Large-Scale Synthesis of Long Double-Walled Carbon Nanotubes

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Long double-walled carbon nanotubes (DWNTs) could be synthesized in a production rate of about 0.5 g per h by an improved catalytic chemical vapor deposition method using xylene solution as carbon feedstock. The argon flowing rate affects the growth of DWNTs sensitively. Raman spectra and HRTEM images show that the DWNTs having inner diameters of about 1.0−2.0 nm dominate in the samples.

Introduction

Double-walled carbon nanotube is a critical type of one-dimensional material between single-walled carbon nanotube (SWNT) and multiwalled carbon nanotube (MWNT). Theoretical calculation[1] and high-resolution transmission electronic microscopy (HRTEM) measurement[2] demonstrated that the interlayer distance between the inner and outer tubes of the DWNTs can vary from 0.33 to 0.41 nm, which is quite different from that of the normal MWNT (0.34 nm). Due to the large interlayer distance, DWNTs are expected to have some anomalous properties, such as electrical properties, optical properties, gas storage, and so on. Several groups have reported their synthesis of DWNTs via different methods, such as heat treatment of the SWNTs samples with C60 encapsulated inside SWNTs,[3] arc-discharge method,[2] and catalytic chemical vapor deposition (CCVD) method,[4−6] while the production rate of the DWNTs is relative low, which is about several milligrams per hour. Recently, Flahaut et al.[7] and Lyu et al.[8] reported the preparation of DWNTs powder in gram scale, independently. Both of their methods need catalyst carriers (such as Al_2O_3, SiO_2, and MgO), which are also the impurity existing in the products and need to be removed from the samples. At the same time, the length of their DWNTs bundles is usually in micrometer scale. Very recently, we synthesized DWNT films in milligram scale per hour by pyrolysis of methane using the CCVD method and purified the raw sample with H_2O_2 and HCl to get highly pure DWNTs.[9] However, it is very difficult to prepare DWNTs in large scale in our previous experiments due to the small feeding of carbon feedstock (methane flowing rate < 8 mL/min). To increase the production rate of the DWNTs, it needs to increase the feeding rate of carbon feedstock in the reaction.

Organic solution (such as xylene, benzene, and *n*-hexane) is usually used as carbon feedstock in preparing an aligned MWNTs array.[10] Although some SWNTs can be also found in sample, MWNTs dominate in the array.[11] It has been successful to prepare SWNTs using organic solution as carbon feedstock with ferrocene-assistant at high temperature (>1373 K) in previous researches.[12,13] Here, we described a simple method to get large quantity of long DWNTs.

Experiments

Our experiments are carried out in an equipment which is usually used to prepare well-aligned MWNTs arrays.[14] The quartz glass, which is usually used as substrate for growing MWNTs arrays, is removed from the equipment and the parameters are fixed to obtain DWNTs. Ferrocene and small amount of sulfur (Fe:S = 10:1, atomic ratio) is dissolved in xylene and form a solution of 0.03−0.12 g/ mL. The solution is injected evenly by a pump into a horizontal quartz tube (reactor) which had an inner diameter of Φ45 mm and a length of 180 cm. The feeding rate of the solution is kept at 0.05−0.15 mL/min with a reaction time of about 10−20 min. In contrast with the parameters of preparing aligned MWNTs array, we increased the reaction temperature to above 1373 K, introduced sulfur (Fe:S = 10:1), and also increased the flowing rate of argon and hydrogen to 2500−3500 and 500 mL/min, respectively. Scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), HRTEM, and Raman spectra were used to characterize and evaluate the samples.

