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Effect of electron beam irradiation on multi-walled carbon nanotubes

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Abstract: Multi-walled carbon nanotubes (MWCNTs) were irradiated with focused electron beams in a transmission electron microscope at room temperature. The results showed that carbon nanotubes had no obvious structural damages but only shell bending under 100 keV electron beam irradiation. However, when the electron energy increased to 200 keV, the nanotubes were damaged and amorphization, pits and gaps were detected. Furthermore, generating of carbon onions and welding between two MWCNTs occurred under 200 keV electron irradiation. It was easy to destroy the MWCNTs as the electron beams exceeded the displacement threshold energy that was calculated to be 83−110 keV. Conversely, the energy of electron beams below the threshold energy was not able to damage the tubes. The damage mechanism is sputtering and atom displacement.
Key words: multi-walled carbon nanotube (MWCNTs); electron beam irradiation; morphology; damage mechanism

1 Introduction

Carbon-based materials are commonly used in aerospace industry or nuclear reactors. Due to the unique chemical and physical properties [1−4], carbon nanotubes (CNTs) reinforced copper or silver composites have been widely used in electric brushes on spacecrafts. However, these materials are sensitive to the environment, particularly to the influence of high-energy particle radiation. The structural stability of such materials under various irradiation conditions is crucial to the safety of aviation facilities. Investigations on structural change of irradiating CNTs are of great importance to provide insights for interactions between energetic particles and CNTs and for controllably protecting radiation damages [5]. Electron irradiation has always been used to simulate the behavior of high-energy particle bombardment for investigating the applicability of materials under harsh outer space radiation environments with a considerable flux of energetic cosmic particles [6]. However, electron beam irradiation of MWCNTs has been seldom reported.

Motivated initially by materials requirement for nuclear reactor development, studies focusing on the irradiation effects have been widely performed by transmission electron microscopy (TEM) [7]. CHOPRA et al [8] reported the first in situ study of the dynamical behavior of CNTs employing TEM. Nowadays, field emission TEM (FETEM) proposes the possibility to achieve the current density of about 10^8 A/cm^2 by focusing the beam to a small spot (less than 1 nm) on the specimen. Additionally, FETEM is equipped with CCD cameras with exposure time of typically 0.5 s which can catch more dynamical details. Thus, TEM takes the advantage of in-situ observation of structural transformations at atomic resolution in real time [9]. Based on all of these, FETEM is always applied in electron beam irradiation experiments.

In this work, the electron irradiation performance of MWCNTs was studied under a focused electron beam in FETEM. Morphology changes and damage mechanism under electron irradiation were investigated. It is expected that the study on the stability of CNTs under electron beam gives insights into material selection.

2 Experimental

The MWCNTs with diameter of 20−50 nm and length of 0.5−500 μm (synthesized by catalytic decomposition method) were provided by Shenzhen Nanotech Port Co., Ltd., China. TEM specimens of

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MWCNTs were prepared by a brief dispersion in an ultrasonic bath of tetrahydrofuran and collected on holey carbon micro grids. In-situ observation and electron bombardment experiment were carried out on a JEM−2100F FETEM with a field emission electron gun operating at 100 kV and 200 kV and equipped with a slow-scan CCD camera. During the experiment, the electron beams were focused to spots with the radius of 5−25 nm to irradiate samples. Imaging and irradiation were always performed on nanotubes protruding into the open space of the holes in the carbon film to avoid the transformation of the nanotubes from being hindered by supports and the contrast overlap of amorphous material in the image.

3 Results and discussion

Electron energy of 100 keV was firstly applied to a MWCNT. Figures 1 (a)−(d) show the sequential bending of the nanotube walls when the beam was irradiated on one side of the wall and the spot size was a little larger than the wall thickness. The visible dark regions of the bending area in Figs. 1 (c) and (d) were caused by the shrinking shell structure. After 60 s irradiation, except for shrinkage of the shells, no structural damage was observed. In addition, the selected area electron diffraction (SAED) patterns in Figs. 1 (e) and (f) displayed no distinct change after irradiation, indicating that no structural changes happened.

