A viable way to tailor carbon nanomaterials by irradiationinduced transformations

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Abstract

Since the discovery of carbon nanotubes (CNT), transmission electron microscopy (TEM) has been the most important tool in their investigation. It is possible to use electron irradiation in a TEM to construct a single-walled carbon nanotube (SWCNT) from an amorphous carbon film. Here we show that such a synthesis method creates a large number of carbon ad-atoms, which after some critical amount of radiation act to restore the system by reconstructing the carbon film. The behavior of the ad-atoms can be controlled by adjusting the current density in the microscope, suggesting that carbon nanomaterials can be tailored by electron irradiation.

Keywords: Carbon nanotubes; Electron irradiation; Nanomaterials; Transmission electron microscopy.

Introduction

Carbon nanostructures such as the fullerene (Kroto et al., 1985) and carbon nanotubes (CNT) (Iijima, 1991) have been primarily studied by transmission electron microscopy (TEM), and for this reason, considerable research into the effects of electron irradiation has been conducted (Banhart, 1999). A CNT synthesis method reported by Troiani et al. (2003) provides an ideal opportunity to study a single-walled carbon nanotube (SWCNT) under irradiation conditions. In this method two through-holes are created in an amorphous carbon film using electron-beam irradiation in a TEM. A thin graphitic fiber forms in between the two holes and is narrowed until forming

a SWCNT (Troiani et al., 2003; Marques et al., 2004). The hole creation and narrowing of the graphitic fiber involves the formation of a large quantity of ad-atoms with high mobility. After some critical amount of irradiation damage is accumulated in the graphitic periphery of the holes, the ad-atoms return to the holes, resulting in a reconstruction of the amorphous carbon film.

Previous irradiation studies of carbon nanostructures indicate that knock-on atom displacements are of primary importance as they can result in displacement cascades, sputtering, and stable interstitial–vacancy pair formation (Banhart, 1999). For example, the collision of an energetic particle, such as an electron in the TEM, with a carbon atom in a SWCNT can result in the displacement of the carbon atom. If the incident energy of the electron is high enough, a vacancy is created and the displaced atom can either leave the tube entirely and be lost to the vacuum or displace other atoms by knockon collisions. If the energy of the displaced atom is low, these atoms can adsorb onto the tube walls as ad-atoms, and assume the role of interstitials in the SWCNT (Krasheninnikov and Nordlund, 2002, 2004; Krasheninnikov et al., 2001, 2002). While vacancies in a SWCNT and in other graphitic structures are considered to be immobile (Niwase, 1995), it has been observed that ad-atoms can migrate along the tube surface and recombine with vacancies in a self-annealing process at elevated temperatures (>300 °C), while at lower temperatures the ad-atoms remain mobile but are less likely to recombine with the vacancies (Banhart et al., 1997). This paper reports for the first time a reconstructive transformation phenomenon in irradiated carbon whereby ad-atoms persist for long periods of time and act to restore the system upon reaching a critical amount of accumulated irradiation damage in a process we refer to as healing.

Experimental

SWCNTs were constructed from an amorphous carbon film by using electron-beam irradiation in a JEOL 2010F field emission gun TEM. Fig. 1a shows the graphitic fiber formation schematically, and Fig. 1b–g shows the overall experiment and healing phenomenon as we observe it in the TEM. Under the action of high current densities in the TEM (highly condensed beam), holes are opened in a carbon film so as to form a thin graphitic bridge separating them (Fig. 1a and b). The beam is spread to soft irradiation conditions, i.e. normal current density observation values, and the thin graphitic bridge is narrowed until forming a SWCNT (Fig. 1c). Due to knock-on displacements, ad-atoms are created and are observed to combine and form small strips (ad-strips) around the periphery of the holes. These ad-strips are observed to be mobile, and after a certain threshold of irradiation damage is reached, the carbon undergoes a reconstructive transformation consisting in the returning of the ad-strips and ad-atoms to the holes (Fig. 1d). This results in an accumulation of amorphous carbon around the graphitic bridge and periphery of the holes (Fig. 1e). The holes close very quickly (1–2 min) at the beginning of the healing process (Fig. 1f). In some cases, enough ad-atoms return to completely close the holes (Fig. 1(g)). After closing of the holes, subsequent condensations of the electron beam on the zones where a hole has closed are not able to re-open holes as easily, suggesting that the reconstructed amorphous carbon has somehow changed the nature of its bonds.

The irradiation conditions are drastically different during the hole formation and the bridge-thinning portions of the experiment. In order to understand the healing, it is

important to first understand the irradiation conditions and effects occurring during (i) hole formation and (ii) thinning of the graphitic bridge.

