

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/carbon

Liquefied petroleum gas containing sulfur as the carbon source for carbon nanotube forests

Jiaqi Huang, Qiang Zhang, Fei Wei*, Weizhong Qian, Dezheng Wang, Ling Hu

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 19 April 2007

Accepted 16 November 2007

Available online 3 December 2007

ABSTRACT

Carbon nanotube (CNT) forests were obtained from liquefied petroleum gas (LPG) as the carbon source in the floating catalyst process. The CNTs obtained in the forest had a thinner diameter and lower growth rate than those obtained with other carbon sources, which was attributed to the existence of sulfur in the LPG. The use of unpurified LPG provides a controllable way to synthesize a CNT forest at low cost.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Since the first synthesis in 1996 [1], vertically aligned carbon nanotube (CNT) forests have become one focus in nanoscience and nanoengineering. These aligned CNTs in the forest-like arrays are of many attractive properties, such as identical tube length, uniform orientation, extra high purity, easy spinning into macroscopic fibers, etc. Therefore, the as-grown forest can be used directly to construct field emission devices, anisotropic conductive materials, multi-functional membranes and super strong yarn. Even after the loss of the original alignment, longer and straighter multi-walled CNTs (MWCNTs) from the CNT forests are found better than randomly aggregated multi-walled or even single-walled CNT (SWCNT) in improving the electronic, mechanic and thermal properties of the polymer [2]. These applications can become feasible if there is a controllable synthesis of CNT forests at a low cost in a scalable way. Various synthesis methods have been developed, which include porosity assisted chemical vapor deposition (CVD) [1], plasma enhanced CVD [3], thermal CVD [4,5], alcohol catalyzed CVD [6] and floating catalyst CVD [7–16]. For further research on CNT forests and the ultimate commercialization of CNT forests, a cheap catalyst, a simple synthesis method and a cheap carbon source are necessary for those methods.

High (>99.9%) purity carbon sources including CO and hydrocarbons such as methane, ethylene, acetylene, *n*-butane, hexane, benzene, toluene, xylene have been used to synthesize CNT forest in previous studies [2–22]. These purified carbon sources were expensive and present in limited supply, compared to cheaper fuels such as natural gas, liquefied petroleum gas (LPG), gasoline, water gas, coal gas, dry gas and coal [23–29]. However, the cheaper fuels contain sulfur in concentration of a few to several hundred ppm, which is expected to severely poison the catalyst, and few reports currently exist on the direct use of LPG, coal or natural gas [23–29]. Prokudina has reported the synthesis of agglomerated CNTs from LPG but no information on the sulfur content was given [23]. Our group had reported the direct synthesis of agglomerated CNTs from the decomposition of the LPG containing 13 ppm sulfur by a Fe/Mo/Al₂O₃ catalyst [24]. There had been no reports on the synthesis of CNT forests, although the CNT forests are fascinating materials which urgently need a large scale production to be useful in the future.

In this contribution, we report the direct synthesis of a CNT forest that is as long as 540 μm from the decomposition of LPG containing 20 ppm sulfur with a one-hour growth. The diameter and growth rate of CNT forest can be modulated by the growth temperature. The fact that a small amount of S in LPG can reduce the diameter of the CNT in the forest was also

* Corresponding author: Fax: +86 10 62772051.

E-mail address: weifei@fotu.org (F. Wei).

0008-6223/\$ - see front matter © 2007 Elsevier Ltd. All rights reserved.

doi:10.1016/j.carbon.2007.11.044

reported. Those findings provide a concept and an example for cheap carbon source and controllable way for CNT forest production.

