



Optical properties of nanotubes / Propriétés optiques des nanotubes

## Synthesis of single-walled carbon nanotubes, their ropes and books

*Synthèse de nanotubes de carbone à paroi simple. Structuration en cordes et en livres*

Bilu Liu, Qingfeng Liu, Wencai Ren, Feng Li, Chang Liu, Hui-Ming Cheng\*

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, P.R. China

## ARTICLE INFO

## Article history:

Available online 6 August 2010

## Keywords:

Carbon nanotubes  
Floating catalyst chemical vapor deposition  
Arc-discharge  
Macrostructures  
Metal-catalyst-free

## Mots-clés:

Nanotubes de carbone  
Dépôt chimique de vapeur à catalyseur flottant  
Arc électrique  
Macrostructures  
Croissance sans catalyseur

## ABSTRACT

The carbon nanotube (CNT) is a model system of one-dimensional nanomaterials, which shows numerous unique properties and vast potential applications. The synthesis and assembly of high-quality CNTs are the basis for studies of their properties and applications. In this contribution, we briefly review our works on the controlled synthesis of single-walled CNTs (SWCNTs) and double-walled CNTs via floating catalyst chemical vapor deposition and arc-discharge methods. The in situ assembly of such CNTs into ordered macrostructures with various dimensions including ropes, films, and buckybooks are also presented. Finally, we introduced our recent findings on metal-catalyst-free growth of SWCNTs.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## R É S U M É

Les nanotubes de carbone (CNT) sont des modèles de nanomatériaux unidimensionnels, qui manifestent beaucoup de propriétés remarquables et ont maintes applications potentielles. La synthèse et l'assemblage de CNT de haute qualité sont essentielles pour leurs propriétés et leurs applications. Dans la présente contribution nous passons brièvement en revue nos travaux sur la synthèse contrôlée de nanotubes de carbone à paroi simple (SWCNT) et de nanotubes de carbone à paroi double par dépôt chimique de vapeur à catalyseur flottant et par la méthode de l'arc électrique. Nous exposons aussi l'assemblage in situ de tels CNT pour former des macrostructures ordonnées tels que des cordes, des films et des livres. Nous en venons enfin à nos récentes découvertes relatives à la croissance de SWCNT sans catalyseur.

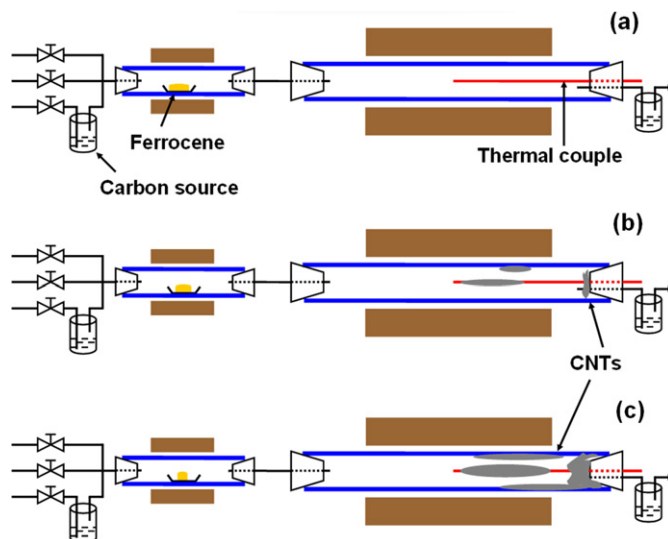
© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## 1. Introduction

