

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231642322>

Synthesis and High Thermal Stability of Double-Walled Carbon Nanotubes Using Nickel Formate Dihydrate as Catalyst Precursor

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · MARCH 2007

Impact Factor: 4.77 · DOI: 10.1021/jp068672k

CITATIONS

39

READS

29

5 AUTHORS, INCLUDING:



Qingfeng Liu

University of Kansas

24 PUBLICATIONS 487 CITATIONS

SEE PROFILE



Feng Li

Chinese Academy of Sciences

213 PUBLICATIONS 14,081 CITATIONS

SEE PROFILE



Hui-Ming Cheng

Shenyang National Laboratory for Materials ...

492 PUBLICATIONS 33,834 CITATIONS

SEE PROFILE

Synthesis and High Thermal Stability of Double-Walled Carbon Nanotubes Using Nickel Formate Dihydrate as Catalyst Precursor

Qingfeng Liu, Wencai Ren, Feng Li, Hongtao Cong, and Hui-Ming Cheng*

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 WenHua Road, Shenyang 110016, China

Received: December 18, 2006; In Final Form: February 4, 2007

Nickel formate dihydrate is demonstrated to be an effective catalyst precursor for selectively synthesizing double-walled carbon nanotubes (DWNTs) with high thermal stability by using a hydrogen arc discharge technique. High-resolution transmission electron microscopy (HRTEM) observations show that the as-synthesized DWNTs are of high quality with good structural integrity and narrow diameter distribution (1.98–3.47 nm and 1.32–2.81 nm, respectively, for the outer and inner diameter). Thermogravimetric analysis (TGA) in air indicates that the DWNTs have excellent oxidation resistance up to ~800 °C, approaching to that of graphitized multiwalled carbon nanotubes and higher than that of DWNTs prepared by other routes or methods. Moreover, Raman analysis and HRTEM observations reveal that these DWNTs can keep good structural stability and other carbon species are removed after oxidation at 650 °C in air flow. The formation of DWNTs with high thermal stability is attributed to the cleaning effect of active radicals such as hydrogen and oxygen originated from the decomposition of nickel formate dihydrate and the in situ defect-healing effect induced by high arc current in the arc growth process. This approach opens various application possibilities for DWNTs with high thermal stability to be used in high-temperature composites, nanoelectronic devices, and electron filed emitters operating at high currents, etc.

Introduction

A great deal of interests have recently paid to double-walled carbon nanotubes (DWNTs) because of their unique structure, promising properties and potential applications.¹ For example, a DWNT can be used as molecular electronic devices, such as cable and capacitor, depending on their electronic properties of the two constituent tubes. Moreover, compared to single-walled carbon nanotubes (SWNTs), DWNTs are expected to exhibit enhanced mechanical properties and structural stability. Therefore, for the application of field emission, for example, DWNTs possess both merits of SWNTs and multiwalled carbon nanotubes (MWNTs); i.e., threshold voltage for electron emission of DWNTs is as low as that for SWNTs, and the lifetime (long-term emission stability) of DWNTs is as excellent as that of MWNTs.²

Several synthesis methods have been developed for the synthesis of DWNTs such as high-temperature treatment of C₆₀@SWNT peapods,³ hydrogen arc discharge,^{4–6} and catalytic chemical vapor deposition (CVD) method.^{7–10} However, current synthesis methods still suffer from the production of DWNTs with significant structural defects, which result in a considerable decrease of thermal stability and the mechanical strength of DWNTs, since these defects are particularly reactive to oxygen at elevated temperatures.^{11–13} Moreover, many important properties of DWNTs strongly depend on their thermal and structural stability, especially for their applications in high-temperature composites, nanoelectronic devices, and electron field emitters operating at high currents, etc. Previous studies indicate that thermal annealing from 1500 to 2800 °C in Ar atmosphere can efficiently remove structural defects of DWNTs.¹⁴ However,

annealing also exerts a crucial influence on the structure and morphology of DWNTs such as tubule coalescence and formation of large-diameter DWNTs, MWNTs and flaky carbons.¹⁴ Therefore, it is still a great challenge to synthesize DWNTs with high thermal stability in order to further realize their potential applications.

Generally, compared to DWNTs synthesized at moderate growth temperatures using CVD method, DWNTs synthesized by arc discharge method have better oxidation stability (~720 °C) due to an in situ defect-healing effect of the high plasma temperature.^{15–17} However, a great deal of amorphous carbon either coats the outer surface or fills the inner cavity of these nanotubes, which, consequently, decreases the structural stability and limits the utilization of their intrinsic properties and potential applications.

Recent studies indicate that introducing an appropriate amount of water into the reaction system can benefit to the production of clean and high-quality SWNTs and DWNTs in the CVD growth process because an appropriate amount of water vapor can effectively enhance the activity and lifetime of catalysts and remove the amorphous carbon without any damage to the nanotubes.^{18,19} However, it is difficult to introduce directly an accurate and controllable amount of water (liquid or vapor) into an arc discharge system. It was reported that nickel formate, which typically exists in the form of a dihydrate, Ni(HCOO)₂·2H₂O, decomposes directly to chemically active metallic Ni nanoparticles with narrow diameter distribution within a residence time as short as 0.1 s at a relatively low temperature of 600 °C.^{20,21} Moreover, an accurate and controllable amount of water can be simultaneously produced in the above decomposition process. Therefore, it may be possible to synthesize clean and high-quality DWNTs using nickel formate

* To whom correspondence should be addressed. E-mail: cheng@imr.ac.cn.