2. Experimental

The CNT forest was grown by the floating catalyst method on a quartz flake growth substrate using ferrocene as the catalyst precursor and LPG as the carbon source. The LPG was directly purchased from a household fuel supplier. The quartz flake was placed inside a horizontal quartz tube with an inner diameter of 30 mm and length of 1200 mm. The quartz tube was heated by a two-stage furnace with length of 300 and 600 mm, respectively. Generally, the reaction zone was first heated to 800 °C with a carrier gas of 90% Ar and 10% H₂ at a flow rate of 600 ml/min. Then the catalyst source was heated to 60 °C in the first furnace stage before LPG was introduced into the reactor. The LPG was flowed into the reactor at a rate of 60 ml/min. It was decomposed by the in situ formed metal catalyst in the second furnace stage. The growth was continued for a specific time. After the experiments, the product was taken out of the reactor and peeled from the substrate.

The LPG and gas product compositions were analyzed by an on-line gas chromatograph (Shimadzu 14B) with a 50 m PLOT Al₂O₃ capillary column and a FID detector. The morphology of the CNT forest was characterized by a JSM 7401F high resolution scanning electron microscope (SEM) operated at 5.0 kV and a JEM 2010 high resolution transmission electron microscope (TEM) operated at 120.0 kV. The sample for the TEM observation was prepared with a common sonication method. Raman experiments were performed with a Renishaw RM2000 Raman spectrophotometer. The spectra are recorded using a He–Ne laser excitation line at 633.0 nm with a

spot size of about 20 μm² on the CNT forest kept at ambient temperature.

3. Results and discussion

Compared to most CNT forest precursor, the LPG had a very complex composition, and even contained some sulfur. The typical composition of the LPG and the gas product from the floating catalyst process is shown in Table 1. It can be seen that the LPG was mainly composed of C₃ and C₄ alkanes and alkenes. Also, 20 ppm H₂S existed in the LPG, which caused an ugly smell. The gas product out from the reactor had lower C₃ and C₄ hydrocarbon weight percentages, which indicated the transformations to other carbon forms, such as the solid carbon product and the other gas hydrocarbons shown in Table 1. The weight percentages of CH₄, C₂H₄ and hydrocarbons above C₅ were increased. Obviously, in this process, the hydrocarbon cracking mechanism is very complex [30]. Apart from producing the solid carbon product, a hydrocarbon gas can also transform into other gaseous hydrocarbons, such as CH₄, C₂H₄ and aromatic hydrocarbons. The details need further studies, but here, we only discuss this on the level that although the LPG was a mixed carbon source, it was effective as a carbon source for CNT growth.

The solid as-grown product obtained from the quartz flake substrate was in the state of a black film. This was characterized by SEM (Fig. 1), which showed that a CNT forest with a length of 540 μm was obtained after a one-hour growth at 800 °C. The CNTs in the forest showed good orientation with parts of straight and curve CNTs (Fig. 1b). This is in agreement with many reports [7–16,21], which have close relationships to forest growth [31]. The curved CNTs were of a little higher curvature, the tortuosity factors of which were about 1.45 ± 0.14 at a calculating scale of 10 μm [32]. This indicated the

Table 1 – Weight percentage composition of the hydrocarbon in the feed LPG and the gas product from the floating catalyst process at the growth temperature of 800 °C

	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈	C ₅ ~
LPG	0.60	2.63	0.28	17.67	6.53	32.59	36.47	3.23
Gas product	21.91	10.25	30.77	2.51	3.18	0.23	3.04	28.11

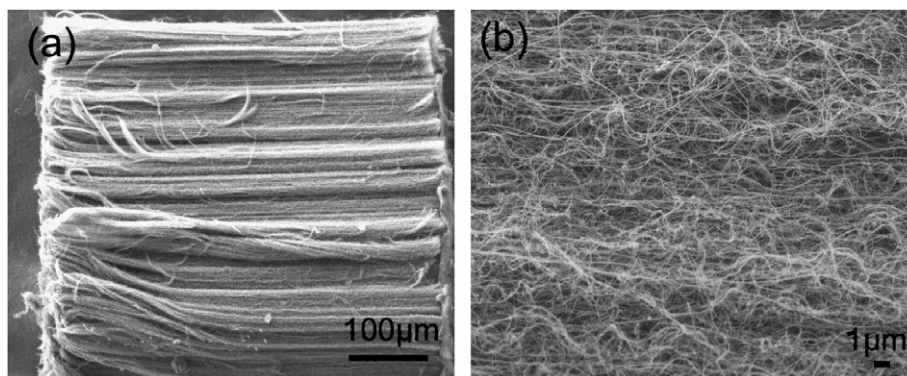


Fig. 1 – SEM images of a CNT forest grown from LPG at 800 °C for 1 h.

