Materials Letters 65 (2011) 2004–2006

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A pressure enhanced CVD method for large scale synthesis of carbon microtubes and their mechanical properties

Hongming Yu [a], Xiaoxiao Huang [a], Guangwu Wen [a,b,*], Bo Zhong [a], Long Xia [b]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China
[b] School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, Weihai, 264209, China

ARTICLE INFO

Article history:
Received 19 January 2011
Accepted 24 March 2011
Available online 31 March 2011

Keywords:
Carbon materials
Chemical vapor deposition
Microstructure
Mechanical properties

ABSTRACT

Carbon microtubes (CMTs) are a new morphological form of carbon with micrometer scale internal diameters and thin walls made of a few graphitic layers. However, compared with carbon nanotubes, there is lack of a feasible and reliable synthetic method. Furthermore, the mechanical properties of CMTs have not been reported. In this paper, we report a gas pressure enhanced CVD method for large-scale preparation of high-purity, crystalline and thin-walled CMTs in a gas pressure furnace using urea as raw material in the absence of catalyst. The as-obtained CMTs have highly graphitized structure and have a homogenous morphology with an internal diameter of about 1 μm, a wall thickness of 5 nm and several millimeters in length. The Young's modulus of the CMTs was determined to be 0.652 TPa on average, which is comparable to that of carbon nanotubes reported in previous research.

1. Introduction

Since the Iijima's landmark paper on carbon nanotubes [1], the unique structure, electronic, mechanical and chemical properties of carbon nanotubes offer enormous potential for various applications. The most promising applications, such as nanoreactor [2,3], separation, storage and nanochannel for the adsorption and transport of various molecules [4,5], relay on the characteristic internal hollow caving peculiar to a tubular shape. However, regarding nanotubes, their potential as reactors or channels is significantly limited due to their relatively small inner diameters, which preclude the entry of large-diameter reactive species or reactants, even if the micromanipulation techniques are available. Therefore, CMTs with larger inner diameter are suitable for large-diameter particles encapsulation. Micrometer-scaled carbon tubes might be ideal candidates for nano/microfluidic and drug delivery applications [6].

Yang and Yu prepared hollow carbon sub-millimeter fibers via the carbonization of spun poly (acrylonitrice) hollow fibers [7]. Han and co-workers synthesized CMTs (outer diameters of 1–100 μm and wall thicknesses ranging from less than 100 nm to a few micrometers) via the pyrolysis of polypyrrole (PPy)-coated poly (ethylene tierephthalate) (PET) fibers [8–10]. Libera and Gogotsi [11,12] used a hydrothermal technique to synthesize carbon tubular structures with outer diameters ranging from 70 to 1300 nm in the C–H–O–Ni system. Hu et al. [13] reported the synthesis of CMTs with diameters in the range of 1–2 μm by heating a mixture of ZnS and activated carbon powers at 1400 °C for 1.5 h. However, compared with carbon nanotubes, the synthetic methods of CMTs have not been fully investigated. There is still lack of a feasible and reliable method to prepare high-purity and crystalline CMTs. Furthermore, the mechanical properties of CMTs have not been studied extensively and the data, such as young modulus, have not been reported.

In this study, we report a gas pressure enhanced CVD method for large-scale preparation of high-purity, crystalline and thin-walled CMTs in a gas pressure furnace using urea as raw material in the absence of catalyst. The obtained-CMTs have uniform internal diameters of about 1 μm, several millimeters in lengths and wall thickness of 5 nm. The Young's modulus of the CMTs has been examined as a key mechanical property.

2. Experimental

In a typical experimental process, 80 g urea was placed into a graphite crucible and annealed at 1250 °C for 2 h under nitrogen atmosphere in a gas pressure furnace. The experimental setup was described in our previous report [14]. The furnace chamber was evacuated to 10^{-3} mbar before the vacuum pump was shutdown, and then it was filled with ultra pure nitrogen gas to 0.2 MPa. After cooling to room temperature, about 5 g CMTs was obtained.

