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Breakage, Fusion, and Healing of Carbon Nanotubes

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ABSTRACT

In-situ breakage of multiwalled carbon nanotubes (MWNTs) under TEM was observed. TEM data suggest that there exist chemical bonds between the broken graphene layer and the inner layer. A "breakage-sliding-fusion" model was proposed to rationalize the experimental observations. Complete load transfer to MWNTs was achieved by co polymerization of MWNTs with the matrix.

Multiwalled carbon nanotubes (MWNTs) have been shown to be extraordinarily strong with Young's modulus in the range of 270−1,250 GPa,[1−5] and are important parts as nanobearings, nanosprings, nanosyringes, nanorotors, and nanopistons for nanomachines.[6−9] Understanding the breakage mechanism of MWNTs is very crucial for the design and thus performance of nanodevices. Previously, a "sword-in-sheath" model,[1−3] based on scanning electron microscopy (SEM) images, was proposed to describe the breaking process of MWNTs. However, some experimental observations cannot be well rationalized by this model. For example, some MWNTs broke without extra "pullout" lengths, whereas most of MWNTs extend 2−12% (or 0.13−0.72 μm) in length before strain failure.[1] According to this model, strain failure should occur at very short length extension immediately after breakage of the outmost graphene layer since the friction due to van der Waals interactions between layers is very weak.[6,10] In addition, dangling carbons at the breakage sites of a broken graphene layer are very reactive and are not likely to remain inert toward the nearby graphene layer(s). Herein, we present consecutive transmission electron microscope (TEM) images to elucidate the in-situ structural changes of a breaking MWNT. TEM data strongly suggest that there exist chemical bonds between the broken layer and the inner graphene layer. A "breakage-sliding-fusion" model was proposed to rationalize the experimental observations.

MWNTs were copolymerized and embedded in a poly (methyl methacrylate) (PMMA) matrix. The MWNT containing PMMA was sliced into thin films of ∼700 nm thickness by a diamond blade in an ultracut microtome. A thin film was then supported by a Cu grid and observed under TEM. It is frequently observed that MWNTs bridge over two sides of a crack, where cracks were created during the slice cutting process. Accumulation of charges from electron beams in the nonconductive polymer film often leads to slow enlargement (or, sometimes, contraction) of cracks, which introduces stress and strain to MWNTs across a crack. Unlike those reported in the literature,[11,12] the copolymerized MWNTs will not be pulled out from one side of the crack. As shown in Figure 1a, the outer layer of the MWNT has been broken and pulled apart by ∼250 nm. The very ends of the broken graphene layer have "fused" (or formed chemical bonds, see further supporting evidences below in Figure 2) with the inner layer at locations shown by arrows. The existence of chemical bonds between the broken graphene layer and the inner layer is supported by the fact that the distance from a fusion point to one side of the polymer matrix remained constant under variable stress during the experiment (see Figure 1a−e). At fusion points, dangling carbons of the broken layer most probably form σ bonds with the olefin carbons of the inner layer. Formation of a σ bond simultaneously breaks a π bond. This bond formation-breaking process is thermodynamically favored (or exothermic), since a carbon−carbon σ bond (p orbit head-to-head bonding) is stronger than a carbon−carbon π bond (p orbit side-to-side bonding). The fusion points are potentially weakened sites for latter breakages, since C−C single bonds, instead of C═C double bonds, exist there. In Figure 1b, the right segment was further pulled out from the left segment, and breakage occurs at the original left fusion site since only a new fusion point (see arrow) is generated. In Figure 1c, the right segment was further pulled out, and its very end can be seen to be buried inside the left segment (see arrow and enlarged image in Figure 1f). In Figure 1d, the sharp end of the right segment was pulled out completely. The dangling carbons at the open end of the multilayered "sheath" segment quickly reorganize (within tenths of seconds under the TEM condition) to form an incomplete, partially closed end upon pullout of the right segment (see

