



The effect of hydrogen on the formation of nitrogen-doped carbon nanotubes via catalytic pyrolysis of acetonitrile [☆]

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Abstract

Nitrogen-doped carbon nanotubes are synthesized by the pyrolysis of CH₃CN with/without H₂ over MgO supported Fe catalysts at 850 °C in argon flow. In both cases nitrogen is introduced to dope the product with quite different amount. TG analysis, Raman spectroscopy, SEM and TEM results showed that the introduction of H₂ is favorable for the formation of multi-walled nanotubes (MWNTs) containing less nitrogen.

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1. Introduction

Carbon nanotubes are starting materials that have attracted much research interest. They are especially intriguing as electronic devices, owing to their unique properties [1–3]. Doping carbon nanotubes with different elements is a promising method to modify the electronic structure of the nanotubes. Boron-doped carbon nanotube was reported to be uniformly metallic via theoretical calculation [4]. On the other hand, nitrogen-doped

carbon nanotubes were found to be either metallic or narrow energy gap semiconductors [5]. Various routes have been applied to synthesize heteroatom-doped nanotubes including arc discharge [6], laser ablation [7] and substitution reaction [8]. Direct pyrolysis of nitrogen/boron-containing carbon feedstock over catalyst processes the advantages of simple apparatus and availability for scaling up. Moreover, its ability to deposit nanotube-based structures on surface is favored for the fabrication of field emission devices and nano-electronic components. From the reasons mentioned above, this method has been given much attention. For example, Terrones [9] pyrolyzed CH₃CN:BCl₃ over Co to form B–C–N nanotubes, Rahul [10] synthesized B–C–N, C–N and B–N nanotubes by the pyrolysis of appropriate

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precursors. Here, we report the growth of C–N nanotubes by pyrolyzing CH_3CN over MgO supported Fe catalysts. It was found that nitrogen could enter the product with identifiable amount (0.9–2.6 wt%), forming bamboo-shaped tube structures. Besides, H_2 would favor the formation of multi-walled nanotubes (MWNTS) containing less nitrogen.

2. Experimental

2.1. Synthesis of carbon–nitrogen nanotubes

The nanotubes were synthesized by the pyrolysis of acetonitrile over MgO supported Fe catalyst, the preparation of which was mentioned in a previous work [11]. Briefly, 20 ml, 10 mg/ml $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution was mixed with 2 g $\text{Mg}_2(\text{OH})_2\text{CO}_3$, followed by sonication and drying to form a yellow powder.

The growth reaction was set in a tube furnace. Typically, 0.3 g catalyst was put in a ceramic boat and set in the middle of the furnace. It was then heated to 850 °C in Ar flow at 300 sccm. Acetonitrile was carried into the tube by Ar flow and hydrogen was fed into the reactor at 100 sccm, as required. The growth period was set as 30 min, after which the furnace was cooled to room temperature. To gain pure nanotube material, the as-prepared material was sonicated first in 4 N HCl and then in water to remove the catalyst.

2.2. Characterization

Raman spectra were recorded on a Renishaw 1000 Raman system in ambient atmosphere, using 50 mW He–Ne laser ($\lambda = 632.8$ nm) and a CCD detector. The elements nitrogen, carbon and hydrogen were analyzed for purified samples by element analysis on an Elementar Vario EL instrument. TGA was conducted on a Universal V25H TA instrument. The samples were heated at a rate of 10 °C/min to 800 °C in airflow. SEM was conducted on a JEOL JBM-6301F instrument at 25 kV. For a SEM characterization, the samples were dispersed in 1,2-dichlorobenzene and dripped on Si wafer. TEM was performed on a Hitachi

H810 at 200 kV. The samples for TEM characterization were dispersed in deionized water and dripped on Cu grid.

3. Results and discussions

Element analysis was first conducted to examine if nitrogen has really entered the tube product. It can be found that for the samples prepared with/without H_2 , nitrogen takes up 0.9% and 2.6% (weight ratio), respectively, while the weight ratios of carbon are both around 93%. Nitrogen is then inferred to be doped into the tube product by the pyrolysis method.

