ELSEVIER

CVD growth of carbon nanotubes directly on nickel substrate

Chunsheng Du, Ning Pan*

Nanomaterials in the Environment, Agriculture, and Technology (NEAT), University of California, Davis, CA 95616, United States

Abstract

Chemical vapor deposition (CVD) growth of carbon nanotubes directly on nickel substrates was carried out at different temperatures. Effects of temperature on the growth of carbon nanotubes were investigated, and the nucleation and growth mechanism of carbon nanotubes at different temperature ranges were also discussed. Based on the growth mechanism of nanotubes, small amounts of Fe nanoparticles were deposited on the nickel substrate to introduce more nucleation sites at elevated temperature, and the density of nanotubes on the surface of the substrate was greatly improved.
© 2005 Elsevier B.V. All rights reserved.

Keywords: CVD growth; Carbon nanotubes; Nickel substrates

1. Introduction

Carbon nanotubes have been the focus of intense interest since their discovery [1] and are shown to have superb properties because of their unique morphological characteristics. Potential technical applications in the areas of molecular electronic devices [2–6], nanocomposites [7–10], and electron field emission [11–15] have been proposed or explored. In addition, because of the nature of their structure and chemical bonding, carbon nanotubes are also interesting 1D host materials for lithium intercalation, and several groups have already investigated the application of carbon nanotubes as the anode for lithium batteries [16–20].

In most cases, the production of nanotube emitters is based on catalytic decomposition of carbon-bearing gases on nanoparticles dispersed on a support. Obviously, such approach involves tedious and time-consuming preparation of supported catalyst nanoparticles. Thus it is particularly attractive to grow carbon nanotubes directly on the surface of catalytically active transition metals such as

nickel and cobalt. At the same time, the growth of carbon nanotubes directly on metallic substrates also resolves the problem of adhesion of nanotubes layers and fulfills the requirement for substrate electroconductivity. Such a one-step method is also advantageous in the electrode preparation for lithium battery application because it avoids laborious procedures for incorporating materials into electrode structure, including the use of binders and/or other adhesives, which may occlude the surface of the nanotubes.

There are several reports on the preparation and characterization of carbon nanotubes on metallic substrates [21–23]. There are also reports on the discovery of carbon nanowires formed on nickel substrates by Fujita et al. [24], and formation of graphite layers during carbon nanotubes growth on Fe–Ni alloy film by Baek et al. [25]. However, either two-step growth process [23] or extreme deposition conditions such as high pressure [21,22] were required in the processes of nanotube growth. Here we report a simple method to directly grow carbon nanotubes on nickel substrate under normal pressure. Furthermore, the effects of temperature on the growth of carbon nanotubes and the microstructure proof of nanotubes growth mechanism on metallic substrate were discussed.

---

2. Experimental

2.1. Growth of the carbon nanotubes

400×400 mesh nickel grids (purity: 99.9%; Ted Pella, Inc.) were used as the catalytic active substrates. The nickel grids were degreased ultrasonically in acetone and dried at room temperature before being loaded into a quartz tube and heated in a high-temperature tube furnace to a desired temperature under a H_2 flow (flow rate: 200 sccm). Upon reaching the desired temperature, ethylene was introduced at a flow rate of 50 sccm, while the flow rate of H_2 was adjusted to 800 sccm. After a period time of growth (2 min, unless otherwise stated), ethylene was shut off and the whole system was cooled down to room temperature under hydrogen protection. CVD growth was carried out at 650 °C, 700 °C, 750 °C, and 850 °C, respectively.

2.2. Microstructure characterization of the carbon nanotubes

The nickel substrates were directly examined after CVD growth by scanning electron microscopy (SEM) (Philips XL30) to investigate the feature of the substrate and the morphology of the carbon nanotubes on the surface. The structure and diameter of the carbon nanotubes were further characterized by transmission electron microscopy (TEM) (Philips CM 120). Specimens for TEM analysis were prepared by sonicating the nickel substrates in a small amount of ethanol for 5 min after CVD growth followed by depositing several drops of the resulted ethanol suspension onto copper gird.

