



# Large-scale synthesis of high-purity well-aligned carbon nanotubes using pyrolysis of iron(II) phthalocyanine and acetylene

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## Abstract

Well-aligned carbon nanotubes (CNTs) with high purity have been produced by pyrolysis of iron(II) phthalocyanine and acetylene at 800 °C. The synthesized CNTs have a length of 75 μm and diameters ranging from 20 to 60 nm. The CNTs have a bamboo-like structure and exhibit good crystallinity of graphite sheets. The growth rate of the CNTs was rapidly increased with adding C<sub>2</sub>H<sub>2</sub>. Our results demonstrate that the proposed growth method is suitable to large-scale synthesis of high-purity well-aligned CNTs on various substrates.

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## 1. Introduction

Since their first discovery in 1991 [1], carbon nanotubes (CNTs) have been the focus of numerous theoretical and experimental studies because of their unusual structure and outstanding properties. Due to their various properties, many applications such as flat panel displays [2], vehicles for large hydrogen storage [3], chemical sensors [4], and nanoscale electronic devices [5] have been proposed.

Various methods, including arc discharge [6], laser ablation [7], and chemical vapor deposition (CVD) [8], have been developed to synthesize CNTs. Among them, the CVD method seems to be the promising method because CNTs can be achieved with high yield, high purity, and good vertical alignment. The alignment of CNTs is very important for both fundamental studies and some potential applications. For example, it is well known that vertically aligned CNTs could be employed as good electron field emitters [9]. There were many reports for the synthesis of aligned CNTs using the CVD method [10–15]. Our group also reported the synthesis of vertically aligned CNTs by catalytic decomposition of acetylene [16]. Although much progress has been achieved for the

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synthesis of aligned CNTs, most methods require catalyst film deposition (Fe, Co, Ni or their mixture) followed by etching or thermal annealing, resulting in a complicated and expensive process. Moreover, conventional CVD methods were very difficult to realize aligned growth of CNTs on a three-dimensional morphological substrate. Sometimes, well-aligned CNTs on the three-dimensional substrates are desired to apply the CNTs to specific system.

Recently, there have been a few reports on the simple growth technique of CNTs by pyrolysis of iron(II) phthalocyanine (FePc) in a quartz reactor. In this method, the catalyst source and carbon source are supplied into the substrate or quartz tube at the same time, which is a very simple and cheap process. Moreover, the process can give well-aligned growth of CNTs on the various shaped substrates such as round substrate, cylindrical substrate, and cubic substrate. Some research groups reported that aligned CNTs could be synthesized by the pyrolysis of FePc in flowing Ar–H<sub>2</sub> mixture at a flow rate of below 100 sccm [17–19]. However, their results showed that the growth rate was very low and amorphous carbon appeared on the surface of CNTs. From the view of practical applications, large-scale synthesis of high-purity well-aligned CNTs based on floating catalyst technique is very desirable. Some research groups reported large-scale synthesis of high-purity well-aligned CNTs using C<sub>2</sub>H<sub>2</sub>–Fe(CO)<sub>5</sub> system [20,21]. Their results showed that acetylene was favorable to synthesize high-purity long CNTs. More recently, we have studied synthesis of high-purity well-aligned CNTs using pyrolysis of iron(II) phthalocyanine (FePc) in a quartz reactor. In order to obtain high growth rate of CNTs, we adapted acetylene gas as a carbon-containing source besides iron(II) phthalocyanine.

In this Letter, we demonstrate synthesis of high-purity well-aligned CNTs by catalytic decomposition of FePc and acetylene. Adding C<sub>2</sub>H<sub>2</sub> to FePc rapidly increases the growth rate of the CNTs. In our method, no preprocessing of substrate is needed and the produced aligned CNTs have high purity. The produced CNTs have a bamboo-like structure and exhibit good crystallinity of graphite sheets.

