Cap Formation Engineering: From Opened C$_{60}$ to Single-Walled Carbon Nanotubes

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ABSTRACT Structural control, and especially chirality control, remains a significant challenge in the synthesis of single-walled carbon nanotubes (SWNTs). We report herein a rational approach to engineering fullerene caps for growing SWNTs with controlled structures via chemical vapor deposition (CVD). Opening of fullerendione via thermal oxidation yields hemispherical caps which can initiate SWNT growth at their open ends. The size and structure of these caps can be engineered by tuning the temperature of thermal oxidation. Results show that pregrowth treatment of the cap is indispensable to successful growth of SWNTs. The temperature used for thermal oxidation strongly affects the size and structure of the cap and further determines the diameter distribution of the as-grown SWNTs. Stronger oxidation treatments (450 °C oxidation in air) promote formation of thinner SWNTs, while weaker oxidation treatments (350 °C oxidation in air) lead to wider SWNTs. Interestingly, SWNTs made using fullerene caps show steplike diameter distributions relative to SWNTs catalyzed by Fe nanoparticles. This cap engineering using opened C$_{60}$ provides a potential approach to grow SWNTs with controlled structures.

KEYWORDS Cap formation, opened C$_{60}$, chemical vapor deposition, single-walled carbon nanotube

Single-walled carbon nanotubes (SWNTs) have been regarded as one of the best candidates for future applications in nanoelectronic devices due to their unique structure and superior electrical properties.[1,2] However, almost all currently available technologies for SWNT growth, including arc discharge, laser ablation, and catalytic chemical vapor deposition (CVD),[3] can only produce a mixture of metallic and semiconducting SWNTs; this limitation largely impedes device performance. Moreover, techniques for producing SWNTs with controlled structure, and specifically controlled chirality, are still in their infancy where a lot of challenges remain. The ability to grow SWNTs with well-controlled structures is highly desirable for both fundamental research and practical applications.

In recent years, much progress has been made toward controlling SWNT structural features such as diameter, conductive properties, and chirality. With respect to diameter control, factors such as temperature,[4] category and size of metal catalysts,[5,6] flow rate of the carbon source,[7] and gas pressure[8] have been investigated rigorously. For most metal-catalyst-involving approaches, however, catalyst particle size is difficult to control at high growth temperatures, thwarting attempts to synthesize SWNTs with uniform diameter. Recently, it was demonstrated that the diameter

of SWNTs can be tuned by changing the growth temperature, which could be applied to forming intramolecular junctions.[9]

To obtain semiconducting SWNTs, many groups have been devoted to developing postgrowth separation methods such as electrophoresis,[10] density gradient induced centrifugation,[11] and gas-phase plasma etching.[12] All of these approaches can effectively synthesize a high percentage of semiconducting carbon nanotubes.[13] In order to avoid chemical decoration, damage, and contamination during the process of removing metallic SWNTs, a simple way has been reported to directly grow semiconducting SWNT arrays with the assistance of ultraviolet (UV) irradiation.[14] Recent progress has demonstrated that metallic SWNTs can be preferentially grown by controlling the annealing conditions of metal catalyst.[15]

Synthesis of SWNTs with identical chirality is essential for their application in nanoelectronic devices because electronic structures are defined by the chiral index (n, m). In this area, bimetal catalysts[16] and carefully selected carbon sources[17] have been exploited to grow SWNTs with narrow (n, m) distributions. Chirality-dependent wrapping by DNA[18] and nucleotides[19] have also been exploited to select carbon nanotubes with specific chiralities. The approaches reported can produce SWNTs with narrow (n, m) distributions or even enrich SWNTs of a single (n, m) index. Recently, it was proposed that chemical synthesis can be used to obtain single-chirality SWNTs.[20] Up until now, it has been difficult to directly grow SWNTs of an arbitrary, desired (n, m) index.
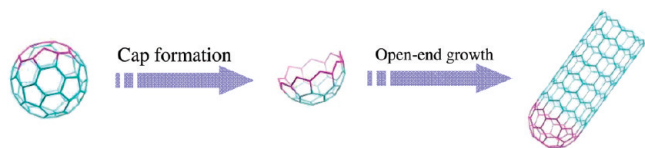
FIGURE 1. Schematic illustration of SWNT growth using fragmented C_{60} as an initiating cap.

