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Bulk morphology and diameter distribution of single-walled carbon nanotubes synthesized by catalytic decomposition of hydrocarbons

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Abstract

Long and wide ropes/ribbons of single-walled carbon nanotube (SWNT) bundles with rope diameters of 100 μm and lengths to 3 cm were synthesized by the catalytic decomposition of hydrocarbons. These ropes/ribbons consist of roughly-aligned bundles of aligned SWNTs. The SWNT diameters, as determined from HRTEM images, are 1.69 ±0.34 nm, which, in combination with resonant Raman scattering measurements, indicates that our SWNTs have larger diameters than those synthesized by other techniques. The larger SWNTs are promising for gas-storage applications. The easy manipulation of the ropes offer special opportunities for their characterization and applications. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Much attention has been paid to both fundamental and applied research on carbon nanotubes [1–3] since the discovery of multi-walled carbon nanotubes (MWNTs) by Iijima in 1991 [4]. In particular, recent progress in research on the properties of single-walled carbon nanotubes (SWNTs), such as their atomic structure and electronic properties [5–8], gas storage properties [9], mechanical properties [10] and property enhancement through nanotube modification [11], has been outstanding, mainly due to the availability of sufficient quantities of SWNTs that can be obtained using the pulsed laser vaporization method [12] and the electric-arc technique [13]. It has been both predicted theoretically and demonstrated experimentally that SWNTs have many especially interesting properties. Since both the laser vaporization and electric-arc methods may not be the best methods for obtaining a continuous process for SWNT production on a commercial scale [14], more emphasis should be given from an applications standpoint to the production of high-purity, high-yield, low-cost, large-scale and easily handled SWNTs. Recently, we reported [15] a novel method for synthesizing SWNTs, the catalytic hydrocarbon decomposition method, in which benzene is catalytically decomposed at 1100–1200°C, yielding SWNTs which are similar, on a nanometer scale, to those obtained by laser vaporization [12] and electric-arc [13] tech-

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niques. This growth method allows lower growth temperatures, permits semi-continuous or continuous preparation and produces a large quantity of SWNTs at relatively high purity and low cost.

In this paper, two specific characteristics of SWNTs synthesized by the catalytic decomposition of hydrocarbons are reported. One is that the products mostly consist of macroscopic ropes and ribbons of aligned bundles of SWNTs, compared to the mats of randomly oriented and entangled carbon filaments reported by both the laser vaporization and electric-arc methods [12,13]. Another characteristic of the catalytically grown material is that the diameters of the SWNTs that we obtained, based on the results from high-resolution transmission electron microscope (HRTEM) images and Raman scattering measurements, are larger than those obtained by the laser vaporization [12] and electric-arc [13] techniques.

2. Experimental

The detailed experimental procedures for the preparation of SWNTs with our hydrocarbon catalytic decomposition method were described in detail elsewhere [15]. Basically, an improved floating catalyst method, similar to that used by Endo et al. for the vapor growth of carbon fibers [16], was employed in which a vapor-phase catalyst precursor (ferrocene) and a SWNT growth promoter (thiophene) were floated into a horizontal reactor to achieve semi-continuous growth of SWNTs. During the preparation of SWNTs, ferrocene was vaporized and carried into the reaction tube with a mixture of benzene and thiophene vapors and hydrogen gas. The vaporized ferrocene was at first reduced by hydrogen to form atomic iron, allowing atomic iron to agglomerate into iron clusters or nanoparticles appropriate for the growth of SWNTs. The reaction temperature was maintained at 1100–1200°C, and typical synthesis times for our runs have been between 1 and 30 min (but they can be much longer). The grown nanotubes were transported out of the reaction zone by the flowing reacted gases and the nanotubes were collected on a graphite plate or on the thermocouple-protecting tube and on the tube wall at the lower-temperature end of the reaction tube. The morphology and microstructure of the SWNTs that were obtained were observed in their as-prepared state using field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). To further characterize the SWNTs, Raman scattering of the radial breathing mode (RBM) of SWNTs in the region around 180cm^{-1} was measured, since the frequency of the RBM is inversely proportional to the tube diameter without any chirality dependence, according to theoretical predictions [17–19].