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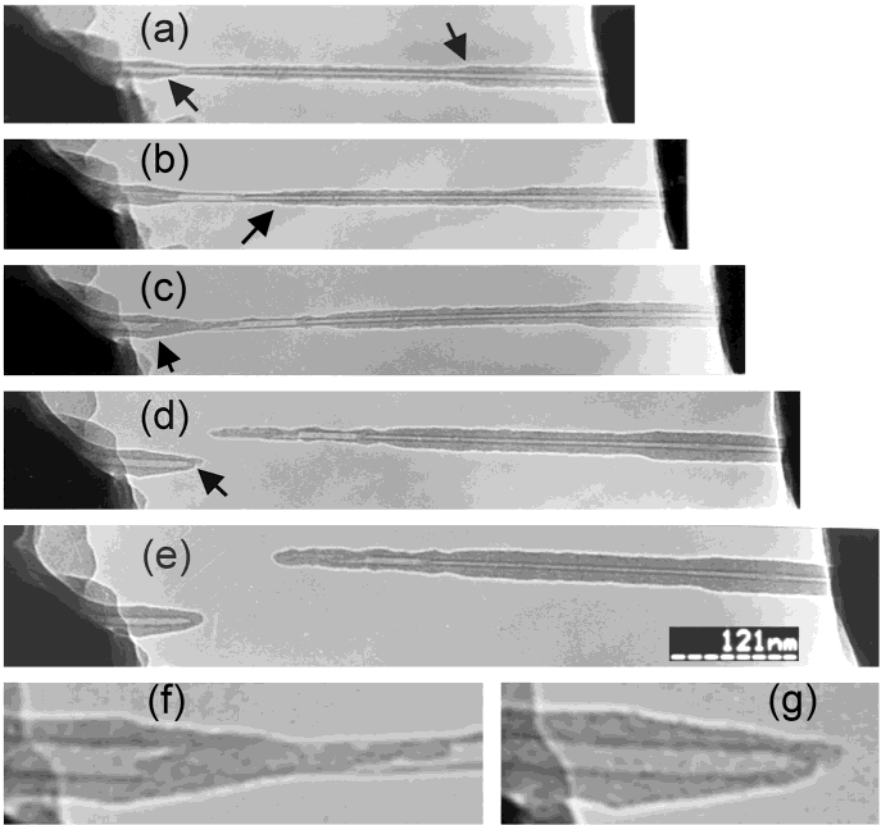

Figure 1. Consecutive TEM (Hitachi, 100 kV) images taken at various time, (a) $t = 0$, (b) $t \approx 2$, (c) $t \approx 6$, (d) $t \approx 10$, and (e) $t \approx 15$ min. The pictures in (f) and (g) are magnified images of those in (c) and (d), respectively. The scale bar in (a)−(e) are all the same.

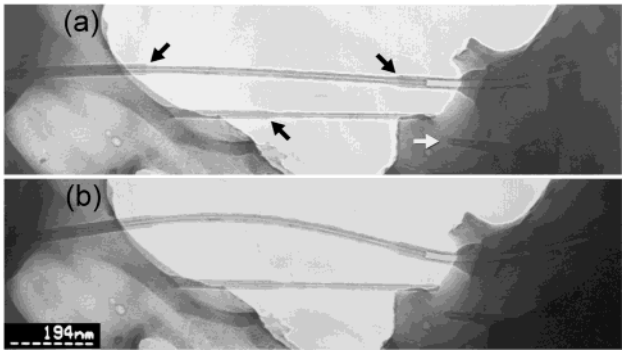

Figure 2. TEM images of two broken CNTs taken at different time, (a) $t = 0$; and (b) $t = 3$ min. The scale bar is the same for both (a) and (b).