It is well-known that SWNT structures are determined by the initial carbon structure as growth begins. The structure of this "cap" is determined during a nucleation stage. It is therefore possible to control the chirality of SWNT by controlling the cap formation process.[21] However, for growth processes using metal catalysts, cap formation at the particle surface is stochastic due to inevitable thermal vibrations during growth. This complicates attempts to control cap formation in catalytic CVD process. One promising concept, "carbon nanotubes cloning", has been proposed to control the chirality of SWNTs during CVD growth process. The concept is based on the use of open-ended SWNTs, a geodesic carbon dome, or other carbon structures as the seed/template for SWNT growth.[22] In our previous work, a rational approach to growing single-walled carbon nanotubes (SWNTs) with controlled chirality was reported based on the concept of cloning. By use of open-end SWNTs as seeds, duplicate SWNTs could be grown and cloned from the parent segments without metal catalysts via an open-end growth mechanism.[23]

In the present work, we report an approach to engineer cap formation and grow SWNT using thermally opened C_{60} as a cap. Figure 1 shows the basic concept of this approach. Specifically, fullerendione was used as precursor to prepare hemispherical fullerenes. With thermal oxidation methods, carbon cages of fullerendione can be opened by breaking C−C bonds to yield an "opened" C_{60} structure. After water treatment to etch away amorphous carbon and removal of oxygen-containing terminal groups introduced by the oxidation process, these activated fullerenes could be applied as caps for growing SWNTs via an open-end growth mechanism. SEM and AFM characterization indicated that SWNTs could be grown with high efficiency and repeatability through this strategy. The pregrowth treatment of the C_{60} derivatives proved to be critical to successful SWNT synthesis. It was found that the diameter distribution of SWNTs grown with such C_{60} fragments is related to the temperature of the thermal oxidation. Higher oxidation temperatures (450 °C in air) promote growth of smaller-diameter SWNTs while lower oxidation temperatures (350 °C in air) promote growth of large-diameter SWNTs. SWNTs from opened C_{60} show discontinuous diameter distributions compared to SWNTs grown from an Fe catalyst.

Experimental Section. A. Preparation of Fullerene Caps. Fullerene caps were obtained from a precursor named as fullerendione derived from pristine C_{60}. The molecular structure of fullerendione is shown in Figure 2 and detailed
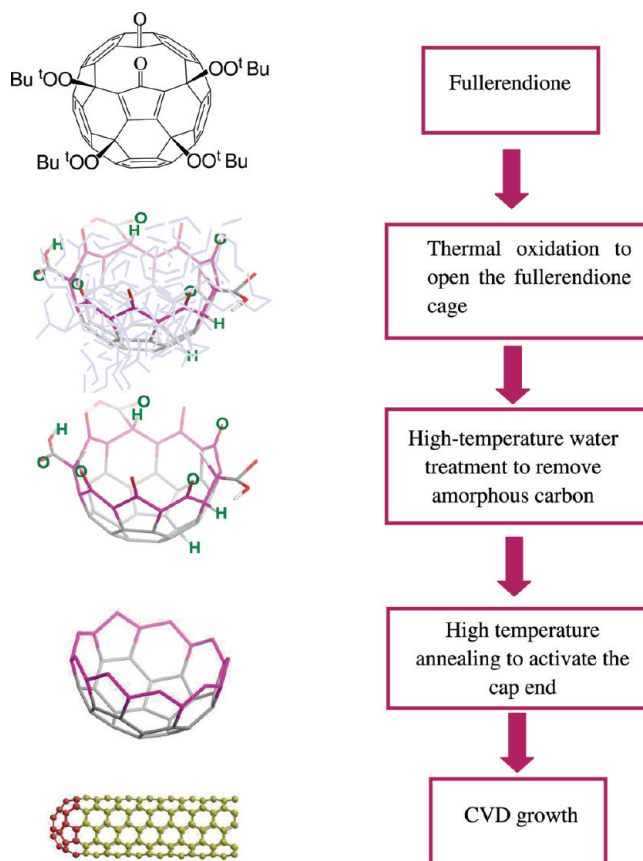

FIGURE 2. Illustration of the process of growing SWNT using opened C_{60} as a cap. The molecular structure of fullerendione is shown on the top left.

information of the synthesis process can be found in previously reported work.[24] Before the experiment, fullerendione in toluene was printed onto a ST cut quartz substrate by poly(dimethylsiloxane) (PDMS) stamp or placed onto the substrate via pipet. After evaporation of the toluene in air, the fullerendione was baked at 150 °C to remove any residual solvent.

