How Does A Carbon Nanotube Grow? An *In Situ* Investigation on the Cap Evolution

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ARTICLE

ABSTRACT Catalyst-free inner growth of single-wall carbon nanotubes has been directly realized and monitored by means of *in situ* high-resolution transmission electron microscopy, with particular attention paid to the evolution of the cap shape. The cap of a carbon nanotube is surprisingly found to be kept closed during the growing/shrinking process, and the cap shape evolves inhomogeneously with a few particular sites growing faster during the growth, while the cap of a carbon nanotube keeps a round shape during the shrinkage process. The closed cap should be specific for noncatalytic growth of carbon nanotubes. We infer, from the results above, the possible atomistic mechanism and how the carbon network can accommodate or release the carbon atoms during the growth/shrinkage of carbon nanotubes.

KEYWORDS: carbon nanotube · noncatalytic inner growth · *in situ* transmission electron microscopy

Understanding the formation mechanism of single-wall carbon nanotubes (SWNTs) is an essential step toward controlled production with desired chirality and diameters.[1] Over the past one and a half decades, numerous efforts have been made in this field;[1–6] especially, recent progress made by environmental transmission electron microscopy (TEM) observations revealed rich details and opened a new insight on the formation of SWNTs.[7–11] Even though, most of them deal with the catalyst-assisted growth, particularly, catalyzed chemical vapor deposition (CVD) of SWNTs, where the carbon atoms are supplied through the catalytic particles.

Noncatalytic growth of SWNTs and other related carbon nanostructures, such as carbon nanohorns,[12] should also be of particular importance. Soon after the discovery of SWNTs, Endo and Saito *et al.* proposed a few possible pathways for the closed-cap growth of a SWNT without any catalyst, where carbon clusters (mainly dimer C_2) could be continuously incorporated into the carbon network,[13,14] while this growth model has never been experimentally observed because the whole reaction might be highly energetically unfavorable. One of the most important approaches is the inner growth of SWNTs, which has been realized based on the so-called peapod structures.[15] By energetic irradiation or heating treatment, the fullerene molecules encapsulated inside the inner hollow cavity of a carbon nanotube (CNT) could coalesce to form a new SWNT,[16–18] which is completed through the initial polymerization and the following series of Stone−Wales (SW) transformations.[19–21] While strictly speaking, this process is "transformation" not real "growth". The fullerene cages are incorporated in whole, not in isolated carbon atoms and clusters. Besides this, it is rather difficult to investigate the dynamical transformation process since this experiment is hard to monitor, partially due to the short time-scale for SW transformations (in the range of nanoseconds or even faster). To solve this drawback, in this paper, we introduce an aboratively designed *in situ* high resolution (HR)-TEM method for the noncatalytic inner growth of SWNTs; by well controlling the supply of carbon feedstock through a thermally activated evaporation process, we are able to observe the evolution of a growing SWNT, with particular attention paid to the following question: How does the cap of a carbon nanotube evolve during the growing process?

In this study, CNTs containing a few discontinuous inner walls (frequently found in the pristine sample) are chosen and then manipulated inside a TEM with a dedicated specimen holder where a piezo-driven stage enables three-dimensional movements, using a tungsten (W) tip to manipulate individual CNTs while under TEM observations. A voltage could be applied to the CNTs and thus induce thermal energy into the specific CNT *via* joule heating.

Ⓦ This paper contains enhanced objects available on the Internet at http://pubs.acs.org/journals/ancac3.

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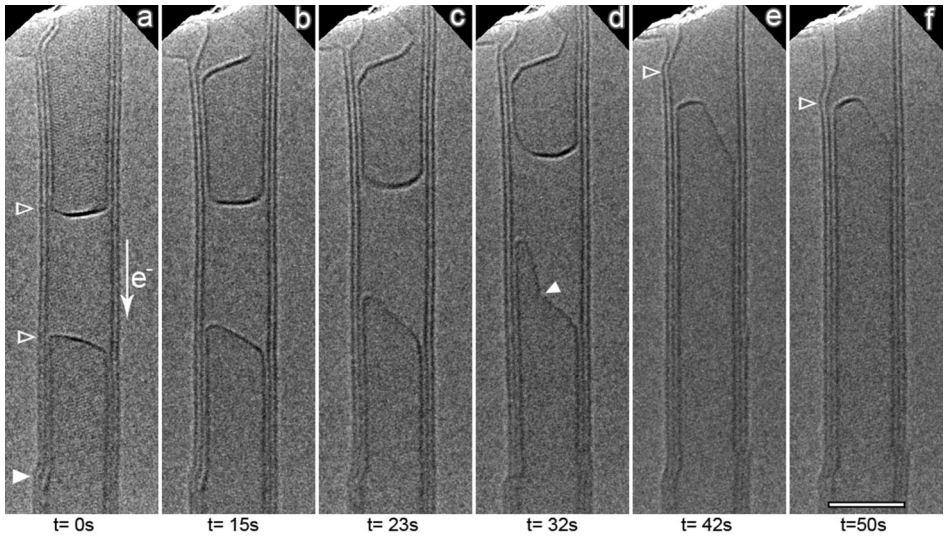