Results and Discussion

During the experiment, DWNTs filaments and films are carried out from the reaction zone (T = 900−1180 °C) by the large argon and hydrogen flow and aggregated at the rear end of the quartz tube (T < 400 °C). The growing speed of the DWNTs is very fast; long DWNTs filaments and large area thin films can be seen blow out by the flowing gas in several seconds after the xylene solution is injected into the reactor. Thus we believe that the DWNTs filaments must be composed of very long DWNTs bundles. Figure 1a shows an optical image of the product prepared in 10 min, which shows two long DWNT filaments with lengths of 35 cm (see arrow A) and 10 cm (see arrow B) and a bulk of DWNT films (see arrow *C*), respectively. The DWNT films are sticky and can be torn into small long films by tweezers.

Figure 1b shows a low magnification SEM image of a DWNTs film. The film is composed of thousands of DWNTs bundles which are aligned in the direction of airflow. The length of the DWNTs bundle measured in the SEM is usually longer than hundreds of micrometer. Some small bundles assemble into

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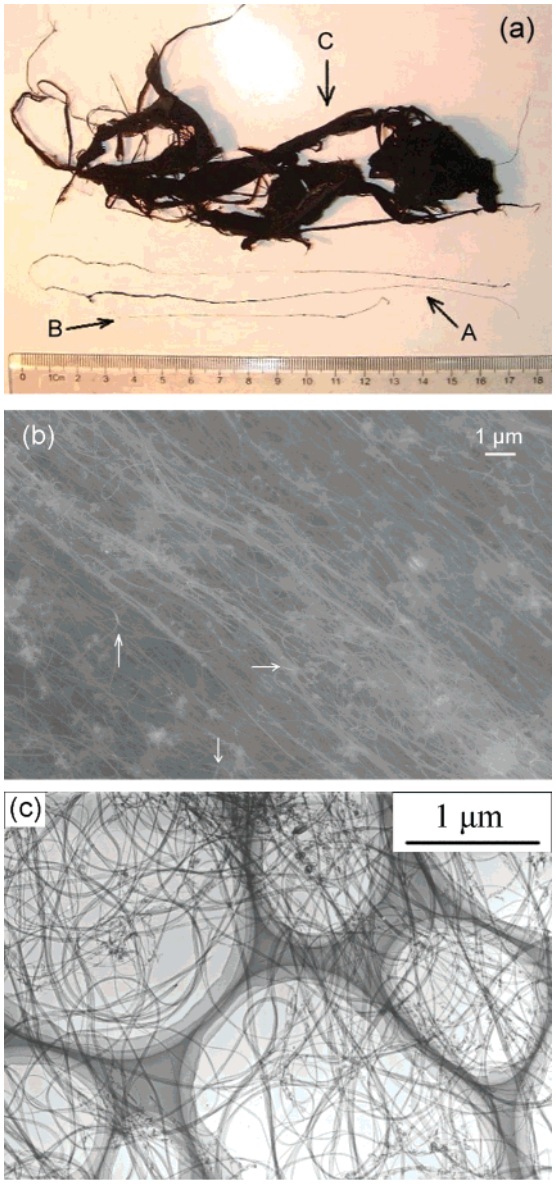

Figure 1. (a) Optical image of the long DWNT filaments and of bulk of DWNT films. (b, c) SEM and TEM images of the DWNTs film, respectively.

a large bundle can be identified (see arrows). Few impurities are seen in the sample during the SEM observation, indicating a high purity of the DWNTs in the film. The DWNTs bundles have diameters of about 5−30 nm.

Figure 1c shows a typical TEM image of the DWNTs film prepared with an argon flowing rate of 3000 mL/min in 10 min. The diameter of the DWNTs bundles mainly distributes in a range of 5−30 nm. Very few impurities are observed in the image, which indicates the highly pure DWNTs in the samples.

