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Electron beam-induced structure transformation of single-walled carbon nanotubes

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Received 1 April 2002; accepted 19 June 2002

Keywords: A. Carbon nanotubes; B. Surface treatment; C. Transmission electron microscopy; D. Defects

Since the discovery of carbon nanotubes in 1991 [1], they have been regarded as ideal materials for use in nanoscale devices because of their small diameter [2], fascinating electronic properties [3], incredible mechanical strength [4] and elasticity [5]. For the application of single-walled carbon nanotubes (SWNTs) in nanoscale devices, it is highly desirable to modify nanotubes in specific positions, especially in an individual tube. Although many efforts have been made to fabricate SWNT-based nanostructures either by post-synthesis manipulation [6] or by controlled growth formation [7], it still remains a great challenge for scientists to find an effective way to modify or transform nanotubes at expected locations.

Transmission electron microscopy (TEM) provides sufficient resolution and it can be used to obtain some direct visualization of the configuration of nanotubes, also it allows in-situ observation of local structure transformation of nanotubes undergoing electron beam irradiation. The electron beam in a high resolution TEM was regarded as a powerful tool to fabricate tubes at a specific position and thus transform the structure of the nanotubes [8,9]. Coalescence [10], jointing [11] and T-junctions [12] of SWNTs were achieved recently by electron beam irradiation. We demonstrate here an in-situ observation of the structural transformations, such as, amorphism, cutting, and welding of the SWNTs under electron beam irradiation in TEM. The results indicate that SWNTs with defects, such as dangling bonds, vacancies, interstitials, pentagon–heptagon pair defects etc., tend to show preferential transformation compared to tubes without defects. Clearly such electron beam fabrication technique might be a useful method to modify the structure of carbon nanotubes.

The SWNTs used in this study were synthesized by chemical vapor deposition (CVD) using Fe catalyst on MgO support [13]. The as-prepared SWNT samples were purified first by acid treatment in 37% hydrochloric acid to remove the catalyst and support material, then microfiltrated with 1.2 μm pore membrane under vacuum after sonication in 0.2% Triton X-100 solution (pH = 10). The properties of nanotubes will be influenced by the presence of defect sites on the walls and/or at the end of the nanotubes [14]. The defects on the walls and/or at the ends of SWNTs were introduced by chemical oxidation using oxidative acid, such as a mixture of concentrated sulfuric acid (98%) and nitric acid (70%) (v/v, 3:1) (alkaline potassium permanganate or dilute nitric acid can be used as oxidant, too). Electron beam irradiation was carried out on a JEOL JEM 2010 TEM under 200 kV. The approximate electron flux at the sample is around 1–0.1 A/cm^2. The samples were prepared by sonicating the soot in water and putting a drop of the suspension onto a homemade carbon-coated copper grid[1] and allowing the solvent to evaporate. As a control, we also did the same experiments on SWNT samples without or with few defects.

Chemical oxidation will introduce some defects on the wall of the nanotubes, and generally the tube ends are opened. Fig. 1 showed the process of amorphism of the defect-containing SWNTs under incessant irradiation of

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[1]Prepared by dropping 0.02 g/ml formvar solution in distilled water to form a thin membrane, transferring the membrane onto copper grids by placing the grids on the water surface, and then coating the membrane with a carbon film using a spray film evaporator.