## 2. Experimental

The pyrolysis set-up consists of a stainless steel gas flow line and a two-stage furnace system filled with a quartz tube. The procedure of FePc catalyzed pyrolysis of acetylene was as follows. ~100 mg of FePc was taken in a quartz boat and placed inside the first furnace. A quartz substrate was put at the center area of the second furnace. Typically, the second furnace was first heated to 800 °C, and then the first furnace was heated to 600 °C. Subsequently, a mixture of C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub> and Ar gases passed through the quartz tube. The flow rates of C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub> and Ar were 10, 30 and 1000 sccm, respectively. The gas mixture carried the Fe and carbon sources into the second furnace maintained at 800 °C, which were generated from FePc at the first furnace. The synthesis of CNTs occurred in the second furnace. After 15 min reaction, the quartz tube was cooled to room temperature in Ar atmosphere.

The morphology of the as-grown samples was first analyzed by scanning electron microscopy (SEM) (Hitachi, S-4700). The structure and crystallinity of the as-grown samples were investigated by transmission electron microscopy (TEM) (JEOL, JEM-3011, 300 kV). The overall crystallinity of CNTs was evaluated by Raman analysis (Bruker, RFS-100/S), using the 1064 nm excitation line from Nd-YAG laser.

## 3. Results and discussion

As a result of the growth of carbon filaments, a layer of dark film fully covers the surface of a quartz substrate. The layer of dark film was scraped from the quartz substrate by a razor for SEM analysis. SEM observation (Fig. 1a) of the resulting dark film indicates that the as-grown black film consists of large amounts of vertically aligned carbon filaments with identical length. To estimate a length of these carbon filaments, a SEM image of these carbon filaments is taken at higher magnification. Fig. 1b shows the medium magnification SEM image of the as-synthesized carbon filaments. It shows that the aligned carbon filaments obtained are densely packed, and have an

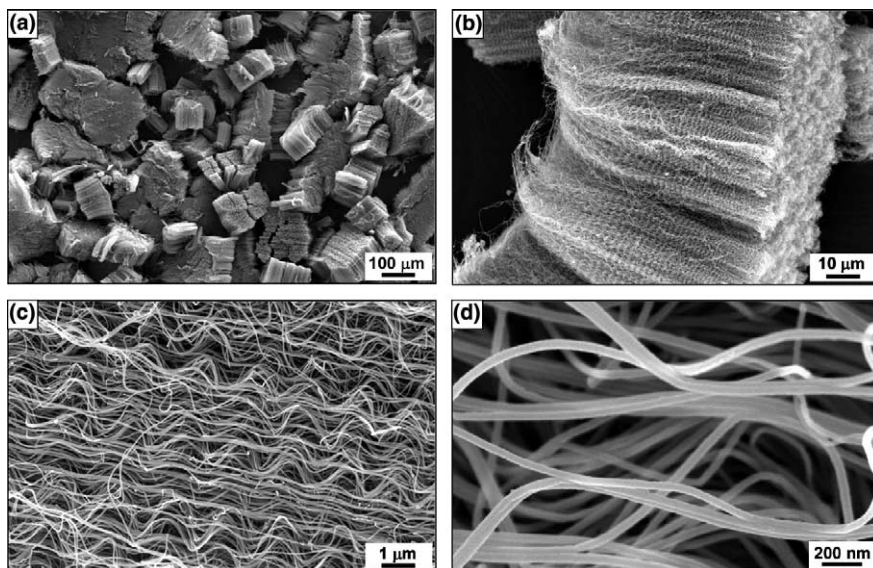


Fig. 1. SEM images of the as-synthesized carbon filaments. (a) and (b) The low magnification SEM image showing large amounts of aligned carbon filaments with high packing density, (c) the medium magnification SEM image of aligned carbon filaments, (d) the high magnification SEM image showing carbon filaments with smooth and clean surface.