Figure 2a shows a typical HRTEM image of the DWNTs prepared with an argon flowing rate of 3000 mL/min. Arrow A shows an individual DWNT with an outer diameter of 2.1 nm and an interlayer distance of 0.4 nm. The double walls structure of the DWNT can be identified clearly. Figure 2b is a HRTEM image of a DWNTs bundle tip, which shows that the most of carbon nanotubes in the bundles have two co-centric graphite cylinders. The DWNTs in the bundles assemble into a planar triangle lattice. The DWNTs are prepared with an argon flowing rate of 3500 mL/ min in 10 min. In the bundle, the DWNTs have similar inner diameters of about 2 nm, which are similar

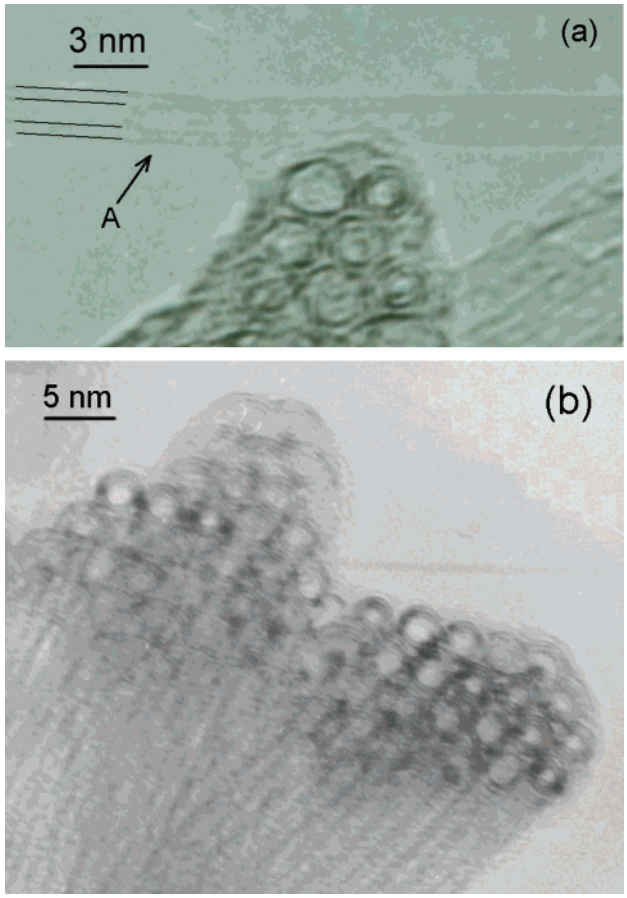

Figure 2. (a) HRTEM image of an individual DWNT with an outer diameter of 2.1 nm and an interlayer distance of 0.4 nm. (b) HRTEM image of a DWNTs bundle tip shows the two co-centric graphite cylinders of the DWNTs; the inner diameter of the DWNTs is about 2.0 nm.

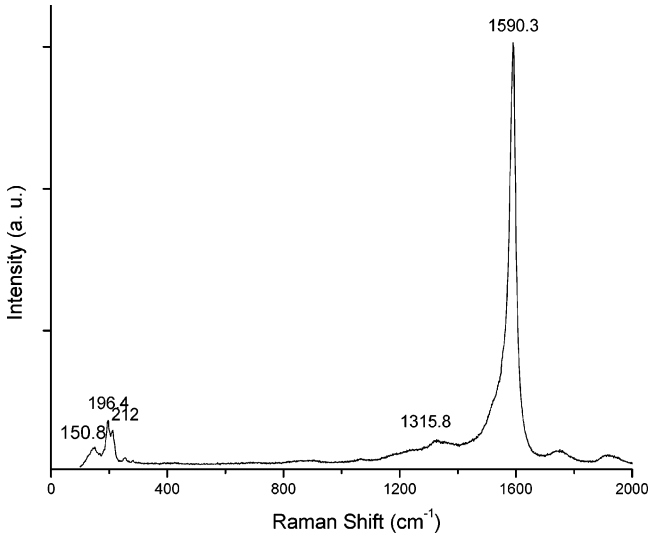

Figure 3. Raman spectrum of the DWNTs film.

to those in Figure 2a. The interlayer distance of the DWNTs in Figure 2b is about 0.4 nm, which is similar to that in Figure 2a. More than 80% of the observed samples are DWNTs by statistical observations of more than 120 carbon nanotubes in the HRTEM images.