3. Results and discussion

3.1. Aligned large ropes and ribbons of SWNT bundles

The bulk morphology of SWNTs prepared by the laser vaporization [12] and electric-arc [13] techniques are reported to be a mat of tangled carbon filaments (SWNT bundles) 10 to 20 nm in diameter and many micrometers long and the axes for the SWNT bundles are randomly oriented within the mat. However, in our vapor grown sample under certain preparation conditions, large quantities of aligned, long and wide macroscopic ropes and ribbons were observed, as shown in Figs. 1 and 2, which look silver-black and appear to be very light, and some ribbons are semi-transparent, but free-standing.

Fig. 1 illustrates a photograph showing the actual

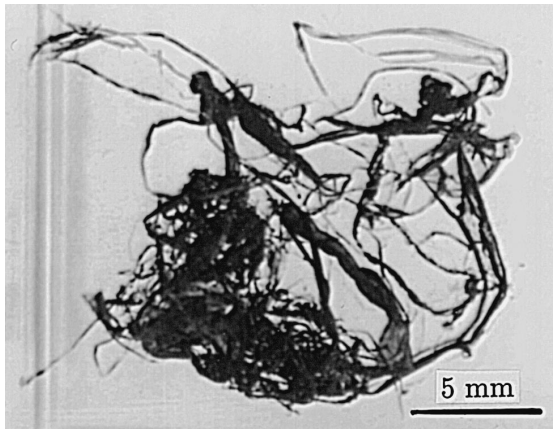

Fig. 1. Optical image of as-synthesized SWNT product obtained from the catalytic decomposition of hydrocarbons.