Actually, interaction between electron beams and materials is interaction between electrons and atoms. When a light electron collides with a nucleus, the momentum transfer arises almost entirely from the change in direction of the electron. The schematic diagram is displayed in Fig. 2 referring to Ref. [10]. The angular dependence of the energy $T(\theta)$ transferred to the nucleus is given by

$$T(\theta) = T_{\max} \cos^2 \theta \quad (1)$$

where θ is the angle between the initial electron motion direction and the scattering direction of the nucleus after collision and $T_{\max}$ is the maximum energy which is transferred by a head-on collision (θ=0). Momentum conservation gives the maximum energy transfer of a relativistic particle (energy E, mass m) to a nucleus (transferred energy T, mass M, θ=0):

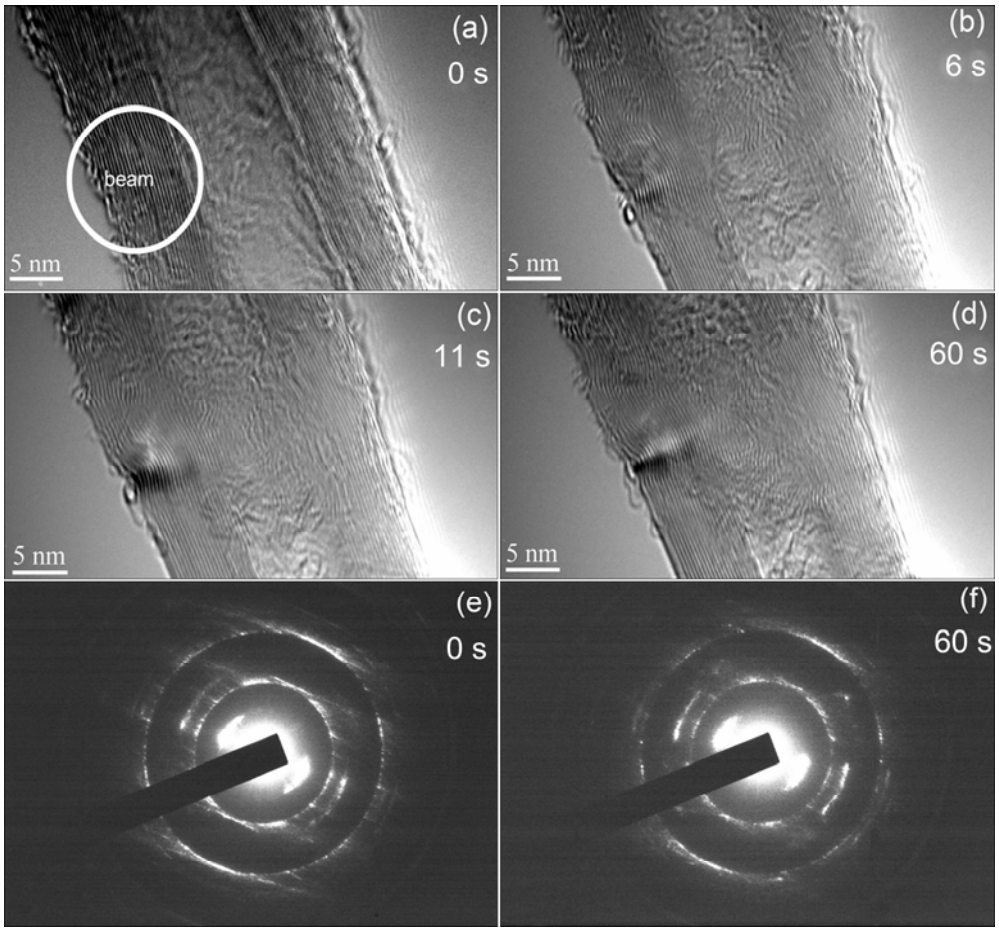

Fig. 1 Bending of shells of MWCNTs under electron irradiation of 100 kV with different irradiation time of 0 s (a), 6 s (b), 11 s (c), 60 s (d) and selected area electron diffraction patterns of 0 s (e) and 60 s (f) (The beam spot size has a radius of about 6 nm)