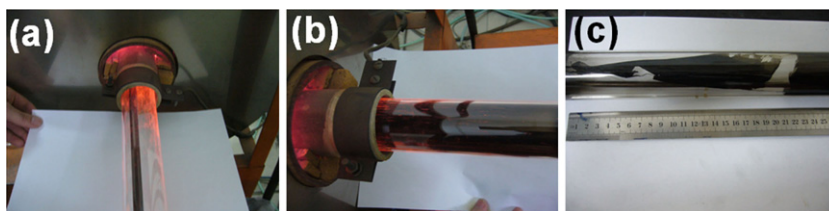
Carbon nanotubes (CNTs) can be conceptually regarded as the rolled-up products of graphene sheets [1,2]. Since their identification by Iijima in 1991 [3], CNTs, especially single-walled CNTs (SWCNTs) [4,5], have attracted huge research interest due to their outstanding mechanical, electronic, optical, and thermal properties. The synthesis of SWCNTs with high quality and large yield is the basis for further investigation of their properties and applications. It is well known that arc-discharge, laser ablation, and chemical vapor deposition (CVD) are the three major methods for the synthesis of SWCNTs. Compared with arc-discharge and laser ablation, CVD shows obvious advantages for the growth of SWCNTs in terms of low growth

\* Corresponding author.

E-mail address: cheng@imr.ac.cn (H.-M. Cheng).



**Fig. 1.** Schematic illustration of the reaction configuration for the FCCVD process: (a) before, (b) during, and (c) after SWCNT growth.



**Fig. 2.** Optical images of the quartz tube before (a) and after (b) SWCNT growth. (c) Quartz tube with as-grown SWCNT film partially peeled off using tweezers.

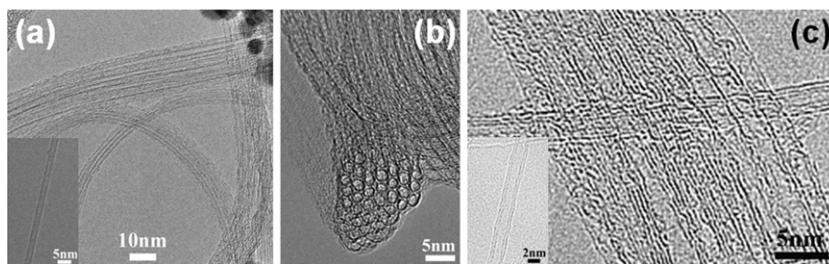
temperature, good controllability, and easiness to scale up. Despite the fact that CVD has become the most popular method for SWCNT growth, only laser ablation [6] and arc-discharge [7] could grow SWCNTs at a relative high yield before 1998. In fact, there were only a few reports on the growth of SWCNTs by CVD over supported catalysts before 1998, but with low yield and purity [8–10].

In 1998, we have developed an improved floating catalyst CVD (FCCVD) process for the semicontinuous synthesis of SWCNTs with relative a large scale, high purity, and low cost [11,12]. In this short review, we briefly summarize our work over the last decade on the controlled synthesis of SWCNTs and double-walled CNTs (DWCNTs) by FCCVD and arc-discharge, their in situ assembly into ordered macrostructures with various dimensions via the direct growth approach, and our recent findings on metal-catalyst-free growth of SWCNTs.

## 2. Controlled synthesis of SWCNTs and DWCNTs

Although FCCVD has been employed for the synthesis of vapor-grown carbon fibers and multi-walled CNTs (MWCNTs) [13,14], there was no report on the growth of SWCNTs using this method before our initial work in 1998 [11,12]. Fig. 1 is a schematic illustration of our SWCNT synthesis system. Two horizontally aligned tube furnaces or one tube furnace with two temperature zones is employed with quartz or corundum as reaction tube for the growth of SWCNTs. Benzene is used as carbon source and bubbled into the reaction tube by  $H_2$ . Ferrocene serves as catalyst precursor, which vaporizes and decomposes at low temperature to form atomic iron which then agglomerates into iron clusters or nanoparticles (NPs) and is transported by  $H_2$  into reaction zone for SWCNT growth at 1100–1200 °C. As an important feature of our FCCVD process, a small amount of sulfur-containing additive, thiophene, is dissolved in benzene at a concentration of 0.5–5 wt% as growth promoter, which plays an important role in the nucleation of the SWCNTs [15]. Without this promoter, SWCNTs can only be grown with very low yield [11]. As shown in Figs. 1a, 1b, and 1c, ferrocene is consumed gradually as the growth proceeds, and the as-synthesized SWCNTs are floated and transferred by the carrier gas to hang on to the thermal couple and reaction tube wall (Figs. 2b and 2c). Since the carbon source and ferrocene flow through the reaction region continuously, SWCNTs can be grown continuously, thus making a full use of the advantages of the floating catalyst method [11].