3. Results and discussion

3.1. Effect of temperature on growth of the carbon nanotubes

Fig. 1 illustrates the typical surface features of nickel substrates before and after CVD growth at 650 °C for 2 min. As shown in Fig. 1(a), the surface nickel substrate prior to the CVD growth is relatively smooth, and the nickel grains and grain boundaries can be clearly seen. After CVD growth, we can see that many carbon nanotubes were grown on the substrate although the growth time was only 2 min (as shown in Fig. 1(b)), which means that nucleation and growth of the carbon nanotubes were really fast at 650 °C under this chosen condition. In addition, the surface of the substrate appears to be totally covered by the carbon deposition, for the nickel grains and grain boundaries can no longer be detected in this sample even at a higher magnification (Fig. 1(c)). It can also be seen that there are cracks in the carbon layer and some nodular structures on the substrate, as shown in Fig. 1(b). We speculate that the carbon deposition was much faster at certain sites (where the nodule formed) so as to cause some internal stress as a result of the different thickness of the carbon layer on the substrate.

Shown in Fig. 1(d) are TEM images of the nanotubes grown on the substrate. They illustrate the uniformity of the
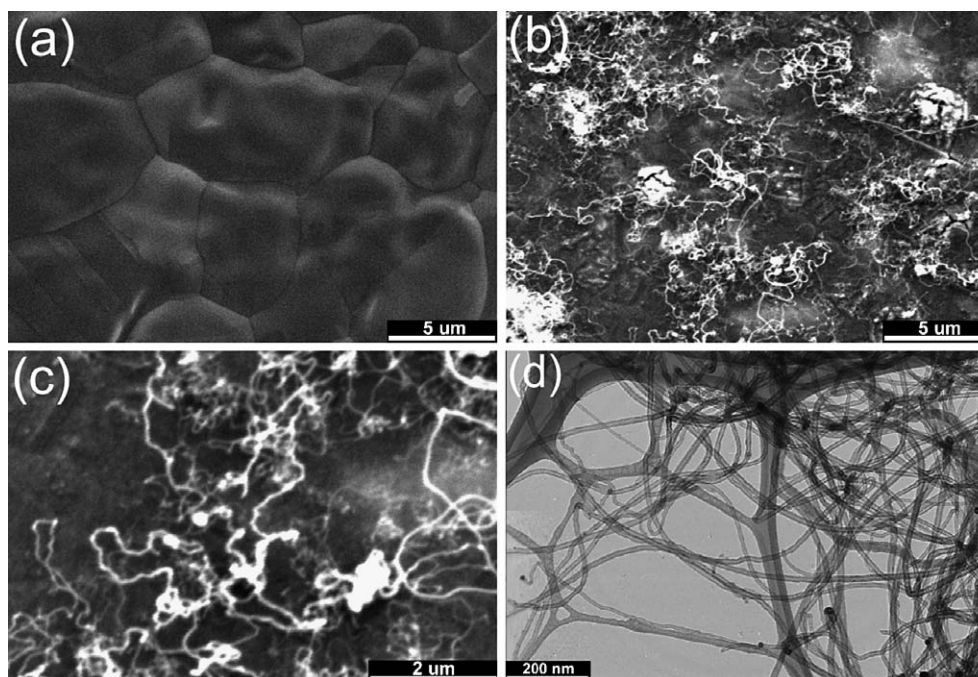

Fig. 1. SEM images of typical features of nickel substrates before and after CVD growth at 650 °C: (a) before CVD growth; (b) and (c) after CVD growth (lower and higher magnification); and (d) TEM image of the carbon nanotubes.
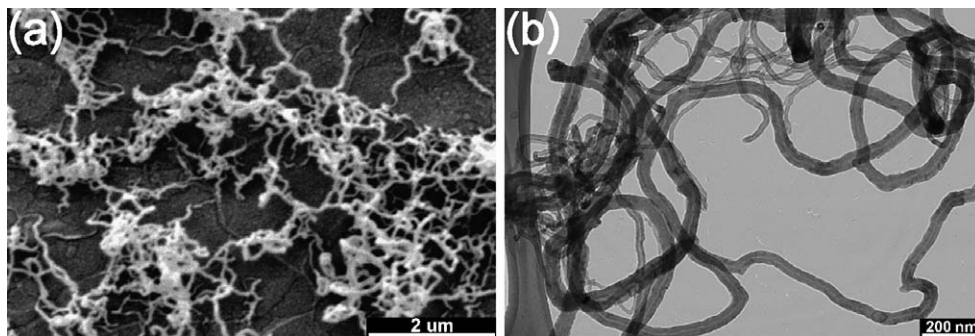
Fig. 2. SEM and TEM images of carbon nanotubes grown on nickel substrate at 700 °C.