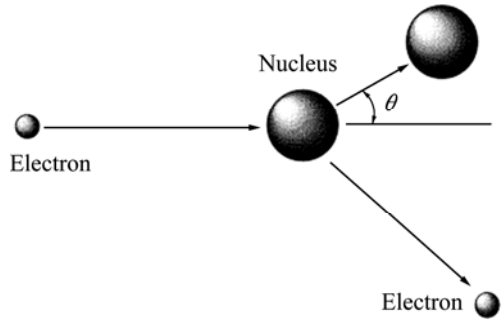

Fig. 2 Schematic diagram of scattering of electron by nucleus

$$T_{\max}=\frac{2ME\left(E+2mC^2\right)}{(m+M)^2C^2+2ME} \tag{2}$$

For electron irradiation ($m_e \ll M$ and $E_e \ll MC^2$), Eq. (2) can be changed to

$$T_d=\frac{2E_e\left(E_e+2m_eC^2\right)}{M_cC^2} \tag{3}$$

where E_e is the electron energy; m_e and M_c are the mass of electron and carbon atom nucleus, respectively; C is the light speed; T_d is the minimum energy transferred to the atom which is required to produce a vacancy-interstitial pair which does not spontaneously recombine. T_d in graphite or MWCNTs is 15−20 eV [10−12]. So, the calculated minimum energy of the electrons, E_e, for atom displacement in MWCNTs is approximately 83−110 keV. Electron beam with energy around 100 keV in our experiment is difficult to cause distinct structure changes because carbon atoms were hard to be displaced far from their positions in a knock-on scattering event with the nucleus. Only a small fraction of carbon atoms were knocked out of their positions as interstitials or sputtering atoms leaving the nanotube to the open space. The loss of atoms led to a reconstruction of the network from a purely hexagonal to a coherent structure containing also non-six-member rings, which produced Stone−Wales defects by forming pentagon−heptagon pairs and thus brought shrinkage to the tube wall. In addition, the removal of carbon atoms left vacancies in the tube walls and also shrank the tube. The small amount of atom loss was responsible for the bending of the shells rather than that of the whole nanotube.