After FCCVD growth, we can obtain a large quantity of web-like, silver-black, very light, and free-standing materials (Figs. 2b, 2c) [11]. Extensive characterization including scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and resonant Raman spectroscopy confirm the formation of SWCNTs with



**Fig. 3.** HRTEM characterizations of FCCVD grown CNTs. (a) Bundles of SWCNTs with an individual SWCNT insert; (b) HRTEM image of the cross section of the tip of an SWCNT bundle, showing the triangular arrangement of SWCNTs inside the bundle; (c) Bundles of DWCNTs with an individual DWCNT insert [16]. Reprinted with permission from Ref. [16].

high quality (Figs. 3a, 3b) [11,12]. Another important feature of this method is that the structures of the CNTs can be easily tuned by changing experimental parameters, such as the sublimation temperature of the ferrocene, the amount of sulfur-containing growth promoter (such as thiophene or sulfur powder), the carbon source and its flow rate, and reaction temperature. By systematically adjusting these parameters, various CNTs with finely tailored structures have been selectively synthesized [11,12,15–18].

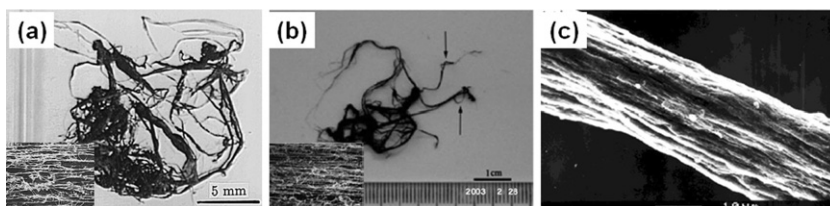
Since the bandgap of semiconducting SWCNTs is inversely proportional to their diameters [1], the diameter-controlled synthesis of SWCNTs is of vital importance for their applications in electronics and optics. Based on further studies on the growth mechanism of CNTs from the FCCVD process [15,19], we can fulfill finely diameter-controlled synthesis of SWCNTs in a  $\text{CH}_4/\text{H}_2$ -based FCCVD process using a powder mixture of ferrocene/sulfur ( $S = 0.5$  wt%) as the catalyst precursor and growth promoter [17]. By introducing an ultralow flow of  $\text{CH}_4$  ( $\leq 6$  sccm) together with a high flow of  $\text{H}_2$  ( $\geq 2000$  sccm), a series of SWCNT samples with large average diameters and narrow diameter distributions at  $1.28 \pm 0.2$ ,  $1.62 \pm 0.2$ ,  $1.72 \pm 0.2$ ,  $1.91 \pm 0.2$ , and  $2.13 \pm 0.2$  nm can be selectively synthesized, as revealed by extensive HRTEM and Raman spectroscopy analyses [17]. The high flow rate of  $\text{H}_2$  is believed to be able to suppress the deposition of amorphous carbon and the formation of small diameter SWCNTs due to its selective etching effect [17]. Large diameter SWCNTs can provide sufficient bandgap for high on/off ratios, enhanced mobility, good electrical contacts with electrodes, and therefore better performance in nanoelectronics than that of small diameter SWCNTs [20]. It is worth noting that we have synthesized SWCNTs with average diameter as large as 2.13 nm, with a narrow diameter distribution, which is not easy to achieve in other synthesis processes.