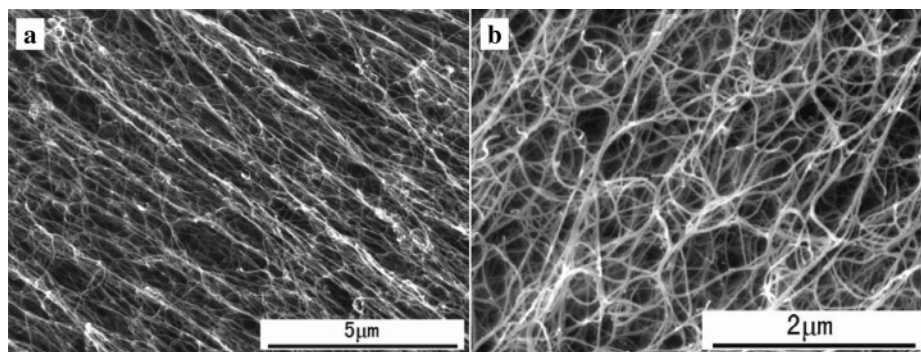


Figure 1. SEM images of the as-synthesized DWNTs under optimum conditions by the formate nickel dihydrate route.

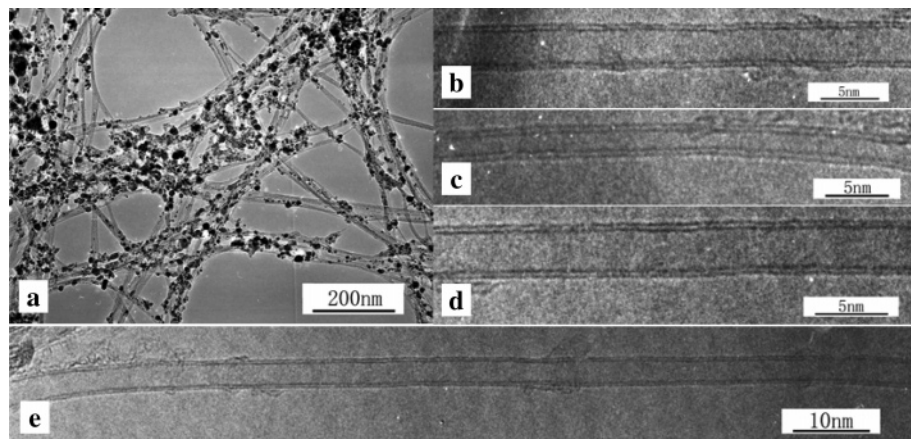


Figure 2. Typical TEM and HRTEM images of the as-synthesized DWNTs under optimum conditions by the formate nickel dihydrate route.

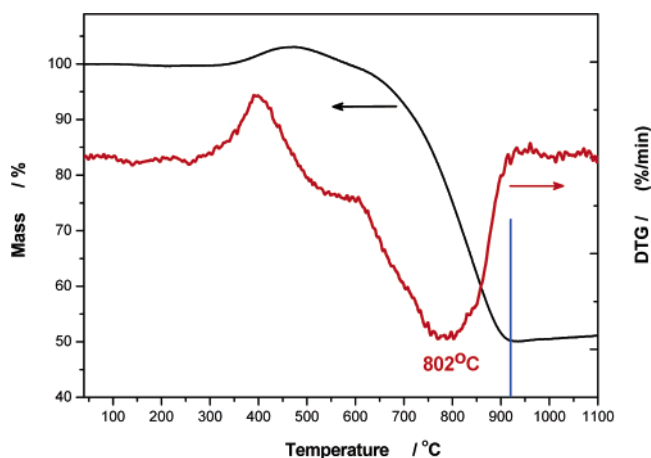


Figure 3. Raman spectrum of the as-synthesized DWNTs excited by a laser energy of $E_{\text{laser}} = 1.96$ eV. The inset indicates the corresponding radial breathing mode (RBM).

dihydrate as catalyst precursor by the hydrogen arc discharge technique, under a careful control of experimental conditions.

In this paper, we try to demonstrate the efficient synthesis of DWNTs with high thermal stability using nickel formate dihydrate as catalyst precursor. Thermogravimetric analysis (TGA) indicates that the as-synthesized DWNTs have excellent high-temperature oxidation resistance up to ~ 800 °C, approaching that of graphitized MWNTs and higher than that of DWNTs prepared by other routes or methods.^{16,17,22} Moreover, Raman analysis and high-resolution transmission electron microscopy (HRTEM) investigation reveal that these DWNTs with narrow diameter distribution can keep good structural stability and amorphous carbon impurities are removed after oxidation at 650 °C in airflow. It is believed that these DWNTs with high thermal stability should benefit from the cleaning effect of active

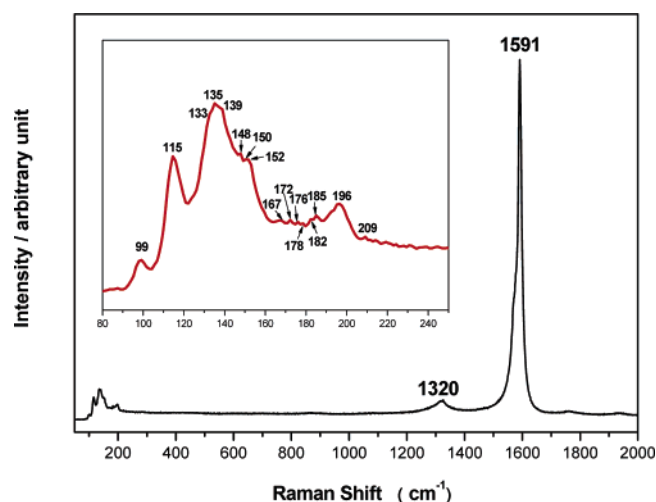


Figure 4. TGA curves of the as-synthesized DWNTs under optimum conditions by the formate nickel dihydrate route in the airflow.

radicals such as hydrogen and oxygen originated from the decomposition of nickel formate dihydrate, which leads to the formation of clean DWNTs free from amorphous carbon impurities. On the other hand, the high thermal stability of these DWNTs is also partially due to the defect-healing effect induced by the relatively high plasma temperature, which is an analogue of in situ high-temperature thermal annealing.