Figure 1. A time sequential TEM images for the catalyst-free growth of SWNT inside a DWNT. (a) Originally, two SWNTs are separated with a head-to-head distance of 8.3 nm. There is a local kink across the nanotube walls. No voltage is applied. The distance between two electrodes is about 52 nm. (b, c) Under 1.40 V and 42 μA, the top SWNT starts to continuously shrink on the cap, and simultaneously, the bottom one grows in its cap. (d) A cone-shaped local protrusion with a height of about 5.5 nm (marked as the filled white triangle) is formed on the cap of the bottom SWNT, while the cap of the top SWNT stays round. (e) About 42 s later, a new and solely one SWNT is formed and the top SWNT completely disappears. (f) With the voltage further increased to 1.42 V (a current of 44 μA), the newly formed SWNT further grows, while the kinks across the nanotube walls migrate downward (marked as the unfilled white triangle). Scale bar = 5 nm.

Ⓦ A HR-TEM movie for the noncatalytic inner growth of the SWNT is available.

A sequential HR-TEM image in Figure 1 shows different stages of noncatalytic inner growth of the SWNT. A double-wall CNT (DWNT) containing two seperated SWNTs inside the inner hollow cavity is chosen. This DWNT is bridged by a Pd electrode (top, Figure 1, not shown) and a W tip (bottom, not shown). Originally, these two close-capped SWNTs are apart from each other with a head-to-head distance of 8.3 nm, and they have the same diameter, 3.6 nm. No voltage is applied yet (Figure 1a).

When the voltage reached about 1.40 V (a current of 42 μA), the apparent shapes of their caps frequently fluctuated, which can be attributed to the structural reconstruction at a high temperature. About 15 s later, as shown in Figure 1b, the length of the bottom SWNT indeed increased, with its growing cone-shaped cap. Simultaneously, the other SWNT suffers shrinkage in its length.[22]

Keeping the applied voltage and current unchanged, the bottom SWNT is continuously growing into a longer one, and the top SWNT is consequently shrinking. Such a relative structural transformation becomes more obvious in Figure 1c. About 23 s later, the top SWNT decreases about 2.3 nm in its length, while the cap still remains round. The growing cap of the bottom SWNT develops inhomogeneously, with a few preferable cites growing faster than the others, leading a local protrusion formed on the cap. This kind of inhomogeneous growth is further "amplified" in Figure 1d; a local cone-shape protrusion with a height of about 5.5 nm forms and develops faster than the other sites on the cap. A negative curvature junction (see arrowhead in Figure 1d) is found on the side of this protrusion, which should involve the existence of a heptagon (or higher polygons) resulting from a generalized SW transformation. Interestingly, the cone angle of this protrusion is about 19°, which is close to that of the carbon nanohorns.[12]

As shown in Figure 1e, about 42 s later, the top SWNT completely shrinks and disappears, and a unique SWNT is solely formed. The cone-shaped protrusion was undergoing a diameter increase and length shrinkage, and the topological defects with negative curvature finally disappeared. The newly formed SWNT shared an identical diameter as the original one, without any observable topological defects found on its side wall. The length of the bottom SWNT increased about 14.0 nm, which is almost the same as the initial length of the top one, about 14.2 nm. From them, we could get an average growth speed of about 0.36 nm/s, which is relatively slower than the conventional CVD process—in the range of nano- to micrometer per second.[1]

From Figure 1, we could infer that here the bottom SWNT acts as the nucleation site and the top SWNT as the carbon source for the growth of new SWNT. The lost carbon atoms or clusters from the top SWNT should have been continuously incorporated into the carbon network of the bottom one to form a new tube. During the whole process, we do not observe any metal atoms or clusters which might come from the electrodes or residual catalyst particles, thus the possibility of metal-catalyzed growth could be strictly excluded since even an individual metal atom is found effective for assisting the tip growth of a close-capped SWNT.[13]