The phase composition of the products was studied by a Shimadzu XRD-6000 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.15418 nm). The morphology and structure of the product were characterized by a FEI Sirion field emission scanning electron microscopy (SEM) and a JEM-2010F high resolution transmission electron microscopy (HRTEM). The mechanical property of the CMTs was performed on a MTS Nano Indenter XP.

* Corresponding author at: School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, Weihai, 264209, China. Fax: +86 451 86413922.
E-mail address: wgw@hitwh.edu.cn (G. Wen).

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.03.092

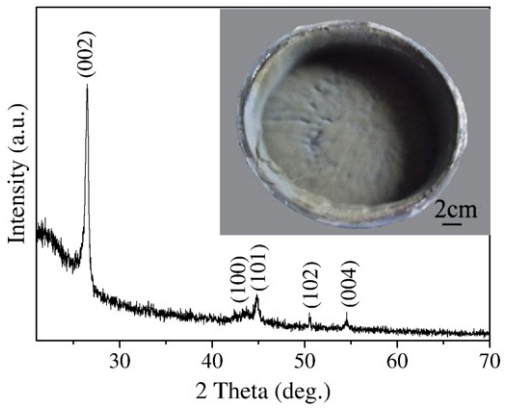

Fig. 1. XRD pattern of the sample. Inset displays the optical image of the products.

3. Results and discussion

The XRD pattern (Fig. 1) shows peaks which are indexed to graphite (JCPDS: 41–1487) and no other phases exist. The diffraction peaks are intense and sharp, indicating that well-developed graphitic structures are dominant in the obtained CMTs. Inset of Fig. 1 presents a digital photograph of the as-grown products. Bulk amount of fibrous products could be observed in the graphite crucible. Typically 5 g CMTs could be obtained in one batch, but the process should be easily scalable to larger amounts.

A low-magnification SEM image (Fig. 2a) reveals the homogeneity and purity of the products, where the typical lengths are several millimeters. Some tubes even reach lengths on the order of centimeters. Most of the tubes are straight throughout their entire lengths. A high-magnification SEM image (Fig. 2b) shows that the as-synthesized CMTs have micrometer-sized diameters. An open-ended microtube is more clearly observed in Fig. 2c, further suggesting a hollow structure and a relatively large tube diameter.

To further investigate the wall thickness and detailed microstructure information of the CMTs, TEM and HRTEM examinations were performed. Fig. 3a shows the typical TEM image, which reveals that the tubes have an internal diameter of 1 μm and remarkably thin walls. The electron diffraction (ED) pattern taken from tube (inset of Fig. 3a) displays strong (002), (100) and (110) diffraction rings, exhibiting graphitization analogous to multiwalled carbon nanotubes [15]. Fig. 3b depicts the HRTEM image of a tube wall segment, showing the tube with a wall thickness of 5 nm. The wall is built up of nearly fifteen graphitic layers. The inset shows the (002) lattice fringes with an interplanar distance of 0.34 nm within the tube wall.

For direct measurements of the elastic properties of CMTs, atomic force microscope (AFM) operating in air was used to apply a load to an individual CMT freely suspending across trenches between the glass pads (the schematic and the microphotograph of the measurement were shown in the upper left and lower right inset of Fig. 4, respectively). An AFM probe tip was positioned near the suspended CMT and the tip hovered about 100 nm above the trench floor. The tip was scanned in a line parallel to the axis of the trench at 1 cycle/s with and amplitude of 1–2.5 μm. The scan center was advanced along the trench in 50 nm increments until a lateral force signal was detected. A typical lateral force versus the displacement curve is shown in Fig. 4. The reduced modulus is derived using the following equation [16]:

$$F = 192\delta EI/L^3 \quad (1)$$

Where F is the lateral force, E is the reduced modulus and I is the momentum of the CMT. δ is the lateral displacement perpendicular to the CMT and L is the suspended length. For a cylinder, the CMT's momentum is