As the thinnest MWCNTs, DWCNTs are an ideal model system to study the interlayer interactions of CNTs. In addition to fundamental studies, DWCNTs show promising applications as nanoscale devices, such as molecular cables and capacitors, depending on the electronic properties of the inner and outer tubes. However, such studies are hindered by the difficulty of synthesis of large amounts of DWCNTs with good controllability [21,22]. By replacing benzene with  $\text{CH}_4$  and adjusting the amount of ferrocene and thiophene and the gas flow rates of  $\text{CH}_4$  and  $\text{H}_2$  introduced into the reaction tube, we have synthesized DWCNTs with a purity of 70% by the FCCVD process at  $1100^\circ\text{C}$  in 2002 (Fig. 3c) [16], as also reported by Ci et al. [23]. HRTEM and Raman spectroscopy studies show that the inner and outer diameters of the as-synthesized DWCNTs range from 0.8–2.8 and 1.6–3.6 nm, with average values of 1.52 and 2.26 nm, respectively [16]. The diameter distributions of inner and outer tubes can be further narrowed to 1.0–1.3 and 1.7–2.0 nm by optimizing the growth parameters [24]. More interestingly, we have found that the interlayer spacing in DWCNTs is not a constant value, ranging from 0.34 to 0.41 nm [16].

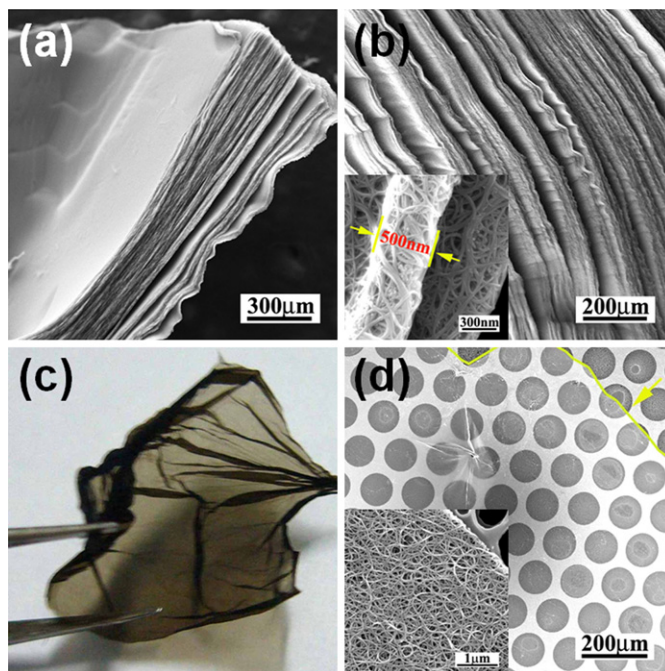
Besides the above FCCVD method, we have also developed a  $\text{H}_2$ -Ar arc-discharge method for the semicontinuous synthesis of SWCNTs [25] and DWCNTs with large scale [26], high purity [27], and high thermal stability [28], by choosing the types of carbon sources and catalysts.

### 3. In situ assembly of CNT macrostructures with various dimensions

The assembly of individual CNTs into ordered macrostructures is an important step in realizing their full potential with unique functionality in integrated systems. Compared with post assembly, direct in situ assembly during the CNT growth process shows obvious advantages in terms of the simple process and lack of damage to the intrinsic properties of the CNTs. Using the above developed FCCVD and arc-discharge methods, we are able to in situ fabricate ordered macrostructures of CNTs with various dimensions including their one-dimensional (1D) long ropes, two-dimensional (2D) films, and three-dimensional (3D) buckybooks during the synthesis process. Shown in Fig. 4 are optical images of the macroscopic 1D long ropes of SWCNTs (Fig. 4a) [12] and DWCNTs (Fig. 4b) [24] synthesized by FCCVD and an SEM image of SWCNT ropes (Fig. 4c) synthesized by arc-discharge. The length of such long ropes can reach 10 cm with width of tens to hundreds of micrometers [12,24,29]. SEM observations show that such ropes comprise many bundles of SWCNTs and DWCNTs that are roughly aligned along the entire rope. Macroscopic long ropes of SWCNTs and DWCNTs are easy for manipulation and thus facilitate fundamental studies of their polarized Raman spectra [30,31] and tensile strength [32], and application exploration, such as field emitters [33] and the filaments of light bulbs [34].