diameter (about 25 nm) and the hollow-core structure of the carbon nanotubes. Although the nanotubes had experienced vigorous ultrasonicating in order to be removed from the nickel substrate during the preparation of the specimens for TEM analysis, some of the catalyst nanoparticles can still be observed at the end of some nanotubes as dark areas, which suggests that the nickel nanoparticles were formed prior to the growth of carbon nanotubes.

Fig. 2(a) shows the SEM images of the nanotubes grown at 700 °C. It can be seen that surface of the nickel substrate is relatively smooth comparing to the 650 °C sample, and there is no trace of nodular morphology. However, TEM image in Fig. 2(b) shows that the tubes are less uniform; the tube diameters show binary distribution, about 25 nm for the smaller ones and about 60 nm for the larger ones. The fact that surface of the nickel substrate of 700 °C sample is relatively smooth after CVD growth indicates that there is less carbon deposition on the nickel surface during CVD growth because the decomposition of ethylene is not favorable at elevated temperature due to the exothermicity of the reaction: $C_2H_4 \rightarrow 2C + 2H_2$.

This was further proved in the samples grown at 750 °C and 850 °C. Shown in Fig. 3(a) are the SEM images of the 750 °C sample for 2 min. The feature of the nickel substrate including the grain boundaries can be clearly seen in the SEM images, and we can also see that some of the carbons were actually initiated at the grain boundaries or at some defects (such as pits) in the substrate. When the CVD growth was carried out at 850 °C, no carbon nanotubes could be detected after 2 min growth on the nickel substrate

under SEM. However, very short carbon nanotubes were found in the sample grown for 15 min at this temperature, as shown in Fig. 3(b). It can be seen that these short nanotubes initiated only at the grain boundaries (indicated by arrows). We also found some carbon nanowires formed at this temperature, which will be discussed elsewhere [26]. This very long nucleation time and/or low growth rate of tubes in the 850 °C sample indicates that the demanding or supplying rate of carbon must be very low. Since the diffusion rate of carbon in nickel substrate is higher at elevated temperature, this low supply rate of carbon should be attributed to the fact that the decomposition of ethylene was somewhat depressed at higher temperature. Another possibility is the increase in the amount of dissolved carbon in the metal at elevated temperature.

3.2. Increasing the nanotubes density on the substrates

Before the tube growth can start, formation of Ni nanoparticles has to take place. TEM analysis in Fig. 1(d) did show the existence of nickel nanoparticles at the end of carbon nanotubes. This could reveal that fragmentation of the nickel metal is a necessity to form catalytically active nickel nanoparticles. It was in fact suggested that saturation of nickel subsurface layer by carbon, and formation of intermediate unstable phase and its further decay would result in the fragmentation of nickel and formation of nickel nanoparticles [22,27]. In our study, we postulate that this is also true for 650 °C and 700 °C samples in our study. However, at higher temperature (750 °C and 850 °C),
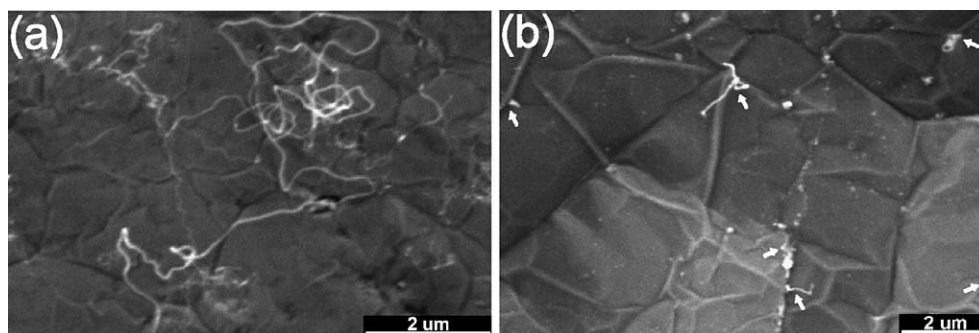