presence of a higher amount of defects, which is one of main reason for curve CNT in the as-grown CNT forests product. It can be seen that the walls of the CNTs were clean and did not have dots that indicated the existence of carbon encapsulated catalyst or carbon sphere. This indicates that the carbon encapsulated catalyst or carbon sphere, which usually pollute the CNT forest in the floating catalyst method [15,16], can be avoided with LPG as the carbon source under our growth condition.

A typical MWCNT structure was seen in the TEM images (Fig. 2a and b). Due to the sonication in the TEM sample preparation, the aligned arrangement of the CNTs was destroyed to obtain a high dispersion of CNTs in the ethanol solution (Fig. 2a). The diameter had a slightly wider distribution, with an average diameter of 12 nm (Fig. 2c), which is in good agreement with the SEM images. About 5–15 layers of graphite can be seen from the TEM images (Fig. 2b). Another important feature of the CNT forest was that the defects density was a little higher for the CNTs from the LPG carbon source. The Raman spectra showed only the D and G peaks with an intensity ratio of 0.98 (Fig. 2d), which is a supporting evidence that the MWCNTs from the LPG had a higher defect density.

In the VLS model of CNT growth, the carbon source is decomposed at the surface of the metal catalyst, and it does not matter whether the carbon source is a pure carbon-containing gas or a mixture of gases. In our case, LPG, which was a cheap and common carbon-containing gas mixture,

was used to synthesize a CNT forest. It can be suggested that it would also be effective with other forms of catalyst for forest formation, such as a metal film in thermal CVD or plasma enhanced CVD.

Another important goal of controllable CNT growth is the diameter of the MWCNTs in the forest, especially in the floating catalyst process. Table 2 summarizes the characteristics of CNTs in forest form that have been reported [8–16]. It can be seen that most works have produced CNTs with a diameter larger than 15 nm. The CNTs can also be thicker when more of the catalyst precursor source is present [11,14,16] or with higher temperatures [11,12,14–16]. In our case, the diameter of the as-grown products was small. It was about 12 nm when the forest growth temperature was 800 °C. When the growth temperature was lowered to 700 °C, the diameter of CNTs in the forest (Fig. 3a) reduced to 6.8 nm (Fig. 3c). There were more defects in the products (Fig. 3b). The Raman spectra showed only the D and G peaks with an intensity ratio of 1.04 (Fig. 3d). The LPG contained 20 ppm H₂S, which was the important difference from other common hydrocarbon sources. The S element plays a key role as a promoter for higher selectivity to SWCNTs or DWCNTs with the floating catalyst method at temperatures higher than 1000 °C [33,35]. The S can partly poison the metal catalyst and promote the presence of small size catalyst particles during the formation process [33–35]. In our case, the S element was in a low concentration compared with other reports [14,33–35]. But it