We have to address a few important issues for the further discussions. First of all, how are the carbon atoms released, transferred, and incorporated into the nucleation CNT? Activation energy is definitely required for the release of carbon from a closed cap and the incorporation into a new one. One important contribution should come from the thermal energy due to the high temperature *via* joule heating. The "hottest" temperature on the DWNT is roughly estimated to range

from 800 to 1800 K by taking the introduced power and the reported thermal conductivity in refs 23 and 24. Note that higher temperatures, 2000 or even 3000 K, have been claimed by Huang *et al.*[25] and by Zettl *et al.*[24] on a similar system. At such a high temperature, the carbon atoms can be thermally sublimated in the form of C_2. O'Brien *et al.* also demonstrated that photoexcited large fullerene cages would release even number carbon clusters, such as C_2 and C_4, until reaching the next stable configurations.[26] Furthermore, here the current density reaches to a high value, approximately 10^8 A/cm^2, therefore the related electromigration mechanism might strongly disturb the carbon network and assist the carbon evaporation/insertion.[27] Even though the electron beam is blanked, the inner growth can still take place with a similar external voltage and current applied. Therefore, the electron irradiation effect should not have a massive contribution to the experiment.

The carbon clusters evaporated from the carbon source, top SWNT, would migrate through the inner cavity or the nearest inner surface of the surrounding DWNT, and the latter one might be preferable due to the binding energy. The polarity of the external electric field does not directly affect the migration of carbon since even we reverse the applied voltage in Figure 1, and the bottom one still grows and the top one still shrinks.

Diffusion of carbon atoms or clusters through the inner surface of CNT could be a fast process at this high temperature. If we follow the proposed diffusion model in refs 28 and 29, on average, it would just take about 1 μs at 1400 K for carbon atoms to transit a distance of about 8.3 nm (cap-to-cap distance of two SWNTs shown in Figure 1). This fast diffusion rate might be one of the possible reasons why we could not observe any carbon atoms and clusters traveling during the whole process because it is far beyond the temporal resolution of our recording device.

Among our numerous experiments, we frequently observe that the SWNTs located around the middle prefer to first shrink, and those SWNTs near the metal electrodes are more likely to act as the nucleation and subsequently grow into a longer SWNT. This is consistent with the temperature distribution along the nanotube in ref 24.

After the carbon clusters evaporate from the closed cap and travel through the DWNT's inner surface, they should be continuously incorporated into the carbon network of the growing SWNT from its closed cap. As already proposed in refs 13 and 14, the carbon atoms or clusters could be inserted into the graphitic network through different pathways. Two topological feasible pathways are schemed in Figure 2a,b, where C_2 is inserted into a hexagon or a heptagon through serial local bond changes. It is suggested that the active sites are in the vicinity of pentagons.[13] Although, two pentagons abut after the insertion, which violates the isolated pentagon rule, while such a transition state should become available at high temperature, and it might be healed through the migration of topological defects.[30–32] As shown in Figure 2b, a pentagon−heptagon pair is annihilated after the insertion of a C_2, which might be responsible for the disappearance of the negative curvature junction, such as shown in Figure 1d. Through the continuous incorporation of radical carbon clusters and the reorganization of the local carbon network, the noncatalytic growth of SWNT with a closed cap should be feasible.

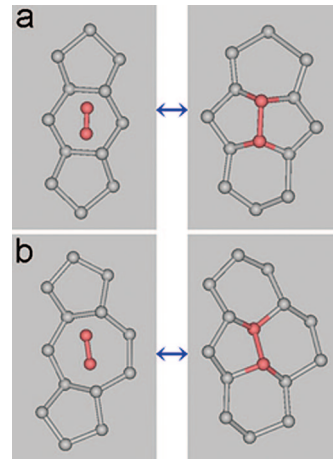

Figure 2. Representative schemes for two possible pathways to incorporate a C_2 into a hexagon (a) and a heptagon (b).

Again, the thermal activation and electromigration at high current density should be the main contribution for the incorporation of carbon and the local rearrangement on the cap. Fortunately, the energy barrier could be greatly reduced due to the presence of extra carbon atoms or clusters which bind loosely with the nucleation site, the so-called "autocatalysis" growth.[33]

During the whole process, the caps for these SWNTs—one growing and the other shrinking—remain closed. This is reasonable since the instability of dangling bonds will lead to spontaneous closure of the cap, especially for SWNTs with a small diameter less than 3 nm, and the thermally induced annealing would also facilitate the cap closure.