Fig. 3. SEM images showing the surfaces of nickel substrates after CVD growth at (a) 750 °C for 2 min and (b) 850 °C for 15 min.
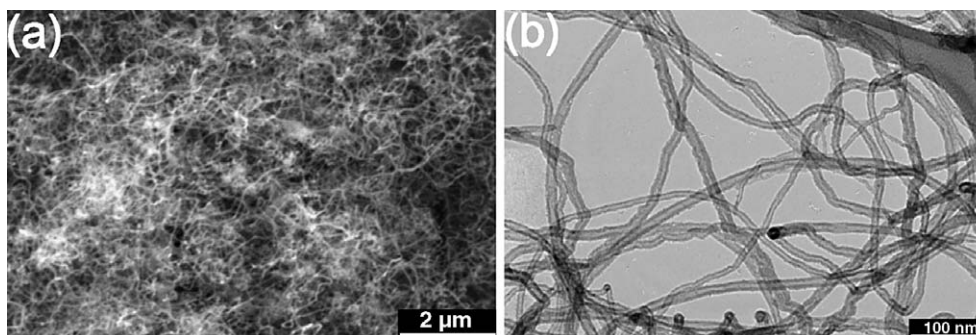
Fig. 4. SEM and TEM images of carbon nanotubes grown at 750 °C on nickel substrate with Fe nanoparticle deposition.

because of the depression of ethylene decomposition and possible increase of the dissolubility of carbon in nickel, the condition to form intermediate phase cannot be satisfied. But the grain boundaries may serve as more effective sites for the formation of such intermediate phase since grain boundaries are always a fast path for mass transportation. In addition, those areas where there are surface defects such as step edges, point defects, dislocations, or pits may also serve as that kind of site for intermediate phase formation. The SEM analysis clearly shows that the carbon nanotubes were initiated from grain boundaries (Fig. 3(b)) or other structure defects (Fig. 3(a)). This was also proved by the fact that the density of carbon nanotubes almost did not change when CVD growth time was prolonged to 15 min for the 750 °C sample (image not shown) because the density of defects in the nickel substrate only depends on the perfection of the substrate.

Therefore, the number of nucleation sites has to be increased in order to increase the density of nanotubes grown on the substrate. One way to do that is to deposit small amounts of Fe nanoparticles on nickel substrate to form alloy particles at elevated temperature. In this experiment, predetermined amount of $Fe(NO_3)_3$ solution (concentration was 5 mM, and ethanol was used as solvent) was deposited on nickel grid and dried at room temperature followed by CVD growth at 750 °C for 15 min. As shown in Fig. 4(a), the density of nanotubes on the substrate was greatly improved. TEM image in Fig. 4(b) shows that the nanotubes are relatively uniform. A control experiment was carried out, in which the nickel substrate was heated in the furnace to 750 °C without introducing ethylene, and no Fe nanoparticles were detected on the nickel substrate under SEM after the heat treatment, indicating that all the Fe nanoparticles formed alloys before nanotube growth started.

4. Conclusion

We have directly grown carbon nanotubes on nickel substrates using chemical vapor deposition method. It was found that growth temperature has a strong effect on the carbon deposition and growth of carbon nanotubes because of the change of nucleation and growth mechanism of carbon nanotubes at different temperature ranges. At lower temperature, nickel nanoparticles formed from fragmentation of nickel are the nucleation sites for carbon nanotubes; however, at higher temperature, carbon nanotubes only nucleate from grain boundaries and defective sites. Based on the growth mechanism of nanotubes at higher temperature, small amounts of Fe nanoparticles were deposited on the nickel substrate to introduce more nucleation sites at elevated temperature, and the density of nanotubes on the substrate was greatly improved by this treatment.