(i) Hole formation: Following the synthesis method reported by Troiani et al. (2003), holes are formed by 200 keV electron irradiation in a 20–30nm amorphous carbon film containing Au nanoparticles of ~2 nm. Highly condensing the electron beam beyond imaging values, current densities greater than 1000 A/cm^2 are reached at the sample, and the radiation dose is sufficiently high to create through-holes in the carbon film. The amorphous carbon around the periphery of the holes as well as in the bridge separating the two holes is observed to graphitize.

(ii) Bridge-thinning: The bridge thinning portion of the experiment commences once the holes are formed and a thin graphitic fiber separates them. The beam is then spread to imaging conditions of current densities between 0.1 and 100 A/cm^2. During this phase, there is a size enlargement of the holes and a subsequent narrowing and lengthening of the bridge structure.

Results and discussion

During the hard irradiation conditions occurring in the first portion of the experiment, holes are created in the carbon film via radiation damage such as sputtering and knock-on atom displacements. However, we emphasize that during the hole formation process, some of the displaced atoms are not lost to the vacuum but rather are adsorbed onto the carbon film surface, presumably around the periphery of the holes.

The amorphous carbon around the periphery of the holes as well as in the bridge separating the two holes graphitizes due to radiation-induced self-organization. The phase transformation from amorphous carbon to graphitic carbon is possible due to self-organization processes occurring during irradiation. The irradiation of the amorphous carbon film creates vacancy–interstitial pairs, but unlike in a SWCNT or in graphitic structures, vacancies are mobile in amorphous carbon and are therefore able to migrate and eliminate energetically high regions, or disordered regions, thus leading to graphitization (Niwase, 1995).

During the bridge-thinning portion of the experiment, we postulate two mechanisms working simultaneously to achieve the narrowing of the bridge structure under the soft irradiation conditions present in the TEM: (1) deformation in response to an axial stress being applied to the bridge due to a contraction of the film and (2) atom displacements due to irradiation occurring in the bridge, resulting in the creation of vacancies and mobile ad-atoms, followed by a diffusion of the ad-atoms to the amorphous region and surface reconstructions due to vacancy formation.

The carbon undergoes a contraction due to graphitization caused by the aforementioned self-organization irradiation process. The higher density of graphite over amorphous carbon causes a contraction in the film which applies an axial tension to the bridge structure.

The graphitic fiber responds by undergoing a series of deformations in a narrowing process which ultimately results in a neck being created somewhere along the bridge and a SWCNT being formed at the neck. The contraction is facilitated by the catalytic effect of the metallic nanoparticles present in the film. The mechanism by

which Au nanoparticles catalyze the carbon transformation is not well understood, but their catalytic effect was verified experimentally by conducting the synthesis method without the presence of Au nanoparticles and observing a much less pronounced contraction in the film as well as an observable difference in the amount of graphitized carbon.

