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Non uniform shrinkages of double-walled carbon nanotube as induced by electron beam irradiation

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Electron beam-induced nanoinstabilities of pristine double-walled carbon nanotubes (DWCNTs) of two different configurations, one fixed at both ends and another fixed at only one end, were *in-situ* investigated in transmission electron microscope at room temperature. It was observed that the DWCNT fixed at both ends shrank in its diameter uniformly. Meanwhile, the DWCNT fixed at only one end intriguingly shrank preferentially from its free cap end along its axial direction whereas its diameter shrinkage was offset. A mechanism of "diffusion" along with "evaporation" at room temperature which is driven by the nanocurvature of the DWCNTs, and the athermal activation induced by the electron beam was proposed to elucidate the observed phenomena. The effect of the interlayer interaction of the DWCNTs was also discussed. © *2014 AIP Publishing LLC*.
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In recent years, much effort[1–12] has been devoted to processing of carbon nanotubes (CNTs) especially single-walled carbon nanotubes (SWCNTs) by energetic electron beam (e-beam) irradiation for their potential applications[13] in nanodevices and nanotechnology. In these studies, the structural changes at nanoscale (called thereafter as nanoinstability for short) of CNTs as induced by e-beam irradiation were generally described in terms of the existing theories such as knock-on mechanism and the subsequent atom reconstruction mostly along with some related simulations. Nevertheless, our recent observations[14] on accelerating shrinkage of diameter of SWCNT under e-beam irradiation demonstrated that nanocurvature effect of SWCNT is much exceeded that predicted from the reported theories and simulations. Moreover, our observations[15] also demonstrated that more curved SWCNT shank faster than a less curved one and with such a nanocurvature effect, SWCNT could also exhibit an extraordinarily plastic flow and wetting ability at room temperature under e-beam irradiation. The above observations confirmed that both the nanocurvature effect and the energetic beam-induced athermal (non-thermal) activation effect (or called as energetic beam induced-atomic vibration instability and soft mode) as we earlier predicted[16–18] for low dimensional nanostructures (LDNs) play a crucial role in energetic beam-induced nanoinstabilities of SWCNT. The above nanocurvature effect and the above energetic beam-induced athermal activation effect are intrinsically of nonequilibrium, disorder (amorphous-like structure) and nonlinearity nature, and cannot be adequately accounted for by the reported simulations or theories including the knock-on mechanism. This is because the reported theories and simulations which were built at the first place based on equilibrium, symmetry, translational periodicity, and linearity nature of bulk crystalline structure or its approximations where the nanocurvature effect[16,17] and the energetic beam-induced athermal activation effect[17,18] have attracted much less attention.

Further from the above studies we can also predict that similar nanocurvature effect and beam-induced athermal activation effect could also be found on e-beam-induced nanoinstabilities of multi-walled carbon nanotubes (MWCNTs). However, up to now, there is not an observation found to confirm such effects on MWCNTs. In order to further explore the nanocurvature effect and the beam-induced athermal activation effect on MWCNTs, we herein specifically investigated nanoinstability of double-walled carbon nanotube (DWCNT) with its unique double-layered tube structure, that is, the simplest structure of MWCNT under e-beam irradiation by our well-developed *in-situ* transmission electron microscopy (TEM) observation technique. It was observed that under e-beam irradiation at room temperature, pristine and straight DWCNT fixed at both ends shrank in diameter uniformly. Nevertheless, it is surprising that pristine and straight DWCNT with its one end fixed shrank preferentially from its most curved cap end in its axial direction whereas its diameter shrinkage was retarded. We proposed that a mechanism of "diffusion" along with "evaporation" at room temperature which is driven by the nanocurvature (surface energy) of the DWCNTs as well as the e-beam athermal activation, but is affected by the interlayer interaction of the DWCNTs could govern the observed nanoinstabilities of the DWCNTs.