Experimental Section

Synthesis of DWNTs. The synthesis method is basically the same as that reported previously.⁶ In brief, a cylinder-shaped reactor chamber with a diameter of 600 mm and height of 400 mm was used. The cathode is a graphite rod (10 mm in

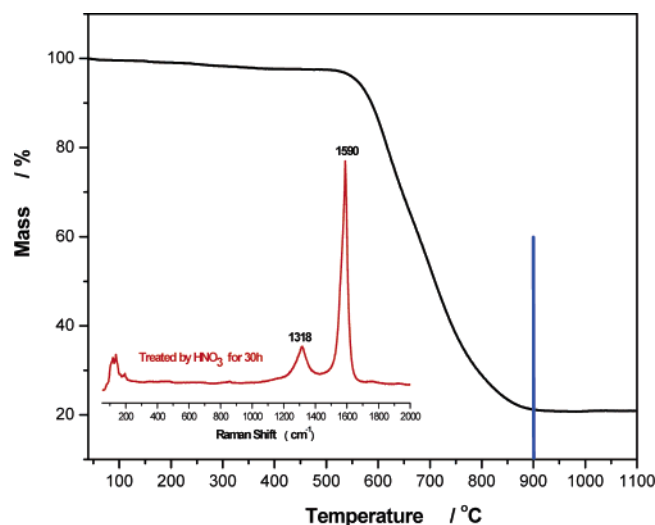


Figure 5. TGA curves of the HNO_3 -treated DWNTs for 30 h. The inset presents the corresponding Raman spectrum of the HNO_3 -treated DWNTs.

diameter and 150 mm in length), and the anode is a big rotatable graphite cylinder with eight holes (20 mm in diameter and 10 mm in depth each), which were filled with the mixture of catalyst precursors, sulfide and carbon feedstock. The electric arc was typically operated in a dc mode at 120–300 A and a hydrogen atmosphere of 32 kPa pressure, with a distance of about 4 mm maintained between the two electrodes. As reported previously, growth conditions play a crucial role in the selective growth of DWNTs. Our results indicate that experimental parameters of arc current ranging from 180 to 270 A and the

molar content of nickel formate dihydrate in the starting mixture ranging from 1.30 to 3.90% are efficient for synthesizing DWNTs. Under these conditions, about 1–2 g of raw products consisting of ~65 wt % DWNTs could be produced in a 10 min operation by the nickel formate dihydrate route in the hydrogen arc discharge method. It is worthy noting that the productivity is higher than those prepared by other methods or routes.^{7–10,16}

Characterization. The thermo-analysis measurements of the as-synthesized DWNTs were carried out in a thermogravimetric analyzer (NETZSCH STA 449C). The morphology and microstructure of the as-synthesized DWNTs were characterized by scanning electron microscope (SEM, JSM-6301F, at 20 kV), high-resolution transmission electron microscope (HRTEM, JEOL2010 at 200 kV), and micro-Raman spectroscopy (Jobin Yvon LabRam HR800, excited by 632.8 nm laser), respectively. To avoid destroying the original morphology and obtain the real structural information of the product, a piece of transparent DWNT film was attached onto the copper grid and then fixed by a drop of ethanol for HRTEM investigations.

Results and Discussion

Figure 1 shows typical SEM images of the as-synthesized tangled DWNT filaments synthesized under the optimum conditions (arc current of 240 A and molar ratio of C:Ni:S = 100:3.25:0.33). Low magnification SEM image (see Figure 1a) shows that these DWNT filaments have lengths of over tens of micrometers, though it is difficult to separate one filament from the rest. Another important feature is that these DWNT filaments have uniform diameters ranging from 20 to 30 nm and clean surfaces (see Figure 1b). Extensive HRTEM observations reveal that more than 90% of the nanotube product is DWNTs, while

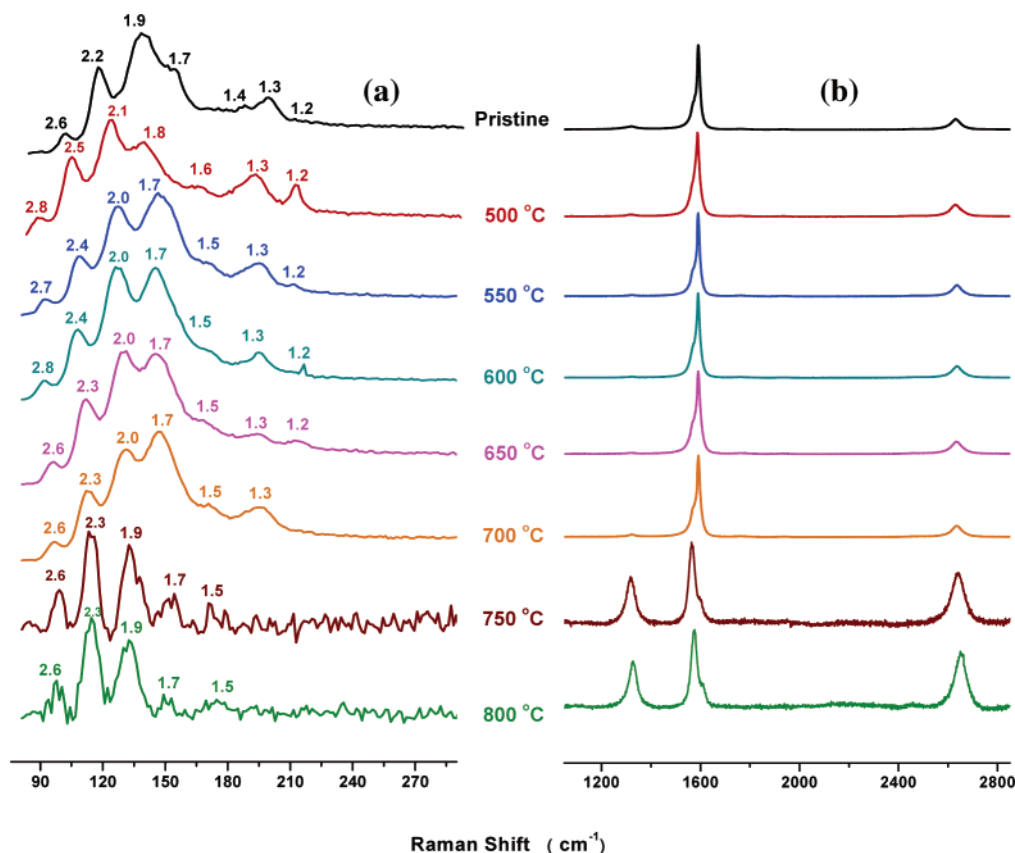


Figure 6. (a) Low-frequency RBM and (b) high-frequency Raman spectra of the as-synthesized DWNTs after oxidation in the airflow at temperatures ranging from 500 to 800 °C. The values on the top of RBM peaks are the corresponding diameters calculated using the equation $\omega_r(d_i) = 254/d$ (nm). The intensities of peaks at 750 and 800 °C were adjusted.