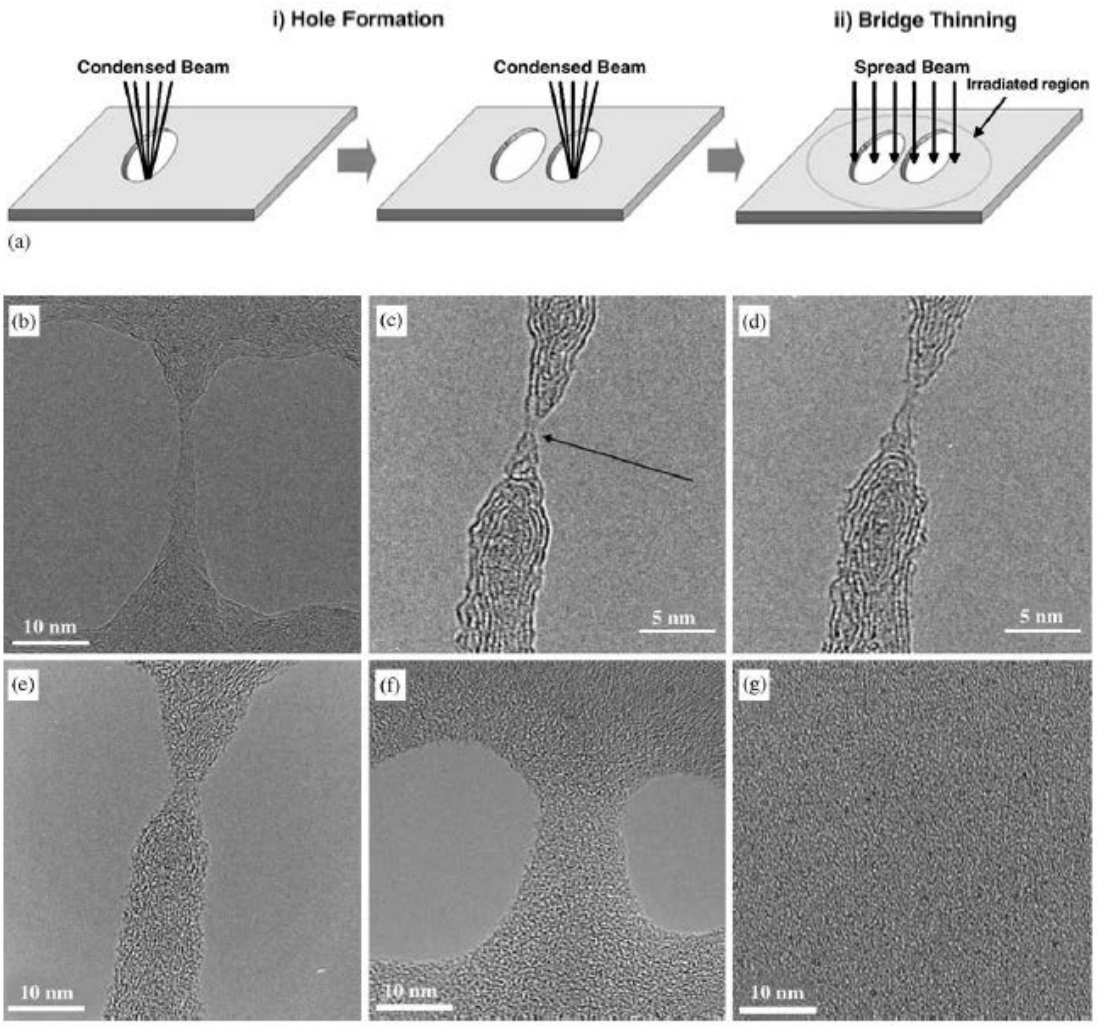

Fig. 1. Carbon nanotube formation and healing phenomenon. (a) Schematic illustration of hole formation by highly condensed electron beam, and bridge thinning during soft irradiation (spread beam) condition (irradiated region is shown). (b–g) Sequence of TEM images depicting healing phenomenon. (b) Low magnification image showing two holes in the carbon film separated by a graphitic bridge. (c) High magnification image of a graphitic bridge that has been narrowed to the point of forming a SWCNT at its neck (signalled by arrow). (d) High magnification image of the beginning of the healing process, showing a graphitic bridge with ad-strips and ad-atoms visible along its edges. (e) High magnification image showing a rapid accumulation of amorphous carbon around the graphitic bridge and periphery of the holes. (f) Low magnification image showing the rapid closing of the holes. (g) Image of the fully reconstructed film after the healing process is completed and the holes have completely closed.

The thinning of the graphitic fiber necessarily involves a diffusion of carbon atoms away from the neck region. Our experiment is conducted close to room temperature, which under our irradiation conditions creates vacancies and mobile ad-atoms. The ad-atoms are able to diffuse away from the neck region, while the vacancies either cluster to form larger holes in the structure or result in surface reconstructions in the CNT by atomic rearrangements. This can occur by dangling bond saturation and Stone-Wales type transformation, leading to reconstruction and dimensional changes (Ajayan et al., 1998). Vacancy clustering likely leads to brittle fracture, whereas atomic rearrangements lead to plastic fracture. As speculated by earlier irradiation studies (Ajayan et al., 1998), the limiting case of surface reconstructions should involve the formation of a single chain of carbon atoms. Troiani et al. (2003) and Marques et al. (2004) have verified carbon chain formation for short lengths of time (seconds) both experimentally and through simulations. In contrast, here we report the formation of a single chain of carbon atoms that was observed to be stable for 5 min prior to increasing the current density and inducing fracture (Fig. 2b).

Our proposed mechanism suggests that higher current densities at the sample should enhance the deformation process in the graphitic fiber. Higher current densities should cause greater graphitization in the surrounding carbon film, thus imparting a larger axial stress to the bridge, as well as enhancing the bridge's ability to respond by deformation processes facilitated by the presence of irradiation-induced vacancies. This is in fact what we observe experimentally. Current densities greater than 20 A/cm^2 result in further thinning of the graphitic fiber until forming a SWCNT, while low current densities (0.1–10 A/cm2) tend to stabilize the bridge structure. For current densities

greater than 75 A/ cm^2, the SWCNT is seen to undergo brittle fracture. For moderate current densities (10–40 A/$cm^{2)}$, low strain rates lead to plastic fracture of the SWCNT by nanotube elongation and linear carbon chain formation prior to fracture (Fig. 2). For the lowest current density conditions (10–20 A/cm^2) leading to plastic fracture, carbon chain lifetimes of up to 5 min prior to fracture were observed (Fig. 2b). It is quite remarkable that it is possible to have amorphous carbon, a graphitic fiber, a SWCNT, and a linear chain of carbon atoms all integrally connected and that such a configuration can remain stable for a considerable amount of time.

