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Vacancy Migrations in Carbon Nanotubes

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ABSTRACT

Activities of vacancy defects in carbon nanotubes have been directly monitored by in situ high-resolution transmission electron microscopy at elevated temperatures. Adatom−vacancy pair defects are first prolific due to the knock-on damage, and then the induced vacancies indeed grow up to 1–2 nm in the size by the following Joule heating. Surprisingly, these large vacancies, or "holes", tend to migrate and coalesce with each other to form even larger ones. It suggests that the activation barrier has been substantially lowered due to the contributions of an electromigration and/or irradiation effect.

Introduction. Defects in carbon nanostructures play a crucial role on the electronic, optical, and mechanical properties. Numerous theoretical efforts have been carried out in order to understand the kinetics of atomic scale defects.[1–8] The recent high-resolution transmission electron microscopy (HRTEM) studies have shown the direct and clear evidence for the presence of point defects like adatoms, monovacancies, interstitial-vacancy defects, pentagon−heptagon pairs, and their evolution over time in carbon nanostructures.[9–11] In the case of a large vacancy or hole (corresponding to a large number of carbon atoms loss) in the carbon network, TEM investigation found the presence of nanometer-sized holes on flat thin graphite flakes.[12] From the theoretical point of view, Kotakoski et al. found that coalescence of monovacancies into a divacancy (or even larger) is an energetically favorable process, and they also pointed out "formation of a large 'hole' on nanotube walls is energetically unfavorable because the vacancies tend to split into smaller defects due to the reconstruction of the nanotube network".[7] Furthermore, a large vacancy is widely believed to be immobile due to its high migration barrier (for example, the migration barrier for just a divacancy is as high as ~5 eV[6]). Thus a clear and direct experimental evaluation on the stability and mobility of these large vacancies in carbon nanotubes (CNT) is obviously intriguing. Here in this letter, we report the first experimental evidence for the migration and coalescence of large vacancies in CNTs.

Methods. To visualize the formation and dynamics of vacancies in CNTs, our experiments are carried out inside a field emission TEM (JEOL-2010F) equipped with a dedicated piezodriven specimen holder (Nanofactory AB). The accelerating voltage has been chosen as 120 kV, which is just close to the knock-on threshold of carbon.[13,14] We are able to precisely drive a sharp tungsten (W) tip and apply a voltage on a selected individual CNT manipulated between two metal electrodes (Figure 1). Thus a direct current passing through the bridging CNT can be induced and monitored. A CCD (Gatan 894) is used for recording images, and the exposure time for each frame is set as short as possible (typically 0.5 s) in order to catch more dynamical details at the cost of a decreased signal-to-noise ratio.

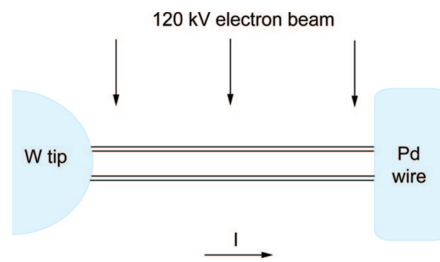

Figure 1. Schematic presentation of the experimental setup: an individual CNT is suspended between a Pd wire and a sharp W tip. The whole CNT is exposed to a uniform electron beam irradiation (120 kV). By applying a voltage between two metallic electrodes, we are able to induce a current through the bridging CNT.

Results and Discussion. The CNT with the reduced number of walls and with a large diameter is suitable for the vacancy observations. These specimens are fabricated in situ by manipulating the starting multiwall CNTs (MWNTs) through a layer-by-layer peeling process[15,16] with a careful control of the induced current. Shown in Figure 2a is an individual CNT with five walls connected by two metallic electrodes (only half of the CNT is shown). The electron