Figure 3 shows a typical Raman spectrum of the DWNTs film excited by a 632.8 nm laser. The DWNTs film is synthesized with an argon flowing rate of 3000 mL/min and a

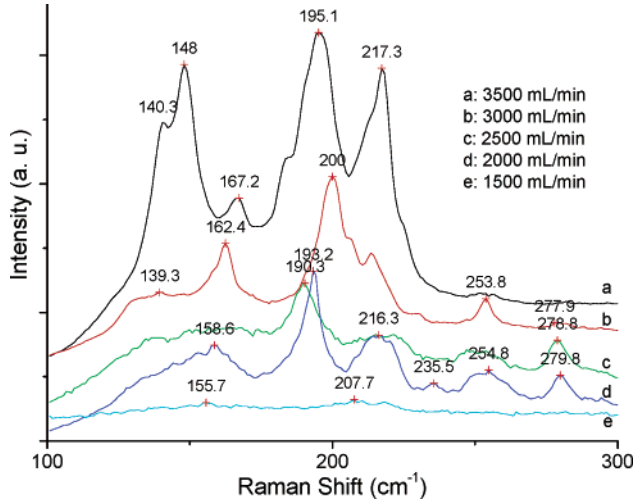

Figure 4. Raman spectra of the products prepared at different argon flowing rate.

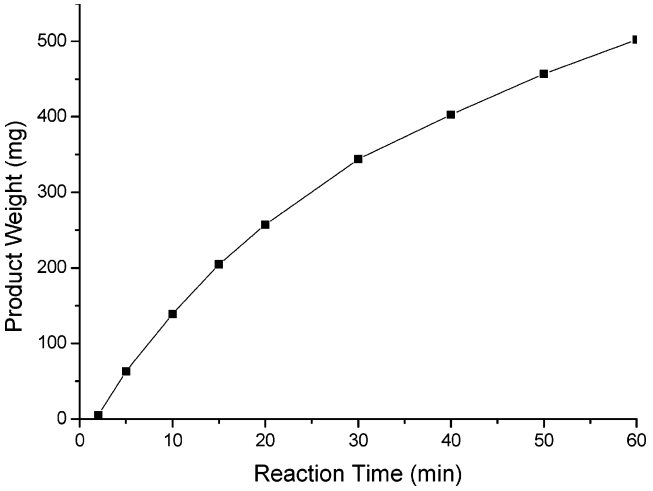

Figure 5. The plot of the product weight of the DWNTs vs reaction time.

xylene solution feeding rate of 0.06 mL/min. The tangential stretching mode (G-band), which is the strongest peak in the Raman spectrum, locates at 1590.3 cm^{-1}. The D-band of the DWNTs locates at 1315.8 cm^{-1}. The frequency of the D-band in our spectrum is lower than that of the normal MWNTs (~1332 cm^{-1}) and SWNTs (~1320 cm^{-1}) at 632.8 nm laser excitation, which is consistent with our recently Raman study on the DWNTs.[15] The ratio between the intensity of the G-band and D-band (I_G/I_D) can be used to show the crystallization of the carbon materials. In our samples, the $I_G/I_D = 14.6$, indicating a high crystallization of the DWNTs in the samples, which is consistent with the HRTEM observation. Several radial breathing modes (RBM) of the DWNTs are identified at the low frequency of the Raman spectrum. Three main RBM peaks, 150, 196.4, and 210 cm^{-1} can be identified in the Raman spectrum. The strongest RBM peak locates at 196.4 cm^{-1}, which indicates that most of the DWNTs have inner diameters of about 1.2 nm.