However, the ratio of nitrogen is quite different, i.e., the introduction of H_2 can reduce the nitrogen amount significantly. We tentatively attribute such a phenomenon to the formation of HCN in gas phase at elevated temperature. At 850 °C, acetonitrile will break into CN and CH_3 free radicals, which are the active fragments for the formation of nitrogen-doped nanotubes. The introduction of H_2 might establish such a balance



Since HCN is more stable than CH_3CN in gas phase, it would prevent nitrogen from doping into the nanotubes. Lower amount of nitrogen is then observed in the sample prepared with H_2 .

Figs. 1a and b show the SEM images of the purified samples prepared with/without H_2 , respectively. SEM showed that most of the nanotubes we prepared were multi-walled, yet in the sample prepared without hydrogen, there also bear some single-walled nanotubes. Furthermore, in both cases very little amorphous carbon could be found, indicating high purity of the product. Highly resolution TEM (shown in Fig. 2) gives the fine structure of the nanotubes. It is found that most of the tubes are bamboo-shaped with integral walls. It is believed that such bamboo-shaped tube structures are generated via base-growth mechanism [12]. In our experiment, closed tips without catalyst nanoparticles can be observed, which is consistent with such a mechanism [12].

Fig. 3 shows the Raman spectra of the samples. For the sample prepared without hydrogen,

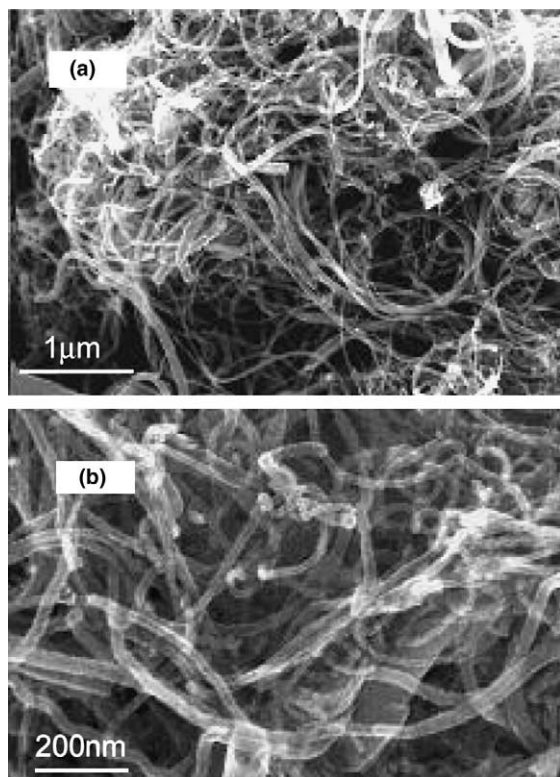


Fig. 1. SEM images of the samples prepared with hydrogen (a) and without hydrogen (b).

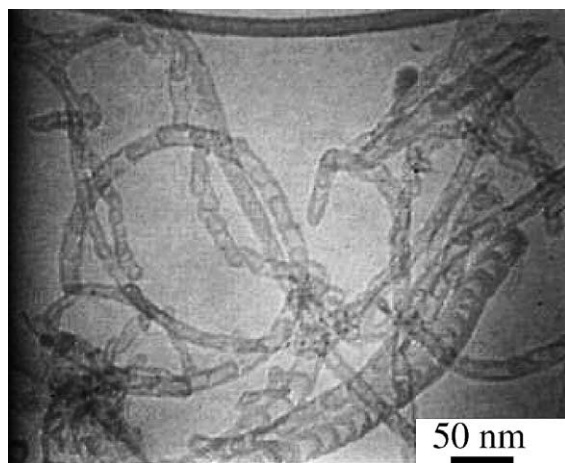


Fig. 2. HRTEM image of the MWNTs bearing bamboo-shaped structure.

