J Mater Sci (2006) 41:4505–4511
DOI 10.1007/s10853-006-0081-0

Irradiation of carbon nanotubes with a focused electron beam in the electron microscope

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Received: 22 November 2005 / Accepted: 10 February 2006 / Published online: 1 July 2006

Abstract The paper reviews in-situ electron irradiation studies of carbon nanotubes in electron microscopes. It is shown that electron irradiation at high specimen temperature can lead to a variety of structural modifications and new morphologies of nanotubes. Radiation defects such as vacancies and interstitials are created under irradiation, but the cylindrically closed graphene layers reconstruct locally and remain coherent. The generation of curvature in graphene layers with non-hexagonal rings allows us to alter the topology of nanotubes. Several examples of irradiation-induced modifications of single- and multi-wall nanotubes are shown. Conclusions about the mobility of interstitials and vacancies are drawn which are important to explain the behaviour and the properties of nanotubes with an atomic arrangement deviating from the hexagonal network of graphene.

Introduction

For more than a decade, carbon nanotubes are considered to be among the most promising nanomaterials for industrial applications [1]. Numerous experimental and theoretical studies have explored their unusual and, in many respects, extreme properties. Nanotubes have been discovered with an electron microscope [2] and since then been found to be ideally suited for transmission electron microscopy (TEM) characterization. Almost the whole present knowledge about the structure of nanotubes (number of shells, helicity, defects, etc.) has been derived from TEM studies. However, it has also been realized that the structure of nanotubes can change under the electron beam [3]. Irradiation of nanotubes with electrons at room temperature causes more or less structural damage in the tubes, depending on irradiation intensity and time and on the energy of the electron beam. Radiation damage is normally an unwelcome artifact in materials characterization by electron microscopy. However, it turned out that under certain experimental conditions, damage can be healed and electron irradiation can lead to new and exciting morphologies of nanotubes.

The structural basis of carbon nanotubes is the graphite lattice [4]. Whereas single-wall nanotubes (SWNT) consist of a cylindrically closed graphene layer (one basal plane of graphite [5]), multi-wall nanotubes (MWNT) are composed of two or more concentric graphene layers with a mutual distance corresponding closely to the distance between basal planes in graphite (0.335 nm). The structural similarity of nanotubes with the graphite lattice suggests to go back to the issue of radiation damage in graphite which has been investigated for many years due to its importance in reactor technology [4]. Although common principles with graphite have been found [6–8], nanotubes exhibit several peculiar phenomena under irradiation. These are due to their small size and to the unique morphology, namely the cylindrical closure of the layers and the inner hollow channel.

Radiation effects in nanotubes

Since the pioneering irradiation experiments of Ugarte in 1992 [9], it became clear that carbon nanoparticles such as nanotubes or graphitic grains behave differently from other

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crystalline structures when exposed to electron irradiation. The first experiments showed that single graphene planes as well as multi-layered graphite sheets bend and curl under intense irradiation, eventually transforming to spherically closed ‘carbon onions’ [9, 10]. However, it remained unclear for a long time how a cylindrical object such as a nanotube can transform to a spherical structure under an electron beam. First it was realized that the temperature rise in such objects is very small, even at high beam intensities, because the particles are small so that most electrons from the beam will not undergo any scattering and the thermal conductivity of graphitic material is high (local heating is low). Therefore, graphitic particles do not melt, and all morphological transformations occur in the solid state.

In order to understand structural alterations in nanotubes under the electron beam, all possible mechanisms of energy (or momentum) transfer from an energetic electron to a graphitic lattice have to be considered. Due to the presence of conduction electrons, all electronic excitations in graphite are quenched within a short time. This has been confirmed by experiments where it was seen that no structural changes could be induced in carbon nanostructures at beam energies below the displacement threshold [10, 11]. The displacement threshold energy is an important parameter which gives us the electron energy necessary to displace an atom permanently from its position in a knock-on scattering event with the nucleus. The threshold electron energies are 86 keV for SWNTs [11] and slightly higher (approximately 100 keV) for MWNTs (depending on the direction of electron incidence) [10]. Due to cascade effects, the displacement rates increase with increasing electron energy within the typical electron energy range of TEMs [10].