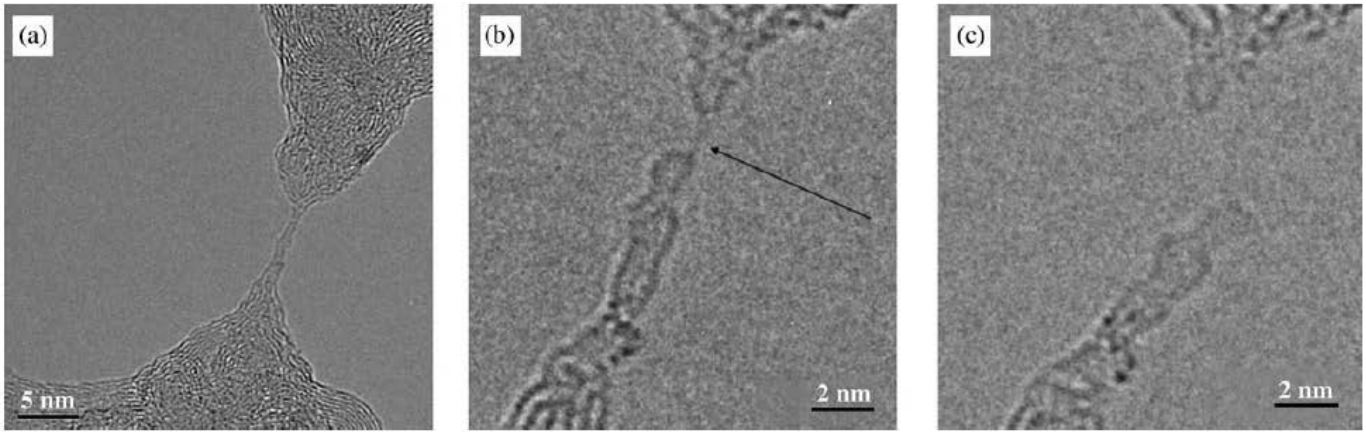

Fig. 2. Sequence of TEM images depicting plastic fracture. (a) A SWCNT is formed in the neck region of the graphitic bridge separating two holes. (b) The SWCNT deforms in response to axial tension and irradiation damage, forming a single chain of carbon atoms of nearly 1 nm in length that remained stable for 5 min (signalled by arrow). (c) The bridge fractures at the chain of carbon atoms upon increasing the current density.