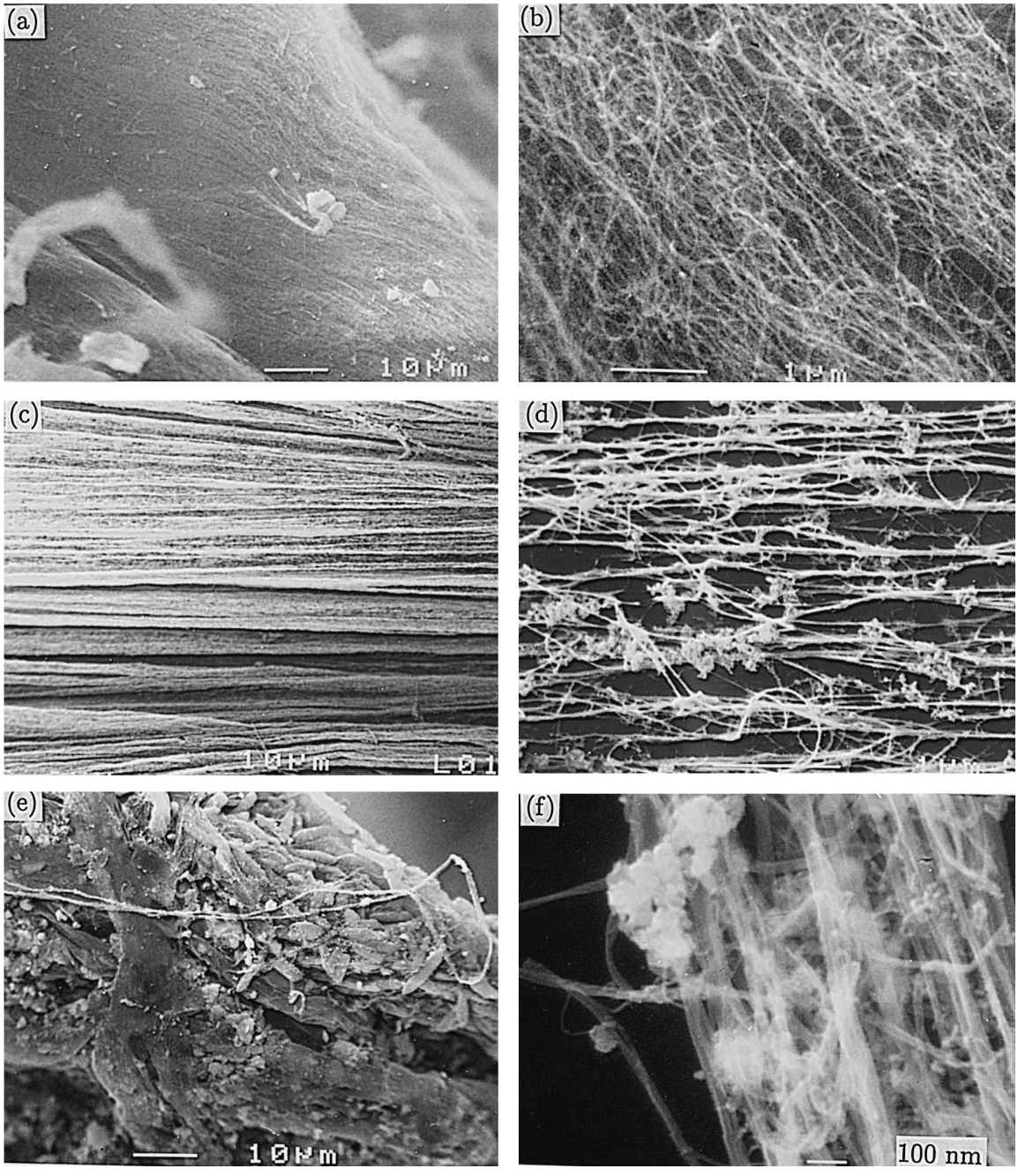

Fig. 2. SEM images of a rope and ribbon from the as-synthesized product prepared by catalytic decomposition of hydrocarbons. (a) A low magnification image of a rope. (b) An enlargement of one portion of the rope in (a). (c) A low magnification image of a ribbon. (d) An enlargement of one portion of the ribbon in (c). (e) A low magnification image of a fine rope. (f) An enlargement of one portion of the fine rope in (e).

size of the products. It shows that the products mainly consist of many ropes and ribbons that can be clearly distinguished to have lengths of several centimeters (the longest rope was about 3 to 4 cm) and with diameters of about 0.1 mm or widths of several millimeters. These ropes and ribbons can be isolated from one another by hand. If we examine one rope or ribbon, which can be observed using SEM, we will see that the rope or ribbon is composed of thousands of roughly-aligned whisker-like filaments, as shown in Fig. 2. These filaments were previously shown to contain SWNT bundles, and TEM observations of the material in Fig. 2 is shown in Fig. 3. For example, a rope with a diameter of about 80 μm is shown in Fig. 2(a) and many small threads in the rope are aligned preferentially along the axial direction of the rope. A magnified SEM image (Fig. 2(b)) illustrates that nanotube bundles are roughly aligned along the axis of the rope, although many bundles are also twisted with respect to one another. Figs. 2(c) and (d) show a ribbon with a width of more than 120 μm, in which the SWNT bundles are very well aligned along the longitudinal direction of the ribbon. The thickness of the ribbons in the product is typically ≤ 10 μm. Figs. 2(e) and (f) show a very thin rope with a length of more than 200 μm within the image and a diameter of about 1 μm. We can see again that the small bundles within the rope are well aligned along the axis of the rope and that the apparent diameters of SWNT bundles range from several nanometers to about 40 nm (Fig. 2(f)). A typical TEM image of the as-synthesized product is given in Fig. 3(a). Here we see that the bundles always consist of many well-aligned SWNTs and their diameters, ranging from several nanometers to 40 nm, are well maintained over the entire length, which is very similar to the SWNT bundles grown by other methods [12,13]. In this figure the cross-section of a SWNT bundle is seen. The bundle has a uniform diameter of 20 nm and consists of tens of SWNTs that are neatly packed.

On the basis of the above observed results, we conclude that the combination texture of the SWNT bundles synthesized by our hydrocarbon catalytic decomposition method, differs in detail from those produced by other major synthesis methods, and our SWNT bundles do have certain preferred orientations and tend to align along their axial direction to