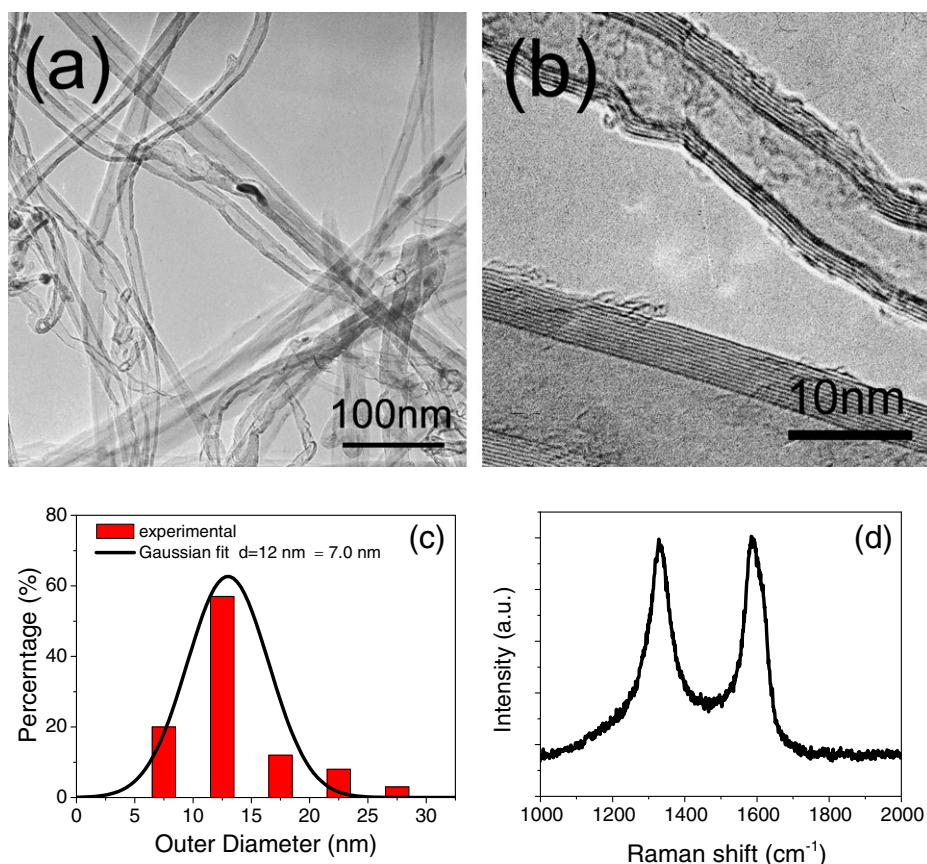


Fig. 2 – (a) and (b) are TEM and HRTEM images of a CNT forest grown from LPG at 800 °C for 1 h (the sample after sonication). (c) and (d) are the diameter distribution and Raman spectra of the CNT forest.

Table 2 – MWCNT forest structure from different carbon sources by the floating catalyst process

Carbon source	Catalyst precursor	Atmosphere	CNT forest length and growth time	CNT diameter	References
LPG	Ferrocene	Ar/H ₂	540 μm, 800 °C, 1 h	12 nm, 800 °C; 6.8 nm, 700 °C	–
Acetylene	Ferrocene	Ar	500 μm, 800 °C, 5 min	20 nm	[8]
Acetylene	Ferrocene	Ar	100 μm, 800 °C, 5 min	15 nm	[9]
Methane, acetylene or n-butane	Ferrocene	Ar	60 μm, 1100 °C	12–18 nm	[10]
Acetylene	Fe film on SiO ₂	NH ₃ , Ar	0.6–20 μm, 3–30 min, 950 °C	60–240 nm	[11]
Xylene	Ferrocene	Ar/H ₂	1.5 μm, 850 °C, 30 min	30–60 nm	[12]
Xylene	Ferrocene	Ar/H ₂	800 °C	20–40 nm	[13]
Benzene or thiophene	Ferrocene	Ar	100–500 μm, 800–1000 °C	25–100 nm	[14]
Toluene	Ferrocene	Ar/H ₂	150 μm, 400 min, 590–760 °C	10–40 nm, 590 °C; 25 ~ 70 nm, 760 °C	[15]
m-Xylene	Ferrocene	Ar/H ₂	820 °C	70–130 nm (13.1 wt%)	[16]