Raman characterization gives a spectrum similar to that of single-walled nanotubes (SWNTs), in which RBM (radial breath mode) peaks can be observed.

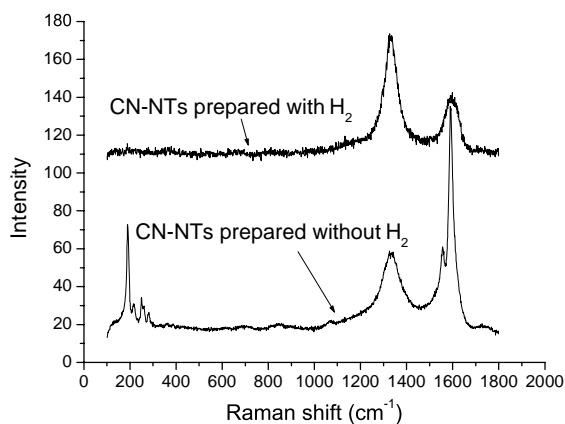


Fig. 3. Raman spectra of the samples prepared with/without hydrogen.

Still, there are some differences. First, compared with the nanotube materials prepared with CH₄, the D-line centered at 1320 cm⁻¹ is much higher. This is understandable since the sample we prepared with acetonitrile was a mixture of single- and multi-walled nanotubes, while in the case of CH₄ most of the product was single-walled. Second, there is an apparent shoulder peak at 1556 cm⁻¹, which is correspondent with metallic tubes [13]. We attribute the appearance of this shoulder peak to the effect of doped nitrogen atoms into the tube structure. For the samples prepared with hydrogen, no RBM peaks can be observed, indicating no single-walled nanotubes in the product, which is in accordance with the SEM result.

Thermal gravity analysis is an effective way to determine the thermal stability of the samples. Besides, analyzing weight loss peaks centered at different temperature can give information on the forms of carbon deposits. In our experiment, for the sample prepared without hydrogen, the derivative of weight loss gives out two peaks, centered at 486 and 579 °C, respectively (Fig. 4a). While for the sample prepared with hydrogen, only one peak centered at 618 °C was observed (Fig. 4b). It is in accordance with SEM and TEM results. In the sample prepared without hydrogen, the weight loss peak at 486 °C can be attributed to the single-walled nanotubes in the sample, while the weight loss at elevated temperature was attributed to the multi-walled nanotubes. This is probably due to

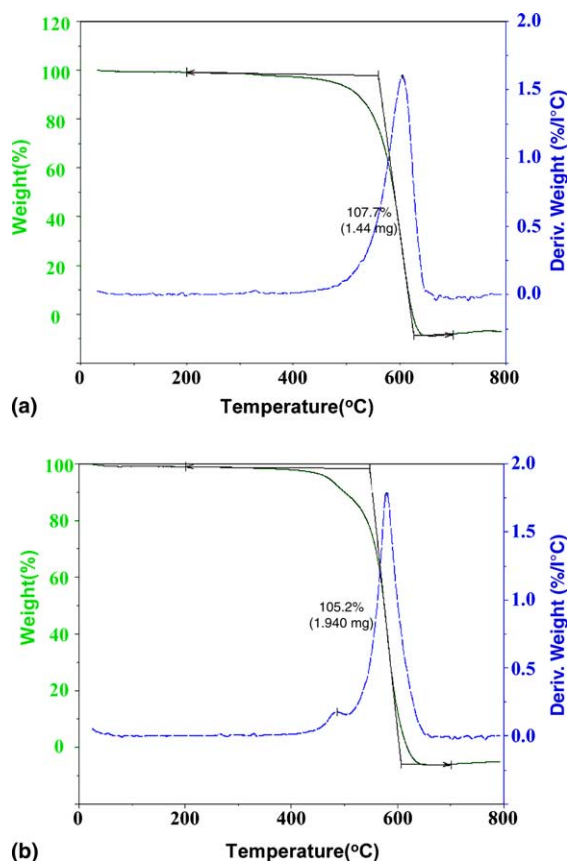


Fig. 4. TG analysis of the samples prepared with H₂ (a) and without H₂ (b).

the fact that the strong interactions between the walls of the MWNTs stabilized the structure and thus makes them thermally more inert than the SWNTs. For the samples prepared with hydrogen, there is only one weight loss peak centered at 618 °C. Since there are no SWNTs observed in SEM and TEM images, this peak is correspondent with the MWNTs in the sample. Moreover, the peak temperature was higher than that of the sample prepared without hydrogen, being attributable to the smaller proportion in which nitrogen entered the tube structure.