References

[1] S. Iijima, Nature 354 (1991) 56–58.
[2] P. Avouris, R. Martel, V. Derycke, J. Appenzeller, Physica. B, Condensed Matter 323 (2002) 6–14.
[3] A. Bachtold, P. Hadley, T. Nakanishi, C. Dekker, Science 294 (2001) 1317–1320.
[4] P.C. Collins, M.S. Arnold, P. Avouris, Science 292 (2001) 706–709.
[5] V. Derycke, R. Martel, J. Appenzeller, P. Avouris, Nano Letters 1 (2001) 453–456.
[6] J. Kong, N.R. Franklin, C.W. Zhou, M.G. Chapline, S. Peng, K.J. Cho, H.J. Dai, Science 287 (2000) 622–625.
[7] A.R. Bhattacharyya, T.V. Sreekumar, T. Liu, S. Kumar, L.M. Ericson, R.H. Hauge, R.E. Smalley, Polymer 44 (2003) 2373–2377.
[8] M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun, A.T. Johnson, J.E. Fischer, Applied Physics Letters 80 (2002) 2767–2769.
[9] M. Cadek, J.N. Coleman, V. Barron, K. Hedicke, W.J. Blau, Applied Physics Letters 81 (2002) 5123–5125.
[10] R.R. Geng, H.Z. Zheng, B. Shimoda, H. Fleming, L. Liu, O. Zhou, Advanced Materials 14 (2002) 1387–1390.
[11] L.A. Chernozatonskii, E.F. Kukovitskii, A.L. Musatov, A.B. Ormont, K.R. Izraeliants, S.G. L'Vov, Carbon 36 (1998) 713–715.
[12] A.L. Musatov, N.A. Kiselev, D.N. Zakharov, E.F. Kukovitskii, A.I. Zhbanov, K.R. Izrael'yants, E.G. Chirkova, Applied Surface Science 183 (2001) 111–119.
[13] Y. Saito, S. Uemura, Carbon 38 (2000) 169–182.
[14] Y. Saito, K. Hata, A. Takakura, J. Yotani, S. Uemura, Physica. B, Condensed Matter 323 (2002) 30–37.

[15] W. Zhu, C. Bower, O. Zhou, G. Kochanski, S. Jin, Applied Physics Letters 75 (1999) 873–875.

[16] B. Gao, A. Kleinhammes, X.P. Tang, C. Bower, L. Fleming, Y. Wu, O. Zhou, Chemical Physics Letters 307 (1999) 153–157.

[17] G. Maurin, C. Bousquet, F. Henn, P. Bernier, R. Almairac, B. Simon, Chemical Physics Letters 312 (1999) 14–18.

[18] G. Maurin, C. Bousquet, F. Henn, P. Bernier, R. Almairac, B. Simon, Solid State Ionics 136–137 (2000) 1295–1299.

[19] M. Sharon, W.K. Hsu, H.W. Kroto, D.R.M. Walton, A. Kawahara, T. Ishihara, Y. Takita, Journal of Power Sources 104 (2002) 148–153.

[20] Z.-H. Yang, H.-Q. Wu, Solid State Ionics 143 (2001) 173–180.

[21] E.F. Kukovitskii, L.A. Chernozatonskii, S.G. Lvov, N.N. Melnik, Chemical Physics Letters 266 (1997) 323–328.

[22] E.F. Kukovitsky, S.G. L'Vov, N.A. Sainov, V.A. Shustov, Applied Surface Science 215 (2003) 201–208.

[23] D. Park, Y.H. Kim, J.K. Lee, Carbon 41 (2003) 1025–1029.

[24] D. Fujita, T. Ohgi, K. Onishi, T. Kumakura, M. Harada, Japanese Journal of Applied Physics 42 (2003) 1391–1394.

[25] Y.G. Baek, S.I. Honda, T. Ikuno, S. Ohkura, M. Katayama, T. Hirao, K. Oura, Japanese Journal of Applied Physics 42 (2003) 579–581.

[26] C.S. Du and N. Pan, in preparation

[27] G.A. Jablonski, F.W. Geurts, A. Sacco, R.R. Biederman, Carbon 30 (1992) 87–98.