Received 15 March 2005; accepted 9 September 2005
Available online 17 October 2005

Abstract

Nitrogen-doped conical hollow and bamboo-like carbon nanotubes (CNTs) have been prepared by pyrolysis of melamine with NaN_3–Fe–Ni and Ni catalysts at high temperature and high pressure, respectively. The conical hollow CNTs with an average diameter of about 70 nm and a length up to 5 μm account for ~50% of the product, whose N/C atomic ratios are about 0.27. The conical bamboo-like CNTs with the diameter of ~65 nm and length of 1–4 μm and wall thickness of 10–20 nm account for ~95% of the product, whose N/C atomic ratios are up to 0.18. The control experiments show that NaN_3 plays a key role in keeping high nitrogen content and high conversion ratio in the CNTs. The possible growth mechanisms have been discussed on the base of the experimental observation. The strategy provides an alternative route to nitrogen-doped CNTs and other carbon nitride materials.

Keywords: Nanotubes; Melamine; HTHP; Morphology

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention due to unique tubular structure and abundant physical and chemical properties including metallic or semiconductor performance, excellent mechanical strength, capability of hydrogen storage, and good adsorption of microwaves [1–5]. Presently, they have been fabricated into various nanodevices such as chemical sensors [6], electronic field emitters [7], nanotweezers [8], and so on. Because the properties of the CNTs are related to the structure, people try to control the structure of the CNTs by designing reaction routes and have obtained single-wall [9], and double-wall carbon nanotubes [10]. Recent research results have shown that the incorporated N in carbon nanostructures can enhance their mechanical, energy storage, and electric properties [11]. The stimulus for this study also originates from the theoretical predictions of the hypothetical metallic CN nanotubes [12] and covalently bonded β-C_3N_4 [13], both possessing an unmatched hardness. Therefore considerable efforts have been made to investigate into the preparation and growth mechanism of the carbon nitrides. Over the past years, many methods have been developed to prepare the carbon nitride nanostructures. They may be divided into five types: (1) chemical vapor deposition (CVD) [14], i.e., C (or CN) gas-precursors were catalytically pyrolyzed to the CN_x nanostructures under N-rich atmosphere at high temperature. However, in this case, whether the N-rich solid precursors or not, the highest N doping level reported so far is only to <13 at.% [15] due to the greater thermodynamic stability of carbon and separate nitrogen molecule at high temperature [16]. (2) high-temperature and high-pressure reaction, i.e., reagents containing nitrogen were sealed in stainless reactor to form carbon niride nanostructures at high temperature and high pressure. For example, cyanuric chloride ($C_3N_3Cl_3$) as an s-triazine building block, and lithium nitride (Li_3N) as a nitrogen-bridging agent, was sealed in stainless reactor to form g-C_3N_4 hollow sphere at 400 °C [17]. CCl_4 (or C_2Cl_6) and NaN_3 were sealed in stainless reactor to produce CN_x (x: 0.01–0.33) nanotubes, nanocubes, and nanospheres at 200–450 °C [18].

* Corresponding author. Fax: +86 25 83317761.
E-mail address: yrtao@hotmail.com (Y. Tao).
[1] Fax: +86 25 83317761.

0925-9635/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2005.09.018

(3) gas–solid reaction of amorphous carbon with NH_3 at high temperature. For instance, high-energy ball milling graphite powders were annealed to produce β-C_3N_4 nanorods in a flowing NH_3 gas at 300–450 °C [19]. (4) solid reaction. For example, cyanuric chloride ($C_3N_3Cl_3$) was reacted with lithium nitride (Li_3N) at 220 °C under N_2 atmosphere to produce nanotubes and nanocages of $C_3N_{3.6-4.5}O_{1.1-1.2}H_{4.1-4.2}$ [20]. (5) solvothermal synthesis. For instance, Guo et al. have reported the synthesis of C_3N_4 nanotubes by using autoclave reaction of cyanuric chloride with NaN_3 in benzene solution [21]. Because of its toxic properties, it is inconvenient to employ the cyanuric chloride as the initial reagent. Therefore it is very necessary to design new route for further investigation in this area.

Melamine ($C_3N_6H_6$) is a low-cost industrial material, and melts or decomposes at 360 °C [22], and can form function polymers with formaldehyde or ethylene carbonate [23,24]. Because of melamine honey-comb atomic arrangement which is very close to the expected one for the structure of C_3N_4 super-hard materials, it was once chosen as precursor to produce C_3N_4 under 3 Gpa and at about 800 °C [25], however, only graphite-C_3N_4 nanoparticles were obtained. In this manuscript, we selected melamine as precursors and added various catalysts to prepare CN_x nanostructures at high temperature and high pressure. Finally, we successfully obtained nitrogen-doped conical hollow and bamboo-like CNTs, and hollow or metal-filled carbon nanospheres. To our knowledge, this is the first example for preparing nitrogen-doped conical hollow and bamboo-like CNTs by this method.