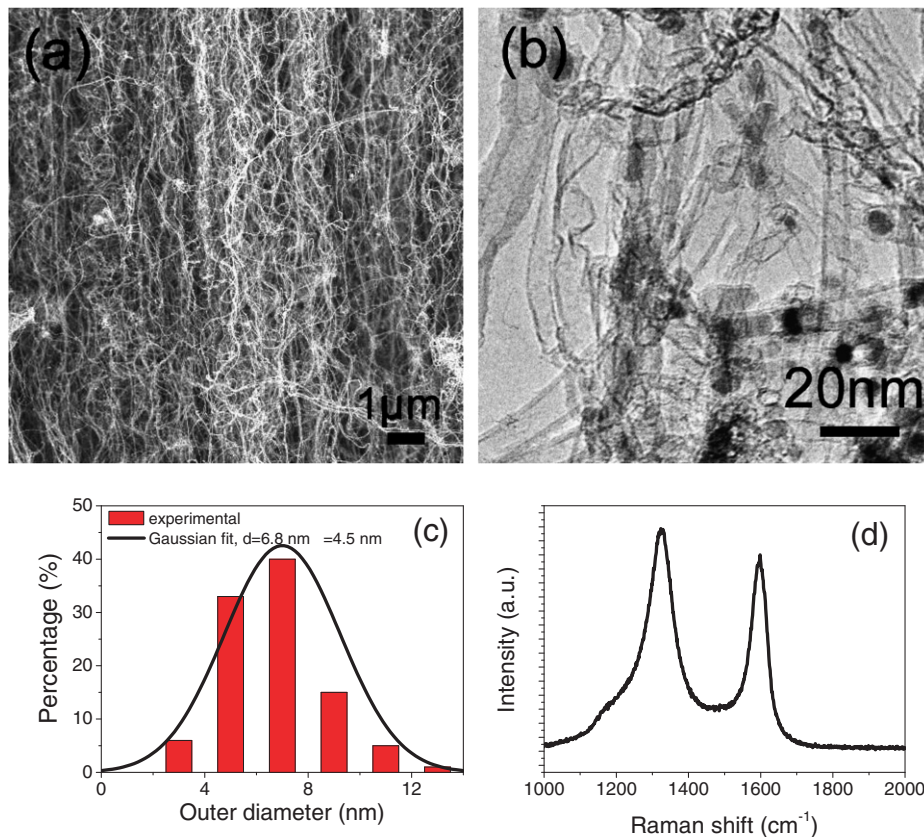


Fig. 3 – (a) and (b) are SEM and TEM images of a CNT forest grown from LPG at 700 °C for 1 h (TEM sample after sonication). (c) and (d) are the diameter distribution and Raman spectra of the CNT forest.

was still effective in keeping the diameter of the CNTs small. At the same time, the defect density was much increased with the continuous introduction of S with the LPG, which was caused by the instability of the catalyst activity. The defects of CNTs increased when in a low growth temperature. As compared to the fast growth at 30 μm/min [12], our thin wall CNT forest growth rate at 800 °C was about 9 μm/min. At the lower temperature of 700 °C, the growth rate was about 1.2 μm/min. Both the CNT product and the growth behavior were much more complex with the sulfur-containing LPG, which needs further researches.

Finally, it can be noted that although the carbon source was very cheap and complex, a good quality CNT forest was synthesized, and its structure can also be modulated by the parameters of the process. The results in this letter indicate a method to lower the production cost of CNT forests.

4. Conclusion

When LPG containing a low S concentration was used as carbon source, CNT forest with a smaller diameter was grown in

the floating catalyst process. LPG was an effective carbon source and it is a small amount of S in LPG that reduced the diameter of the CNTs. However, the product had more defects and a lower growth rate. Since LPG is very cheap, this suggests that more controllable CNT forests can be produced at a lower price in future.

Acknowledgements

The work was supported by the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (No. 200548), Natural Scientific Foundation of China (No. 20606020), China National Program (No. 2006CB0N0702), Key Project of Chinese Ministry of Education (No. 106011).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2007.11.044.