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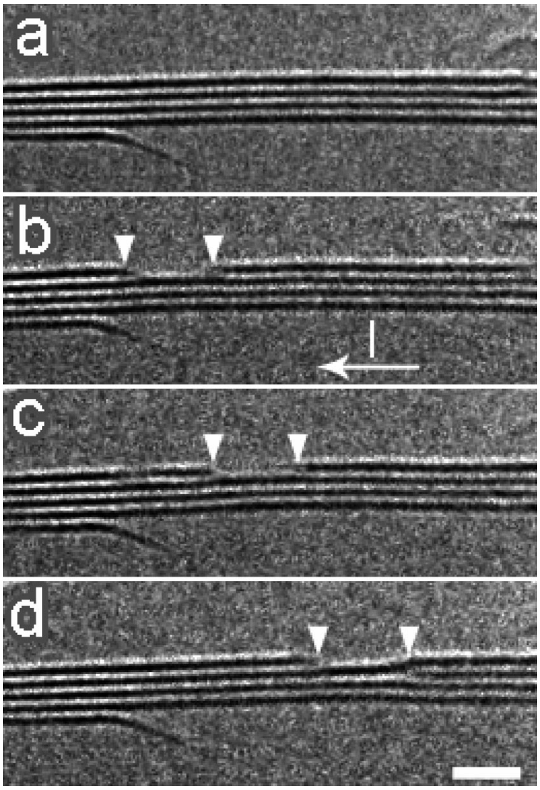

Figure 2. Serial HR-TEM images showing the formation and migration of a large vacancy on a CNT. (a) A CNT having five walls is chosen without any voltage applied. Only half of this CNT is shown here. (b) A concaved step (marked as two white arrowheads) is created on the outmost wall when the gradually increased voltage reaches about 1.2 V and a current of 98 μA. It has a length about 2 nm, corresponding to a large vacancy or hole by losing a group of carbon atoms. The arrow displays the direction of electric current. (c–d) Keeping on a constant voltage, this hole migrates toward the right end of the CNT, as marked by the white arrowheads. The electron dose is about 4×10^4 electrons/nm^2. Scale bar = 2 nm.