2. Experimental sections

To prepare nitrogen-doped nanostructures, analytical grade melamine (2.0 g), sodium azide (2.0 g), iron (0.2 g), and nickel powders (0.1 g) were sufficiently ground for about 20 min, and then the mixtures were transferred into stainless steel autoclave (25 ml). The autoclave was sealed, heated to 650 °C, and maintained at temperature for 10 h under condition of about 35 Mpa, and then allowed to cool to room temperature. The dark products were collected and washed with absolute ethanol, dilute HCl aqueous solution, and distilled water, respectively. The final products were dried at 100 °C for 2–4 h, yielding about 0.50 g of the product. In addition, keeping the other experimental constant, the pyrolysis of melamine (2.0 g) without and with other reagents such as nickel powders (0.1 g), Fe (0.2 g)–Ni (0.1 g) powders, metallic sodium (2.0 g), and NaN_3 powders (2.0 g) were carried out, respectively.

The morphology of the samples was observed on a field emission scanning electron microscope (SEM, LEO-1530VP). Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV. The microstructures of the carbon nanotubes were characterized by high-resolution transmission electron microscope (HRTEM, JEOL-2010). The chemical composition was analyzed by EDX (Thermo NORAN) that was attached to the HRTEM equipments. Micro-Raman spectrum was recorded at ambient temperature on a T64 000 Raman spectrometer at room temperature. C, H, and N elements was quantified by an elemental analyzer (Foss Heraeus CHN-O-Rapid, Ger.) Infrared spectrum of the samples was recorded on BRUKER VECTOR 22 infrared spectrometer.

3. Results and discussion

3.1. Morphologies and microstructures of the products

The morphology of the product (sample 1) obtained by the reaction of melamine with NaN_3–Fe–Ni is shown in Figs. 1a and 2, respectively. The SEM image (in Fig. 1a) reveals that the product contains a large number of CNTs and a modicum of carbon particles, and the CNTs account for about 50% of the product. The typical CNTs have the diameter of 70–300 nm and length up to 5 micrometers. TEM image (in Fig. 2a) further confirms that they are conical hollow CNTs with the inner diameter of about 10 nm and the outer diameter of about 70 nm. Fig. 2c obviously displays the conical hollow structure of the CNT, and the inclination angle of the tube wall in respect to the axial direction can be estimated about 5°. Fig. 2b reveals HRTEM image of a single nanotube with the inner diameter of 1.5 nm and wall thickness of 15 nm, and the lattice fringe shows herringbone motif. They clearly indicate that the layers are inclined from outside to inside of the nanotube along the growth direction. The inclination angle of the layers in respect to the axial direction is about 20°. The buckling structure of the graphite layers (Fig. 2b) has been commonly observed in the

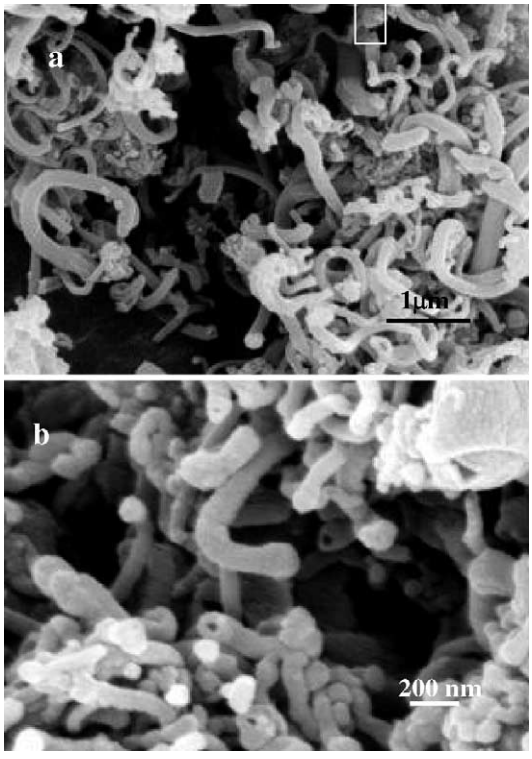

Fig. 1. SEM images of the samples prepared by pyrolysis of melamine with NaN_3–Fe–Ni powders (a), and Ni powders (b) at high-temperature and pressure.