Figure 3 shows the amorphization of a MWCNT

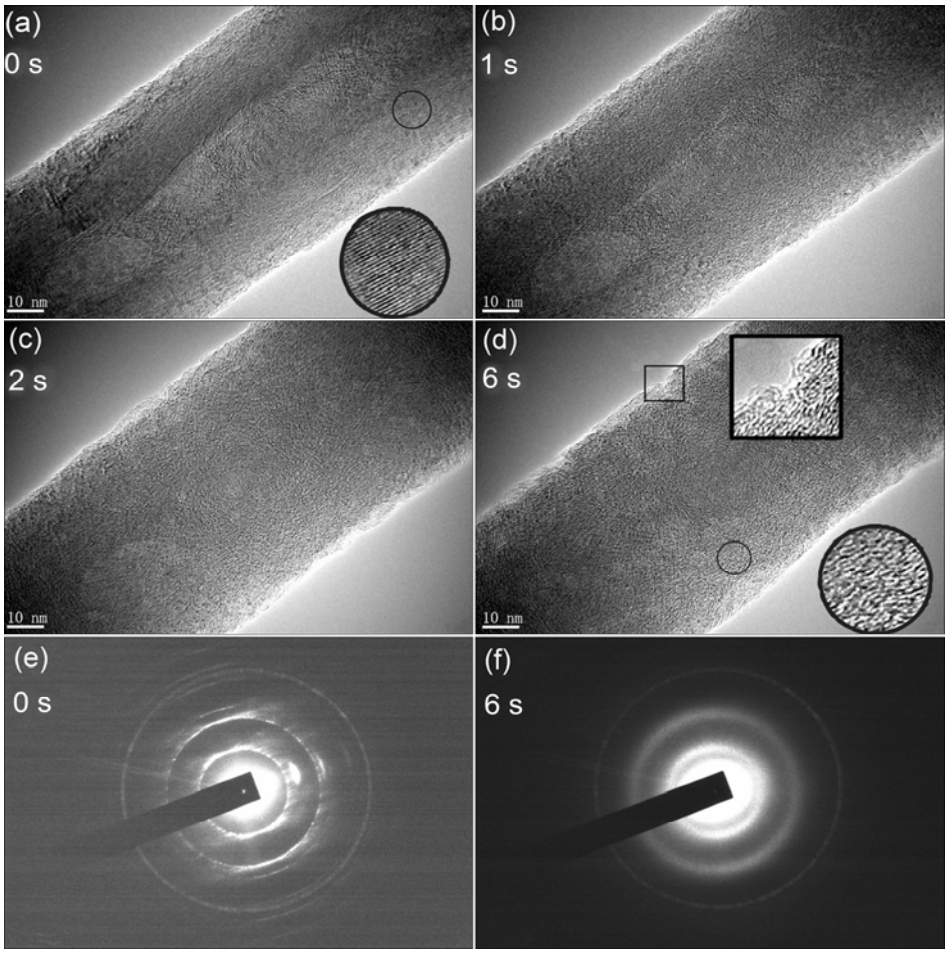

Fig. 3 Amorphization of MWCNT under moderate electron irradiation of 200 keV with different time of 0 s (a), 1 s (b), 2 s (c), 6 s (d) and selected area electron diffraction patterns of 0 s (e) and 6 s (f) (The insets of (a) and (d) are detailed enlargements in order to observe the CNTs walls clearly)

and the corresponding SAED patterns under irradiation of 200 keV electron beam which spreads over the nanotube in visual field. Even gentle irradiation with large beam spot caused distorted and disordered tube walls as shown in the inset in the box of Fig. 3(d), compared with the clear and straight shells of the pristine nanotube before irradiation displayed in the inset of Fig. 3(a). The SAED patterns of the nanotube in Figs. 3(e) and (f) show that the patterns before irradiation are smeared out by diffuse rings after 6 s irradiation, which demonstrates that the amorphous carbon was introduced into the nanotube. Furthermore, during the irradiation process, the tube lost its shape structure step by step due to the gradual absence of the hollow structure (see Figs. 3(a)−(d)) and several pits formed on the surface shown by the circular detail enlargement of Fig. 3(d). As the cross section for damage production in nanotubes dramatically increases with the increase of electron energy, electron beam of 200 keV energy, about twice the threshold energy for displacement of carbon atoms in MWCNTs, could bring much more damage to the tube in terms of knock-on mechanism. Carbon atoms were ejected off their original position which produced Frank defects (interstitials and vacancies) and sputtering atoms. However, the accumulation of interstitials and vacancies due to their poor mobility at room temperature (temperatures above 200−300 °C is high enough for point defects migration to a fast reconstruction of the graphite lattice during irradiation [10]) destroyed the lattice plane and created a lot of dangling bonds possessing high energy. Irradiation-induced cross-linking of the carbon bonds would be expected to appear throughout the nanotube and convert the shell structure to amorphous carbon. The mechanism of amorphization of CNTs was like that of graphite under electron irradiation [13]. In addition, nanotubes can act as nanoscale pipes for the transport of atoms at elevated temperatures [14]. Interstitial atoms cannot migrate along the inner hollow at room temperature so they block up the channel which caused the vanishing of the hollow structure of the nanotube.

Another result of electron irradiation is the cutting effect and the formation of carbon onions as displayed in Fig. 4. When an intense elongated electron beam was applied on one side of the nanotube walls (see Fig. 4(a)) for 60 s, a big gap was observed in Fig. 4(b) due to the loss of a large number of atoms by displacement and sputtering. Two carbon onions were obtained between the two halves of the tube (Fig. 4(c)) after continuous irradiation on the rest of the incomplete nanotube with a circle beam (Fig. 4(d)) for 130 s. The inset in Fig. 4(d) shows the enlargement of the carbon onion in the box. The close-up gives us the details that the carbon onion contains about 12 shells. It is generally known that MWCNTs with smaller inner diameter and thicker tube wall under intense electron irradiation are more likely to form carbon onions. The current density in Fig. 4(b) was estimated as high as 10^5 A/cm^2. The perfectly spherical onions are the only stable form of carbon under such intense irradiation in common sense.