**Fig. 4.** CNT ropes. Optical images of FCCVD-synthesized SWCNT ropes (a) [12] and DWCNT ropes (b) [24]. Reprinted with permissions from Refs. [12,24]. Insets in (a) and (b) are SEM images showing the ropes comprise the aligned SWCNT and DWCNT bundles. (c) SEM image of an SWCNT rope synthesized by arc-discharge [29]. Reprinted with permission from Ref. [29].

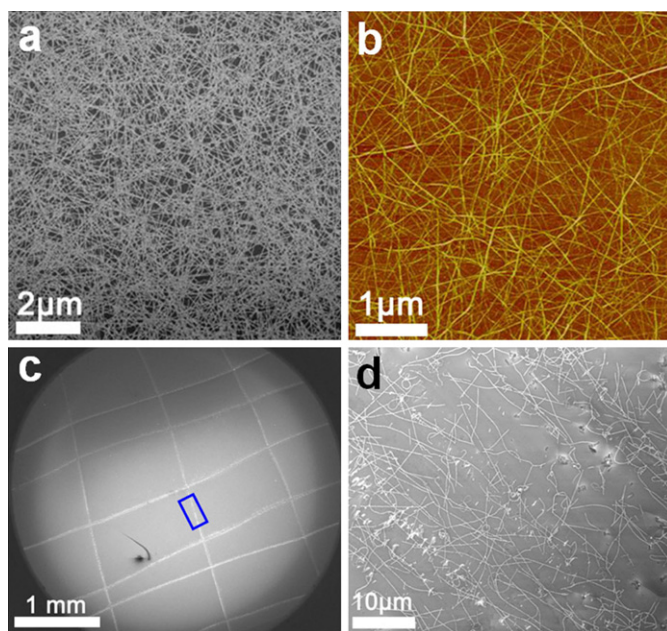


**Fig. 5.** CNT buckybooks [18]. (a) Top view and (b) cross section SEM images of the as-grown SWCNT buckybooks. The insert in (b) is an enlarge SEM image showing the thickness of one page of the book. (c) Optical image and (d) SEM top view of a book page from a buckybook, peeled off using tweezers. The insert in (d) is an enlarged SEM image showing that the page comprises of many entangled SWCNT bundles. Reprinted with permission from Ref. [18].

We have also fabricated 2D and 3D CNT macrostructures by direct growth approaches in the FCCVD process. By applying a specifically-designed porous membrane placed the downstream of the reaction tube as the receiving substrate for the as-grown SWCNTs, book-like SWCNT 3D macrostructures can be formed in situ during their growth [18]. SEM images (Figs. 5a, 5b) show the layered structures of the as-formed SWCNT 3D macrostructures, viz., SWCNT buckybooks, which comprise thousands of book pages with thickness of several hundreds of nanometers for each page. Moreover, such a book can be easily peeled off by using tweezers to obtain an isolated single sheet that is a continuous, semitransparent, conductive, and free-standing 2D SWCNT film (Fig. 5c). SEM examinations reveal that the SWCNT film consists of random tangled SWCNT bundles (Fig. 5d). Such directly synthesized SWCNT films have been demonstrated to possess superior electrical and mechanical properties compared with those made from the solution-based filtration process [35]. By adjusting the sublimation temperature of the ferrocene/sulfur mixture powder and other parameters correspondingly, sophisticated sandwich-like SWCNT/MWCNT/SWCNT buckybooks with good control over the CNT diameters, sheet packing density, and book thickness have also been fabricated [18]. Such CNT buckybooks show promising applications as high-efficiency molecular separation and binder-free electrodes for supercapacitors [18].