The samples of DWCNT were fabricated by the floating catalyst method. They were well-dispersed in ethanol and deposited onto holy carbon film on Cu grids for TEM studies. The DWCNT TEM specimens as prepared were then irradiated at ambient room temperature to different doses or times

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and the structure evolutions of DWCNTs were *in-situ* observed by a high-resolution transmission electron microscope operated at 200 kV. The irradiation was always focused on segments of single clean tubes crossing over or protruding into the open space of the holes in the carbon film of microscopy grid so that local structure transformations or deformation of the tubes are not affected by any support within the holes. During the experiment, we always tilted the sample to make sure that axis of the tube was normal to the electron beam if there was any deviation of the tube from this position. In doing so, we ensured that there was no reduction in the projected or measured length of the tubes, which may be caused by any upward or downward tilting of the tubes. We took micrographs of the individual tube at each dose (or time) for observation and the contrast of the micrographs was enhanced through Fourier filtering by cutting frequencies beyond the information limit of the microscope. The tube diameter was taken as an averaged value of several tube radii which were measured at different representative positions across the tube from each micrograph to take account of any tube radius non uniformity after being deformed during the irradiation. During the irradiation, the current density at the specimen was kept at about 100 A/cm^2, which was uniform over an area larger than the zone observed. Furthermore, the beam was spread to an around 100 times weaker intensity in cycles for the observation or taking a picture. In doing so, the irradiation effect during the observation or taking a picture can be minimized to a negligible degree and at the same time the image contrast can also be improved. Note also that during the electron irradiation, the beam was expected to heat the specimens by no more than a few degrees[8] due to their extremely large ratio of surface to volume and the dominant irradiation effect should be athermal. Therefore, it could be considered that the tube DWCNT essentially remained at room temperature throughout the irradiation time.

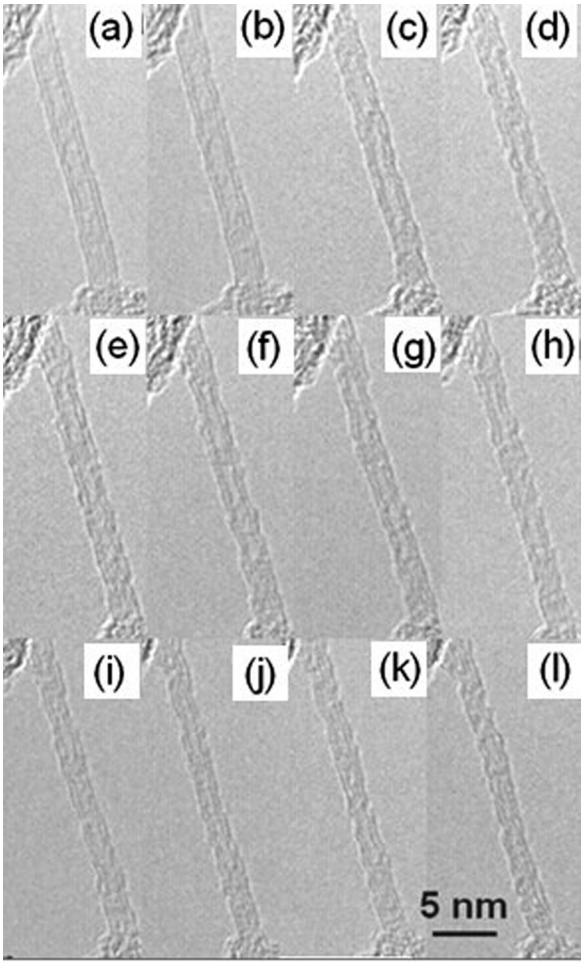

FIG. 1. Sequential *in-situ* TEM micrographs showing typical structure evolution of DWCNT with its two ends being fixed as induced by the e-beam irradiation to different irradiation time (s): (a) 0; (b) 60; (c)180; (d) 300; (e) 360; (f) 420; (g) 540; (h) 660; (i) 780; (j) 900; (k) 1080; and (l) 1140.

