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Controllable growth of single wall carbon nanotubes by pyrolizing acetylene on the floating iron catalysts

Lijie Ci, Sishen Xie *, Dongsheng Tang, Xiaoqin Yan, Yubao Li, Zuqin Liu, Xiaoping Zou, Weiya Zhou, Gang Wang

Institute of Physics, Center for Condensed Matter Physics, Chinese Academy of Science, Group 412, P.O. Box 603-92#, Beijing 100080, PR China

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Abstract

Single wall carbon nanotubes (SWNTs) without amorphous carbon coating were prepared by thermally decomposing acetylene (C_2H_2) at the temperature range 750–1200 °C in a floating iron catalyst system. The C_2H_2 partial pressure was controlled to make a carbon supply limiting growth of SWNTs. The higher reaction temperature above 1100 °C seemed not to favor the SWNT production due to the quick thermal decomposition of C_2H_2.

1. Introduction

Single wall carbon nanotubes (SWNTs) exhibit many exceptional and useful electronic and mechanical properties and will be a promising candidate for application in nano-scale technologies [1,2]. The most established methods to produce SWNTs currently include laser-ablation method [3] and carbon arc method [4]. By pyrolizing carbon-containing molecules such as CO [5], CH_4 [6] and C_2H_4 [7] on supported nanometer-sized metal particles, chemical vapor deposition (CVD) method can be a promising way to up-scale the production of SWNTs. During the past three years, a continuous CVD synthetic method, in which SWNTs are grown in a flowing gaseous feedstock mixture, was developed to provide a mass-production method of SWNTs [8–11]. Cheng et al. [8] first reported that they obtained ropes of SWNTs in high yield by pyrolizing a benzene–ferrocene–thiophene mixture at a temperature of 1200 °C. After that, Rao and coworkers [9], Nikolaev et al. [10] and Bladh et al. [11] also demonstrated that SWNTs could be produced in similar experiments by pyrolyzing other carbon-containing gases (C_2H_2, CO and CH_4) at a temperature range 800–1200 °C.

In those studies, CO was shown to be a better carbon feedstock to produce clean SWNTs without amorphous carbon coating [10]. In contrast, SWNTs produced from hydrocarbon sources such as C_2H_2 [9] and C_6H_6 [8] often suffer from amorphous carbon coating due to their self-pyrolysis at the reaction temperature. However, the reaction

* Corresponding author. Fax: +86-10-82-64-95-31.
E-mail address: ssxie@aphy.iphy.ac.cn (S. Xie).

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rate of CO disproportionation at a given temperature and pressure is much slower than hydrocarbon thermal decomposition, and a larger CO flow amount (1000–2000 sccm) is always needed to grow SWNTs [10].

Other reports showed that it was difficult to produce pure SWNTs from hydrocarbon precursors such as C_6H_6 [12] and C_2H_2 [11] under their experimental conditions. It means that this kind of SWNT synthesis process needs to be improved. Hydrocarbons are more common carbon-containing gases, and synthesizing SWNTs from hydrocarbon gas by this kind of process may provide a good way to scale up SWNT production for commercial application.

In this communication, we report that C_2H_2 can also be a very ideal carbon feedstock to produce clean and pure SWNTs by controlling the experimental parameters carefully. In our studies, we found that the reaction temperature of SWNT from C_2H_2 can be in a wide range 750–1200 °C, which is different from other report [9]. We also found that the partial pressure of hydrocarbon is much crucial to synthesize SWNTs. Experiments here may be helpful to grow SWNTs from other hydrocarbon by the floating catalyst process [13].