REFERENCES

- [1] Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, et al. Large-scale synthesis of aligned carbon nanotubes. *Science* 1996;274(5293):1701–3.
- [2] Moissala A, Li Q, Kinloch IA, Windle AH. Thermal and electrical conductivity of single- and multi-walled carbon nanotube-epoxy composites. *Compos Sci Technol* 2006;66(10):1285–8.
- [3] Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, et al. Synthesis of large arrays of well-aligned carbon nanotubes on glass. *Science* 1998;282(5391):1105–7.
- [4] Fan SS, Chapline MG, Franklin NR, Tomblor TW, Cassell AM, Dai HJ. Self-oriented regular arrays of carbon nanotubes and their field emission properties. *Science* 1999;283(5401):512–4.
- [5] Hata K, Futaba DN, Mizuno K, Namai T, Yumura M, Iijima S. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. *Science* 2004;306(5700):1362–4.
- [6] Murakami Y, Chiashi S, Miyauchi Y, Hu MH, Ogura M, Okubo T, et al. Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy. *Chem Phys Lett* 2004;385(3–4):298–303.
- [7] Andrews R, Jacques D, Rao AM, Derbyshire F, Qian D, Fan X, et al. Continuous production of aligned carbon nanotubes: a step closer to commercial realization. *Chem Phys Lett* 1999;303(5–6):467–74.
- [8] Lee YT, Kim NS, Park J, Han JB, Choi YS, Ryu H, et al. Temperature-dependent growth of carbon nanotubes by pyrolysis of ferrocene and acetylene in the range between 700 and 1000 °C. *Chem Phys Lett* 2003;372(5–6):853–9.
- [9] Kim KE, Kim KJ, Jung WS, Bae SY, Park J, Choi J, et al. Investigation on the temperature-dependent growth rate of carbon nanotubes using chemical vapor deposition of ferrocene and acetylene. *Chem Phys Lett* 2005;401(4–6):459–64.
- [10] Satishkumar BC, Govindaraj A, Rao CNR. Bundles of aligned carbon nanotubes obtained by the pyrolysis of ferrocene-hydrocarbon mixtures: role of the metal nanoparticles produced in situ. *Chem Phys Lett* 1999;307(3–4):158–62.
- [11] Lee CJ, Lyu SC, Cho YR, Lee JH, Cho KI. Diameter-controlled growth of carbon nanotubes using thermal chemical vapor deposition. *Chem Phys Lett* 2001;341(3–4):245–9.
- [12] Zhang XF, Cao AY, Wei BQ, Li YH, Wei JQ, Xu CL, et al. Rapid growth of well-aligned carbon nanotube arrays. *Chem Phys Lett* 2002;362(3–4):285–90.
- [13] Wei BQ, Vajtai R, Jung Y, Ward J, Zhang R, Ramanath G, et al. Organized assembly of carbon nanotubes – cunning refinements help to customize the architecture of nanotube structures. *Nature* 2002;416(6880):495–6.
- [14] Tapasztó L, Kertész K, Vertesy Z, Horváth ZE, Koos AA, Osvath Z, et al. Diameter and morphology dependence on experimental conditions of carbon nanotube arrays grown by spray pyrolysis. *Carbon* 2005;43(5):970–7.
- [15] Singh C, Shaffer MS, Windle AH. Production of controlled architectures of aligned carbon nanotubes by an injection chemical vapor deposition method. *Carbon* 2003;41(2):359–68.
- [16] Barreiro A, Selbmann D, Pichler T, Biedermann K, Gemming T, Rummeli MH, et al. On the effects of solution and reaction parameters for the aerosol-assisted CVD growth of long carbon nanotubes. *Appl Phys A* 2006;82(4):719–25.
- [17] Zhu LB, Xu JW, Xiao F, Jiang HJ, Hess DW, Wong CP. The growth of carbon nanotube stacks in the kinetics-controlled regime. *Carbon* 2007;45(2):344–8.