The sequential TEM micrographs in Figure 1 show the typical structural change and evolution of clean and straight DWCNT with its two ends fixed at ropes of nanotubes during irradiation of the electron beam up to about 1200 s. Figure 1(a) shows the DWCNT prior to the irradiation, which has a quite well-defined double-walled tube structure with a tube diameter of about 2 nm. Figures 1(b)–1(h) show the gradual change of the shape, structure, and size of the DWCNT after the irradiation to different irradiation time (or electron dose). As the tube ends are both fixed, the tube cannot shrink in its axis (we call it axial shrinkage) and can only shrink in its diameter (we call it radial shrinkage) to minimize its surface energy with reducing in its surface area. The average shrinkage rate for the tube diameters is about 5×10^{-4} nm/s. During the irradiation, the tube structure and the interlayer distance between adjacent outer and inner wall layers seems essentially kept unchanged. This indicated that during the dynamic competition between atomic defect creation and annihilation, the atomic defect annihilation may overall dominates over the atomic defect creation, giving rise to an ability for the tube to restore to its double-layered, curved sp^2 structure by atomic rearrangements or self-mending.[19,20] In this way, the tube became instable and was able to shrink *even at room temperature with e-beam activation* to form a tube of smaller diameter of another metastable structure configuration. The phenomena are similar to these as observed in SWCNT.[14] Thus, Fig. 1 clearly presents a direct experimental evidence for pure loss or escaping (ablation or "evaporation" at room temperature) of atoms as activated by the energetic e-beam irradiation as well as by the high surface energy as associated with highly curved tube surface. On the other hand, along with the shrinkage, an increasing number of beam-induced, local, small deformations, or structure defects such as necking, breaking, or fragmenting of tube walls can be observed. Although the intrinsic nonuniformity or fluctuation at nanoscale either of local beam current density or of local tube structure or in both during the irradiation may be one reason, the easy aggregation of local defects as observed herein in DWCNT compared with that in SWCNT as observed in Ref. 14 may be another reason. This indicates that during the dynamic competition between creation and annihilation of atomic defect, the ability for creation of atomic defect in a DWCNT or a MWCNT may be much stronger than that for a SWCNT. This may be due to the fact that the interlayer defects in-between adjacent graphene layers produced in a DWCNT[21] or in a MWCNT can be stable for a macroscopic time at the temperature below 450 K whereas defects in a SWCNT cannot.

In order to understand the mechanisms of both axial shrinkage and radial shrinkage of DWCNT under e-beam irradiation, we further investigate structural change of segment of clean and straight DWCNT which protrudes from a rope of nanotubes during the electron beam irradiation. The typical result is illustrated in Figure 2. Figure 2(a) shows the very initial DWCNT before irradiation. The original length of the tube segment was about 15 nm and the tube diameter was also about 2 nm. Figures 2(b)–2(i) show the gradual structural evolution of the DWCNT during the irradiation to different irradiation time (or electron dose). In this case, the most curved cap end of the tube became amazingly the most instable and the DWCNT shrank preferentially from the most curved cap end along the tube axial direction whereas the radial shrinkage is almost restrained. The axial length shrinks continuously with irradiation at an average rate of about 6×10^{-3} nm/s in the measured time interval whereas the average tube diameter almost remains unchanged. Similar to Figure 1, during the shrinkage, although the essential features of the double-walled tube structure remained unchanged, the tube wall structure became increasingly defected and the tube segment deflected in plan. Note that as mentioned in the experiment section, during the experiment, we always tilted the sample to make sure that axis of the tube is normal to the electron beam if there was any deviation of the tube from this position. In this way, we ensured that there is no reduction in the projected or measured length of the tubes, which may be caused by any upward or downward tilting of the tubes. The same irradiation on other tube segments of the similar configuration was repeated several times. It was observed that the features of the structure changes were essentially the same as shown in Figure 2, where a preferential axial shrinkage from free cap end of the tubes along with retardation in shrinkage of their diameter always occurred. Similar preferential axial shrinkage from free cap end along with retardation in shrinkage of their diameter has been also observed in SWCNT and MWCNT as well as in nanowire (X. F. Zhu *et al.*, manuscripts in preparation or to be submitted). This means that this kind of non-uniform shrinkage is probably a well-defined universal phenomenon in one dimensional nanostructure.

Obviously, the above difference between two shrinkages of the DWCNTs, as shown in Figures 1 and 2, is hardly expected from the existing knock-on mechanism employed in the literature. The above structural transformations could be well interpreted by athermal carbon atom "diffusion" and "evaporation" mechanisms, as we proposed based on the surface nanocurvature effect,[16,17] and the energetic beam-induced athermal activation effect.[17,18] As described in our previous papers,[14–17] when a planar monoatomic graphite layer is curved to a SWCNT and the radius of the SWCNT approaches the carbon atomic bond length, an additional nanocurvature effect would form and cause a tensile stress on electron cloud structure of outer surface of the SWCNT's wall and a compressive stress on that of inner surface of the SWCNT's wall as well. Such stresses would lead to a dramatic increase in the SWCNT's surface energy which leads to a strong thermodynamic force to drive the SWCNT to shrink. As the DWCNT can be considered to form by two coaxial SWCNTs, we assert that the surface tension of the highly nanocurved tube surface can be similar in DWCNT and plays a key role as well as in its beam-induced structural transformations. In addition to this, under e-beam irradiation, there may be not enough time for the deposited energy from the incident electrons to transfer to atom vibration energy within one single period of the atom vibration.[17,18] In doing so, the irradiated carbon atoms of DWCNT could lose stability or vibration mode of atoms would be softened and then energy