#### 4. Metal-catalyst-free growth of SWCNTs

The growth of SWCNTs often requires the assistance of metal catalysts, predominately, iron group metals Fe, Co, and Ni. Recent experimental [36,37] and theoretical [38] studies have shown that the chiralities of the synthesized SWCNTs can be controlled to some extent by the type of catalyst, which has greatly stimulated the exploration of new catalysts for SWCNT growth to realize the chirality-controlled synthesis of SWCNTs. However, the metal catalysts used can bring difficulty for both intrinsic property investigations and applications of SWCNTs and are not easy to be removed completely without



**Fig. 6.** Metal-catalyst-free growth of SWCNTs [41,42]. SEM (a) and AFM (b) images of SWCNTs grown from 30-nm-thick sputtering deposited SiO<sub>2</sub> film. (c), (d) SEM images of the scratching grown SWCNTs on Si/SiO<sub>2</sub> substrate with a crossed pattern. Reprinted with permission from Ref. [41].

introducing defects to SWCNTs. Although there are a few reports on the growth of CNTs without the use of metal catalysts, the CNTs obtained suffer from low yield and poor quality, and the growth processes are complex [39,40].

Recently, we have developed a simple metal-catalyst-free process for the growth of SWCNTs [41]. In our method, a 30-nm-thick SiO<sub>2</sub> film is sputter deposited onto a Si/SiO<sub>2</sub> or Si wafer and serves directly as substrate for SWCNT growth in a CH<sub>4</sub> CVD process at 900 °C [41,42]. Atomic force microscopy (AFM) characterizations confirm the formation of abundant SiO<sub>2</sub> NPs with an average size of 1.9 nm after H<sub>2</sub> pretreatment which serve as catalyst for the SWCNT growth [41]. Panels a and b in Fig. 6 are the SEM and AFM images of as-grown SWCNTs on Si/SiO<sub>2</sub> wafer, respectively, showing the formation of a densely populated SWCNT network on surface. Raman spectroscopy and HRTEM characterizations confirm the growth of SWCNTs with high quality [41], indicating the activity of SiO<sub>2</sub> NPs for the growth of SWCNTs. Such metal-free and pure SWCNTs can find applications in the fields span catalysis, electronics, biology, etc. Moreover, we have also developed a simple “scratching growth” method for the metal-catalyst-free growth of SWCNTs, as also reported by Huang et al. [43]. In this process, a Si/SiO<sub>2</sub> wafer is scratched by another one with a sharp tip to obtain the desired patterns (both Si/SiO<sub>2</sub> wafers are free of SiO<sub>2</sub> film deposition). After the same CH<sub>4</sub> CVD process mentioned above, high quality SWCNTs grow only at those scratched domains, as presented in Figs. 6c and 6d [41]. This scratching growth process is simple and cheap, without using any complex patterning process [41,44] and could be adopted for the growth of SWCNTs at a precisely predefined position for device fabrication, e.g., by employing a Si AFM tip to “write” a pattern onto a Si/SiO<sub>2</sub> wafer.

The growth of high quality SWCNTs from a nonmetal catalyst could provide valuable information for an in-depth understanding of the growth mechanism of SWCNTs. Our further studies on this topic indicate that SiO<sub>2</sub> catalyzed grown SWCNTs has an extremely low growth velocity of 8.3 nm/s, more than 300 times slower than that of commonly used Co catalyst for SWCNT growth at the same reaction condition [42]. Based on such slow growth velocity of SWCNTs from SiO<sub>2</sub> catalyst, we can realize direct length-sorted growth of short SWCNTs with average lengths of 149, 342, and 483 nm by simply adjusting the growth durations correspondingly [42]. Moreover, the short SWCNTs obtained by our direct growth method are free of defects, which is the predominant advantage over the currently established top-down cutting methods for the preparation of short SWCNTs. Such short SWCNTs are expected to show intriguing physics and have some unique applications due to the finite length effect. Moreover, benefiting from the slow growth velocity, patterned growth of SWCNTs well-restricted in a width narrower than 5 μm is fulfilled from a SiO<sub>2</sub> catalyst, showing obvious better pattern precision than the commonly used metal catalysts where severe cross-linking usually take place due to the high growth velocity and consequently long length of the SWCNTs obtained [42].