average length of about 75  $\mu\text{m}$  for the reaction time of 15 min, indicating the aligned carbon filaments in our method have a higher growth rate of 5  $\mu\text{m}/\text{min}$  compared with most previous results reported in the literatures [17,18]. This fact demonstrates that the addition of acetylene significantly promote the growth of carbon filaments. In our experiment, without acetylene feeding into the reactor, we could confirm that produced carbon filaments had a lower growth rate of 0.67  $\mu\text{m}/\text{min}$  at the same process condition. Previous studies also indicated that acetylene CVD was effective method to realize large-scale production of long CNTs using  $\text{Fe}(\text{C}_5\text{H}_5)_2$  and  $\text{Fe}(\text{CO})_5$  as floating catalyst precursor [20,21]. From Fig. 1c, one can observe that these filaments are well aligned along the one direction although each single nanotube has a curly shape looking like a ripple. It has been known that the pores on the substrate can control the alignment of CNTs [10]. But in our method, without the presence of the pores, the perpendicular arrangement of CNTs can be obtained. We consider that in our experiment, the carbon filaments are forced to grow perpendicular to the substrate due to the presence of densely packed nucleation sites [16]. Fig. 1d shows the high mag-

nification SEM image of the as-synthesized carbon filaments. It shows that the carbon filaments have a smooth surface and a fairly uniform diameter. There is no trace of carbonaceous particles to be detected in our samples. This result demonstrates that the as-synthesized carbon filaments have very high purity. It was well known that the passage of gas with high flow rate could avoid the amorphous carbon coating on CNTs [22].

From Fig. 1d, the diameter of carbon filaments ranges from 20 to 60 nm. In addition, we note that the aligned carbon filaments can grow on all of heating zone in the second furnace besides the quartz substrate, indicating large-scale production of aligned carbon filaments could be realized using this method.

To study the microstructure of the synthesized carbon filaments, TEM observation was performed. Fig. 2a shows the low magnification TEM image of the as-grown carbon filaments. It clearly shows that the prepared carbon filaments indicate multiwalled carbon nanotubes (MWNTs) with centrally hollow inside, not solid fibers. The produced MWNTs have a uniform diameter, and the compartment layers of nanotubes indicate a bamboo structure [23].

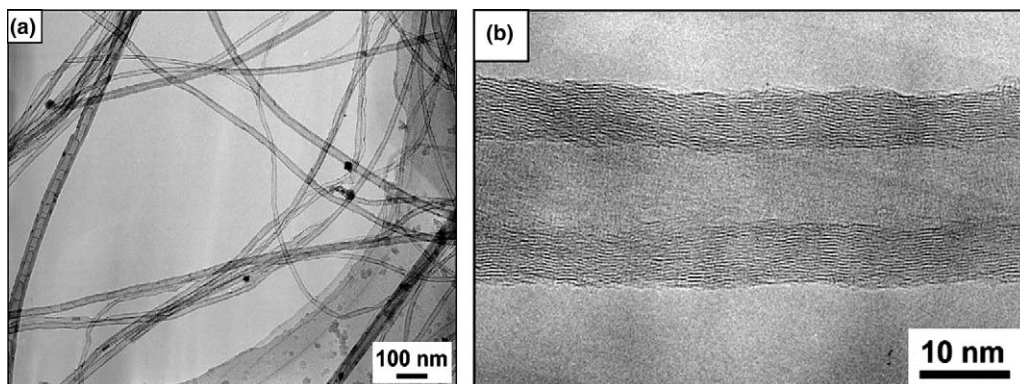


Fig. 2. TEM images of the as-synthesized CNTs. (a) The low magnification TEM image indicating MWNTs with compartment layers, (b) the HRTEM image of a typical CNT showing fairly good crystallinity of graphite sheets and little amorphous carbon covering on the surface.

Especially, the HRTEM image of a typical CNT shows little amorphous carbon materials covering the periphery of the CNTs as shown in Fig. 2b. This indicates that the as-synthesized CNTs are of high purity. The lattice fringes of the each side of the CNT represent individual cylindrical graphitic layers. The lattice fringes are well resolved, which indicates the synthesized CNTs have fairly good crystallinity of graphite sheets even though the graphite sheets of CNTs have a waving structure over a short range, revealing that the produced CNTs have some defects within the graphite sheets.

Raman spectroscopy was used to further characterize overall information of the structure and crystallinity of the synthesized CNTs. Raman spectrum of the produced CNTs shows two main frequency peaks as shown in Fig. 3. The clear G band at  $1597.2\text{ cm}^{-1}$  identifies the MWNTs, and the D band at  $1284.4\text{ cm}^{-1}$  indicates the level of the disorder carbon. High peak intensity ratio of  $I(G)/I(D)$  indicates that the as-grown CNTs have good crystallinity of graphite sheets. In this work, the result of Raman analysis is in agreement with the HRTEM observation.