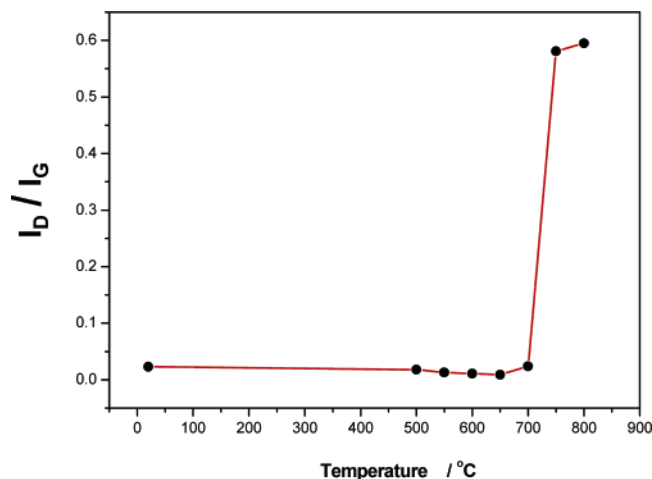


Figure 7. Intensity ratio of D band to G band (I_D/I_G) of the DWNTs treated at different temperatures presented in Figure 6.

the rest is SWNTs. Figure 2a–e shows typical TEM images of the isolated DWNTs with different magnifications. A great deal of HRTEM observations reveal that the outer and inner diameters of most DWNTs are in the range of 1.98 to 3.47 nm and 1.32 to 2.81 nm, respectively. Additionally, the interlayer spacing is not constant, ranging from 0.33 to 0.41 nm. Compared with those previously prepared by arc discharge method,^{4–6,16,17} the as-synthesized DWNTs have relatively smaller outer and inner diameters and a narrower diameter distribution, but similar interlayer spacing. It is worthy noting that rare amorphous carbon is found to coat the outer surface or fill inside the inner cavity of the DWNTs. Moreover, the walls of the DWNTs are well resolved and free from defects, indicating a good structural integrity. Therefore, an excellent thermal stability is expected for these high-quality DWNTs.

To further reveal the structural features and provide a quantitative assessment of the quality of the DWNT samples, Raman measurements were performed on the as-synthesized DWNTs. Figure 3 shows a typical Raman spectrum of the as-synthesized DWNTs excited by a laser energy of 1.96 eV. Previous studies indicate that Raman frequency of the radial breathing mode (RBM, ω_r) can be used to evaluate the diameter (d_t) of inner and outer diameters of DWNTs based on the relation $\omega_r(d_t) = 254/d$ (nm).⁷ Therefore, it is estimated from

RBM frequencies in Figure 3 that the as-synthesized DWNTs have a diameter distribution from 1.22 to 2.57 nm, in agreement with the results from HRTEM observations. It should be noted that the RBM peaks shown in Figure 3 should originate from most of the inner tubes and some of the thin outer tubes of DWNTs since the low-frequency RBM peaks are difficult to detect due to the reduced Raman cross-section for large diameter nanotubes (>3 nm). The G band at 1591 cm^{-1} originates from the C–C stretching mode, while the D band at 1320 cm^{-1} is associated with defects and amorphous carbon in the nanotube samples. Generally, the ratio of the intensities of D to G band (I_D/I_G) can be used as an indicator of the quality of the nanotubes. For the as-synthesized DWNTs, the G band is very narrow and strong, while the D band is much weak. The I_D/I_G is ~ 0.023 , much smaller than those reported for DWNTs prepared by arc discharge method,^{4,17} indicating a higher purity and quality of these DWNTs.

Thermogravimetric analysis (TGA) is employed to characterize the thermal stability of the as-synthesized DWNTs toward high-temperature air oxidation. Figure 4 shows the TGA curve of the as-synthesized DWNTs in the airflow. It can be found that there is a slight weight increase at around $350\text{ }^\circ\text{C}$ and a little weight loss at around $500\text{ }^\circ\text{C}$, which can be ascribed to the oxidation of metallic catalyst particles and other minor byproducts such as amorphous carbon and SWNTs in the raw product. Even though the residual metal is up to $\sim 50\%$, the DWNTs themselves are oxidized in a temperature range of $630\text{--}920\text{ }^\circ\text{C}$ and have an oxidation resistance up to $802\text{ }^\circ\text{C}$, approaching that of graphitized MWNTs ($\sim 800\text{ }^\circ\text{C}$) and higher than the reported highest oxidation resistance temperature for DWNTs ($\sim 720\text{ }^\circ\text{C}$) prepared by other routes or methods.^{16,17,22} The presence of transition metals is known to catalyze the gasification of carbon, but the mechanism by which the transition metal catalysts affect this is not fully understood.²³ However, there seems to be a weak catalytic influence on the oxidation resistance temperatures of the as-synthesized DWNTs, because most of the catalyst particles are encapsulated by pyrolytic carbon layers. On the other hand, even after the treatment of concentrated HNO_3 ($\sim 65\text{ wt } \%$) for 30 h at room temperature, the oxidation resistance of the DWNTs is not obviously decreased (see Figure 5). Furthermore, after the acid treatment, the structural features of these DWNTs are rarely changed, as indicated by the Raman spectrum of the inset of Figure 5.