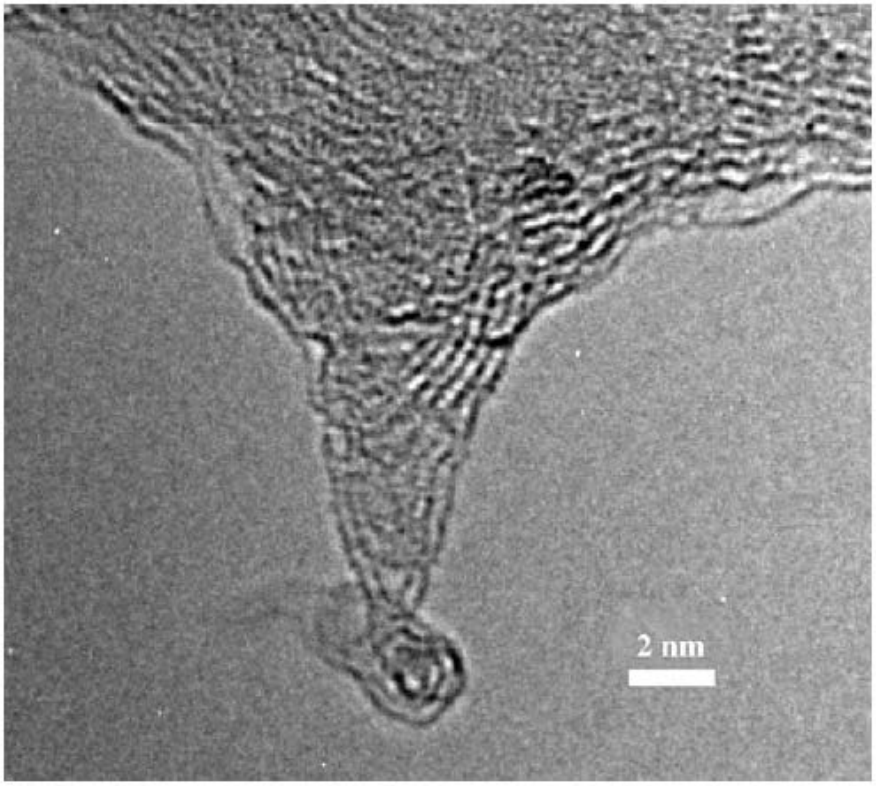

Fig. 3. TEM images of one side of a bridge that has fractured and bent into the beam, so as to be parallel to the beam direction and thereby provide a cross-sectional view of the bridge structure. The cross-sectional view clearly indicates that the bridge neck consists of a CNT that itself necks into some smaller structure, possibly a CNT of smaller diameter.

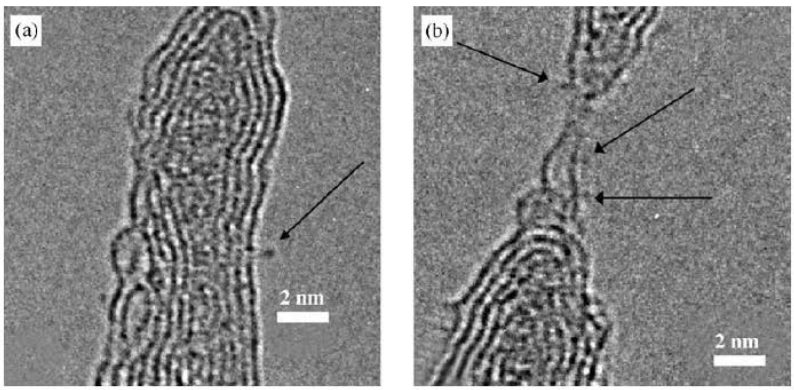

Fig. 4. TEM images of ad-strips. (a) Ad-strip (signalled by arrow) on the surface of graphitic bridge diffusing rapidly during the healing process. (b) Numerous ad-strips (signalled by arrows) returning to CNT neck during the healing process.

While it may not be obvious from the planar view TEM images that the neck indeed consists of a SWCNT rather than, for example, a carbon strip, we were able to obtain cross-sectional TEM images of a bridge immediately after fracture, clearly showing the presence of a CNT neck. Fig. 3 shows one side of a bridge structure that has fractured and bent into the direction of the electron beam, thereby providing a cross-sectional view of a portion of the bridge neck. The structure is clearly not a 2-dimensional carbon strip, but rather a 3- dimensional CNT. In addition, the CNT appears to neck even further at its tip into some smaller structure, possibly a CNT of smaller diameter.

The above discussion is concerned with effects occurring prior to the healing phenomenon; however, they are essential to understanding the healing. Our observations, as well as the proposed mechanism, indicate that some of the atoms displaced during the hole-forming and bridge-thinning process are not lost to the vacuum but rather remain as ad-atoms which diffuse to the amorphous regions. Once some critical accumulated irradiation damage is reached, the ad-atoms try to restore the previous state and rapidly diffuse back to the graphitized bridge and periphery of the holes (Fig. 4).The observed, sudden pronounced diffusion confirms that at least some of the carbon atoms removed during hole formation and thinning of the graphitic fiber, instead of going to the vacuum, become ad-atoms which are able to persist for extended lengths of time, possibly as interstitials in the surrounding amorphous carbon. They likely return to the holes because the heavily graphitized periphery of the holes and bridge region accumulate radiation damage faster than the amorphous regions due

to vacancies being relatively immobile in graphite. These graphitic regions are the first to become highly damaged and unstable, and therefore provide an ideal site for the ad-atoms or interstitials to return.

Our observations agree well with the proposed mechanism, and lead one to suggest that the tempo of the experiment can be controlled. Indeed, by adjusting the current density we were able to form the CNT neck, return to a thicker graphitic bridge structure after irradiation-induced healing occurred, and then again formed a CNT neck. It is remarkable that the process is somewhat reversible and that its directionality as well as tempo can be controlled. The results indicate that the carbon ad-atoms generated by electron irradiation are very active and can be used to tailor the structure and properties of carbon nanomaterials as well as to induce self-repair. This clearly opens up the possibility of developing electron beam lithography methods for the synthesis and design of carbon nanomaterials and nanodevices.

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