In most crystalline structures, knock-on displacements of atoms lead to either spontaneous recombination of the vacancy-interstitial pair or to persistent structural damage (visible as dislocation loops, voids, or amorphization). This also holds for the graphite lattice when irradiated at room temperature. The accumulation of interstitials (leading to new lattice planes between the basal layers) or of vacancies (leading to holes in the planes and, finally, to a rupture of the hexagonal network) destroys the lattice and does not result in new morphologies. The situation is different, however, when the temperature is high enough so that interstitials and/or vacancies are getting mobile. Then, the lattice can reconstruct during the irradiation, and defect agglomerates are avoided. Experimental [8, 10, 12] and theoretical [13] studies indicate that at temperatures above 200–300 °C the mobility of point defects is high enough for a fast reconstruction of the graphite lattice during irradiation. Initially, it was believed that the mobility of vacancies in graphite is orders of magnitude lower than of interstitials, but in the light of new theoretical work [13], this assumption is now questionable. It appears that (opposite to naïve expectation) vacancies are getting quite mobile already at moderate temperatures. This enables the graphitic network to reconstruct and to form stable structural defects such as pentagonal, heptagonal, or octagonal rings (instead of the hexagonal defect-free arrangement).

Since the discovery of the fullerenes it is known that pentagonal rings lead to positive, heptagonal rings to negative curvature of the graphitic network. Therefore, transformations between different ring structures (pentagonal, hexagonal, heptagonal), e.g., of the Stone–Wales type [14], lead to local changes of the curvature of graphene planes. The ability of the graphitic lattice to reconstruct when atoms are removed is unique among all known crystalline structures. The strong tendency of the graphene network to close firmly even after defect generation and to develop local curvature enables us to generate new morphologies on the nanoscale [15, 16]. Figure 1 shows an example of structural changes in a nanotube as obtained by atomistic computer simulations [17, 18]. A single-wall nanotube reconstructs when a number of atoms are displaced or removed. Primary radiation defects are single vacancies (S) or interstitials as adatoms (A). Coalescence of single vacancies may lead to the formation of divacancies (D) which are, however, not stable but close by saturating dangling bonds. Such a reconstruction of the lattice leads to a stable arrangement of non-six-membered rings. Furthermore, the tube shrinks when atoms are removed, but the lattice remains coherent.

While the dynamics of vacancies determines the structural evolution of nanotubes under irradiation, the mobility and diffusion pathways of interstitials gives information about the loss of material when atoms are removed from their positions. It has been assumed that most carbon atoms which are displaced in SWNTs or outer shells of MWNTs are sputtered off and lost. However, as recent studies indicate [19], the majority of the atoms is trapped inside the hollow channel in the tubes where they diffuse in axial direction. Simulations show that the migration barrier for interstitials is lower on the inner than on the outer wall of

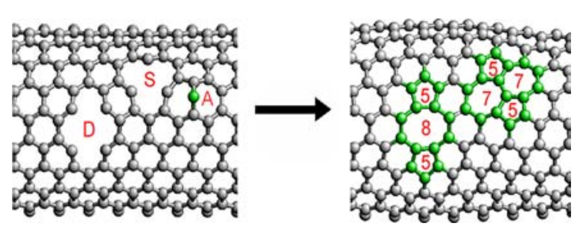

Fig. 1 Relaxation of a defective single-wall nanotube. The starting configuration (left) contains a single vacancy (S), a divacancy (D) and an adatom (A). After relaxation (right), an arrangement of non-six-membered ring defects forms and the tube is shrinking. (Molecular dynamics simulation, courtesy of A. Krasheninnikov)

the tubes. As will be shown below, this is of importance during the evolution of nanotubes under the electron beam.

