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Field-ion microscopy observation of single-walled carbon nanotubes*

Zhang Zhao-Xiang(张兆祥)[a], Zhang Geng-Min(张耿民)[a]†, Du Min(杜 民)[a], Jin Xin-Xi(金新喜)[a], Hou Shi-Min(侯士敏)[a], Sun Jian-Ping(孙建平)[a], Gu Zhen-Nan(顾镇南)[b], Zhao Xing-Yu(赵兴钰)[a], Liu Wei-Min(刘惟敏)[a], Wu Jin-Lei(吴锦雷),[a] and Xue Zeng-Quan(薛增泉),[a]

[a] *Department of Electronics, Beijing University, Beijing* 100871, *China*

[b] *College of Chemistry and Molecular Engineering, Beijing University, Beijing* 100871, *China*

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Field-ion microscopy (FIM), a tool for surface analysis with atomic resolution, has been employed to observe the end structure of single-walled carbon nanotubes (SWCNTs). FIM images revealed the existence of open SWCNT ends. Amorphous carbon atoms were also observed to occur around SWCNTs and traditional field evaporation failed to remove them. Heat treatment was found to be efficacious in altering the end structures of SWCNT bundles. Carbon and oxygen atoms released from heated tungsten filament are believed to be responsible for the decoration imposed on the SWCNT ends.

Keywords: field-ion microscopy, carbon nanotubes
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1. Introduction

The carbon nanotube has been intensely studied since its discovery.[1,2] Graphitic layers can curl into single-walled carbon nanotubes (SWCNTs) with different chiral vectors. A large aspect ratio and small curvature radius make the SWCNT a promising candidate for field emitters, such as the cathode of a planar display and the tip of a scanning tunnelling microscope (STM).

Much work has been done in the research on field emissive characteristics of SWCNTs.[3−6] Emissive characteristics of SWCNTs depend remarkably on their surface structure. The structure of the SWCNT is often observed using a high resolution transmission electron microscope (HRTEM), but atomic images are unavailable. The STM is capable of revealing the atomic structure of SWCNTs,[7−9] but so far only the flank wall of a SWCNT has been studied and the atomic image of the end is still beyond STM observation. Field-emission microscopy (FEM) can give field emissive images and characteristics of SWCNTs but, generally speaking, atomic resolution is not achievable.[10−17] Only when a single SWCNT protrudes from a bundle of SWCNTs, is the atom-resolvable image of field emission observable after sample heating.[17,18] Field-ion microscopy (FIM) is a tool for surface analysis with atomic resolution. SWCNTs are considered to be very suitable for FIM observation due to their pointed ends. For instance, Lovall *et al*[19] observed FIM images of SWCNTs, but neighbouring atoms were not distinguished. As reported in this paper, we have observed the open ends of SWCNT bundles using FIM and we have also studied the change in composition of residual gas during heat treatment.

2. Experimental details

We fabricated SWCNTs using the dc discharge method, the details of which were given in Ref.[20]. Transmission electron microscopy (TEM) observation revealed the existence of a large number of SWCNTs in the samples after purification. After further oxidation, samples of SWCNT bundles with a purity of 90% were obtained. The SWCNTs were stored in the form of water colloid.

The system was evacuated by sequentially using the mechanical pump, turbomolecular pump, sputter ion pump and titanium sublimation pump when necessary. After baking, the ultimate vacuum was bet-

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†Author to whom any correspondence should be addressed.

ter than 4×10^{-7}Pa. A fluorescent screen and a multichannel plate were employed to show the FIM images. The images were eventually recorded by a camera. The distance between the multichannel plate and the sample tip was approximately 7.5cm. A ϕ0.2mm tungsten wire served as a filament, on to which a tip chemically eroded from a ϕ0.1mm tungsten wire was spot-welded. A SWCNT bundle, which was treated ultrasonically beforehand, was assembled on to the tungsten tip by van der Waals force and then the tip was mounted into the system.

3. Results and discussion

Just before FIM observation, the sample was cooled to below 100K using liquid nitrogen and the sputter ion pump was switched off. Highly pure helium was introduced into the system as an imaging gas until the pressure increased to 6×10^{-3}Pa and then nominal voltages were applied to the multichannel plate and the fluorescent screen, separately. In normal cases, irregularly distributed bright spots appeared on the screen as a high voltage was applied between the tip and the multichannel plate, and the number of spots increased with the rising voltage. When the voltage reached a certain value, some bright spots were seen to form circles or, more precisely, approximate ellipses.

Figure 1 gives a helium FIM image of the end of a SWCNT bundle, the optimal imaging voltage being 6130V. According to the FIM mechanism,[21] helium atoms were ionized in the high field in the vicinity of the tip, and the generated ions were accelerated and flew on to the multichannel plate at a high speed so that the end structure of the SWCNTs was imaged. Consequently, in an ideal case a bright spot on the screen arose from a carbon atom. Since SWCNTs stood on the tungsten tip, Fig.1 actually presents an atomic image of the end of a SWCNT bundle. It is noticed that no other spots can be found inside the circle, suggesting that the open end of the observed SWCNT was free from impurity atoms. In Fig.1, two atoms at the same height are imaged as two partially resolvable spots with similar brightness. Two atoms at different heights are not entirely distinguishable from each other although their relative height can be known from the different brightness of the corresponding spots. If the distance between the pair of atoms indicated by the arrow is assumed to be 0.144nm, the nearest distance between two atoms in a SWCNT, the diameter of the observed SWCNT can be calculated to be approximately 1.8nm. It is generally believed that FIM resolution depends mainly on the sample temperature and curvature radius. As reported previously, the best resolution for a single tungsten crystal in FIM observation is 0.25nm. Since some locally protruding structure might exist on the SWCNT ends, we think that it is possible for the local resolution to exceed the limit in the tungsten case.