In order to grow SWNTs using opened C_{60} as a cap, the precursor fullerendione needs to be opened prior to CVD growth. Several pretreatment procedures were employed to obtain hemispherical fullerene. As shown in Figure 2, the fullerendione first underwent thermal oxidation in air at various temperatures to open the carbon cage. This process was performed in a 1.8 cm tube furnace at temperature 300−500 °C for 30 min. The tube was designed to be movable so that the substrate position within the tube could be easily changed. After thermal oxidation treatment, the furnace temperature was elevated to 900 °C and the thermally opened C_{60} was treated in the presence of water to remove amorphous carbon. The sample was moved away from the hot zone during temperature elevation to avoid serious decomposition or sublimation of the fullerene caps. Lastly, the sample was annealed at 900 °C for 3 min to activate the carbon cap by removing carboxyl groups at the
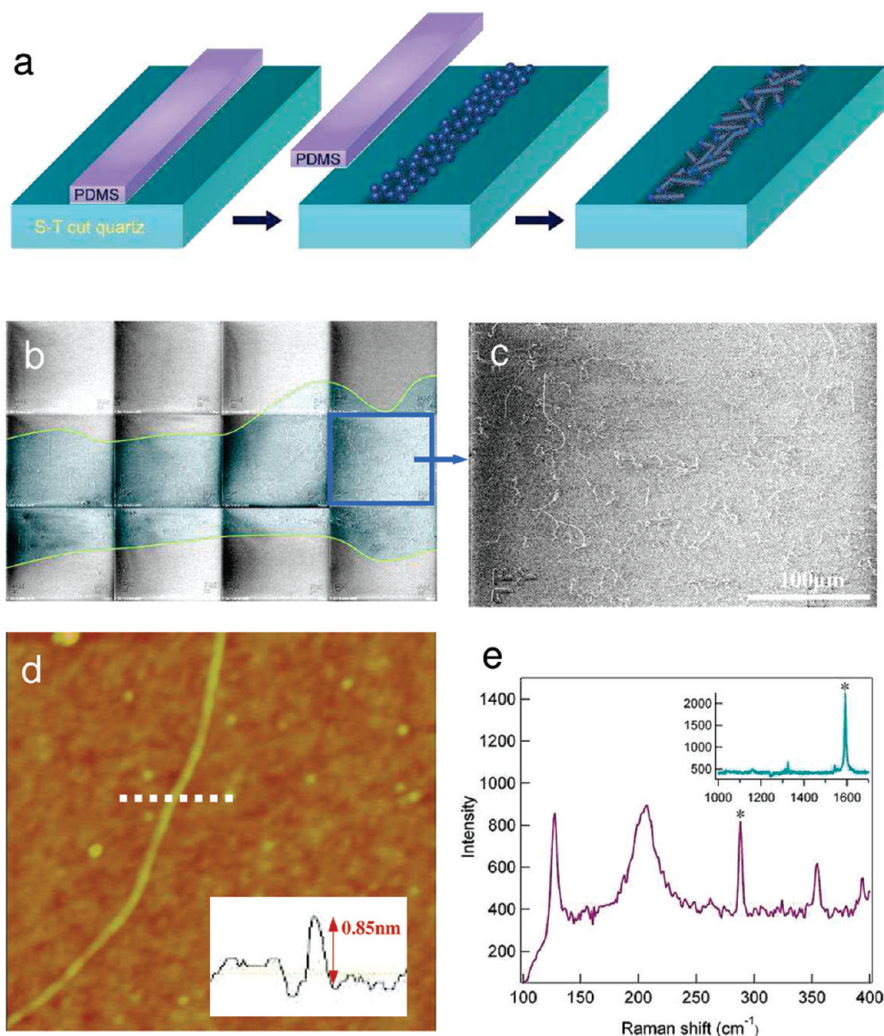
FIGURE 3. (a) The process of growing SWNTs using a fullerene cap. (b) Combined SEM images of the grown SWNTs. The SWNT region is highlighted in color for clarity. (c) A full SEM image of the pane-marked image in (b). (d) AFM image and section analysis of a SWNT. (e) RBM peak and G band (inset) of a SWNT on S-T cut quartz. Excitation laser wavelength is 633 nm.

open end of the cap. The treated caps were then used for SWNT growth.