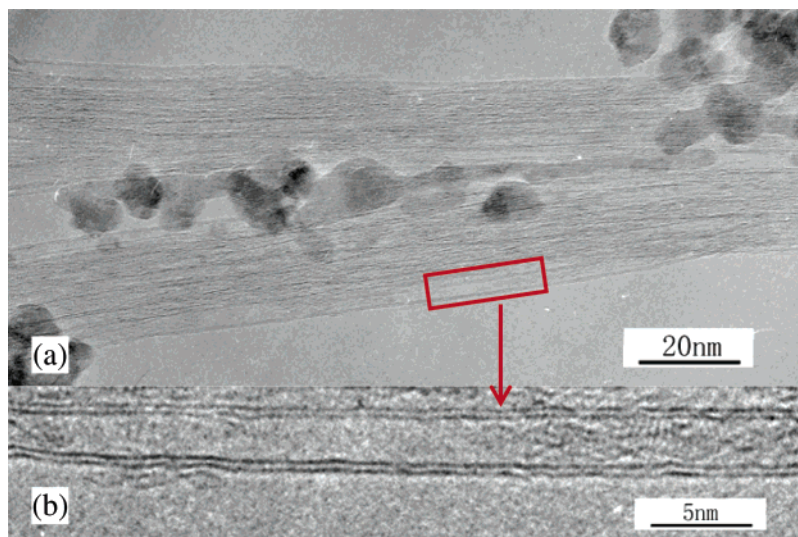


Figure 8. HRTEM images of the DWNT bundles (a) and an isolated DWNT (b) after oxidation in the airflow at $650\text{ }^\circ\text{C}$.

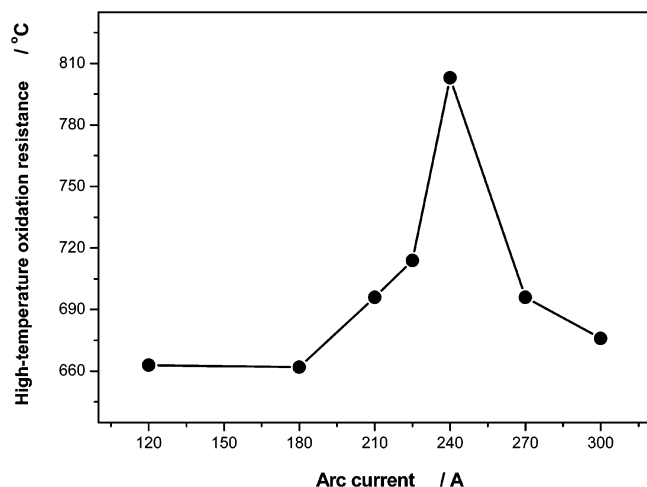


Figure 9. Dependence of the arc current used for the growth of DWNTs on thermal stability of DWNTs.

To further evaluate the thermal stability of DWNTs to oxidation, Raman spectroscopy was used to characterize the structural changes of the DWNTs at temperatures ranging from 500 to 800 °C during the above TGA measurement process. We note from Figure 6a that, for temperatures between 500 and 700 °C, the Raman profile of the DWNTs remains similar. This result indicates that the DWNTs keep their structural stability up to 700 °C, demonstrating excellent high-temperature oxidation resistance. However, remarkable changes in the profile and intensity of Raman spectra are found in the DWNTs treated at temperatures above 750 °C, indicating a substantial damage of the structure of DWNTs. The high-frequency Raman spectra of DWNTs at each stage of TGA measurements in airflow are shown in Figure 6b. It is apparent that both the absolutely intensities of both D band and G band are remarkably decreased and the I_D/I_G ratio is remarkably increased with the increase of oxidation temperature above 750 °C, implying a violent damage

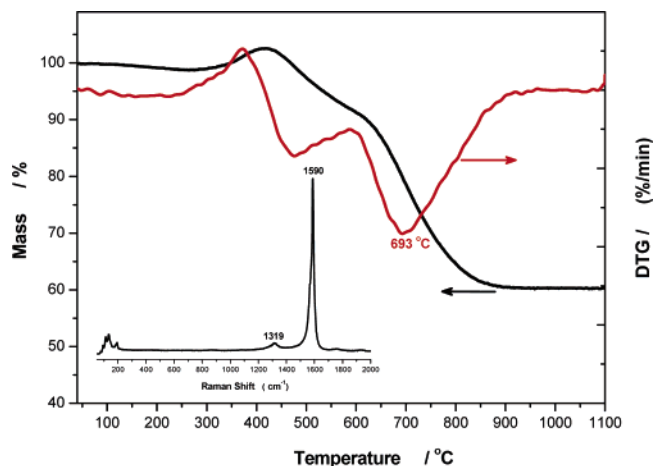


Figure 11. TGA curves of the as-synthesized DWNTs using Ni powder as catalyst. The inset indicates the corresponding Raman spectrum.

of structure of DWNTs caused by air oxidation. In order to quantitatively evaluate the quality of the DWNTs after oxidation treatment, the I_D/I_G of the DWNTs at various oxidation temperatures are shown in Figure 7. It can be seen that the I_D/I_G ratio slight decreases before 700 °C but increases sharply above 750 °C. We believe that the initial small decrease of I_D/I_G ratio is mainly attributed to the removal of amorphous carbon and hydrocarbons absorbed on the surface of DWNTs (the synthesis was conducted in a hydrogen atmosphere). The smallest ratio, $I_D/I_G \approx 0.009$, for the DWNTs oxidized at 650 °C reveals that (i) 650 °C is the optimum temperature for removal of other carbon species such as amorphous carbon and (ii) this temperature is not high enough to destroy the structure of the DWNTs. Moreover, after oxidation at 650 °C in the airflow, HRTEM observations (see Figure 8) show that the obtained DWNTs have a clean surface and perfect structure without amorphous carbon impurities, in agreement with the above Raman analysis. Furthermore, SWNTs are rarely found