$$I = \pi D^4/64 \quad (2)$$

Where D is the diameter of the CMT. As such, the reduced modulus is given by:

$$E = 64FL^3/192\pi\delta D^4 \quad (3)$$

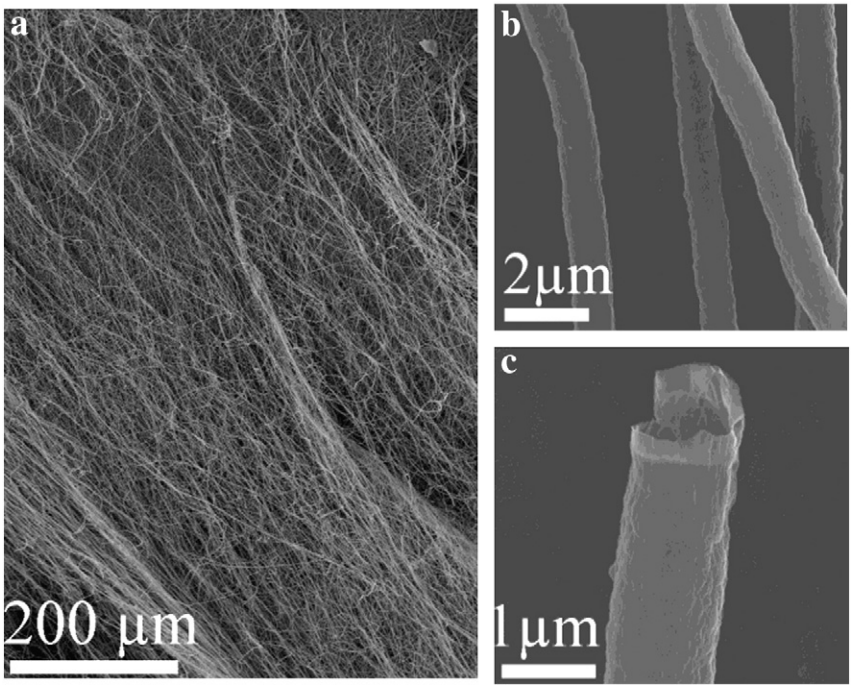

Fig. 2. (a) Low-magnification SEM image of the CMTs. (b and c) High-magnification SEM images displaying micrometer-sized diameters and the open end of the microtubes.

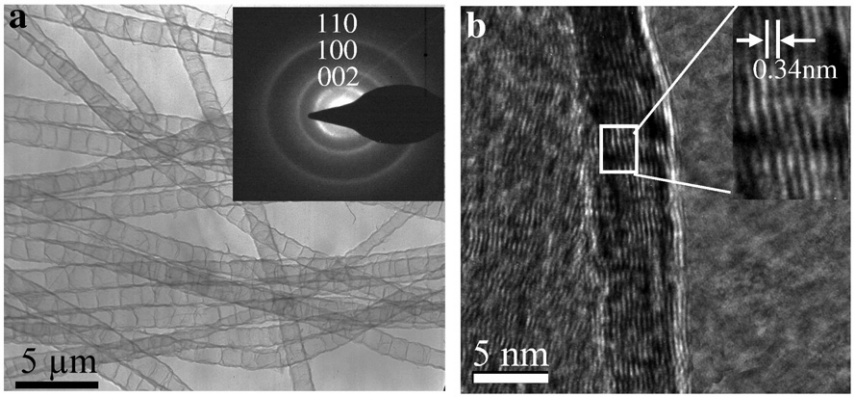

Fig. 3. (a) TEM image showing the uniform diameters and ultra-thin walls of the CMTs; inset depicts the ED pattern taken from the tube. (b) HRTEM image taken from a carbon microtube wall (wall thickness ~5 nm); inset displays an interplanar spacing of the graphitic (002) lattice fringes.