- [18] Wang MZ, Li F, Yang QH, Cheng HM. Advances in synthesizing and preparing carbon nanotubes from different carbon sources. *New Carbon Mater* 2003;18(4):250–64.
- [19] Wang Y, Wei F, Luo GH, Yu H, Gu GS. The large-scale production of carbon nanotubes in a nano-agglomerate fluidized-bed reactor. *Chem Phys Lett* 2002;364(5–6):568–72.
- [20] Xiong GY, Wang DZ, Ren ZF. Aligned millimeter-long carbon nanotube arrays grown on single crystal magnesia. *Carbon* 2006;44(5):969–73.
- [21] Xiang R, Luo GH, Qian WZ, Zhang Q, Wang Y, Wei F, et al. Suction, compensation, and substitution of catalyst particles during continuous growth of carbon nanotubes. *Adv Mater* 2007;19(17):2360–3.
- [22] Zhang Q, Qian WZ, Wen Q, Liu Y, Wang DZ, Wei F. The effect of phase separation in Fe/Mg/Al/O catalysts on the synthesis of DWCNTs from methane. *Carbon* 2007;45(8):1645–50.
- [23] Prokudina NA, Shishchenko ER, Joo OS, Kim DY, Han SH. Carbon nanotube RLC circuits. *Adv Mater* 2000;12(19):1444–7.
- [24] Qian WZ, Yu H, Wei F, Zhang QF, Wang ZW. Synthesis of carbon nanotubes from liquefied petroleum gas containing sulfur. *Carbon* 2002;40(15):2968–70.
- [25] Bonadiman R, Lima MD, de Andrade MJ, Bergmann CP. Production of single and multi-walled carbon nanotubes using natural gas as a precursor compound. *J Mater Sci* 2006;41(22):7288–95.
- [26] Wang ZY, Zhao ZB, Qiu JS. In situ synthesis of super-long Cu nanowires inside carbon nanotubes with coal as carbon source. *Carbon* 2006;44(9):1845–7.
- [27] Wang ZY, Zhao ZB, Qiu JS. Synthesis of branched carbon nanotubes from coal. *Carbon* 2006;44(7):1321–4.
- [28] Qiu JS, Li QX, Wang ZY, Sun YF, Zhang HZ. CVD synthesis of coal-gas-derived carbon nanotubes and nanocapsules containing magnetic iron carbide and oxide. *Carbon* 2006;44(12):2565–8.
- [29] Qiu JS, An YL, Zhao ZB, Li YF, Zhou Y. Catalytic synthesis of single-walled carbon nanotubes from coal gas by chemical vapor deposition method. *Fuel Process Technol* 2004;85(8–10):913–20.
- [30] Kuwana K, Li TX, Saito K. Gas-phase reactions during CVD synthesis of carbon nanotubes: Insights via numerical experiments. *Chem Eng Sci* 2006;61(20):6718–26.
- [31] Zhang Q, Zhou WP, Qian WZ, Xiang R, Huang JQ, Wang DZ, et al. Synchronous growth of vertically aligned carbon nanotubes with pristine stress in the

- heterogeneous catalysis process. *J Phys Chem C* 2007;111(40):14638–43.
- [32] Zhou WP, Wu YL, Wei F, Luo GH, Qian WZ. Elastic deformation of multi-walled carbon nanotubes in electrospun MWCNTs–PEO and MWCNTs–PVA nanofibers. *Polymer* 2005;46(26):12689–95.
- [33] Barreiro A, Kramberger C, Rummeli MH, Gruneis A, Grimm D, Hampel S, et al. Control of the single-wall carbon nanotube mean diameter in sulfur promoted aerosol-assisted chemical vapour deposition. *Carbon* 2007;45(1):55–61.
- [34] Luo T, Chen LY, Bao KY, Yu WC, Qian YT. Solvothermal preparation of amorphous carbon nanotubes and Fe/C coaxial nanocables from sulfur, ferrocene, and benzene. *Carbon* 2006;44(13):2844–8.
- [35] Ren WC, Li F, Cheng HM. Evidence for, and an understanding of, the initial nucleation of carbon nanotubes produced by a floating catalyst method. *J Phys Chem B* 2006;110(34):16941–6.