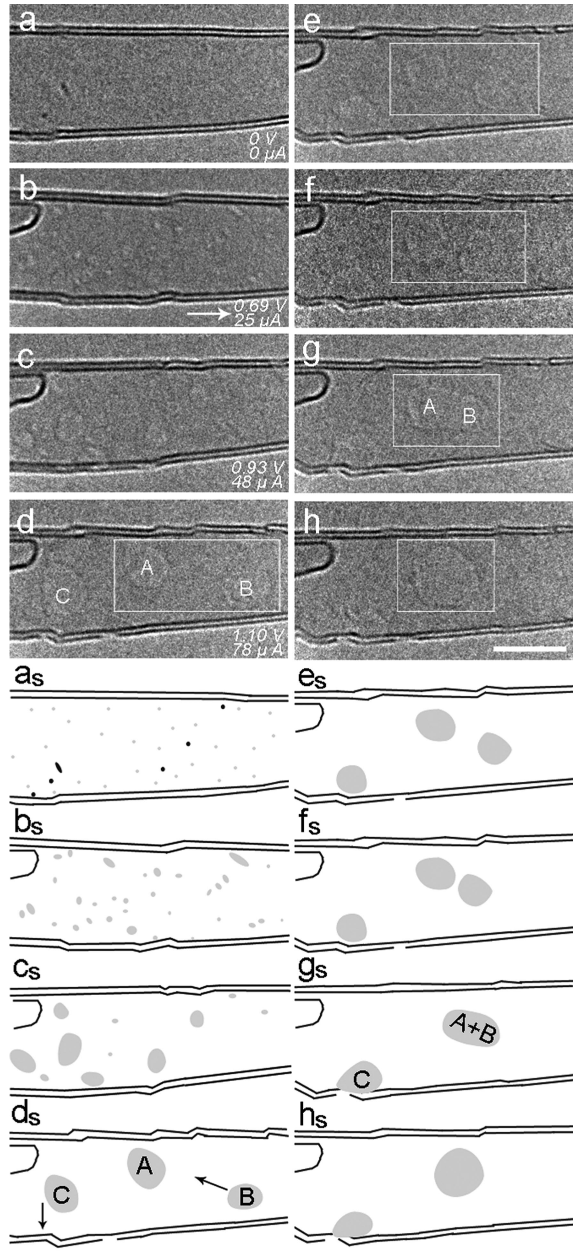

Figure 3. Time sequential HR-TEM images for the formation, migration, and coalescence of large vacancies in a DWNT (a–h) and their respectively schematic images (a_s−h_s). (a) Carbon adatoms or clusters (dark spots) and monovacancies (white spots) are created on the nanotube wall after 30 s irradiation with a electron beam dose of 2×10^5 electrons/nm^2. No voltage is applied on. (b) At t = 52 s, most of the carbon adatoms or clusters disappear, while the vacancies remain, when the voltage is increased to about 0.69 V and a current of 25 μA. The direction of current is indicated by the arrow. (c) At t = 108 s, a few large "holes" with a diameter of about 1–2 nm forms on the nanotube wall when the voltage reaches about 0.93 V (a current of 48 μA). (d) At t = 170 s, even larger vacancies are formed on the nanotube wall if we further increase the input voltage to 1.10 V (a current of 78 μA). Three large vacancies with a similar average diameter of about 2.8 nm are marked as A, B, and C, respectively. A white rectangular marks the region of interest where vacancy A and B are located. (e–f) Vacancy B is found to migrate toward A, and C migrates downward. (g) At t = 190 s, vacancies A and B join each other to form a larger one with a prolonged shape. (h) The newly formed larger vacancy is annealed to a round-shaped one. The input voltage is constant in (d–g). Scale bar = 5 nm.

dose is set as low as 4×10^4 electrons/nm^2 here. When the applied voltage reaches about 1.2 V (a current about 98 μA), an obvious step with a length about 2.2 nm appears on the outermost wall of this CNT (marked by the arrowheads in Figure 2b), which corresponds to the local loss of a group of carbon atoms, i.e., a large vacancies (or hole). As shown in Figure 2b−d, the induced large hole continuously migrates toward the right end of the CNT with the constant applied voltage and current, but never in the reverse direction.[17] The formed hole prefers to migrate along the tube axis because the concaved step always lies in the upper edge of the CNT, therefore it is presumably difficult for this hole to migrate toward the peripheric direction of the CNT.

To investigate the shape and size of the large vacancies (which was unclear in the experiment above), we have also prepared another nanotube specimen with fewer walls so that the top view of the large vacancies can be studied.

Shown in Figure 3 are time-sequential HR-TEM images for the whole story from the formation and migration of the vacancies to the coalescence of the large holes in a double-wall CNT (DWNT) with an outer diameter of ~7.1 nm. At the beginning, the DWNT is kept at room temperature for the first 30 s without any voltage applied. Because of a uniform irradiation of 120 kV electrons for this period (electron dose is about 2×10^5 electrons/nm^2), a number of carbon adatoms (or interstitials) and monovacancies (dark and white spots, respectively) are created on the nanotube wall (Figure 3a,a$_s$). The formation of adatom−vacancy pair defects is consistent with the earlier report of Hashimoto et al.[9] Most of the created defects are more likely to lie on the upper or lower plane of the nanotube walls, which is reasonable due to the anisotropic knock-on threshold energies.[14]

In the second step, a voltage is gradually applied on the DWNT. When the voltage reaches about 0.7 V (a current about 25 μA), most of the dark spots are wiped out although the bright spots remain there, as shown in Figure 3b (also schemed in Figure 3b$_s$). This suggests the migration and diffusion of carbon adatoms (or interstitials) out of the observed area because the carbon adatoms are more mobile than the vacancies due to the lower migration barriers.[13] The temperature gradient[18] along the DWNT and the induced current may also facilitate the diffusion.[19] In addition to the disappearance of carbon adatoms and clusters, a few vacancies with an enlarged size are newly formed on the nanotube wall (Figure 3b). They might correspond to the multivacancies such as di-, triple-, or octavacancies created either by the coalescence of nearby monovacancies (energetically favorable process as mentioned in ref 7) or through the further carbon loss around the monovacancies.

When we further raise the temperature by increasing the input voltage to 1.1 V (a current about 78 μA), most of the smaller vacancies disappear and no more obvious carbon adatoms or clusters (dark contrast spots) can be observed, as shown in Figure 3c (also schemed in Figure 3c$_s$). Instead, a few even larger vacancies with a diameter of about 1–2 nm are created, corresponding to tens of carbon atoms loss. They are mostly formed due to the coalescence of those mobile smaller vacancies in neighbors (please see also Movie S1 in the Supporting Information). We never observe any of them split into smaller ones. Also they are still surprisingly mobile and could further coalescence each other into an even larger one.