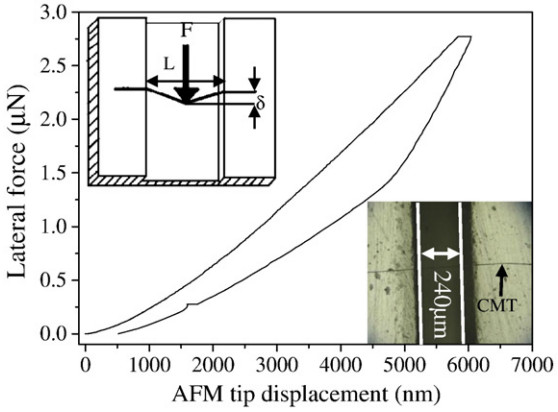

Fig. 4. Lateral force on an individual CMT as a function of AFM tip position; the upper left inset is the schematic of the measurement; the lower right inset shows the microphotograph of the measurement.

From the measured data we calculate the average reduced modulus of the CMT to be about 0.652 TPa, which is only slightly lower than that of carbon nanotubes [17].

4. Conclusions

We reported a low cost and convenient method to synthesize high-purity CMTs on a large scale using urea as precursor in a gas pressure furnace via a pressure assisted chemical vapor deposition route in the absence of catalyst. The as-prepared CMTs have uniform internal diameter of 1 μm, ultra-thin wall thickness of 5 nm and several millimeters in length. The calculated reduced modulus of the CMTs is about 0.652 TPa on average, which is similar to that of carbon nanotubes. Mass production and excellent mechanical property of this kind of CMTs provide possibilities for diverse applications in future microdevices.

Acknowledgments

The authors are grateful to the financial support from the 863 Program of China (No. 2007AA03Z340), the excellent team in Harbin Institute of Technology, Fundamental Research Funds for the Central Universities (HIT. ICRST. 2010009) and the Fundamental Research Funds for the Central Universities (HIT. NSRIF. 2010121).

References

[1] Iijima S. Nature 1991;354:56–8.
[2] Dai HJ, Wong EW, Lu YZ, Fan SS, Lieber CM. Nature 1995;375:769–72.
[3] Han WQ, Fan SS, Li QQ, Hu YD. Science 1997;277:1287–9.
[4] Che GL, Lakshmi BB, Fisher EB, Martin CR. Nature 1998;393:346–9.
[5] Skoulidas AI, Ackerman DK, Johnson JK, Sholl DS. Phys Rev Lett 2002;89:185901–4.
[6] Wang XF, Liu XQ, Lai LF, Li SY, Weng J, Zhou ZM, et al. Adv Funct Mater 2008;18:1809–23.
[7] Yang MC, Yu DG. J Appl Polym Sci 1998;68:1331–6.
[8] Han CC, Lee JT, Yang RW, Chang H, Han CH. Chem Commun 1998;19:2087–8.
[9] Han CC, Lee JT, Yang RW, Chang H, Han CH. Chem Mater 1999;11:1806–13.
[10] Han CC, Lee JT, Yang RW, Han CH. Chem Mater 2001;13:2656–65.
[11] Libera J, Gogosti Y. Carbon 2001;39:1307–18.
[12] Gogotsi Y, Dimovski S, Libera JA. Carbon 2002;40:2263–7.
[13] Hu JQ, Bando Y, Xu FF, Li YB, Zhan JH, Xu JY, et al. Adv Mater 2004;16:453–6.
[14] Yu HM, Huang XX, Wen GW, Zhong B, Zhang T, Bai HW. Mater Res Bull 2010;45:1013–6.
[15] Ebbesen TW, Ajayan PM. Nature 1992;358:220–2.
[16] Salvetat JP, Briggs GD, Bonard JM, Bacsa RR, Kulik AJ, Stockli T, et al. Phys Rev Lett 1999;82:944–7.
[17] Lu JP. Phys Rev Lett 1997;79:1297–300.