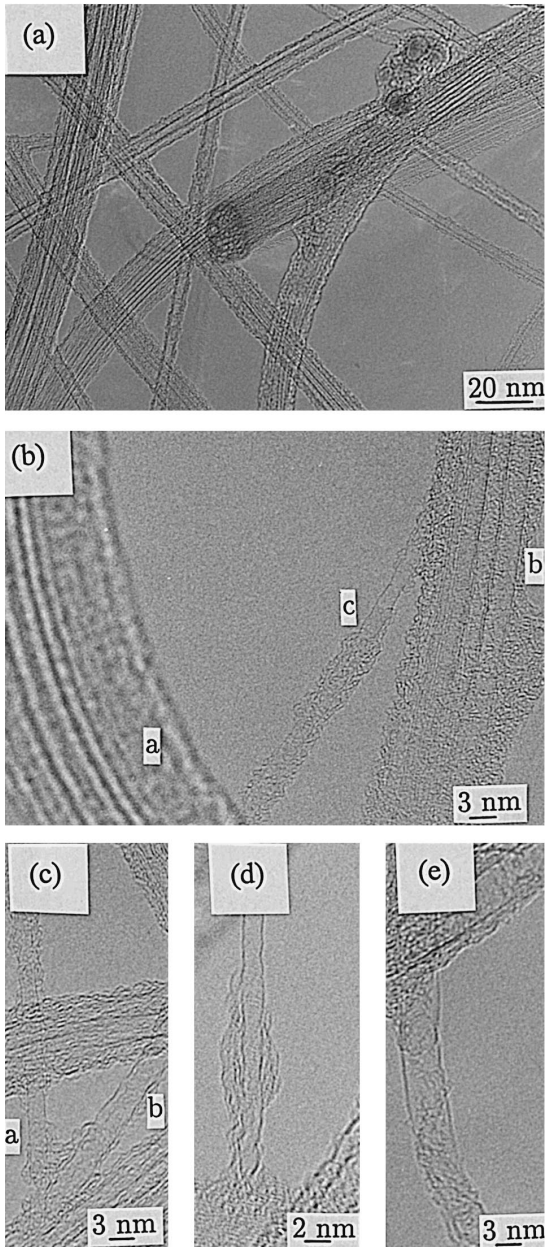

Fig. 3. HRTEM images of the as-synthesized SWNTs by the catalytic decomposition of hydrocarbons. (a) Bundles of aligned SWNTs. (b) Two bundles of aligned SWNTs and an isolated SWNT. (c) Two isolated SWNTs. (d) An isolated SWNT with a wavy morphology. (e) An isolated SWNT having the largest observed diameter of 4.3 nm.

form large ropes or ribbons. We consider that the formation mechanism for large SWNT ropes and ribbons is most probably related to the following physical process. The hydrocarbon catalytic decomposition method [15] works at normal atmospheric pressure within a certain gas flow rate, flowing in one direction. During their synthesis, the SWNTs in a bundle that are simultaneously grown in the reaction zone are transported out of this zone by the flowing gases, and the SWNTs adhere to the graphite plate or to the thermocouple protecting tube or to the reaction tube wall. The gas phases continuously flow into the reaction zone and the newly formed nanotubes continuously flow out of the reaction zone with the flowing gas phases. The newly formed SWNT bundles may adhere to the previously formed SWNT bundles due to a Van der Waals force, or they will mechanically twist or knit together to form long and wide ropes and ribbons. (Even during the preparation of samples for characterization, the tubes tend to adhere to one another or to other surfaces like a glass plate). Moreover, since the SWNT bundles thus formed are very fine and light, it is likely for the bundles to align along the flowing direction of the gas phases when the bundles are binding to each other to form ropes or ribbons. Because other main methods [12,13] for the synthesis of SWNTs basically involve a low vacuum environment and no obvious gas phase flow, it is unlikely for them to obtain long and wide SWNT bundles aligned into ropes or ribbons. Therefore, this SWNT rope/ribbon forming process can be considered to be one of the unique characteristics of our hydrocarbon catalytic decomposition method.

From Fig. 2, we also observe that some particles or particle clusters, which are considered to be impurities in SWNTs, such as carbon nanoparticles, catalyst particles and carbon blacks, exist on the surfaces of or among the SWNT bundles. This suggests that purification may need to be carried out before a precise characterization of the physical properties of the SWNTs is carried out.