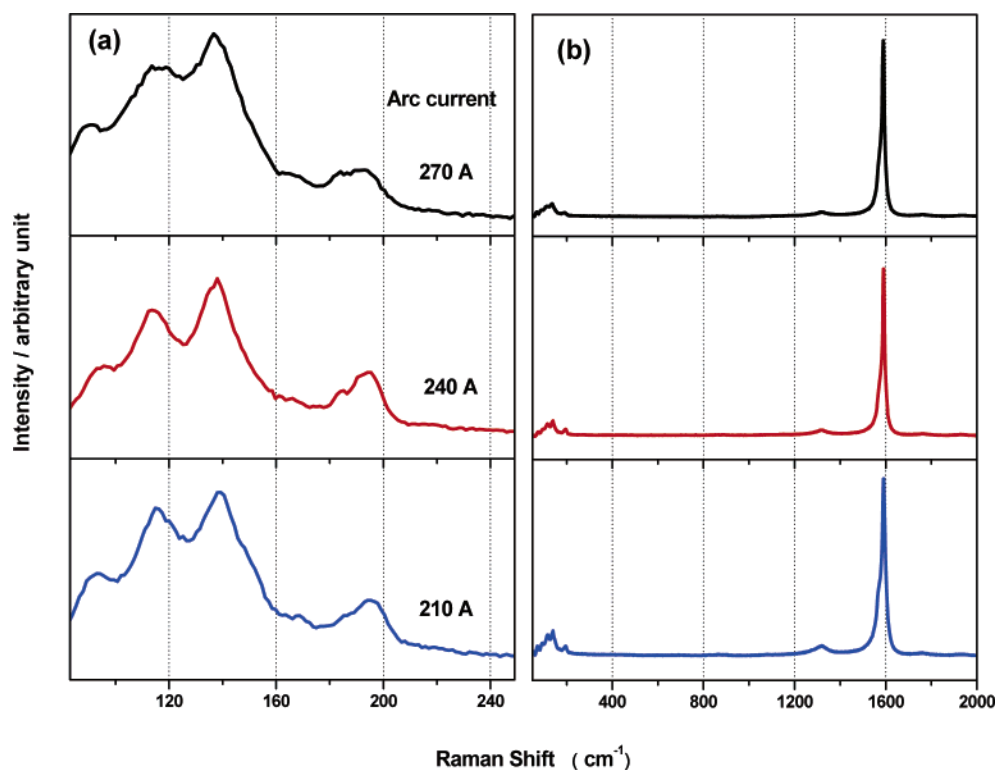


Figure 10. (a) Low-frequency RBM and (b) Raman spectra of the as-synthesized DWNTs with different arc currents.

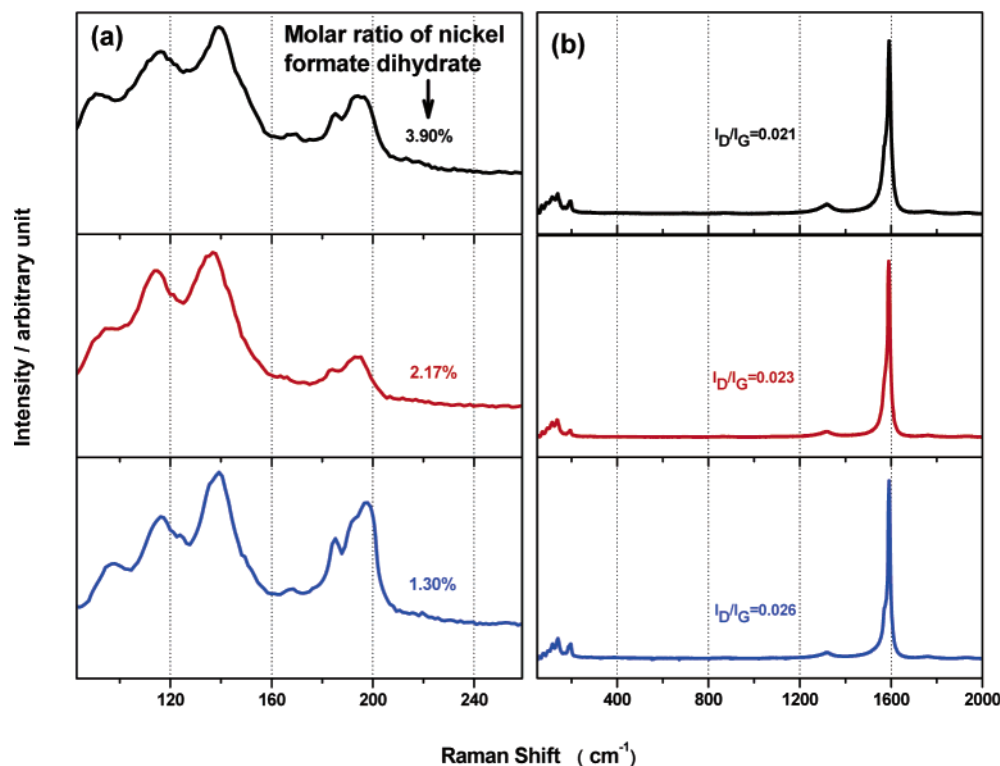


Figure 12. (a) Low-frequency RBM and (b) Raman spectra of the as-synthesized DWNTs with different molar contents of nickel formate dihydrate in the starting mixture.

during TEM observations. Obviously, these results further prove experimentally that DWNTs have higher thermal stability than SWNTs, and oxidation is an effective method to remove amorphous carbon and SWNTs in the sample, and they can also provide some useful information on determining the ideal oxidation conditions for the purification of DWNTs without loss or structural damage.