B. Growing SWNTs Using Fullerene Caps. SWNT growth was carried out in a 1.8 cm tube furnace using a thermal ethanol CVD technique. CVD growth was performed at a furnace temperature of 900 °C. Pure Ar and H_2 were used as carrier gases (total flow 50 standard cubic centimeters per minute (s.c.c.m.)). Ethanol was introduced as the carbon source by bubbling pure argon through ethanol (gas flow 20 s.c.c.m.) for 20 min during SWNT growth.

C. Eliminating the Influence of Other Catalysts. The following procedures were used to ensure that SWNT growth was not caused by residual catalysts: (a) A new commercial quartz tube was installed for the growth experiment. Before use this tube was cleaned thoroughly with concentrated hydrochloric acid to remove any metal catalysts. (b) The quartz boat used to load the sample was cleaned with hydrochloric acid before use for the same purpose. (c) ST-cut quartz substrates were annealed at 900 °C for 8 h to obtain ideal crystalline surfaces. Cautions were taken to prevent abrasions of the crystal surface. As a control, a bare ST cut quartz substrate was used to grow SWNTs with no added substances.

D. Characterization of Grown SWNTs. A resonant micro-Raman spectrometer (633 nm excitation wavelength) and atomic force microscopy (AFM) using tapping mode were applied to characterize the structure of the grown SWNTs. In order to measure SWNT diameters, SWNTs grown on quartz were transferred to intrinsic silicon substrates using PMMA.[25] Before AFM measurement, the SWNTs on silicon were annealed at 700 °C for 2 h under an Ar/H_2 flow to remove any residual PMMA adhered to the SWNTs. Scanning electron microscopy (SEM) characterization was performed on a Hitachi S4800 scanning electron microscope.

Results and Discussions. A. Growing SWNTs Using Fullerene Caps. As illustrated in Figure 3a, with fullerendione as an ink, a fullerendione stripe pattern was formed on a clean quartz substrate via microcontact printing with a

PDMS stamp. The patterned fullerendione was then used to initiate SWNT growth. After thermal oxidation, high-temperature water treatment, and cap activation, CVD growth was performed at 900 °C. Figure 3b shows the combined SEM images of carbon nanotubes (CNTs) obtained by continuously scanning a region of ~1.2 mm × 0.8 mm. It can be observed that the grown carbon nanotubes form a stripe pattern (Figure 3c). Figure 3d is a typical AFM image of an individual CNT. Section analysis indicates the diameter is ~0.85 nm. The Raman spectrum (Figure 3e) shows a sharp peak at 288.2 cm^{-1}, which is attributed to the radial breathing mode (RBM) of a SWNT. The diameter of the SWNT is estimated about 0.86 nm using the equation of d (nm) = $248/\omega$ (cm^{-1}). Inset is the G band at 1592.5 cm^{-1} of the same SWNT. These characterization results indicate that SWNTs were grown from patterned fullerendione.

With thermally opened C_{60} as an initiating cap to grow SWNTs without metal catalysts, the growth mechanism may proceed in the open-end growth mode,[23] such that carbon radicals C_1, C_2, or C_3 are directly added to the end of the cap to form a SWNT. Although fullerendione is an open-cage fullerene (Figure 2),[24] the single broken C−C bond does not create a large enough opening to successfully initiate SWNT growth. Therefore, the cage of fullerendione needs to be further opened prior to CVD growth. The described thermal oxidation method, which has been reported previously,[26,27,30,31] was introduced to open the fullerene cage within a 350−450 °C temperature range. Panels a−e of Figure 4 show SEM images of SWNTs grown from fullerendione oxidized in air at temperatures of 300, 350, 400, 450, and 500 °C, respectively. It is clear that at oxidation temperatures of 350, 400, and 450 °C, SWNTs were grown with high efficiency, but growth efficiency drops significantly at temperatures below ~300 °C or above ~500 °C. For comparison, pristine, unopened C_{60} was also used to grow SWNTs. It turns out that SWNT could not be grown from C_{60} when the thermal oxidation was performed below ~450 °C. Interestingly, when thermal oxidation was performed at 500 °C, SWNTs were grown efficiently via CVD (Figure 4f). The result indicates that both fullerendione and C_{60} can be used as seeds/caps for growing SWNTs, but they must be fully oxidized prior to CVD growth to open the carbon cage. The effective cage opening temperature for pristine C_{60} is higher than that of fullerendione.