The absence of SWNTs in the sample prepared with H₂ can be explained in two aspects. First, H₂ is more apt to cause the fusion of Fe catalyst particles, since it can reduce Fe oxide into Fe more readily. These larger particles would then favor the formation of MWNTs rather than SWNTs. Second, C

atoms are believed to be critical for the nucleation of SWNTs [14]. The break-up of CH₃CN into free C atoms would give out H₂ at the same time. Thus the existence of H₂ in the reaction system would hinder such a process and further prevent the formation of SWNTs. It has to be admitted that such an explanation is based much on hypothesis, because of the little knowledge that has been gained about the growth mechanism of carbon nanotubes. However, introducing H₂ is probably an effective method in controlling the doping amount of nitrogen, which is of great interest in studying the electronic properties of such doped nanotubes. It would also shed light on understanding the growth process of heteroatom nanotubes.

In summary, we have successfully prepared nitrogen-doped carbon nanotubes by catalytic pyrolysis of acetonitrile over MgO supported Fe catalyst. It is found that the nanotubes are mostly multi-walled and bamboo-shaped. The introduction of H₂ is found to have great impact on the growth process, which can reduce the nitrogen amount in the tube products and hinder the formation of SWNTs.

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References

- [1] R. Satio, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
- [2] J.W.G. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker, *Nature* 391 (1998) 59.
- [3] C.T. White, T.N. Todorov, *Nature* 393 (1998) 240.
- [4] D.L. Carrol, Ph. Redlich, X. Blase, J.C. Charlier, S.P.M. Ajayan, S. Roth, M. Ruhle, *Phys. Rev. Lett.* 81 (1998) 2332.
- [5] Y. Huang, J. Gao, R. Liu, *Synth. Met.* 113 (2000) 251.
- [6] Z. Weng-Sieh, K. Cherrey, N.G. Chopra, X. Blase, Y. Miyamoto, A. Rubio, M.L. Cohen, S.G. Louie, A. Zettl, R. Gronsky, *Phys. Rev. B* 51 (1995) 11229.
- [7] Y. Zhang, H. Gu, K. Suenaga, S. Iijima, *Chem. Phys. Lett.* 279 (1997) 264.

- [8] D. Golberg, Y. Bando, W. Han, K. Kurashima, T. Sato, *Chem. Phys. Lett.* 308 (1999) 337.
- [9] M. Terrones, N. Grobert, J.P. Zhang, H. Terrones, J. Olivares, W.K. Hsu, J.P. Hare, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, *Chem. Phys. Lett.* 285 (1998) 299.
- [10] R. Sen, B.C. Satishkumar, A. Govindaraj, K.R. Harikumar, Garge Raina, Jin-Ping Zhang, A.K. Cheetham, C.N.R. Rao, *Chem. Phys. Lett.* 287 (1998) 671.
- [11] Q.W. Li, H. Yan, Y. Cheng, J. Zhang, Z.F. Liu, *J. Chem. Mater.* 12 (2002) 1179.
- [12] C.J. Lee, J.H. Park, J. Park, *Chem. Phys. Lett.* 323 (2000) 560.
- [13] M.A. Pimenta, A. Marucci, D.M. Brown, M.J. Matthews, A.M. Rao, P.C. Eklund, R.E. Smalley, G. Dresselhaus, M.S. Dresselhaus, *J. Mater. Res.* 13 (1998) 2396.
- [14] P.M. Ajayan, *Chem. Rev.* 99 (1999) 1787.