To elucidate the origin of the high thermal stability and high quality of these DWNTs, we analyzed the experimental conditions used for the synthesis of DWNTs in our method. It is worthy noting that the arc current used in our route is remarkably higher than those previously used for DWNT synthesis.^{4–6,16,17} Higher arc current can lead to higher plasma temperature, which is helpful to heal structural defects during the growth process of DWNTs, similar to in situ high-temperature thermal annealing.¹⁶ Therefore, we believe that high thermal stability of the as-synthesized DWNTs partially benefits from the above in situ defect-healing effect. In order to verify this point, comparative experiments were performed to demonstrate the role of arc current in the thermal stability of DWNTs. Figure 9 shows the dependence of arc current used for DWNT growth on high-temperature oxidation resistance of DWNTs. It can be found that the oxidation stability of the DWNTs is greatly improved with increasing arc current from 120A to 240A, but drastically decreased as the arc current is larger than 240A. Therefore, we consider that the plasma temperature plays a competition role in the structure of DWNTs. That is, it can heal the structural defects on DWNTs through in situ annealing during growth process, and on the other hand, simultaneously, it can also enhance reactive radicals such as hydrogen and oxygen (from the decomposition of water due to high arc current) to etch the walls of DWNTs. As a result, an appropriate current is very critical for the synthesis of DWNTs with high thermal stability by the nickel formate dihydrate route. It should be noted the diameter of a DWNT may affect its thermal stability. However,

it is found that the diameters of the as-synthesized DWNTs do not depend on the arc current, which can be seen from the corresponding Raman spectrum (Seen Figure 10). Therefore, we believe that high arc current leads to a high thermal stability through improving the structural integrity of DWNTs by in situ annealing.

We consider that another crucial reason responsible for the high thermal stability and purity of DWNTs should be attributed to the addition of water during the preparation process. When nickel formate dihydrate is replaced by comparable molar content of metallic Ni powder as catalyst and other parameters remain the same, uniform DWNTs still can be obtained; however the productivity of DWNTs was decreased significantly. Raman spectroscopy (see the inset of Figure 11) shows that the DWNTs synthesized by Ni powder have a similar structure to these synthesized by the nickel formate dihydrate route. However, the oxidation temperature of the DWNTs is only 693 °C, as suggested by the DTG peak in Figure 11. Additionally, the molar content of nickel formate dihydrate in the starting mixture ranging from 1.30% to 3.90%, as mentioned above, is efficient for synthesizing DWNTs with comparable quantity. Moreover, note that the RBM profile of the DWNTs prepared by different amount of Ni in the above range remains similar (Seen Figure 12), indicating that the change of Ni concentration does not cause a structural alteration for DWNTs such as the diameter distribution. However, the oxidation resistance temperature is increased with increasing the amount of catalyst precursor, because of the removal of amorphous carbon in the products resulting from the increase of addition amount of water. This can be further verified by the decrease of I_D/I_G for these samples. Therefore, we conclude that the addition of water plays an important role in the selective growth of DWNTs and the improvement of thermal stability. It is worthy noting that due to the high arc plasma temperature, H_2O should be in situ decompose to reactive radicals such as hydrogen and oxygen

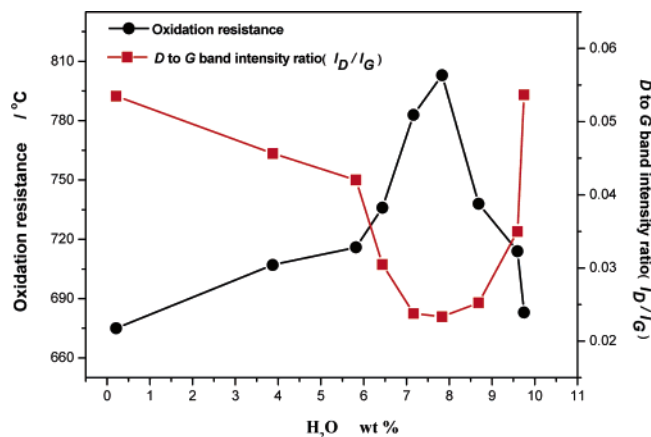


Figure 13. Thermal stability and the corresponding intensity ratio of D band to G band (I_D/I_G) of the DWNTs synthesized at various weight percents of water produced from the pyrolysis of nickel formate dihydrate in the starting mixture for the growth of DWNTs.

in our synthesis method. Although the water-assisted growth mechanism may be different, the cleaning effect on the synthesis of DWNTs such as removing amorphous carbon and enhancing the activity and lifetime of metal nanoparticles as a protective agent against amorphous carbon coating in arc discharge system should be comparable with that in CVD system.¹⁹

In order to further verify the role of water in the synthesis of DWNTs, we systematically investigated the dependence of thermal stability of DWNTs on the quantity of water produced from the pyrolysis of catalyst precursor by means of modifying the content of nickel formate dihydrate in the starting mixture. Figure 13 shows thermal stability and the corresponding I_D/I_G of DWNTs synthesized at different weight percent of water to the raw materials. It is interesting to find that the thermal stability of DWNTs is closely related to the corresponding I_D/I_G . That is, the higher the thermal stability, the lower the I_D/I_G . This result further proves that the high thermal stability of DWNTs originate from their structural integrity. Moreover, similar to the role of arc current on the thermal stability of DWNTs, the addition of water plays a competition role in the growth of DWNTs. An appropriate amount of water can effectively assist the synthesis of clean DWNTs with high crystallization and structural integrity, and accordingly enhance the thermal stability of DWNTs. However, excess water may oxidize or damage substantially the DWNTs themselves, and thus greatly decrease the thermal stability of DWNTs.

It should be noted that nickel formate dihydrate was reported as an effective catalyst precursor not only for SWNTs but also for versatile growth of CNTs with varied structures. However, the advantages of this precursor, which is dispersed on the support materials like silica powder, may be not fully realized in the CVD growth process.^{20,21} First, the effect of water is eliminated, since the water produced from the decomposition of dihydrate at low temperatures (<300 °C) is out from the CVD system with the carrying gases before reaching the growth temperature (usually over 850 °C) of nanotubes in CVD system. On the other hand, Ni nanoparticles are inevitably sintered beyond the size limit suitable for nanotube growth because of the relatively long duration time before reaching the growth temperature and high density of particles. In contrast, the high temperature in arc discharge method can result in instantaneous pyrolysis of nickel formate dihydrate and the formation of a great deal of catalytically active Ni nanoparticles suitable for the growth of DWNTs, avoiding sintering Ni nanoparticles

beyond the size limit due to a short duration time. Therefore, as demonstrated above, a high-efficiency growth of DWNTs is achieved using nickel formate dihydrate as catalyst precursor by hydrogen arc discharge method.