After thermal oxidation, other forms of carbons, including amorphous carbon, were also produced due to the complexity of the oxidation process.[27] These unwanted carbons need be cleared away before SWNT growth or they may cover the caps and hinder SWNT growth. Thus high-temperature water treatment was performed to remove amorphous carbons from the oxidized products.[28] Our experiments demonstrated that SWNT growth efficiency was extremely low without the water treatment process (Figure 5a). Growth efficiency increased remarkably when the thermally opened
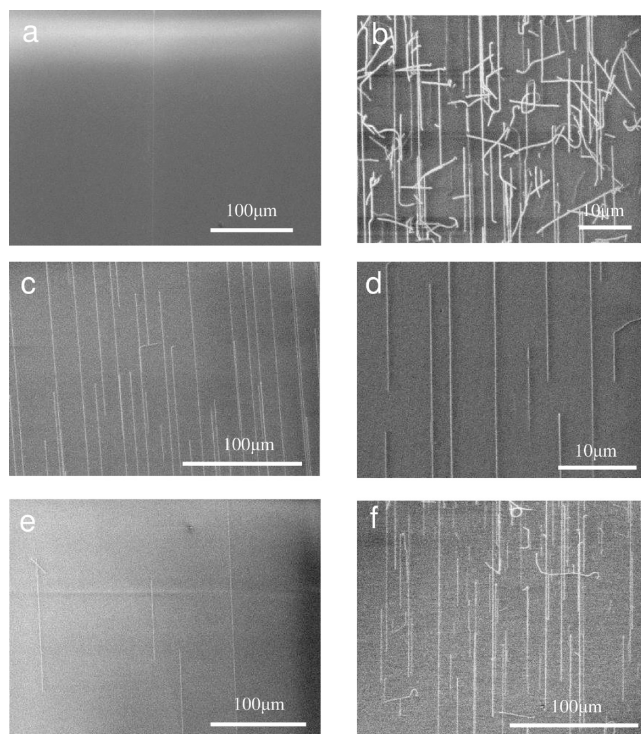
FIGURE 4. SEM images of SWNTs grown from fullerendione on ST cut quartz surface using thermal oxidation treatment at 300 (a), 350 (b), 400 (c), 450 (d), and 500 °C (e), respectively. (f) SEM image of SWNTs grown from pristine C_{60} using thermal oxidation treatment at 500 °C.
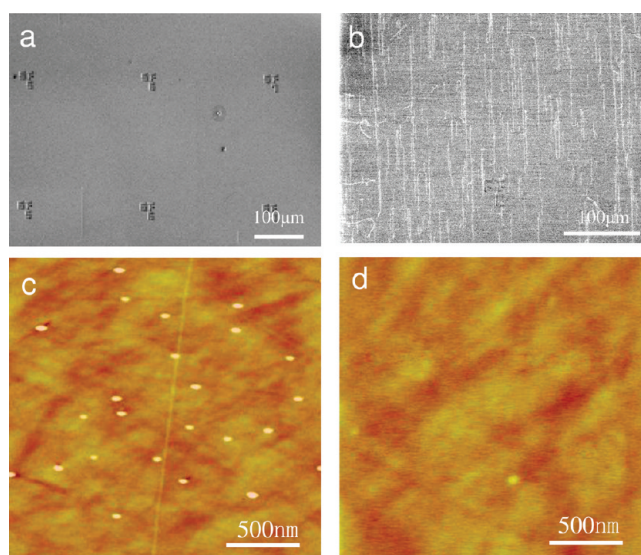
FIGURE 5. SEM images of the SWNTs grown from fullerendione without (a) and with (b) water treatment. The AFM images of a SWNT sample after CVD growth (c) and 700 °C heat treatment of (c) in air (d).

C_{60} was heated in the presence of water for only 2 min at 900 °C (Figure 5b). The water gas was introduced by bubbling pure argon through water under ambient conditions. The content of water in the gas should be sufficient. It was also observed that large amounts of water can reduce

growth efficiency, which is attributed to excess etching of opened C_{60} caps.