3.2. Diameter distribution of the SWNTs

We have carried out further HRTEM observations on the as-synthesized samples and Figs. 3(b) to (e) show typical images of isolated SWNTs. Fig. 3(b) shows a well-aligned SWNT bundle with a diameter of 30 nm, four parallel SWNTs aligned one-by-one, and an isolated SWNT with a diameter of 1.7 nm, as denoted by a, b and c, respectively. Most of the isolated SWNTs that were observed have diameters ranging from 1.2 to 2.0 nm, as shown in portion c of Fig. 3(b) , portion a of Fig. 3(c) and Fig. 3(d). A few very large SWNTs were also observed, such as those shown in portion b of Fig. 3(c) (3.2 nm) and in Fig. 3(e) (4.3 nm), where the nominal projected diameters were given in parentheses. Although no SWNTs with diameters larger than 2 nm were reported in the as-synthesized form by the laser vaporization and electric-arc methods, Nikolaev et al. [20] reported that as many as 60% of the SWNTs prepared by laser vaporization coalesced with neighbors after annealing at 1400 or 1500°C, resulting in nanotubes with twice (2.7 nm) and occasionally three times (4.1 nm) the diameter of the (10, 10) tube. These results suggest that big SWNTs, such as (20,20) tubes (2.75 nm) or (30,30) tubes (4.12 nm), can also be stabilized and synthesized. In addition, it can be observed that some SWNTs (Fig. 3(d)) have a wavy morphology, which is considered to be an imperfect structure. Such structures may be due to the low synthesis temperature and sulfur addition used in our hydrocarbon catalytic decomposition method.

The diameters of 74 isolated SWNTs were measured, with an accuracy of about ± 0.1 to 0.15 nm, based on HRTEM images similar to those shown in Fig. 3. From these measurements a diameter distribution for our SWNTs was deduced, and the results are shown in Fig. 4. Since only one SWNT with a diameter larger than 3.2 nm (4.3 nm as shown in Fig. 3(e)) was observed, we put this diameter value into the 3.0 to 3.2 nm diameter group of SWNTs to simplify Fig. 4. We can see that more than 75% of the SWNTs have diameters ranging from 1.2 to 2 nm, with a Gaussian mean diameter of 1.69 ± 0.34 nm. These results show that the SWNTs synthesized by our hydrocarbon catalytic decomposition method have larger diameters than those grown both by the laser vaporization method, whose diameters have a mean value [12] of 1.38 nm or a Gaussian mean value of 1.39 ± 0.1 nm, as fitted by the authors to the STM measurements by Wildöer et al. [6] and by the electric-arc method [13], whose diameters are about 1.4 nm.

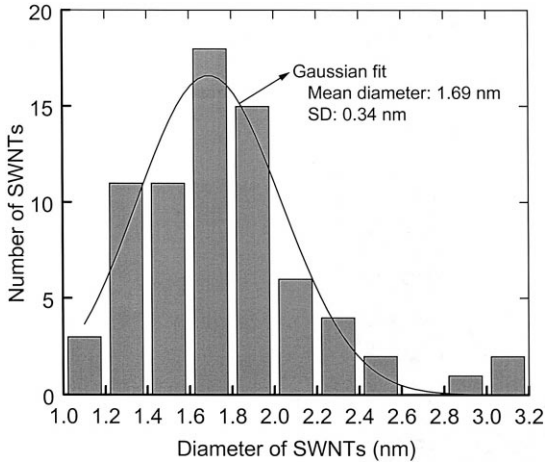

Fig. 4. Diameter distribution of the SWNTs obtained by the catalytic decomposition of hydrocarbons using data obtained from HRTEM images. The Gaussian fit to these data gives a mean diameter of 1.69 $\pm$0.34 nm for our SWNTs.

It is known theoretically [17–19] that the resonant Raman scattering from SWNTs associated with the radial breathing mode (RBM) depends strongly upon the diameter of SWNTs. The larger the diameter of the SWNTs, the lower the frequency of these RBM peaks. Therefore, resonant Raman scattering measurements of the as-synthesized SWNTs were performed for the RBM spectral region with a laser excitation energy of 2.54 eV, and the scattering profile for these results is shown in Fig. 5a. For comparison, we also measured the Raman band associated with the radial breathing mode of the SWNTs prepared by the laser vaporization method at the same laser excitation energy (Fig. 5b). Comparing Fig. 5a with b, the RBM frequency of the maximum intensity of the Raman bands for our SWNTs is shifted to lower frequencies by about 25 cm^{-1}, which indicates that our SWNTs do have larger diameters than those produced by laser vaporization, consistent with our HRTEM observations, as discussed above. However, the RBM spectra for our SWNT sample is fitted by only two Lorentzian-fitted curves with peaks at 159 and 154 cm^{-1} (Fig. 5a) and has a smaller bandwidth than that for the laser vaporization SWNT sample (Fig. 5b) which has a quite broad Raman band composed of more individual peaks (164, 168, 177, 182, 187, 194, 199 and 205 cm^{-1}), although our sample seems to have a wider diameter distribution from HRTEM observations. It is predicted that the Raman cross-section of the RBM decreases as the diameter increases. Thus the intensity of the RBM Raman peaks becomes weak, preventing their experimental observation for nanotube diameters in the wings of the diameter distribution, thereby resulting in a relatively narrow spectrum from the RBM, giving more weight to the contributions from the smaller diameter SWNTs.