Experimental techniques

Structural alterations of carbon nanotubes require electron beams with an energy exceeding the threshold for atom displacements. The studies presented in this paper were carried out with a field emission TEM operating at 300 kV or a high-voltage TEM (LaB_6 cathode) at 1250 kV. Whereas the high-voltage instrument can be used to obtain high displacement rates on a large specimen area, the focused beam of a field emission TEM enables us to selectively irradiate specimen areas with nanometre precision and to achieve extreme beam current densities. In conventional TEMs with LaB_6 filaments, maximum beam currents of typically 100–300 A/cm^2 can be attained if the condensor apertures are retracted. In field emission TEMs, 2–3 orders of magnitude higher beam intensities are feasible within a small spot on the specimen.

As mentioned above, the dynamics of interstitials and vacancies which are created under irradiation determines the perfection of the modified structures. To ensure high defect mobility, the temperature of the specimens should exceed 300 °C. Holding the specimen at high temperature during high-resolution microscopy and irradiation puts high demands on dedicated heating stages. Thermal specimen drift has to be compensated and mechanical vibrations from water cooling have to be avoided. Additional heating by the electron beam can mostly be neglected. The temperature in the irradiated area is difficult to measure and can be calculated only for simple geometries. But nanotubes have an exceptionally high thermal conductivity along their axis so that heat which is generated locally is most efficiently conducted away. Assuming a typical MWNT which is suspended at one end on a metal grid (the grid is acting as a heat sink) and irradiation conditions as used in typical irradiation experiments (300 keV, 1000 A/cm^2), local heating is found to be much less than 1 K above the temperature of the holder.

Most irradiation-induced structural changes in nanotubes occur on a time scale between several seconds and hours, therefore fast video recording is often dispensable. Fast processes can be slowed down by just decreasing the irradiation intensity. Recording static images with a slow-scan CCD camera (exposure times of typically 0.1 s), refreshing the image every second, and saving the images where structural changes are clearly visible, proved to be a convenient technique.

Nanotubes are usually collected on holey carbon grids or on pure metal grids for irradiation and imaging in the TEM. It is important that a self-supporting web of tubes is spanning over the holes in the grid. This avoids contrast overlap of amorphous material in the image.

Irradiation of nanotubes

In early irradiation experiments, the nanotubes were always at room temperature (the minimal heating by the electron beam can be neglected). Since the low defect mobility at room temperature prevents reconstruction and leads to rapid destruction of the graphite lattice, new structures or insights into the properties of nanotubes were hardly obtained. Later, irradiation experiments at specimen temperatures above 300 °C revealed a variety of new morphologies.

Electron irradiation of SWNTs leads to a shrinkage and collapse of the tubes. This was already seen to happen very fast at room temperature [11, 20]. At higher temperature, the collapse is observable as well, but happens clearly slower. The collapse eventually leads to a breakage of the tubes when the innermost diameter falls below approximately 0.4 nm. From such experiments a value for the stability limit of small SWNTs can be deduced, but the tubes which shrunk under irradiation are not atomically perfect. Nevertheless, this value is surprisingly similar to the lowest diameter which was observed in (presumably) perfect SWNTs [21, 22].

MWNTs show a more complex behaviour under irradiation. Several scenarios have been observed, depending on the diameter of the tube or its inner hollow and on the size of the beam spot on the tube. Smaller tubes with a few layers (typically 5) and a sufficiently large inner hollow (typically 5 nm or more) show a remarkable behaviour when they collapse under the electron beam as shown in Fig. 2 [19]. While the outer shell remains intact (though shrinking), the innermost shells break successively and close their ends by cone-like caps. Such a behaviour of the tubes demonstrates that the stability of tubes decreases with decreasing diameter: the inner tubes are smaller and therefore less stable and vanish first [23]. Furthermore, it is observable that eroded material aggregates inside the tubes but at some distance from the irradiated area. From the temporal evolution of the morphology and diameter of the tube, we can conclude that irradiation leads to a preferential transport of material inwards instead of sputtering towards the outside as has been assumed earlier. The collapse occurs fast as long as the inner hollow is wide and open so that interstitials can vanish in axial direction. Once the collapse is complete (hour-glass shape of the tube), the shrinkage occurs much slower because the inner channel is blocked.