During the thermal oxidation process, oxygen-containing functionalities such as carboxyl groups were introduced to the ends of the opened caps, deactivating them toward SWNT growth. For this reason the sample was further annealed at 900−1000 °C just prior to CVD growth to activate the cap. Experimental results show that the CVD growth tended to form amorphous carbon rather than SWNTs without this cap activation process. It should be noted that the water treatment and thermal annealing were all performed at high temperatures; thus the treating time was set cautiously to avoid serious decomposition or sublimation of the carbon caps. Experimentally, when water treatment was performed for 2 min and thermal annealing was performed for 3 min, SWNTs could be grown efficiently.

AFM characterization shows that the growth process also produced solid particles in addition to SWNTs (Figure 5c). These particles are either located on the substrate or attached to the ends of grown SWNTs (Figures S1 and S2 in Supporting Information). Heat treatment was conducted to study the stability of these particles. It was found that all of these solid particles can be burned away in air at ~700 °C for 10 min (Figure 5d) and are attributed to carbon particles formed during the CVD growth process.

The above results demonstrate that SWNTs can be grown repeatedly and consistently using fullerendione as a seed/cap. To ensure that SWNT growth was not caused by catalyst contamination or morphological changes of substrate by water (or H_2) etching,[29] a control experiment was done using a bare quartz substrate and AFM characterization was conducted afterward. The results showed that no SWNTs could be grown on bare substrate in the absence of fullerendione or C_{60}, and no morphological changes occurred on the quartz substrate during the whole process. Therefore the SWNT growth did not originate from residual catalysts or morphological changes of the substrate but from the existence of fullerendione or pristine C_{60} on the substrate.

B. Features of SWNTs Grown from Fullerene Caps. A marked feature of SWNTs grown from thermally opened C_{60} is that the diameter distribution is strongly dependent on the conditions of the thermal oxidation treatment. Figure 6a shows the diameter distribution of SWNTs from four samples obtained under different growing conditions. One SWNT sample was synthesized with an Fe catalyst using the typical catalytic CVD method. The three others were obtained using fullerendione as the precursor following the strategy described above. Fullerendione was oxidized at temperatures of 350, 400, and 450 °C, respectively. For each sample, AFM measurements were conducted to obtain the diameters of 100 SWNTs which were imaged randomly at different positions of the sample. It is evident from the figure that the diameter distribution of SWNTs from fullerendione depends strongly on the oxidizing temperature: stronger thermal oxidation treatment (450 °C) promotes growth of thinner
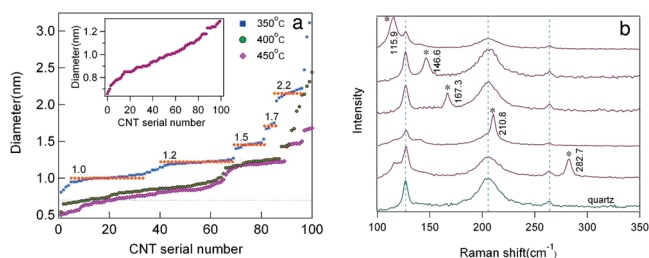

FIGURE 6. (a) Diameter distribution of SWNTs grown from fullerendione oxidized in air at different temperatures of 350, 400, and 450 °C, respectively. Inset is the diameter distribution of SWNTs grown with Fe catalysts. *X* axis denotes the serial numbers of SWNTs lined up from 1 to 100 according to the magnitudes of SWNTs diameters. (b) Raman spectra (RBM) of SWNTs showing similar diameters with the AFM measurements. RBM peaks are labeled by stars and wavenumbers. Excitation laser wavelength is 633 nm.

SWNTs, while weaker thermal oxidation treatment (350 °C) prefers to grow wider SWNTs. Under 450 °C oxidation conditions, around 20 % of the measured SWNTs are distributed below a diameter of 0.7 nm (the diameter of C_{60}); 80 % of the SWNTs are distributed above 0.7 nm. For the 400 °C thermal oxidation, 10 % of the SWNTs are distributed below 0.7 nm while 90 % of the SWNTs are distributed above 0.7 nm. For the 350 °C thermal oxidation, very few of the measured SWNTs are distributed below a diameter of 0.7 nm. Because the diameter of a SWNT is determined by the cap structure at the nucleation stage, the dependence of the diameter distribution on oxidizing temperature indicates that the cap formation process is strongly affected by the thermal oxidation conditions.