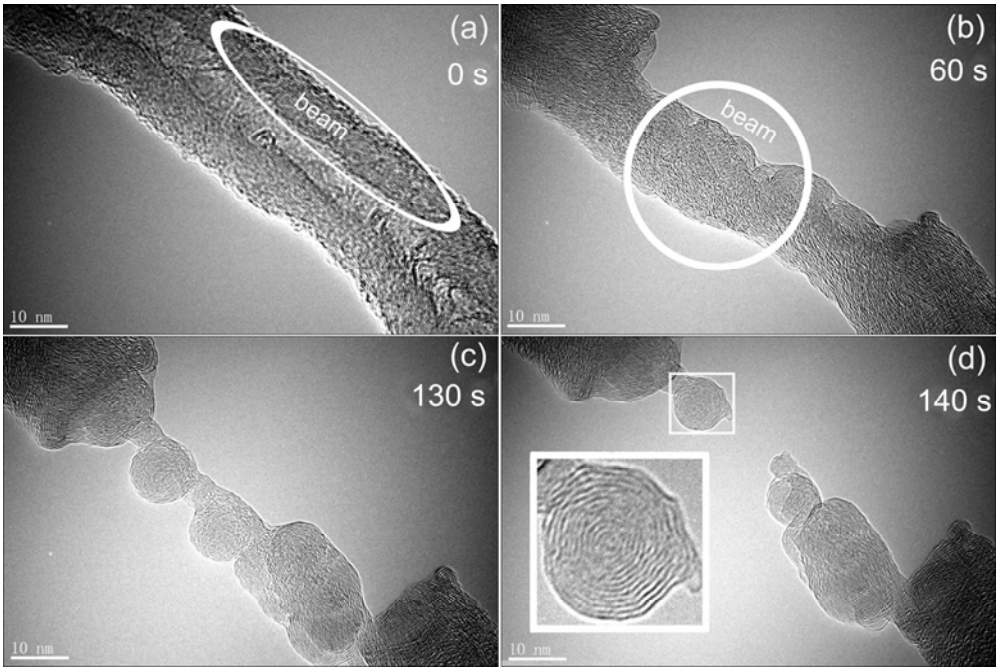

Fig. 4 Morphological evolution of MWCNT under 200 keV irradiation with different shapes of beam spot: (a) Pristine MWCNT; (b) Cutting of gap into tube with intense elliptical beam after 60 s irradiation; (c) Formation of carbon onions with moderate circular beam after 130 s irradiation; (d) Fracture of tube after 140 s irradiation (The inset in (d) is the close-up of the carbon onion in the box)

The formation of carbon onions was driven by the minimization of surface area due to the physical tendency of the lowest energy. Reducing area of nanotubes due to vacancies under irradiation led to the surface tension and the graphitic sheet bent in an attempt to eliminate the highly energetic dangling bonds by electron bombardment, which favored the formation of spherical structures. Symmetry breaking could come about by the tendency of bending of graphene layers after a large amount removal of carbon atoms under irradiation. The curling of the first planes could influence their environment in such a way that adjacent planes find favorable positions by wrapping around the initially curled structure and lead to spherical structure, and no longer changed its shape under electron irradiation. Finally, the nanotube broke in half after 140 s irradiation.

Figure 5 presents the welding evolution of two crossed nanotubes under electron irradiation with a beam of about 20 nm in radius. The two nanotubes were linked together through the junction of the outside shells after irradiation for 30 s as shown in Fig. 5(d). The welding of the tubes was ascribed to the irradiation-induced vacancies and energy gain by dangling bonds saturation. Vacancies play the most dominant role in directing the coalescence of nanotubes. Other defects such as dangling bonds, interstitials and Stone−Wales can be responsible for connections between nanotubes that promote their polymerization through sp^3 bonding [15]. Dangling bonds around vacancies at contact point of the two tubes can serve as bridges for the merging process. The inherent ability of carbon atoms to form structures with different coordinations of atoms, such as heptagonal or octagonal rings, on the surfaces introduced negative curvature and promoted the welding of nanotubes. NIE et al [16] reported that electron irradiation, Joule heating and electromigration could create large vacancy clusters in the specific areas which were specially designed as the merging centers of double-walled nanotubes at room temperature. In our case, just intense electron irradiation created a lot of defects and thus provided enough highly reactive dangling bonds as bridging sites on the edge of the two tubes' shells, which led to the coalescence of MWCNTs even at room temperature.