According to theoretical predictions, the frequency of the radial breathing mode is inversely proportional to the diameter of the SWNTs. Recent calculations show that the frequency for the RBM for a (10,10) armchair nanotube is around 162 cm^{-1}, which leads to the expression $\omega = 223.75/d$, where ω is in units of cm^{-1} and d in nm [21]. Application of this expression to the experimental results from our sample, in which the RBM band is centered about 158 cm^{-1}, would give an average diameter of 1.42 nm, which is significantly smaller than the value obtained by HRTEM observations. Similarly, the average diameter of the laser vaporization sample obtained from the maximum of the RBM band (about 184 cm^{-1}) and using the above $\omega(d)$ versus $1/d$ expression [21] is around 1.21 nm, which is also

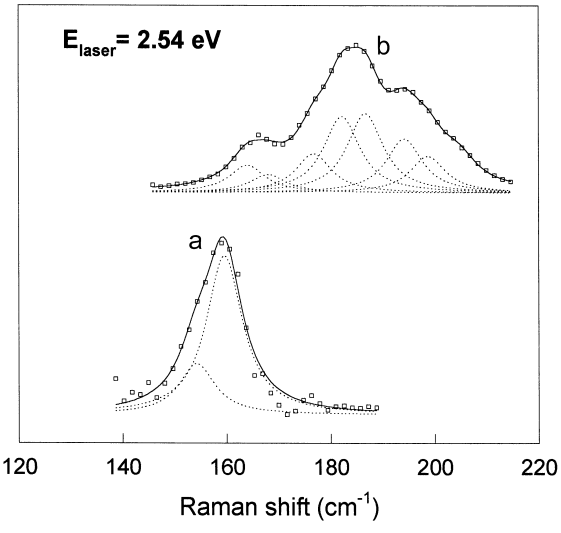

Fig. 5. Raman spectrum, using an excitation laser energy of 2.54 eV, of the radial breathing mode for the SWNTs prepared by the catalytic decomposition of hydrocarbons (a) and by laser vaporization (b). The dotted curves represent the individual Lorentzian curves and the solid curve represents the fit to the experimental data.

smaller than the average nanotube diameters for the laser vaporization sample (1.38 nm reported from X-ray diffraction results [12] and 1.39 nm by our Gaussian fit to the STM measurements by Wildöer et al. [6]). Although the reason for this difference is not yet fully understood, it may be explained by the decreases in the Raman cross-section of the RBM with increasing tube diameter, as discussed above. This discrepancy may also be ascribed to the underestimation of the RBM peak frequency for the (10,10) nanotube in the theoretical prediction. If we fit the experimental results of the mean diameter (1.38 nm) and maximum RBM Raman peak (184 cm^{-1}) obtained from the laser vaporization sample, the above expression will be adjusted to be $\omega = 254/d$. With this expression, we can obtain a mean diameter of 1.61 nm from the RBM Raman peak (158 cm^{-1}) for our sample, which is much closer to the HRTEM results. In addition, Kahn and Lu [22] pointed out that the RBM frequency of SWNTs in a bundle is expected to be higher than that of an isolated SWNT because of interactions between nanotubes. Since most of our SWNTs are observed to be in bundle form, the measured RBM frequency could be higher, which, as a consequence, results in a lower estimation of the diameters of SWNTs.