0008-6223/02/$ – see front matter
PII: S0008-6223(02)00203-8

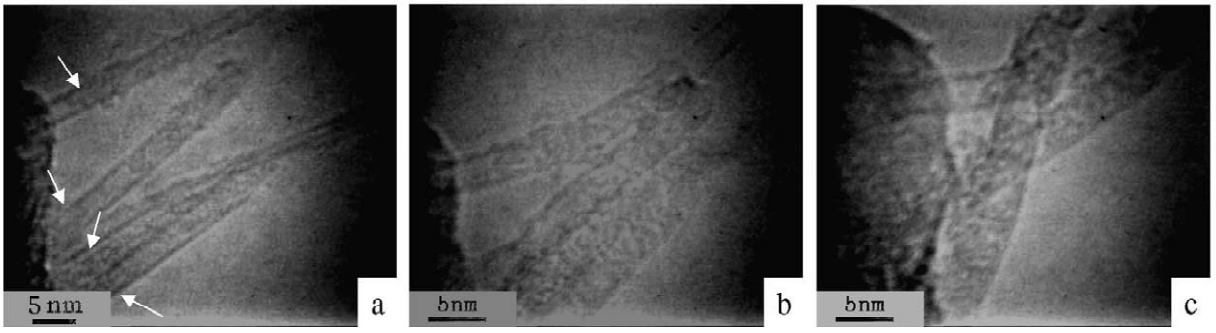

Fig. 1. Amorphism of nanotubes under irradiation of electron beam. (a) There were defects on the walls of nanotubes before irradiation. The arrows point to locations where defects appear. (b) Small ripples present in the nanotube walls, and the tubes began to bend at the defect sites. (c) The tubes collapsed and eventually broke.

the electron beam. When we focused the electron beam on the region of a defect, the most common phenomenon was the amorphism of the nanotubes. Firstly, small ripples began to be present in the nanotube walls (Fig. 1b), and then the deformation increased until ultimately the tubes collapsed and broke (Fig. 1c). We can see that the deformation began at the site of defects (Fig. 1a and b), and the spots where the tubes bent and collapsed were at defect sites (Fig. 1a and c). During the whole process, the tubes were thickened gradually. Occasionally, the tubes were cut into two parts by electric beam irradiation.

In-situ observation of cutting tubes under about 50-s intervals of electron beam irradiation is shown in Fig. 2. A tube initially has a defect in its wall (Fig. 2a). After being irradiated for 50 s, the tube began to disintegrate into two parts at the defect positions (Fig. 2b). The contact between

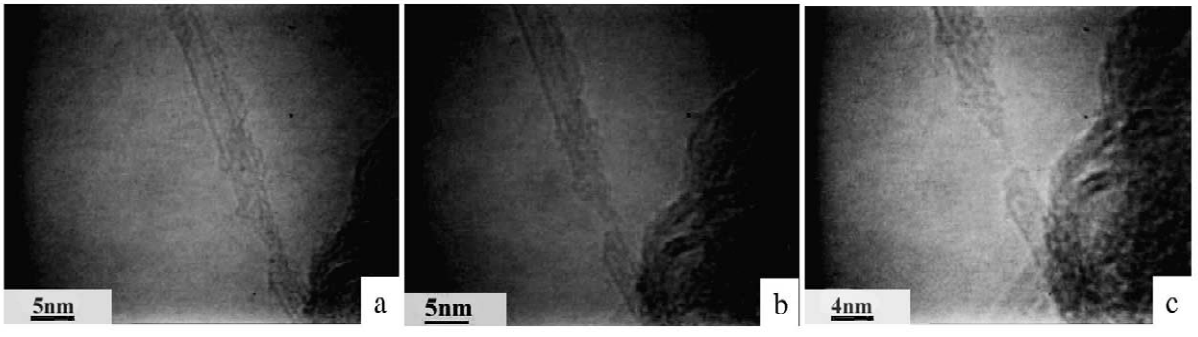

Fig. 2. Nanotube severed under electron beam heating. (a) Nanotube initially with a defect in its wall. (b) The tube began to disintegrate into two parts (A and B). (c) The tube was finally severed into two parts.