arrow, and also the enlarged image in Figure 1g). In Figure 1e, the broken end of the left segment completely "heals" and becomes a seamlessly perfect CNT end. In literature, it was reported that prolonged (10−20 min) irradiation by focused high-energy (300 keV) electron beam could result in conversion of amorphous carbons into thermally more stable spherical carbon onions.[13] High energy (1.25 MeV) electron beam irradiation at high temperataure (800 °C) can also result in coalescence of single-walled CNT.[14] It was never observed that unfocused, low energy (100 keV) electron beam irradiation could result in the same reorganization of carbonaceous materials. In this study, the electron beam (Hitachi, 100 kV, unfocused) irradiation may offer some energy for the "healing" of the open CNT end in Figure 1e and g; the chemical instability of the dangling carbons at the open tip certainly provides a significant driving force for the reorganization of the open tip into a closed end. It was also noticed that the outer diameters of the CNT increase gradually from Figure 1a to e, which is attributed to the long-term (>10 min) deposition of carbonaceous materials from evaporation of the neighborhood polymer matrix upon electron beam irradiation. When a CNT is under electron beam for short time (e.g., < 5 min), the carbonaceous deposition phenomena was not observed (such as the conditions in Figures 2 and 3). Physical absorption of these carbon materials is not expected to affect the structural properties of a CNT. However, if the deposited carbon materials form chemical bonds with the outer graphene layer of a CNT, it may create a weakened site (i.e., a location of C−C single bonds, instead of unsaturated carbons). Creation of a new weakened site may alter the CNT breakage location, but not the mechanism.

The above MWNT breaking pattern can be well described by a repeating "breakage-sliding-fusion" process. Important supporting evidences are the observations of fusion points, a multilayered CNT "sheath", and a pullout segment with gradually diminished diameters. According to the "sword-in-sheath" model,[1] the sheath segment should be a single layer, and the strain failure should occur immediately after breakage of the outmost layer (i.e., at very short length extension). The previous observations that strain failure of MWNTs occurs after significant length extension, can be well rationalized by the current "breakage-sliding-fusion"

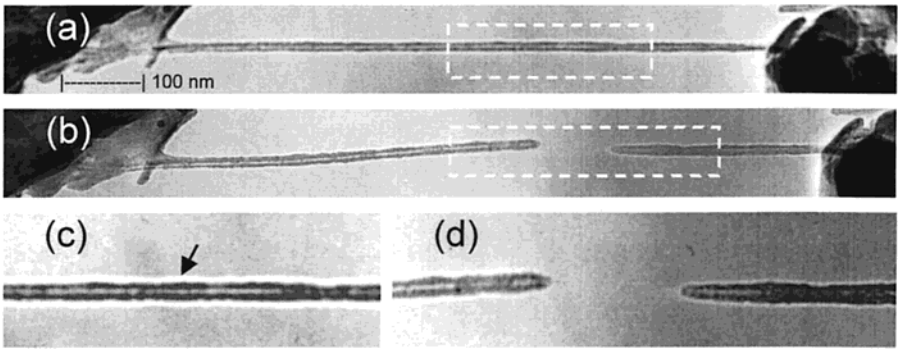

Figure 3. TEM images of a CNT taken at different time, (a)$t = 0$; and (b) $t = 2$ min. Images (c) and (d) are magnified pictures of the rectangular region of (a) and (b), respectively.

model. Concerning the "healing" of the CNT end in Figure 1d and e, it is known that the nanotube wall region is made of hexagons. Similar to fullerenes, any carbon nanotube end cap must follow the Euler's rule; that is, an end cap must contain six pentagons (for CNTs with the same diameter as that of C_{60}, or more than six pentagons for CNTs of larger diameters).[15] Therefore, to form a closed cap, the carbons at the open-end tip have to rearrange to form thermally more stable, pentagon-containing closed end cap. Most likely, such kind of rearrangements in Figure 1d were partially induced by electron beam irradiation. In plasma discharge processes, cationic carbon species are attracted by the negative electric field, fly to the cathode surface, and form an open-end growing CNT.[16−18] The CNT elongation process competes with the cap closing process. Upon discontinued supply of carbon atoms, the CNT end cap closing process dominates.[18] Similar to the observation in Figure 1c−e, high temperatures (3000−4000 K) at the arcing site can offer heat to overcome energy barriers and to promote rearrangements of dangling carbons to form an end cap. The data in Figure 1c−e provide an important "visual" evidence for the cap closing process of CNTs in carbon-arc growth processes at high temperatures. In literature, various CNT end cap opening methods[19−21] and metal filling into the CNT internal void space[22−24] have been reported. Figure 1c−e indicates that it should be possible to reseal the CNT end after filling of various substances by using electron beam irradiation or other high energy irradiations.