2. Experimental

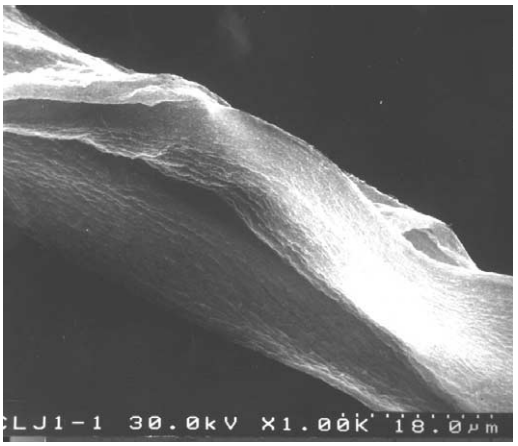
Our experimental set-up is a two-stage furnace system fitted with a quartz tube (30 mm i.d.) [12]. Ferrocene (dicyclopentadienyl iron), acting as the source of catalyst, was sublimed in the first furnace at the temperature 60–90 °C. The sublimed ferrocene was carried by the flowing Argon (1200 sccm) and acetylene (3–10 sccm) mixture into the second furnace. The SWNT growth temperature (the temperature of the second furnace) can vary from 750 to 1200 °C. The pressure inside the quartz tube was held constant at 1 atm in all the following experiments. To collect the SWNT product, we fitted a water-cooled collector in the end of second furnace. We found that most of the products condense on the water-cooled collector to form a SWNT film, and only a small faction of the products were found on the cold part of the quartz tube.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and micro-Raman spectroscopy were performed to characterize the products. Because the film of the products were not easy to disperse even after ultrasonic treatment for several hours, TEM samples were prepared by simply tearing apart a small piece of product and attaching it on the carbon copper grid, then dropping a drop of ethanol and drying it.

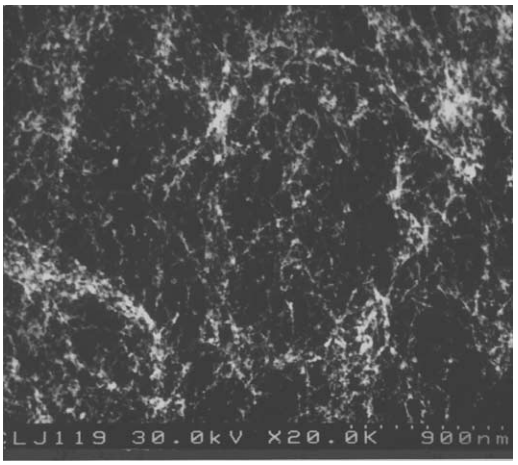
3. Results and discussion

The products in our typical experiments can be peeled easily off the water-cooled collector in large sheets. Fig. 1a shows a SEM macro-appearance of a small piece of the products, and Fig. 1b is a local enlarged image of this piece. It shows that the products mainly consist of thousands of entangled filaments with very small diameter and small particles, and most of the small particles seem decorate on those filaments and are shown as bright color in the image. High resolution TEM image (Fig. 1c) shows that all of those filaments are SWNT bundles or individual SWNTs, and the particles are metal catalysts encapsulated by two or three graphite layers. Analysis of XRD indicates that the particles are iron. In the as-grown film (as shown in Fig. 1c), SWNTs are not easy to form large bundles due to the small particles supporting. SWNTs tend to congregate to form a large bundles where there are no particles supporting. No amorphous carbon was found in the sample, which indicates that there is no hydrocarbon thermal decomposition on the SWNTs and the encapsulated particles.

The partial pressure of the C_2H_2 was shown as a crucial factor to produce SWNTs in our experiments. Fig. 2 shows the partial pressure of C_2H_2 vs. the yield of SWNTs. We found that when the C_2H_2 partial pressure was higher than 12 Torr, almost no SWNTs could be obtained from the collector. Hafner et al. [7] showed evidences that the growth rate of SWNTs, which are prepared by catalytic decomposition of C_2H_4 and CO on the supported catalyst, is limited by the supply of carbon to the catalyst particles. The above exper-



(a)



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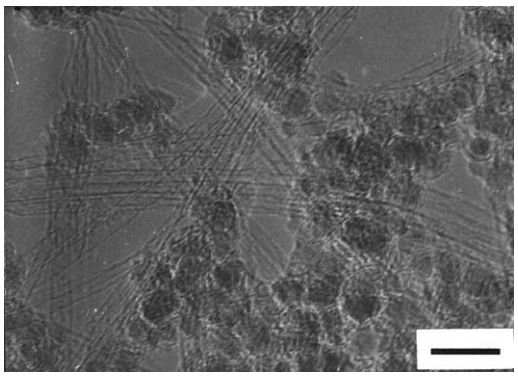

(c)

Fig. 1. (a) SEM macro-appearance of a small piece of the as-grown products; (b) a local enlarged image of a; (c) HETEM image of the as-grown film, and the inserted bar is 10 nm.