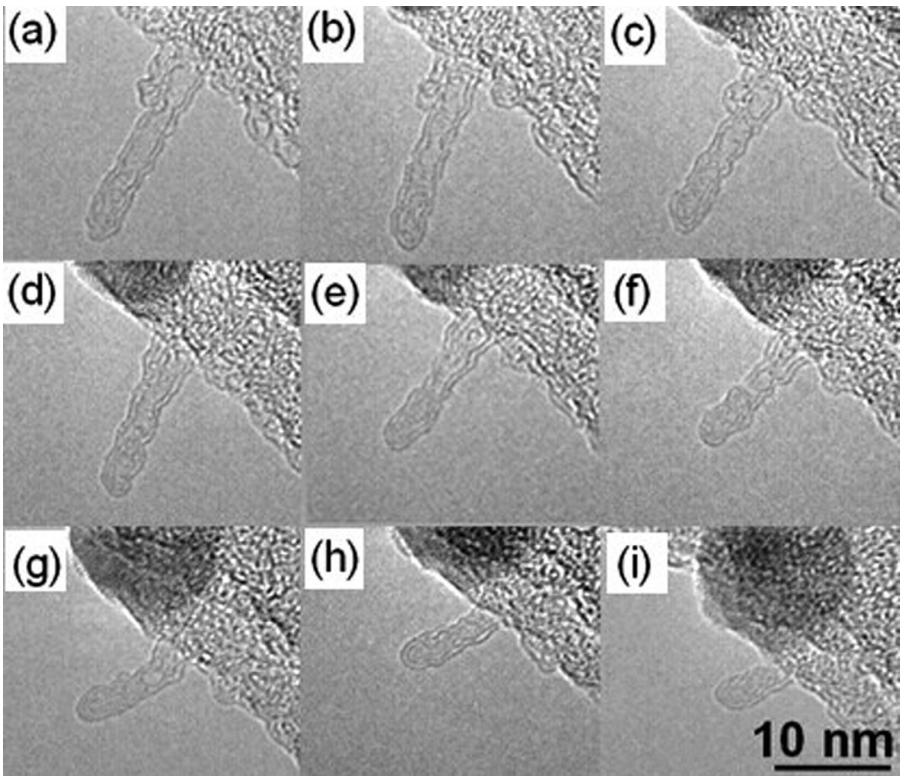

FIG. 2. Sequential *in-situ* TEM micrographs showing typical structural evolution DWCNT with only one end being fixed as induced by the e-beam irradiation to different irradiation time (s): (a) 0; (b) 140; (c) 280; (d) 440; (e) 560; (f) 700; (g) 840; (h) 1060; and (i) 1260.

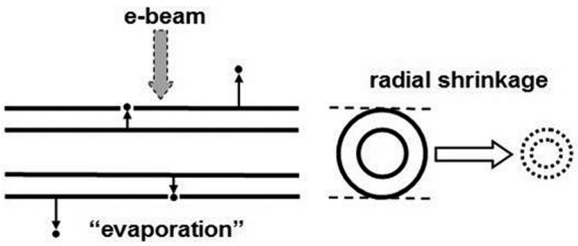

FIG. 3. Schematic to illustrate the e-beam-induced athermal "evaporation" processes of atoms from the DWCNT with its two ends fixed as shown in Figure 1.

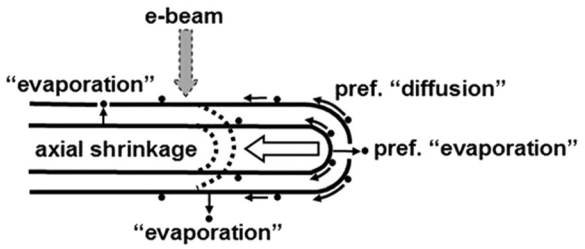

FIG. 4. Schematic to illustrate the e-beam-induced "evaporation" and "diffusion" processes of atoms from the DWCNT with only one end fixed as shown in Figure 2.

barrier for the atoms to overcome during their migration or escape would be greatly suppressed or even totally disappear. Thus, the atoms could escape easily from restriction of their adjacent carbon atoms, leading to the following athermal "diffusion" or athermal "evaporation" of the atoms and thus the nanocuvature-dependent shrinkages of DWCNT.