## 5. Conclusions and remarks

The controlled synthesis of CNTs with a large scale and high quality is the first step for their fundamental studies and applications. In this review, we have summarized our studies on the controlled synthesis of SWCNTs and DWCNTs from FCCVD and arc-discharge methods. The in situ and nondestructive fabrication of CNT macrostructures with various

dimensions, including 1D long ropes, 2D films, and 3D buckybooks, during growth process, has also been presented. We lastly discussed our recent findings on metal-catalyst-free growth of SWCNTs.

Compared with some commercial SWCNT samples such as HiPCO [45,46], CoMoCAT [36], etc., SWCNTs synthesized from the FCCVD possess larger diameters. However, there are relative few studies on the detailed structure information of large diameter SWCNTs due to the limitation of conventional characterization tools such as Raman spectroscopy, optical adsorption spectroscopy, and photoluminescence excitation/emission. New characterization techniques are expected to be developed and more efforts are required to reveal the structure information of such large diameter SWCNTs. The large diameter SWCNTs are superior to those of small ones in areas such as nanoelectronics [20], and the applications of SWCNTs in such areas need more attention. Metal-catalyst-free growth of SWCNTs is a newly emerging topic whose the growth mechanism deserves further study. In addition, most of the current synthesis processes using new catalysts focus only on the surface growth with a limited amount of SWCNTs obtained. The development of methods for large scale metal-catalyst-free growth of SWCNTs can greatly promote their applications in various fields where metals are harmful.

## Acknowledgement

We acknowledge support from MOST of China (Nos. 2006CB932701 and 2008DFA51400), NSFC (Nos. 50921004, 90606008 and 50702063), and CAS (No. KJCX2-YW-M01).