Another feature illustrated in Figure 6a is that the diameter distribution of SWNTs from opened C_{60} is not continuous but shows a steplike aspect. Along the steps of the 350 °C curve, dotted lines were plotted to demonstrate the mean diameters of the data points included in each step. The average gap between two successive steps is estimated to be 0.2−0.3 nm. To examine whether the diameter gap is caused by statistical variation, the diameter distribution of SWNTs grown with Fe catalyst is shown in the inset of Figure 6a for comparison. It is evident that the diameters of the Fe-grown nanotubes are distributed continuously from 0.6 to 1.3 nm and no diameter "steps" can be observed. The clear distinction suggests that the steplike feature is not caused by statistical reasons but is an intrinsic property of SWNTs grown from opened C_{60}. Figure 6b shows the RBM peaks of SWNTs in Raman spectra, indicating the diameters from RBM peaks are similar to those obtained with the AFM measurements.

C. Mechanism of Growing SWNTs from Fullerene Caps. The above results demonstrate that SWNTs can be grown from thermally opened C_{60} using the established strategy. The growth of SWNTs from opened C_{60} cannot be explained by the vapor−liquid−solid (VLS) mechanism commonly accepted for growing SWNTs using transition metal particles as catalysts. Under the VLS model, the active carbon species in the vapor phase diffuses into a liquid

nanoparticle and nucleates at the liquid/solid interface leading to the growth of a SWNT. For CVD growth of SWNTs from thermally opened C_{60}, the diffusion of carbon radicals into the carbon seed can be neglected. We propose that the growth of SWNTs from thermally opened C_{60} follows a vapor–solid (VS) mechanism, for which the opened C_{60} serves as a carbon cap for growing SWNT via an open-end growth mode. We have previously reported that an open-end SWNT segment can be used as the carbon seed for growing SWNTs following a similar mechanism.[23] Previous thermogravimetric analysis (TGA) experiments showed that pristine C_{60} starts to lose weight above ∼450 °C in air.[30,31] Emission FTIR studies showed that the C_{60} cage can be broken by thermal oxidation.[26] In the present work, thermal oxidation treatment was introduced to open the fullerendione (or C_{60}) cage at various suitable temperatures (Figure S3 in Supporting Information). After the cage-opening process, broken bonds are formed at the edge of cage-opened C_{60} which can deoxygenize and form dangling bonds during the process of high-temperature annealing. These active dangling bonds can react with carbon species in the subsequent CVD process, allowing the cage-opened C_{60} to play the role of "cap" in the growing of SWNT. The cap-directed growth mechanism here is different than the case where nanoparticle was proposed to provide a curved surface for cap nucleation and no chemical bonds can be formed at the particle surface.[32,33]

AFM characterization shows that in most cases SWNTs are free of solid particles at the two ends (Figure S1 in Supporting Information). In such cases, SWNTs can be grown from a single carbon cap residing on the surface or floating in the gas by sublimation. Under some circumstances, carbon particles were found attached to the ends of SWNTs after the CVD process (particles can be burned away by heating in air at ∼700 °C). However, there appears to be no correlation between particle size and SWNT diameter (Figure S2 in Supporting Information). Considering the pretreatment processes prior to CVD growth, it is possible that the oxidation and annealing processes can introduce dangling bonds to the curved surface of the fullerene fragment, which can react with carbon species during the CVD process and grow into larger carbon particles at the end of a SWNT. Using special carbon structures as seeds for growing SWNTs in open-end growth mode, the chemical activity of seed is essential to growth results. When growing SWNTs using thermally opened C_{60} as the cap, growth efficiency was critically dependent on the high temperature water treatment and high temperature annealing, which were performed to keep the cleanliness and activity of the cap. During the process of cage opening, the thermal oxidation conditions can determine the size and structure of the opened caps. Oxidation treatments of fullerendione at higher temperatures tend to open the cage to a larger extent and produce smaller carbon caps, and vice versa. This is supported by the comparison of AFM morphology of fulleren-
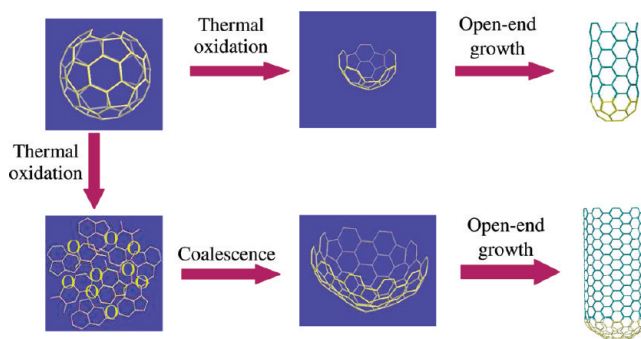