The collapse of MWNTs finally ends in a last SWNT before the tube breaks, as shown in Fig. 2d. The whole process can be considered as a transformation from a

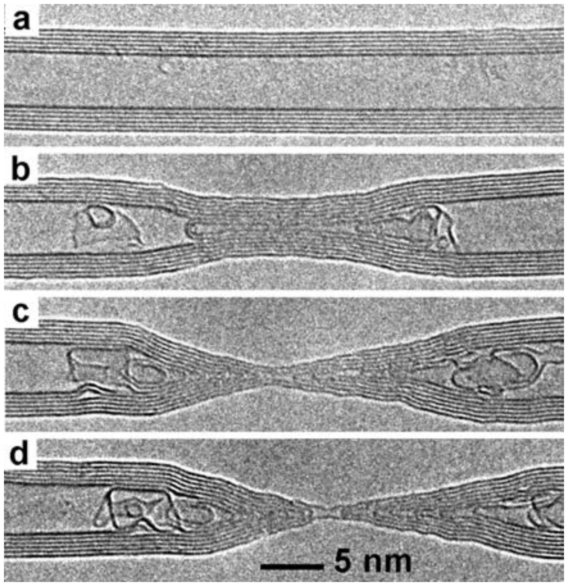

Fig. 2 Collapse of a multi-wall nanotube of 15 nm in diameter during irradiation with an electron beam (300 keV, 450 A/cm^2). While the inner shells vanish, the outermost shell remains intact. Material which is lost from the shells aggregates inside the central hollow. The total irradiation time until (d) was approximately 14 min (specimen temperature: 600 °C)

MWNT to a SWNT under the electron beam. The reverse transformation can also be achieved, though in a different mechanism. When a bundle of SWNTs is exposed to an electron beam (Fig. 3), the collapse of all SWNTs and subsequent graphitization can result in a MWNT which, in turn, can be transformed to a single SWNT as described above [24]. The major driving force of these transformations is the tendency of surface area reduction of all closed shells as shown in Fig. 1. When atoms are knocked from their positions, each shell contracts by applying pressure onto the structure. The surface energy of a defective shell (containing vacancies) is enormous because the formation energies of all vacancies have to be summed up. Since graphene layers can anneal their vacancies by reconstruction of the lattice (cf. Sect. 2), there is a strong tendency towards reduction of surface area and, thus, reduction of surface energy. Local positive curvature (e.g., the caps of the tubes) is due to the presence of pentagons, negative curvature (e.g., the hour-glass shape in Fig. 2) to heptagons.

Bundles of SWNTs can be cut with the fully focused beam in a field emission TEM [25]. This is achieved when the beam spot is moved with sufficiently low speed over the SWNT bundle. Each SWNT which is exposed to the intense beam shrinks and finally breaks while caps close the broken ends. An unexpected phenomenon was observed when attempts were undertaken to cut such a bundle twice. A second cut close to the first cut required approximately twice the electron dose of the first cut. Thus, the radiation hardness of the SWNTs increases once their end is closed by a cap. This can be explained by the preferential loss of interstitials towards the inner channel during irradiation. Interstitials have a high mobility inside the channel and are reflected at closed ends of the tube. Therefore, the tube is filled with interstitials which are available for defect annealing when vacancies are formed under the beam. Such an effect of self-healing makes cutting more difficult and, thus, the tubes more resistant to irradiation once their ends are closed.