Conclusions

A new approach was developed for the synthesis of DWNTs with high thermal stability, using nickel formate dihydrate as catalyst precursor in a simple hydrogen arc discharge method. TGA results show that the as-synthesized DWNTs have excellent oxidation resistance up to ~800 °C, which approaches that of graphitized multiwalled carbon nanotubes and higher than that of DWNTs prepared by other routes or methods. HRTEM observations and Raman analyses indicate that the high thermal stability of DWNTs is attributed to their good structural integrity. From systematic experimental studies, we consider that the structural integrity of DWNTs arise from two important factors: (1) the high-temperature defect-annealing effect induced by high arc current; and (2) the cleaning effect of active radicals such as hydrogen and oxygen originated from the pyrolysis of nickel formate dihydrate. Another feature of this approach is that the diameter distribution (1.98–3.47 nm) of the DWNTs is much narrower than those (usually 1.5–5.5 nm) reported using conventional arc discharge method. This nickel formate dihydrate route is quite simple to implement, and may provide a realistic approach to mass production of the DWNTs with high quality, which may stimulate various applications of DWNTs as nanoelectronic devices, high-temperature composites and electron field emitters operating at high currents, etc.

Acknowledgment. The work was supported by the Ministry of Science and Technology of China (No. 2006CB932700), the National Science Foundation of China (No. 90606008), and the Chinese Academy of Sciences.

References and Notes

- (1) Saito, R.; Matsuo, R.; Kimura, T.; Dresselhaus, G.; Dresselhaus, M. S. *Chem. Phys. Lett.* **2001**, *348*, 187.
- (2) Kurachi, H.; Uemura, S.; Yotani, J.; Nagasako, T.; Yamada, H.; Ezaki, T.; Maesoba, T.; Loutfy, R.; Moravsky, A.; Nakagawa, T.; Katagiri, S.; Saito, Y. *Proceedings of 21st International Display Research Conference/8th International Display Workshops*; Nagoya, Japan; Society for Information Display: San Jose, CA, 2001; p 1245.
- (3) Bandow, S.; Takizawa, M.; Hirahara, K.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2001**, *337*, 48.
- (4) Hutchison, J. L.; Kiselev, N. A.; Krinichnaya, E. P.; Krestinin, A. V.; Loutfy, R. O.; Morawsky, A. P.; Muradyan, V. E.; Obratsova, E. D.; Sloan, J.; Terekhov, S. V.; Zakharov, D. N. *Carbon* **2001**, *39*, 761.
- (5) Saito, Y.; Nakahira, T.; Uemura, S. *J. Phys. Chem. B* **2003**, *107*, 931.
- (6) Li, L. X.; Li, F.; Liu, C.; Cheng, H. M. *Carbon* **2005**, *43*, 623.
- (7) Ren, W. C.; Li, F.; Chen, J. A.; Bai, S.; Cheng, H. M. *Chem. Phys. Lett.* **2002**, *359*, 196.
- (8) Wei, J. Q.; Jiang, B.; Wu, D. H.; Wei, B. Q. *J. Phys. Chem. B* **2004**, *108*, 8844.
- (9) Li, W. Z.; Wen, J. G.; Sennett, M.; Ren, Z. F. *Chem. Phys. Lett.* **2003**, *368*, 299.
- (10) Zhu, J.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2003**, *380*, 496.
- (11) Lu, X. K.; Ausman, K. D.; Piner, R. D.; Ruoff, R. S. *J. Appl. Phys.* **1999**, *86*, 186.
- (12) Bendall, J. S.; Ilie, A.; Welland, M. E.; Sloan, J.; Green, M. L. H. *J. Phys. Chem. B* **2006**, *110*, 6569.
- (13) Bom, D.; Andrews, R.; Jacques, D.; Anthony, J.; Chen, B. L.; Meier, M. S.; Selegue, J. P. *Nano. Lett.* **2002**, *2*, 615.
- (14) Kim, Y. A.; Muramatsu, H.; Hayashi, T.; Endo, M.; Terrones, M.; Dresselhaus, M. S. *Chem. Phys. Lett.* **2004**, *398*, 87.
- (15) Ramesh, P.; Okazaki, T.; Sugai, T.; Kimura, J.; Kishi, N.; Sato, K.; Ozeki, Y.; Shinohara, H. *Chem. Phys. Lett.* **2006**, *418*, 408.
- (16) Huang, H. J.; Kajiura, H.; Tsutsui, S.; Murakami, Y.; Ata, M. J. *Phys. Chem. B* **2003**, *107*, 8794.
- (17) Qiu, H. X.; Shi, Z. J.; Guan, L. H.; You, L. P.; Gao, M.; Zhang, S. L.; Qiu, J. S.; Gu, Z. N. *Carbon* **2006**, *44*, 516.

- (18) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004**, *306*, 1362.
- (19) Yamada, T.; Namai, T.; Hata, K.; Futaba, D. N.; Mizuno, K.; Fan, J.; Yudasaka, M.; Yumura, M.; Iijima, S. *Nat. Nanotechnol.* **2006**, *1*, 131.
- (20) Geng, J. F.; Singh, C.; Shephard, D. S.; Shaffer, M. S. P.; Johnson, B. F. G.; Windle, A. H. *Chem. Commun.* **2002**, 2666.

- (21) Geng, J.; Li, H. W.; Golovko, V. B.; Shephard, D. S.; Jefferson, D. A.; Johnson, B. F. G.; Hofmann, S.; Kleinsorge, B.; Robertson, J.; Ducati, C. *J. Phys. Chem. B* **2004**, *108*, 18446.
- (22) Zhang, H.; Sun, C. H.; Li, F.; Li, H. X.; Cheng, H. M. *J. Phys. Chem. B* **2006**, *110*, 9477.
- (23) McKee, G. S. B.; Vecchio, K. S. *J. Phys. Chem. B* **2006**, *110*, 1179.