## References

- [1] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, 1998.
- [2] A. Jorio, G. Dresselhaus, M.S. Dresselhaus, *Carbon Nanotubes: Topics in Applied Physics*, vol. 111, Springer-Verlag, Berlin–Heidelberg, 2008.
- [3] S. Iijima, *Nature* 354 (1991) 56.
- [4] S. Iijima, T. Ichihashi, *Nature* 363 (1993) 603.
- [5] D.S. Bethune, C.H. Kiang, M.S. Devries, et al., *Nature* 363 (1993) 605.
- [6] A. Thess, R. Lee, P. Nikolaev, et al., *Science* 273 (1996) 483.
- [7] C. Journet, W.K. Maser, P. Bernier, et al., *Nature* 388 (1997) 756.
- [8] H.J. Dai, A.G. Rinzler, P. Nikolaev, et al., *Chem. Phys. Lett.* 260 (1996) 471.
- [9] A. Peigney, C. Laurent, F. Dobigeon, et al., *J. Mater. Res.* 12 (1997) 613.
- [10] A. Fonseca, K. Hernadi, P. Piedigrosso, et al., *Appl. Phys. A – Mater. Sci. & Process.* 67 (1998) 11.
- [11] H.M. Cheng, F. Li, G. Su, et al., *Appl. Phys. Lett.* 72 (1998) 3282.
- [12] H.M. Cheng, F. Li, X. Sun, et al., *Chem. Phys. Lett.* 289 (1998) 602.
- [13] R. Sen, A. Govindaraj, C.N.R. Rao, *Chem. Phys. Lett.* 267 (1997) 276.
- [14] A. Oberlin, M. Endo, T. Koyama, *J. Cryst. Growth* 32 (1976) 335.
- [15] W.C. Ren, F. Li, H.M. Cheng, *J. Phys. Chem. B* 110 (2006) 16941.
- [16] W.C. Ren, F. Li, J.A. Chen, et al., *Chem. Phys. Lett.* 359 (2002) 196.
- [17] Q.F. Liu, W.C. Ren, Z.G. Chen, et al., *ACS Nano* 2 (2008) 1722.
- [18] Q.F. Liu, W.C. Ren, D.W. Wang, et al., *ACS Nano* 3 (2009) 707.
- [19] W.C. Ren, F. Li, S. Bai, et al., *J. Nanosci. Nanotech.* 6 (2006) 1339.
- [20] W. Kim, A. Javey, R. Tu, et al., *Appl. Phys. Lett.* 87 (2005) 173101.
- [21] J.L. Hutchison, N.A. Kiselev, E.P. Krinichnaya, et al., *Carbon* 39 (2001) 761.
- [22] S. Bandow, M. Takizawa, K. Hirahara, et al., *Chem. Phys. Lett.* 337 (2001) 48.
- [23] L.J. Ci, Z.L. Rao, Z.P. Zhou, et al., *Chem. Phys. Lett.* 359 (2002) 63.
- [24] W.C. Ren, H.M. Cheng, *J. Phys. Chem. B* 109 (2005) 7169.
- [25] C. Liu, H.T. Cong, F. Li, et al., *Carbon* 37 (1999) 1865.
- [26] L.X. Li, F. Li, C. Liu, et al., *Carbon* 43 (2005) 623.
- [27] Z.G. Chen, F. Li, W.C. Ren, et al., *Nanotechnology* 17 (2006) 3100.
- [28] Q.F. Liu, W.C. Ren, F. Li, et al., *J. Phys. Chem. C* 111 (2007) 5006.
- [29] C. Liu, H.M. Cheng, H.T. Cong, et al., *Adv. Mater.* 12 (2000) 1190.
- [30] A. Jorio, G. Dresselhaus, M.S. Dresselhaus, et al., *Phys. Rev. Lett.* 85 (2000) 2617.
- [31] W.C. Ren, F. Li, H.M. Cheng, *Phys. Rev. B* 71 (2005) 115428.
- [32] F. Li, H.M. Cheng, S. Bai, et al., *Appl. Phys. Lett.* 77 (2000) 3161.
- [33] C. Liu, Y. Tong, H.M. Cheng, et al., *Appl. Phys. Lett.* 86 (2005) 223114.
- [34] Z.G. Zhao, F. Li, C. Liu, H.M. Cheng, *J. Appl. Phys.* 98 (2005) 044306.
- [35] W.J. Ma, L. Song, R. Yang, et al., *Nano Lett.* 7 (2007) 2307.
- [36] S.M. Bachilo, L. Balzano, J.E. Herrera, et al., *J. Am. Chem. Soc.* 125 (2003) 11186.
- [37] X.L. Li, X.M. Tu, S. Zaric, et al., *J. Am. Chem. Soc.* 129 (2007) 15770.
- [38] F. Ding, P. Larsson, J.A. Larsson, et al., *Nano Lett.* 8 (2008) 463.
- [39] T. Uchino, K.N. Bourdakos, C.H. de Groot, et al., *Appl. Phys. Lett.* 86 (2005) 233110.
- [40] D. Takagi, H. Hibino, S. Suzuki, et al., *Nano Lett.* 7 (2007) 2272.
- [41] B.L. Liu, W.C. Ren, L.B. Gao, et al., *J. Am. Chem. Soc.* 131 (2009) 2082.
- [42] B.L. Liu, W.C. Ren, C. Liu, et al., *ACS Nano* 3 (2009) 3421.
- [43] S.M. Huang, Q.R. Cai, J.Y. Chen, et al., *J. Am. Chem. Soc.* 131 (2009) 2094.
- [44] D.N. Yuan, L. Ding, H.B. Chu, et al., *Nano Lett.* 8 (2008) 2576.
- [45] P. Nikolaev, M.J. Bronikowski, R.K. Bradley, et al., *Chem. Phys. Lett.* 313 (1999) 91.
- [46] M.J. Bronikowski, P.A. Willis, D.T. Colbert, et al., *J. Vac. Sci. Technol. A* 19 (2001) 1800.