There are different ways of modifying MWNTs by an electron beam. With the focused beam in a field emission TEM, the outermost layer can be selectively removed as shown in Fig. 4a. Here, only a few atoms have been displaced and sputtered off [24]. Since the surface layer is known to carry the majority of charge during electrical transport, the conductivity of MWNTs could be modified by perforating the outermost layer. When the electron beam is spread over half the diameter of the tube, the removal of material on one side only leads to a bending of the tube as shown in Fig. 4b–d. The bending angle can be controlled precisely by adjusting the irradiation time. Spreading the electron beam over the whole diameter of the tube can either lead to the collapse (as described above) when the inner hollow is large enough, or to the transformation of the tube to a spherical carbon onion when the tube is large and the inner hollow is narrow [24].

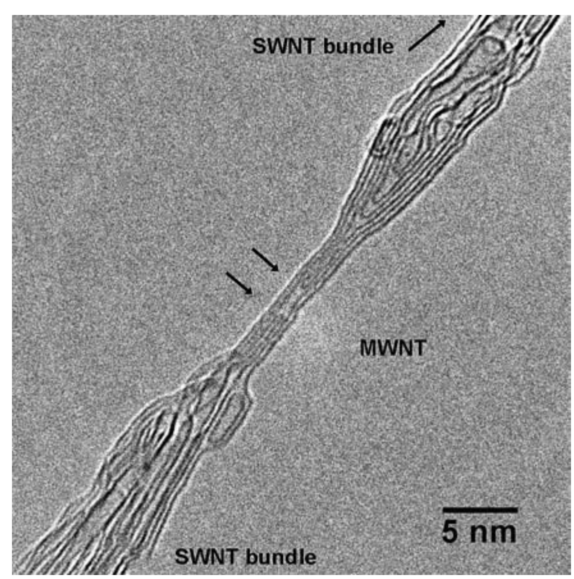

Fig. 3 Transformation of a bundle of single-wall nanotubes (seen in the upper right and bottom left corner) into a multi-wall nanotube under irradiation with an electron beam (300 keV) of 15 nm in diameter. After several minutes of irradiation with a beam current density of approximately 100 A/cm^2, the multi-wall tube in the center shrinks by losing its innermost shell as also seen in Fig. 2. The ends of the broken innermost tube close by caps (arrowed). (Specimen temperature: 600 °C)