In summary, we demonstrated the synthesis of high-purity well-aligned CNTs by pyrolysis of FePc and acetylene. Adding  $\text{C}_2\text{H}_2$  rapidly increased the growth rate of the produced CNTs. The synthesized CNTs had a bamboo-like structure and fairly good crystallinity of graphite sheets. We suggest that our growth method is very simple and efficient to realize

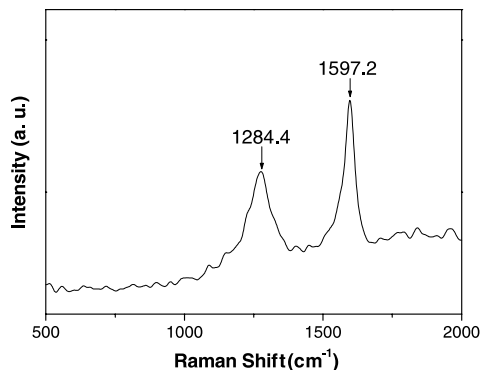


Fig. 3. Raman spectrum of the as-synthesized aligned MWNTs.

large-scale synthesis of high-purity well-aligned CNTs on various shaped substrates.

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### References

- [1] S. Iijima, Nature 354 (1991) 56.
- [2] W.B. Choi, Y.W. Jin, H.Y. Kim, S.J. Lee, M.J. Yun, J.H. Kang, Y.S. Choi, N.S. Park, N.S. Lee, J.M. Kim, Appl. Phys. Lett. 78 (2001) 1547.

- [3] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, *Science* 286 (1999) 1127.
- [4] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, *Science* 287 (2000) 622.
- [5] P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, *Science* 278 (1997) 100.
- [6] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, *Nature* 363 (1993) 605.
- [7] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fischer, R.E. Smalley, *Science* 273 (1996) 483.
- [8] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanov, J.B. Nagy, *Science* 265 (1994) 635.
- [9] W.A. de Heer, A. Chatelain, D. Ugarte, *Science* 270 (1995) 1179.
- [10] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, *Science* 274 (1996) 1701.
- [11] M. Terrones, N. Grobert, J. Olivares, J.P. Zhang, H. Terrones, K. Kordatos, W.K. Hsu, J.P. Hare, P.D. Townsend, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, *Nature* 388 (1997) 52.
- [12] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, *Science* 282 (1998) 1105.
- [13] C.N.R. Rao, R. Sen, B.C. Satishkumar, A. Govindaraj, *Comm. Commun.* (1998) 1525.
- [14] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, *Science* 283 (1999) 512.
- [15] M. Sveningsson, R.-E. Morjan, O.A. Nerushev, Y. Sato, J. Bäckström, E.E.B. Campbell, F. Rohmund, *Appl. Phys. A* 73 (2001) 409.
- [16] C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, Y.H. Lee, W.B. Choi, N.S. Lee, G.S. Park, J.M. Kim, *Chem. Phys. Lett.* 312 (1999) 461.
- [17] S. Huang, L. Dai, A.W.H. Mau, *J. Phys. Chem. B* 103 (1999) 4223.
- [18] D.C. Li, L. Dai, S. Huang, A.W.H. Mau, Z.L. Wang, *Chem. Phys. Lett.* 316 (2000) 349.
- [19] S. Huang, L. Dai, *J. Phys. Chem. B* 106 (2002) 3543.
- [20] F. Rohmund, L.K.L. Falk, E.E.B. Campbell, *Chem. Phys. Lett.* 328 (2000) 369.
- [21] C.J. Lee, S.C. Lyu, H.W. Kim, C.Y. Park, C.W. Yang, *Chem. Phys. Lett.* 359 (2002) 109.
- [22] J. Kong, H.T. Soh, A.M. Cassell, C.F. Quate, H. Dai, *Nature* 395 (1998) 878.
- [23] C.J. Lee, J. Park, *Appl. Phys. Lett.* 77 (2000) 3397.