The above MWNT-breakage pattern can be observed repeatedly under TEM. Figure 2a shows two MWNTs in a PMMA matrix; one has been broken into two segments and another one has a broken outmost layer. Both of the CNTs show the presence of "fusion" points (see black arrows). The broken sheath segment of the bottom CNT has rehealed to become a closed end (see white arrow). The right segment is a multilayered sheath segment (the picture of the bottom CNT right before complete breakage was not shown). In Figure 2b, the polymer matrix contracts, which introduces compression stress and makes the upper CNT become bent. The "sword" segment does not reinsert into the "sheath" segment, which is most probably due to the presence of chemical bonds between the broken layer and the inner intact layer at the fusion point. Recently, it was reported that the inner intact segment of a peeled MWNT can be pulled out of (or pushed into) the outer broken sheath segment like a telescope without any friction between the intact and the innermost broken graphene layers.[6] This can be true only when the broken graphene layers form chemical bonds among themselves without forming bonds with the inner intact layer. Probably, different ways of creating broken graphene layers result in different patterns. The bond formation between a broken layer and the inner intact layer can rationalize why strain failure of MWNTs always occurs after large length extension.[1] The fusion behavior between a broken layer and an inner layer indicates that an inner graphene layer can also contribute tensile strengths when MWNTs were used as reinforcement additives in composite materials.

The breakage of CNTs in Figures 1 and 2 can be well described by the three-steps "breakage-sliding-fusion" model. The picture in Figure 3, however, shows a special example of this model; that is the absence of the "sliding" process. Figure 3a shows a MWNT bridging over the polymer matrix. The TEM resolution is not high enough to show the number of graphene layers. However, the thickness and the diameter indicate that the CNT is not single-walled. Upon expansion of the polymer matrix, the MWNT broke without length extension as evidenced by the nearly equal lengths of the segments to that of the original tube. The CNT segment near the breakage site (white square in Figure 3a) was enlarged and shown in Figure 3c. From the length, the breakage site can be assigned to the location as indicated by the arrow in Figure 3c. The breakage is expected to occur at the weakest defect site of the CNT, which, in this particular example, is not the thinnest location along the tube. The uneven tube wall is probably due to the presence of the PMMA copolymer on the CNT surface. When the polymer matrix expands, the outmost layer of the CNT was broken. The dangling carbons at the broken sites form chemical bonds with the inner layer, which weakens the inner layer and leads the breakage of the inner at the same location upon stress. The absence (or near absence) of the "sliding" process is probably due to a faster bond formation (or fusion) process than the sliding process (or a very slow sliding process). The extent of the sliding process is related to the magnitude of pulling force at two ends of the CNT. The breakage pattern in Figure 3 can be treated as a special example of the "breakage-sliding-fusion" model. In fact, breakage of CNTs without obvious

length extension was also observed in previous SEM experiments.[1] Again, the multiwalled, broken CNT segments soon (within tenths of seconds in the TEM chamber) "heal" to seamlessly perfect closed ends (see Figure 3d). The data in Figures 1−3 demonstrate for the first time that load can be completely transferred to copolymerized CNTs, which leads to complete CNT breakages but not being pulled out from the matrix.

In summary, different real-time breakage patterns of MWNTs have been observed under TEM. The CNT breakage patterns can be well rationalized by a "breakage-sliding-fusion" model. Observations of fusion points, a multiwalled CNT sheath segment, and a CNT segment with gradually diminished diameters strongly support the above model. TEM data strongly suggest that there exist chemical bonds between the broken layer and the inner graphene layer. Contrary to the previous prediction,[11,12] this chemical bond formation makes the inner graphene layer able to contribute tensile strengths when used as reinforcing additives in composite materials. The realization of MWNT breaking mechanism is very crucial to the future designs of CNTs as elements in mechanical nanodevices. Data in Figures 1−3 demonstrate that an open CNT end can form a seamlessly perfect closed end by reorganization of dangling carbons at the tip. The data here also provide a solution for the first time to the literature problem that poor interactions between CNTs and the matrix[11,12,25] can be significantly improved by copolymerization of CNTs with the matrix, which makes it possible to have complete load transfer to CNTs and thus to use CNTs as additives for reinforcement of composite materials.

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