For the DWCNT with its two ends fixed as shown in Figure 1, the curvature is uniform over surface of the tube and any extension in the tube length is prohibited. Thus, there is no force to drive the atoms as activated by the nanocurvature effect and the beam-induced athermal activation effect to diffuse to a site of smaller nanocurvature or lower surface energy and the activated atoms would be only able to escape into space during irradiation. The process could give rise to the athermal "evaporation" or the pure loss of atoms. Figure 3 presents a schematic to illustrate the athermal "evaporation" processes. The escaped carbon atoms on the outer surface of tube wall would leave vacancies or dangling bonds in their positions temporarily. On the other hand, as the CNT has a strong ability to restore to its cylindrical shape with the rolled, sp^2 hybrid atomic layer structure,[19,20] the vacancies or dangling bonds as generated would refilled with adjacent atoms by a rearrangement or self-healing processing. After such an atom readjust process, the tube diameter becomes smaller and leads to a radial shrinkage of the tube.

In comparison to the DWCNT with its two ends fixed in Figure 1, the DWCNT with only one end fixed in Figure 2 has a free end cap which has a much larger nanocurvature or a higher surface tension than that of the tube wall. Thus, under the nanocurvature effect and the beam-induced athermal activation effect, the atoms at the end cap would become more unstable and thus either preferentially "diffuse" toward the tube wall or preferentially "evaporate" into space. Both the preferential "diffusion" and the preferential "evaporation" could give rise to the preferential axial shrinkage at room temperature. The detailed processes can be schematically illustrated in Figure 4. Similar to the DWCNT with its two ends fixed in Figure 1, the tube wall herein would also lose its carbon atoms by the "evaporation" under the tube wall nanocurvature effect and the beam-induced athermal activation effect. But in this case, the atoms "diffused" preferentially from the cap end to the tube wall would fill in partial or all of the vacancies as left by the atoms evaporated from the tube wall. In this way, the "diffused" atoms would offset the "evaporated" atoms to some degree and the radial shrinkage of the tube is retarded or restrained as observed in Figure 3.

It should be noted that owing to the atomic interaction between the outer wall and the inner wall in DWCNT, the shrinkages both of the outer wall and of the inner wall would be slowed down compared with SWCNT. Especially, during the processes, the activated atoms on the inner wall would be able to escape into outer space only by the vacancies or dangling bonds[12] as generated on the outer wall as illustrated in Figures 3 and 4. In doing so, along with the shrinkage of the outer wall, the inner wall was able to shrink simultaneously. However, both the shrinkage of the inner wall and the shrinkage of the outer wall could be delayed due to possible refilling of the partial vacancies or dangling bonds as generated on the outer wall during the escape of the atoms of the inner wall. Similar analysis could be applicable to shrinkages of other MWCNTs.

Our experimental study revealed two distinct nanoinstabilities of DWCNT under *in-situ* TEM electron beam irradiation: (a) DWCNT with its two ends fixed shrank in its radial direction uniformly; (b) DWCNT with only one end fixed intriguingly shrank preferentially from its free cap end in the axial direction whereas its radial shrinkage was retarded. The observed phenomena cannot be adequately accounted for by the knock-on mechanism but could be well elucidated by a mechanism of "diffusion" and "evaporation" at room temperature which are driven by the nanocurvature of the DWCNTs and the athermal activation induced by the electron beam.

In this letter, although we are only able to report our experimental result on the nanoinstability of DWCNTs of two different configurations which was induced by a limited duration of irradiation of e-beam with a beam current fixed at about 100 A/cm^2 and a beam accelerating voltage fixed at 200 kV, we believe that the result and principle reported herein can be extended for elucidation of irradiation of electron beam of other beam parameters such as beam current, beam accelerating voltage, or irradiation time. Actually, even more universally, along with other experiments[14,15,22,23] (also X. F. Zhu *et al.*, manuscripts in preparation or to be submitted), the experiment herein further confirms that the general principle of nanosize effect (i.e., nanocurature effect as specified in this letter and also including low dimension-confinement effect at nanoscale) and nanotime effect (i.e., energetic beam-induced athermal activation effect or energetic beam induced-atomic vibration instability and soft mode effect as specified in this letter) as predicted in earlier publications[16–18] can be extended for elucidation of nanoinstability of LDNs of different types under such irradiations as well as for elucidation of irradiation of other energetic beams such as ion or photon (i.e., laser) beam.

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