The growth mechanism of larger-diameter SWNTs from the catalytic decomposition of hydrocarbons with the addition of sulfur is not yet clear. One possibility attributes the larger diameters to the low growth temperature in the catalytic hydrocarbon decomposition method. The growth temperature for our method is relatively low (1100–1200°C), compared to the laser-generated and electric-arc-generated temperatures of graphite targets (about 3000°C) for other growth methods. This lower growth temperature may result in larger-diameter SWNTs, since the strain energy per atom for curving a graphene sheet into a cylinder is much higher at smaller diameter. In addition, the growth rate of SWNTs at lower temperature is slower, which gives more time to make larger tube diameters.

3.3. Expected applications for the above two characteristics of SWNTs

Brown et al. [23] have recently discussed the reversible hydrogen uptake in carbon-based materials. They estimated that, if hydrogen at the density of solid hydrogen with a hexagonal close-packed lattice were to fill the entire hollow of typical (10,10) SWNTs and the interstitial volume between these SWNTs, then the total hydrogen uptake would be [H/C] = 114 atom% for (10,10) SWNTs, but for larger SWNTs with a 2 nm diameter, the amount of hydrogen that could be stored within the nanotube core at the solid hydrogen density would be increased to a [H/C] ratio of about 250 atom%, using the same set of assumptions. On the basis of their prediction [23], we estimate that the amount of hydrogen that could be stored within our SWNTs with a median diameter of 1.69 nm could be as high as about 150 atom%, a rather optimistic value for practical energy-related applications.

Dillon et al. [9] investigated experimentally the hydrogen absorption capacity of SWNTs with a mean diameter of about 1.2 nm in comparison with that of activated carbon. They showed that hydrogen can condense to a high density inside the narrow core of SWNTs under conditions that do not induce adsorption within a standard mesoporous activated carbon. The hydrogen uptake capacity of their SWNTs was found to be 5–10 wt%, or an [H/C] ratio of about 60–120 atom%. They also pointed out that the amount of hydrogen stored for a practical vehicle powered by a fuel cell required system densities approaching 6.5 wt% and 62 kg H_2 m^{-3}, and no storage technology is currently capable of meeting these goals. However, they predicted that SWNTs with diameters of 1.63 nm and 2.0 nm would come close to the target densities and could operate near room temperatures if modest H_2 over-pressures compensated for the lower heats of adsorption expected in the larger cavities. High energy storage efficiencies can also be achieved, if the system could be operated at or near ambient temperatures and pressures. Therefore, larger diameter SWNTs synthesized by our hydrocarbon catalytic decomposition method appear to be very promising for this application.

Since the long and wide ropes and ribbons of aligned SWNT bundles can be easily handled and manipulated by hand or with the aid of a low-magnification optical microscope, the availability of such nanotubes will be of importance for many property characterizations and application explorations of

SWNTs. For example, by incorporating such an aligned SWNT rope into a resin matrix to form a mini-composite structure, the mechanical properties of the SWNTs can be characterized through a combination of experimental measurements and modeling predictions for composite materials. This research is in progress and preliminininary results show that it is promising.

4. Conclusions

1. The products synthesized by the catalytic decomposition of hydrocarbons consist mainly of long and wide, macroscopic ropes or ribbons of aligned SWNT bundles with rope diameters of about 100 μm or ribbon widths of several millimeters and lengths of about 3 cm. The microstructure observations show that the ropes consist of many roughly-aligned bundles and the bundles consist of well-aligned SWNTs.
2. The formation of aligned ropes and ribbons of SWNT bundles is considered to be one of the unique characteristics of the hydrocarbon catalytic decomposition method, mainly due to the action of the van der Waals force, the flow of the gas phases in one direction and the mechanical interlocking and twisting of the bundles.
3. The diameters of our SWNTs, which were determined from high-resolution transmission electron microscopic images, mostly range from 1.2 to 2.0 nm and have a mean value of 1.69 ± 0.34 nm from a Gaussian distribution analysis, which, in combination with the Raman scattering results for the radial breathing mode frequencies, indicates that our SWNTs have mean diameters that tend to be larger than those obtained by the laser vaporization and by the electric-arc techniques.
4. The SWNTs with larger diameters will be more promising in gas-storage applications, such as a hydrogen-storage material for fuel-cell operated electric vehicles. The easy handling and manipulation of the long and wide ropes and ribbons of aligned SWNT bundles will be of importance for the characterization of the properties of these vapor grown SWNTs and for the exploration of new applications for these SWNTs.

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