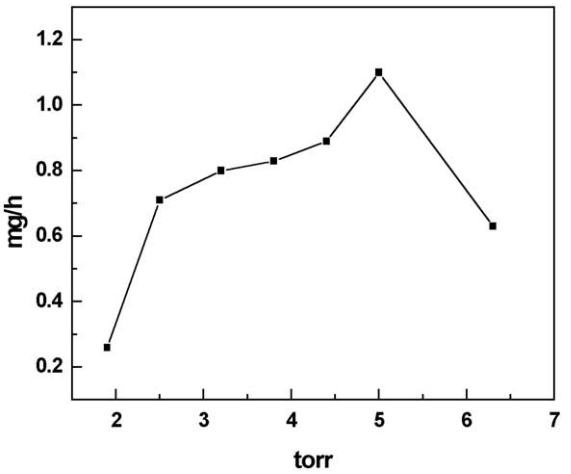

Fig. 2. The partial pressure of C_2H_2 vs. the yield of SWNT. The reaction temperature is 900 °C and the amount of sublimed ferrocene 3.74×10^{-5} mol/h.

imental data indicate that the rate-limiting step in our floating catalyst system is also the carbon supply to the catalysts, which was achieved by controlling the partial pressure of C_2H_2. Fig. 2 shows that at the controllable C_2H_2 partial pressures blow 5.0 Torr, the product mass were grown with the C_2H_2 partial pressure increased. However, when the C_2H_2 partial pressure excess 5.0 Torr, more thermal decomposed carbon was produced, which may make the catalyst particles inactive, and the SWNT production began to decrease.

Reaction temperature is also an important parameter to grow SWNT. The growth temperature of SWNTs from hydrocarbon were reported at 1100–1200 °C [8,9]. In our experiments, we found that SWNTs could be synthesized at a wide temperature range 750–1200 °C. Table 1 shows the yield of SWNTs vs. the reaction temperature. At a low temperature below 800 °C, we found that there is only small piece of the product covered on the collector. On the other hand, most of the products obtained at a temperature over 1100 °C are amorphous carbon, which looks gray and cannot peel them off the collector as sheets. The optimized temperatures for the growth of SWNTs are in the range 900–1000 °C, which is different from other reports that the highest SWNTs' yield

Table 1
The relation between production rate and reaction temperature

Temperature (°C)	Sublimed ferrocene $\times 10^{-5}$ (mol/h)	C_2H_2 Partial pressure (Torr)	Production rate (mg/h)
800	4.68	5.0	0.16
850	4.68	5.0	0.36
900	3.74	5.0	1.2
1000	4.68	5.0	1.1
1100	4.33	5.0	0.72

Table 2
The relation between the production rate and the amount of the sublimed ferrocene

Sublimed ferrocene $\times 10^{-5}$ (mol/h)	Temperature (°C)	C_2H_2 Partial tressure (Torr)	Production rate (mg/h)
11.29	900	6.3	4.4
8.55	900	6.3	3.0
5.91	900	6.3	1.52
3.74	900	6.3	1.2

were often achieved at their highest available temperature up to 1200 °C [10,11]. The reason that we did not obtain highest SWNTs' yield at the higher temperature may be ascribed to the rate-limiting step for growth of SWNT is changed due to the much quicker thermal decomposition of C_2H_2 at the higher temperature.

As shown above, the main products in our experiments are SWNTs and encapsulated iron particles. We found that the fraction of the encapsulated particles was controllable by adjusting the sublimed temperature of ferrocene. More ferrocene was introduced into the second furnace with the temperature of the first furnace increased, and the yield of the products was increased due to the mass fraction of the encapsulated particles increased (as listed in Table 2). The purer SWNT film can be obtained at the lower sublimed temperature.

The diameter distribution of the SWNTs was shown in Fig. 3, which were measured from HRTEM images. The average diameter we measured is 1.1 nm, and we did not observed SWNTs with diameter larger than 2 nm. However, many SWNTs as small a 0.7 nm in diameter, which is about the diameter of a C60 molecule, were found in our samples.

Raman spectroscopy was always employed to identify SWNTs. Fig. 4 shows micro-Raman spectra for an as-grown film, measured with a laser excitation wavelength of 514.5 nm. The Raman spectra consist of two main groups of peaks, which are typical for SWNTs and indicate SWNT existing in the film. The first group includes the peaks