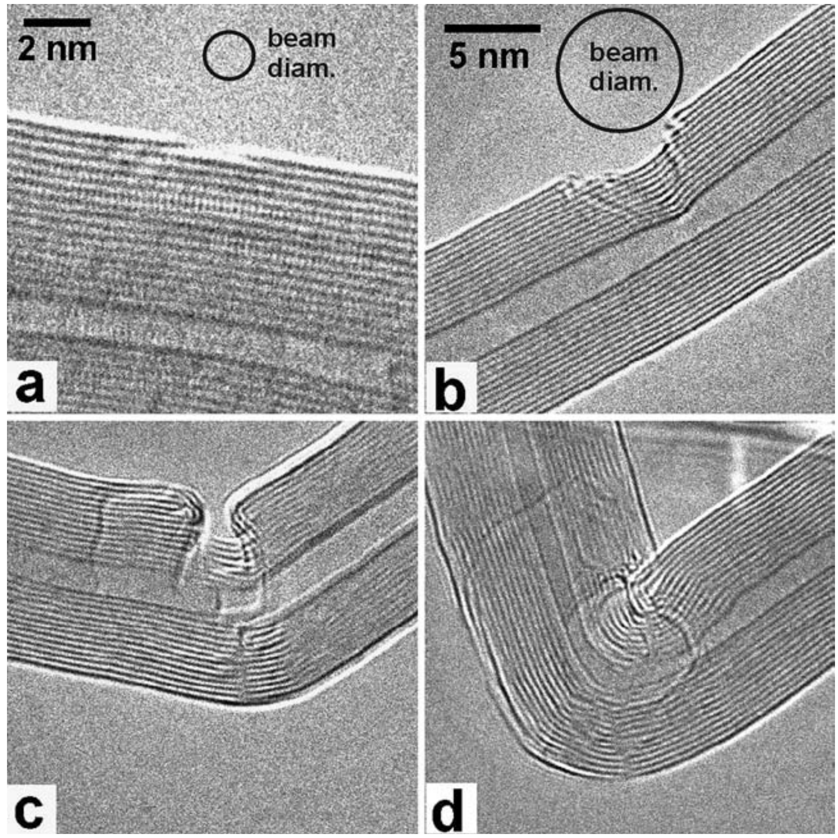

Fig. 4 Manipulation of a multi-wall nanotube with an electron beam. (**a**) A focused beam of extreme current density (2 nm diameter, 10^4 A/cm^2, 300 keV) can be used to remove just a few atoms from the outermost layer by irradiation for a few seconds. (**b–d**): Irradiation with a beam diameter corresponding to approximately half the diameter of the tube (5–10 nm) leads to a one-sided collapse and thus to bending of the tube (beam current density: 10^3 A/cm^2, total irradiation time: 15 min, specimen temperature: 600 °C)

The transformations of SWNTs and MWNTs as described until here were all achieved under an intense electron beam. More careful irradiation with a weaker beam can be used to join SWNTs at high specimen temperatures. The irradiation of SWNT bundles with a moderate beam can lead to the spontaneous coalescence of two adjacent tubes when the tubes are of the same (n,m) type (n and m are the 'crystallographic' coordinates characterizing the lattice structure of the tube [1]). Because of the conservation of surface area, a new tube with double diameter is formed and can be viewed clearly in a cross-section of the bundle as shown in Fig. 5 [26]. Crossing SWNTs can also be joined by moderate electron irradiation as shown in Fig. 6 [27, 28]. Such a 'molecular junction' of two SWNTs might be useful in nanoelectronics applications of nanotubes.

From the electron irradiation studies described above, several conclusions can be drawn about the properties of carbon nanotubes that have not been accessible by other techniques. The electron beam removes atoms from the graphene layers, but nevertheless, the layers are not destroyed at temperatures above 300 °C. Instead, the morphology of the tubes changes and their surface area is shrinking. This has recently been explained in terms of the formation of rather mobile single vacancies which combine to immobile divacancies [13]. Divacancies can close by the formation of non-six-membered rings so that the surface area is getting smaller and the tube collapses without breakage of the shell. Furthermore, the presence of such defects allows almost every type of curvature in the graphene network.

The stability of tubes as a function of temperature, as observed in the above-mentioned examples, gives us useful information about the migration behaviour and mobility of vacancies and interstitials. Both is essential when different topologies of tubes and their mechanical stability is considered. The fact that interstitials are preferentially injected into the tubes by the electron beam shows that the tubes act as pipelines for interstitial transport. This has also been confirmed by theoretical studies which show that the migration barrier for interstitials inside tubes is lower than on the outer surface [19].

Conclusions

Many remarkable properties of nanotubes were discovered in electron irradiation experiments. The reconstruction of graphene layers after defect formation by maintaining almost the same stability as the perfect structure is a unique phenomenon which gives carbon nanotubes some of their

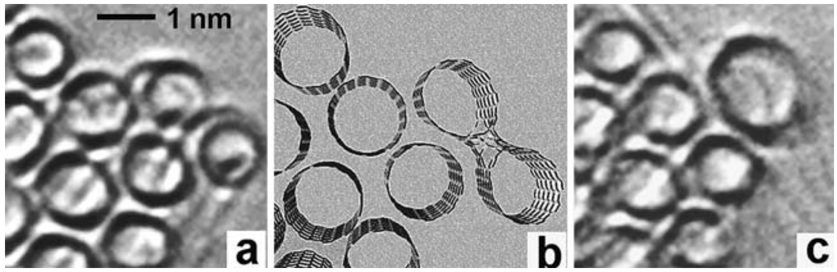

Fig. 5 Irradiation of a bundle of single-wall nanotubes (seen here in cross-section) leads to a merging of two tubes. (**a**): initial configuration before irradiation; (**b**) schematic model showing the coalescence (courtesy of M. Terrones); (**c**) after irradiation: the two tubes (right hand side) have merged into a tube of double diameter. Electron energy: 1250 keV; beam current density: approx. 10 A/cm^2; specimen temperature: 800 °C