The flowing rate of argon plays an active role in the growth of the DWNTs. Figure 4 shows the Raman spectra of the DWNTs films prepared by the different argon flowing rate. It is clear to see that the component of the product depends on the argon flowing rate sensitively. At the argon flowing rate of 1500 mL/min, very few small RBM peaks can be identified in the Raman spectrum, which shows that very few DWNTs or SWNTs are found in the sample. When the argon flowing rate is larger than 2000 mL/min, the RBM peaks at about 190, 210, and 150 cm^{-1} become clearer and stronger as the argon flowing rate increases, which indicates that more and more DWNTs present in the product. The RBM peaks at about 195 and 217 cm^{-1} shift slightly as the argon flowing rate, which indicates small changes in the diameter of DWNTs in different airflow. Although some small diameter nanotubes can be identified in the Raman spectra (RBM peaks at about 254 and 278 cm^{-1}), the inner diameters of DWNTs in the samples mainly distribute in 1.0−1.2 nm and about 1.6 nm according to the Raman spectra in Figure 4.

The influence of the argon on the long DWNTs may be explained in the following two cases. First, the large flowing rate of argon reduces both the carbon and catalyst concentration in the reactor. The organic solution evaporates and decomposes into carbon clusters rapidly when they are injected into the reactor. The carbon clusters are diluted by the large airflow of argon and hydrogen, which can prevent DWNT from growing up to a multiwalled carbon nanotube. At the same time, large airflow of argon can prevent catalyst clusters decomposed from ferrocene from gathering into a large particle. The small catalyst particles are fitted for growing DWNTs or SWNTs. In the appropriate argon flowing rate, MWNTs are not observed in the samples.

Second, the flowing rate of argon determines the growing time of the DWNT in the reaction. When the flowing rate of argon is lower than 1500 mL/min, the products deposit on the quartz wall very near to the reaction zone. In this case, MWNTs and DWNTs coated with a thick amorphous layer can be found in the samples. The time when the catalyst particles stay in the reaction zone is only about 5 s in an argon flowing rate of 3000 mL/min. The time DWNTs stay in the reaction zone is also about 5 s. DWNTs are blown out from the reaction zone by the carrier gas before they grow up in the diameter direction. While the production rate of DWNTs decreases quickly if the flowing rate of argon is larger than 4000 mL/min. Thus, the optimized flowing rate of argon is about 2500−3500 mL/min. On the other hand, only SWNTs were obtained in the similar system without argon in the literatures.[12,13] In the experiments described in ref 12, carbon resources were evaporated by the carrier gas of hydrogen, and the carbon concentration in the reactor was so low that it fits for growing SWNTs, so they can get SWNTs in the samples. However, they product rate is rather low due to the small amount of the carbon feedstock in the reaction.

In the optimized argon flowing rate, DWNT films are blown out from the reaction zone quickly and deposit on the rear end of the quartz tube, where the temperature is below 400 °C. When the DWNTs are carried out from the reaction zone, they stop growing up in both axis and diameter direction. It is quite different from the situation of preparation of aligned MWNTs array on a substrate, which carbon nanotubes stay at the reaction zone during the whole reaction.

Figure 5 shows the dependence of the product weight on the reaction time. The feeding rate of the organic solution is 0.08 mL/min, and the argon flowing rate is 3000 mL/min. The weight of the product keep on increasing as the as the reaction time in our experimental system, but the growing speed slows down when the reaction time over 20 min. About 0.5 g DWNTs films and long filaments are obtained in 1 h. The product weight varies with the feeding rate of the organic solution. But as the feeding rate accesses 0.15 mL/min, MWNTs and DWNTs bundles coated with a thick amorphous carbon layer dominate in the product.

Conclusions

In summary, we developed an efficient method to synthesize very long DWNTs in a production rate of about 0.5 g/h using xylene as carbon feedstock. The inner diameter of the DWNTs varied from 1.0 to about 2.0 nm, and the interlayer distance of the DWNTs was about 0.4 nm. The argon flowing rate affected the growth of DWNTs sensitively.

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