Now the inhomogeneous evolutions for a SWNT's cap during its growth can be reasonably understood as follows. Originally, the distribution of pentagons on the cap of the bottom SWNT could not be realistically homogeneous, and the structural fluctuation at high temperature will lead to a local change. In this way, some local active sites where a hexagon in the vicinity of two pentagons might first facilitate the incorporation of carbon clusters and a small protrusion, as shown in Figure 1b. Due to the curvature effects (the energy barrier for carbon incorporation should be lower for a SWNT with a smaller diameter), the newly formed pro-

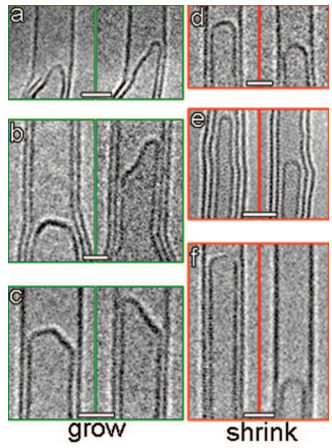

Figure 3. Image gallery for (a−c) the inhomogeneous growth of the SWNTs on the caps (green rectangular mark) and (d−f) nearly homogeneous shrinkage of the SWNTs on the caps (red rectangular mark). Scale bar in all panels is 2 nm.

trusion could preferably grow faster than the other sites on the cap, as evidenced by Figure 1.

There is an important and obvious difference between the growth and shrinkage of SWNT. By a careful comparison of the dynamics of two SWNTs in Figure 1, we found that the end (or cap) grew inhomogeously, while the other SWNT's cap always remained round during the whole shrinkage process. In order to exclude the casual accidents, a systematic investigation on a large number of specimens has been performed. Shown in Figure 3 is an image gallery for the cap evolution of growing or shrinking caps of CNTs. One could infer that the free carbon radicals (such as C_2 or in any other form) can be emitted from the symmetric end but not re-adsorbed to a stable geometry. However, at the asymmetric tip, the carbon radicals can be incorporated and the tube hence grows. Such inhomogeneous tip growth of SWNT, to our best knowledge, is the first time to be reported.

The outer DWNT plays a key factor for the catalyst-free inner growth of SWNT. Besides the reaction cell and resistive heating, it is also an indispensable template. It guided the supply of carbon atoms and the growth of a new SWNT (only longitudinal growth is permitted). As shown in Figure 1, the wall on the body of the newly formed SWNT matched the outer DWNT wall with an interwall distance of about 0.36 nm. In addition, the outer DWNTs could also directly act as the carbon source. As shown in Figure 1e,f, when the applied voltage was raised to about 1.42 V (and a current of 44 μA), the kinks (marked as the unfilled white arrowhead) on the side walls started to migrate downward, leading a ~0.4 nm diameter decrease for the portion of tube where it passed. Simultaneously, the SWNT was found to grow during the kink migration. Without this template, it would become intrinsically difficult to observe the noncatalytic growth of SWNTs with the cap closed.

In summary, we have presented *in situ* HR-TEM studies on the noncatalytic inner growth of SWNTs. The cap of a SWNT remains closed rather than open during its growing process, and the cap of a SWNT is found to develop inhomogeneously with a few preferable sites growing faster than the other sites on the cap. In contrast with the growth process, the cap remains a round shape during its shrinkage. Our results give another point of view on the formation mechanism of SWNTs and may shed light of future controllable production of SWNTs and other related carbon nanostructures. In addition, the presented method can be possibly used to repair defects of inner tubes by applying high current/temperature, and this may be of great interest for electronic applications of CNTs.

METHODS

This experiment was carried out with a transmission electron microcope (JEOL-2010F) operating at 120 kV. It was equipped with a dedicated holder, where a piezo stage drives a sharp tungsten tip (made from electrochemically etching) to manipulate an individual nanotube with a precision better than 0.5 nm. Commercially available MWNT samples were directly assembled onto a clean Pd wire by van der Waals force and then mounted onto the stationary side of the holder, opposite to the W tip. Many isolated individual MWNTs were found to extend out to the edge of the Pd wire under TEM observations. After the W tip contacts the free end of a selected sample, we were able to apply a voltage between the W tip and the Pt wire, thus inducing a current that passes though the object nanotube. TEM images were recorded by slow-scan CCD (Gatan 894), and the exposure time was set as short as 0.5 s in order to catch more dynamical process at the expense of degrading signal-to-noise ratio. The typical electron density is about 6×10^4 electrons/nm.^{2}

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