4 Conclusions

The effects of electron beam irradiation on MWCNTs were investigated by a transmission electron microscopy at room temperature. Electron beams with energy larger than the threshold energy for MWCNTs (approximately 83−110 keV) can destroy the nanotubes and generate new morphologies, such as amorphization, little pits and big gap on the surface, carbon onions and the welding of two nanotubes through sputtering and knock-on displacement mechanism. However, electron beams with energy of 100 keV can hardly influence the nanotubes except the formation of shell bend. The small amount of atom loss was responsible for the bending of the shells.

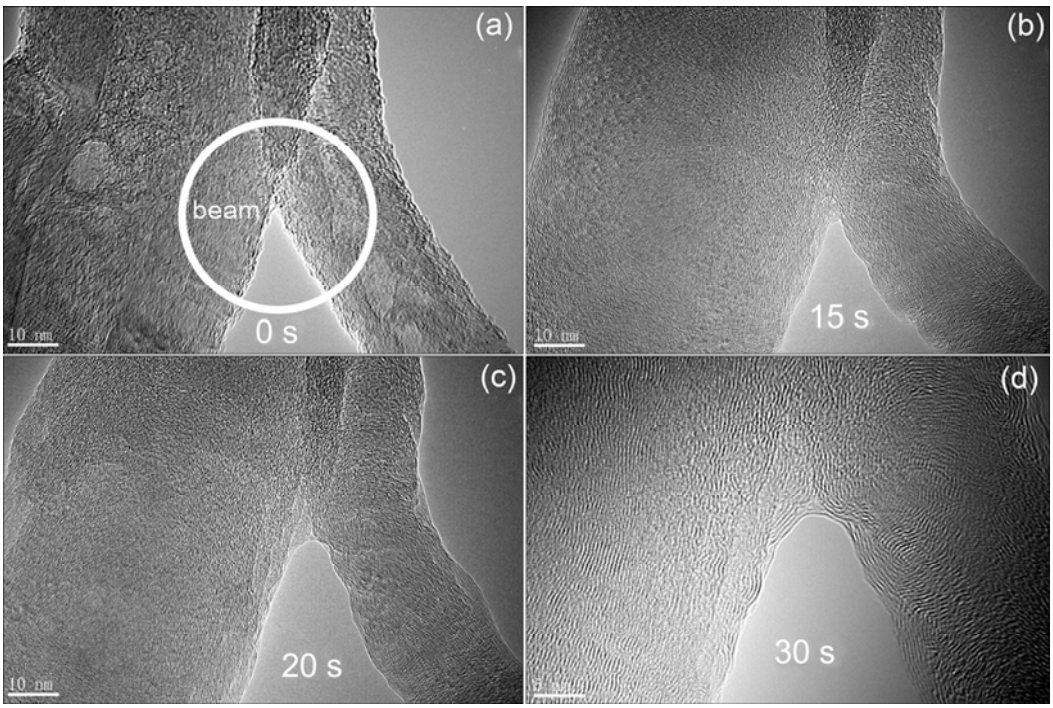

Fig. 5 Welding evolution of two MWCNTs with electron irradiation of 200 keV at different irradiation time (The beam spot size in (a) has a radius of about 20 nm)

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电子束辐照对多壁碳纳米管的影响

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摘 要：在室温下采用透射电子显微镜中汇聚的电子束辐照多壁碳纳米管。结果表明，在能量为 100 keV 的电子束辐照下除了碳纳米管管壁有一些弯曲外没有其他结构被破坏；当电子能量增加到 200 keV 时，纳米管有明显的损伤，可以观察到纳米管的无定型化、纳米管外壁的凹坑和缺口。200 keV 的电子束辐照还能形成碳洋葱和 2 根多壁纳米管的焊接。多壁碳纳米管的离位阀能为 83~110 keV。能量超过阀能的电子束可以很轻易地损伤纳米管而低于阀能的电子束则很难损坏纳米管，其损伤机理为溅射和原子离位。

关键词：多壁碳纳米管；电子束辐照；形貌；损伤机理

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