FIGURE 7. Proposed mechanism of growing SWNTs using thermally opened C_{60} caps.

dione oxidized at 300 and 400 °C, respectively (Figure S4 in Supporting Information). Smaller caps can therefore grow thinner SWNTs, and larger caps can grow wider SWNTs. This agrees well with the fact that in the case of 450 °C oxidation, there are more SWNTs observed to be below 0.7 nm in diameter than in the case of 350 °C oxidation.

Diameter characterization shows that, in addition to small-diameter SWNTs (thinner than 0.7 nm), there are many large-diameter SWNTs wider than 1.4 nm. The proportion of large-diameter SWNTs in the total amount of SWNTs for the 350 °C thermal oxidation is 20 % greater than that observed for the 450 °C thermal oxidation. Obviously, the large-diameter SWNTs cannot be grown from individual caps of cage-opened C_{60}. Early work has demonstrated that, during thermal oxidation, oxygen can be inserted in the C_{60} layer and bridge C_{60} molecules together.[27] After thermal oxidation processing, fullerendione was broken into carbon caps and fragments existing either as individual caps or as oxygen-bridged cap/fragment aggregates. At the CVD growth temperature (900–1000 °C), oxygen atoms can be removed and the bridged caps/fragments can coalesce into larger carbon caps which serve as seeds for growing large-diameter SWNTs. The overall proportions of the large-diameter SWNTs are dependent on the size and proportions of the coalesced caps. Under constant annealing condition, the diameter of a coalesced cap is determined by the size of individual opened caps/fragments. This can lead to the observation that more large-diameter SWNTs were formed in the case of lower-temperature oxidation treatment compared with higher-temperature oxidation treatment. The proposed mechanism of forming individual and coalesced carbon caps is shown in Figure 7.

For the usual catalytic CVD method, cap nucleation occurs at the particle surface; therefore the size of the cap is closely related to the diameter of nanoparticle.[34] Because the diameters of nanoparticles are continuously distributed in a certain range, it is natural that the diameters of SWNTs grown with Fe catalyst are also continuously distributed in a certain range. A different pattern is seen with fullerene caps. It can be reasoned that under certain thermal oxidation and annealing conditions, the carbon cage of fullerendione

tends to be selectively opened at the broken C−C bond, resulting in limited possibilities for carbon caps; the categories of coalesced caps from individual caps/fragments should therefore also be limited. Therefore the diameter distribution of caps derived from fullerendione should not be continuous but are instead discrete.[35] This elucidates the origin of the steplike distribution of SWNTs grown from thermally opened C_{60}.

Conclusions. We report a rational approach to engineering the structures of thermally opened C_{60} using thermal oxidation techniques. The opened C_{60} can be applied as caps to grow SWNTs with controlled diameters using the strategy we established. After thermal oxidation treatment to open the fullerendione cage, water treatment for etching amorphous carbon, and thermal annealing for removing terminal oxygen-containing groups, the fragmented C_{60} was applied as a cap to grow SWNTs. Size and structure of fullerene caps could be engineered by tuning the temperature of the thermal oxidation. The results indicated that the cage-opening temperature directly affects the diameter distribution of SWNTs. Higher cage opening temperatures are favorable for growing small-diameter SWNTs, while lower cage opening temperatures are favorable for growing large-diameter SWNTs. In addition, the as-grown SWNTs by thermally opened C_{60} show a steplike diameter distribution compared to SWNTs grown by Fe catalyst. This cap formation engineering using opened C_{60} has potential applications in growing SWNTs with controlled structure.

Supporting Information Available. AFM characterization of a 40 μm long SWNT grown from fullerendione, AFM characterization of carbon particles at the end of SWNTs grown from fullerendione, characterization of thermally opened C_{60} and ST cut quartz after the pretreatment processes before CVD growth, and AFM images of fullerendione oxidized at different temperatures.This material is available free of charge via the Internet at http://pubs.acs.org.

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