A typical example is given in Figure 3d−h (also schemed in Figure 3d$_s$−h$_s$), where particular attention is paid on three large vacancies marked as A, B, and C respectively in Figure 3d. Vacancies A and B are separated with a center-to-center distance of about 7 nm at $t = 170$ s (Figure 3d). Vacancy B migrates toward A, and vacancy C migrates downward to the sidewall, while vacancy A strolls itself around its original position. The migration of vacancies B and C is quite smooth, and they do not cause any massive structural distortions on the nanotube walls. Although each of them is trying to keep an energy-favored round shape and their edge-shapes are slightly and frequently changing, suggesting the diffusion of carbon atoms through the edge would become easier at this high temperature. It takes about 18 s for vacancy B to arrive at vacancy A. Once they get in touch, coalescence starts gradually and a narrow neck forms between them. Within 0.5 s, coalescence process completes and a much larger hole is formed. Soon after, it is annealed into again a round-shaped one with a diameter of about 4 nm, and its surface area is roughly equal to the sum of vacancies A and B (please also see Movie S2 in the Supporting Information for the whole process). More importantly and surprisingly, this large hole is still mobile. As shown in Movie S3 in the Supporting Information, it moves upward and finally migrates to the left end of this DWNT. When it reaches the sidewall, we could recognize that the large hole lies in the outer shell of DWNT because a portion of outer wall disappears, not the inner wall, and consequently so do vacancies A, B, and C. Note that this newly formed large hole could survive without any splitting, even at the room temperature after removing the applied voltage.

In the above experiments, we find the vacancies in the outer wall are definitely more likely to migrate. This is reasonable because most of the current is supposed to flow through the outmost shells,[20] therefore the "hotter" outer wall is more favorable for the formation and migration of vacancy, and a CNT with a larger diameter is more likely to accommodate a large vacancy due to the weakened curvature effect. The presence of inner wall is also playing a key factor here. When a large hole is formed on the outer wall by losing tens of carbon atoms or even more, the outer shell is hardly able to reconstruct by a diameter shrinkage because of the existence of inner walls.

By adopting the previously proposed thermal conductively for a suspended CNT,[18,21] the temperature on the CNT is estimated to range from ∼1000 to ∼1800 K. For the migration of the vacancy B in Figure 3, we know the traveling distance within a given time (about 7.3 nm for 18 s). On the basis of the diffusion model on the migration of metal atoms and carbon adatoms on CNTs in refs 22, 23, the estimated migration energy barrier of our experiments is ranging from 2.2 to 4.0 eV. This is apparently an underestimated value because the migration barrier for a divacancy could be theoretically predicted to be as high as 5 eV.[6] Larger vacancy should have a larger migration barrier (more carbon atoms have to participate the vacancy migration). This discrepancy may suggest some other contributions rather than the simple thermal activation should be considered for the vacancy migration in the present experiment.

Effect of 120 kV energetic electrons irradiation is not negligible in this study because electron irradiation is an unavoidable factor for the TEM study. Also, electron irradiation is used to produce smaller vacancies on the nanotubes at the beginning stage, as shown in Figure 3. A previous report found electron irradiation could assist the migration of topological defects along the CNTs.[11] Other mechanisms such as electromigration[24] may also have some contributions, especially for those "border" atoms in the edge of vacancy, and because the current density on the DWNT reaches as high as 10^{8-9} A/cm^2 here, the effect of electromigration will become of prime importance.[25]

Conclusions. In summary, the migration and coalescence behavior of the large holes of ∼4 nm created on a nanotube wall during the electron irradiation associated with the Joule heating is directly investigated by the in situ HR-TEM. By carefully controlling the irradiation and heating process, we might be able to carry out the "vacancy engineering" on the nanotube wall, e.g., creating vacancies with a desirable size and position, which could facilitate potential applications of nanotubes like molecular anchoring or drug delivering.

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Supporting Information Available: Movies for the formation, migration, and coalescence of large vacancies in nanotube walls. This material is available free of charge via the Internet at http://pubs.acs.org.

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