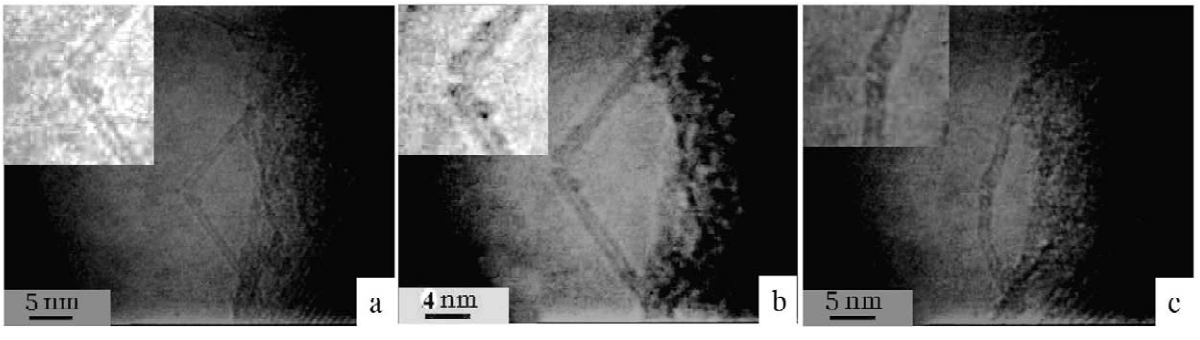

Fig. 3. HRTEM images of the weld process of two vertically aligned SWNTs taken with about 1 min interval. (a) Two tubes with caps were vertically aligned to each other. (b) The tubes began to contact. (c) The tubes were welded by fusion of two adjacent tips.

the two parts slowly decreased, and finally the tube was cut (Fig. 2c). Meanwhile the two parts are enveloped by some carbon particles and thickened. When we focus the electron beam on the SWNTs without or with few defects, however, the structure of the tubes tends to show no change for the same irradiation condition.

It is hence deduced that the structure transformation might have a close relationship with defects in SWNTs. How the above phenomena happened can be rationalized by considering high strain at the sites of defects (such as dangling bonds, vacancies, interstitials, pentagon–heptagon pair defects etc.). With defects expanding, the increased tensile force leads to a less stable structure compared with a perfect hexagonal carbon network, hence making the structure delicate to outside disturbance. It is deduced that the continuous electron beam heating may easily break C–C bonds from defects, causing C atom sublimation and further evaporation of a graphene fragment. The sublimed carbon may deposit on the walls of nearby nanotubes, thus making the tubes thicker [12].

The process of welding two vertically aligned nanotubes was also observed in situ. Fig. 3 shows a succession of images of two tubes taken at about 1-min intervals. The tubes were originally vertical to each other, and there were caps at the tips of the tubes (Fig. 3a). After 1 min of operation, the tubes came into contact (Fig. 3b). And finally, the two tubes fused together to form one tube (Fig. 3c). At the same time, we found that the total length of the tubes decreased. We do not observe a similar situation for two randomly aligned nanotubes. Ho also showed that vertically aligned carbon nanotubes exhibit preferential nanojunction formation as compared to randomly aligned carbon nanotubes due to the proximity of adjacent open tips [12], but they did not show in-situ experimental evidence supporting their reasoning. As we have inferred above, the strain at the nanotube tips made them unstable. When they are opened by electron beam heating, many dangling bonds remain. As the two tubes are so close, they may connect through sp^3 bonding to satisfy most of the dangling bonds.

The application of an electric field may provide an alternative way of fabricating structures of nanotubes for foundation of nanoelectronic devices. The choice among deterioration, separation and fusion of nanotubes depends on the sites of defects, degree of oxidative treatment (size and density of defects), bond formation environment and heat distribution. As a comparison, we irradiated tubes without oxidative treatment under the same condition and we did not get similar phenomena. We can utilize the effect of heating to generate various reconstructions of nanotubes, which may result in a new desirable nanostructure/morphology. Under appropriate conditions, the tubes might be snipped or connected and thus become elements of nanodevices. Further study on this area is underway.

We can conclude that in-situ fabrication and transformation of SWNTs can be realized using high resolution electron irradiation. Structural transformations, including amorphism, cutting and welding, have been demonstrated. Analysis of these processes of transformation indicates that introduction of defects on the wall of the nanotubes is the key step for the fabrication of SWNTs using electron beam irradiation. This could also be a useful method to modify the structure of nanotubes on a molecular scale, thereby providing an approach to the fabrication of nanoelectronic devices.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (NSFC 6989022, 59910161982, 29973001, 30000044), the Ministry of Science and Technology of China (2001CB6105) and SRF for ROCS, SEM.

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