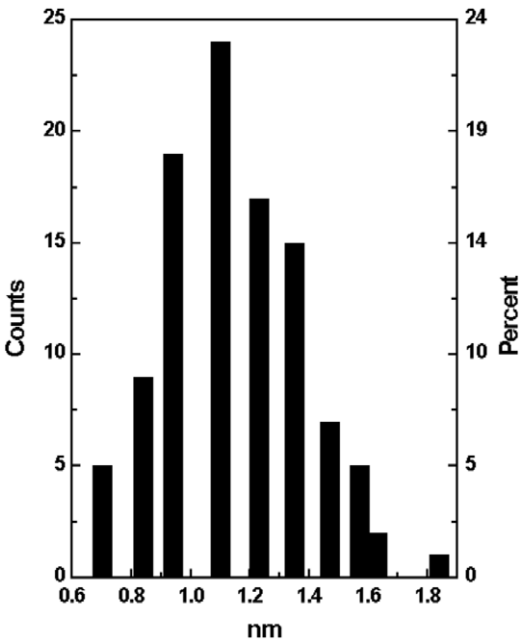

Fig. 3. The diameter distribution of the typical SWNT products.

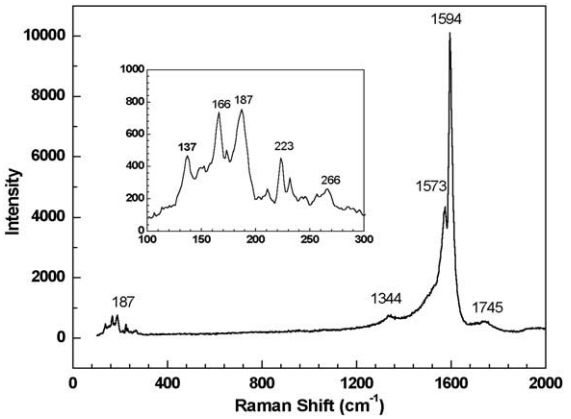

Fig. 4. The Raman spectrum of an as-grown film, obtained with an excitation wavelength of 514.5 nm. The inset shows details of the peak distribution in the low frequency range.

at 137, 166, 187, 223, 266 cm^{-1}, which consists of the radial breathing modes (RBM) whose frequencies depend on the SWNT's diameters (see inserted graph). According to the relation between diameter and frequency [14], the SWNT's diameter in the measured sample is 1.63, 0.84 nm for 137 and 266 cm^{-1}, respectively, which agrees with the HRTEM observation. The second peak group consists of the peaks at 1573 and 1594 cm^{-1}, which are related to the Eg2 graphite mode. The D-line around 1344 cm^{-1} indicates that the amount of amorphous carbon in the sample is very small.

4. Conclusion

We have demonstrated that clean SWNTs without amorphous carbon coating could be produced by thermally decomposing C_2H_2 in the floating catalyst system. The rate-limiting step for the growth of SWNTs must be controlled to be the supply of carbon to catalyst particles by adjusting the C_2H_2 partial pressure and the reaction temperature. Our experiments here may be helpful to produce SWNTs from other hydrocarbon gas by the floating catalyst method, which is a promising process for bulk SWNT production.

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References

[1] C. Dekker, Phys. Today 22 (1999).
[2] E. Hernandez, C. Goze, P. Bernier, A. Rubio, Appl. Phys. A 68 (1999) 287.
[3] T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. 243 (1995) 49.
[4] S. Iijima, T. Ichihashi, Nature (London) 364 (1993) 603.
[5] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. 260 (1996) 471.
[6] J. Kong, A.M. Cassell, H.J. Dai, Chem. Phys. Lett. 292 (1998) 567.
[7] J.H. Hafner, M.J. Bronikowski, B.R. Azamian, P. Nikolaev, A.G. Rinzler, D.T. Colbert, K.A. Smith, R.E. Smalley, Chem. Phys. Lett. 296 (1998) 195.
[8] H.M. Cheng, F. Li, X. Sun, S.D.M. Brown, M.A. Pimenta, A. Marucci, G. Dresselhaus, M.S. Dresselhaus, Chem. Phys. Lett. 289 (1998) 602.
[9] B.C. Satishkumar, A. Govindaraj, R. Sen, C.N.R. Rao, Chem. Phys. Lett. 293 (1998) 47.
[10] P. Nikolaev, M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert, K.A. Smith, R.E. Smalley, Chem. Phys. Lett. 313 (1999) 91.
[11] K. Bladh, L.K.L. Falk, F. Rohmund, Appl. Phys. A 70 (2000) 317.
[12] L. Ci, J. Wei, B. Wei, J. Liang, C. Xu, D. Wu, Carbon 39 (2001) 329.
[13] M. Endo, T. Koyama, Japanese patent 60-32818, 1985.
[14] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. B 57 (1998) 4145.