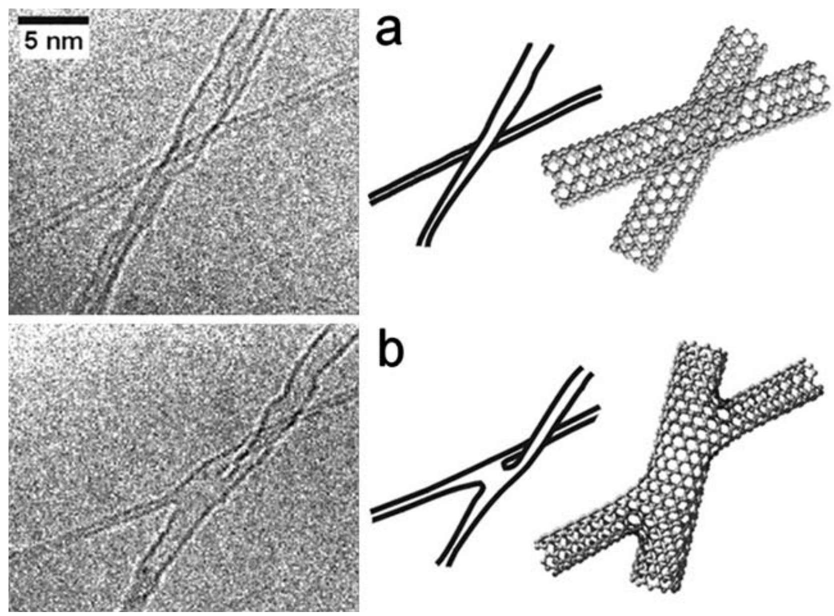

Fig. 6 Formation of an X-junction between two single-wall nanotubes under electron irradiation. (**a**): initial configuration: two crossing nanotubes; (**b**) after a few minutes of irradiation: the two tubes have merged at the crossing point. Electron energy: 1250 keV; beam current density: approx. 10 A/cm^2; specimen temperature: 800 °C

exceptional properties. Hence, electron irradiation can modify the structure locally or the overall morphology of nanotubes. The introduction of non-six-membered rings allows us to create a huge variety of different topologies as has been suggested theoretically [15, 16]. With the electron beam, these defects can now be created so that new topologies appear. Of course, not every conceivable structure is realized because defects are created randomly under the beam. But it became clear that nanotubes exist in many possible configurations, some of them being far from the atomic arrangement in a perfect hexagonal graphene sheet. Nevertheless, a high mechanical stability of the tubes is maintained. Measuring the electrical properties of defective nanotubes [29] will be a challenge for future studies.

Electron beam irradiation of nanotubes could be useful in several applications. The nano-engineering of tubes by selectively thinning or bending them would be of advantage when individual nanotube devices have to be tuned for dedicated functions. Creating junctions of SWNTs would be useful for making multi-terminal nanotube devices such as transistors on a chip. The coalescence of tubes within a bundle could be used to increase the diameter of the tubes. The injection of carbon atoms into tubes by an electron beam is of interest when nanotubes are used as pipelines for the migration of atoms. In such a way, nanotubes could act as channels for mass transport on the nanoscale.

Acknowledgments The author is grateful to J.X. Li, L. Sun, A. Krasheninnikov, M. Terrones, P.M. Ajayan, D. Tománek, J.-C. Charlier, N. Grobert, Ph. Kohler-Redlich, T. Füller, and M. Ozawa for good collaboration during many years.

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