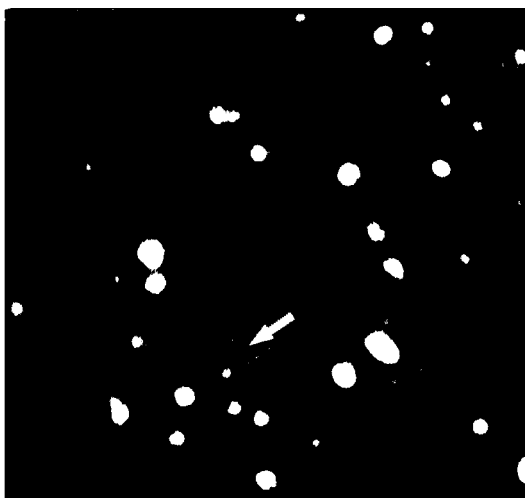


Fig.1. FIM image of a SWCNT end. The imaging voltage used is 6130V.

Owing to the carbon vacancies caused by oxidation cutting, it is difficult to observe perfect atomic images of SWCNT ends. In FIM images, some irregular spots also manifest themselves, which actually result from amorphous carbon atoms surrounding the SWCNTs. These undesired atoms also contribute to field emission when SWCNTs are studied by FEM. Thus the measured work function reflects the average effect only, i.e. an impurity-free end is a prerequisite for the precise measurement of the work function of a SWCNT.

Figure 2 shows an FIM image of another SWCNT bundle, the optimal imaging voltage being 4650V. In Fig.2(a), one can see three imperfect ellipses, indicated by '1', '2' and '3'. Their major axes are oriented similarly and are almost equal in size, inferring that they are images of the ends of three SWCNTs quite uniform in diameter. The axial direction of the SWCNTs was probably not parallel to that of the FIM system, thus the SWCNT ends were imaged as ellipses instead of circles. It is easy to know that the length of the major axis is equal to the SWCNT diameter. Figure 2(b) shows an amplification of '1' in Fig.2(a). There are nine bright spots along the ellipse, six being almost equal in size. A model of end structure (7,7) corresponding to Fig.2(b) is given in Fig.2(c).

The small circles with crosses represent the spots in Fig.2(b), while hollow circles are added for the purpose of achieving a perfect end structure. If two adjoining spots are considered to represent two carbon atoms spaced by 0.144nm, the diameter of the corresponding SWCNT is then calculated to be 0.979nm, which is in good agreement with the theoretical value 0.963nm for the (7,7) structure.

It should be stressed that the observation of the images in Figs.1 and 2 was foregone by heat treatment.

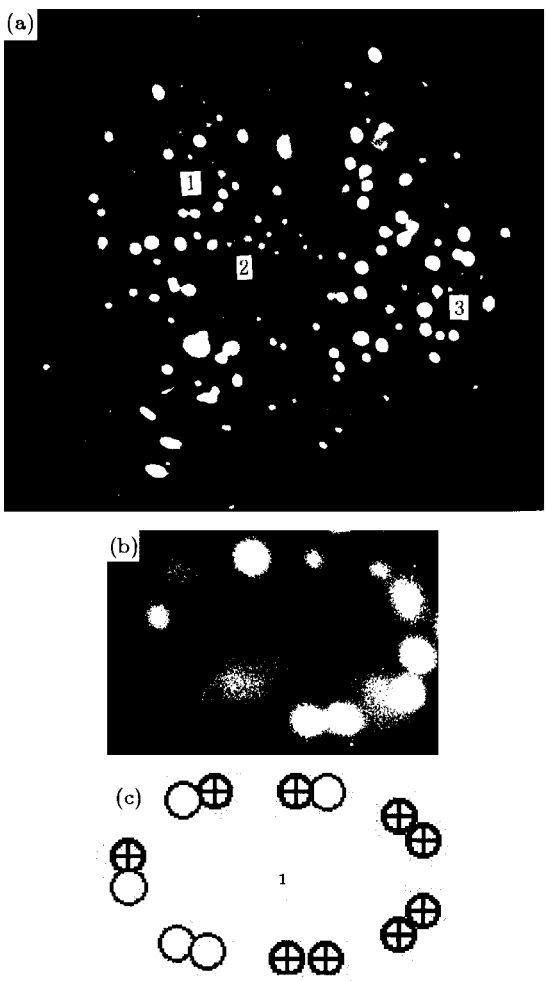


Fig.2. (a) A FIM image of another SWCNT bundle. (b) An amplification of '1' in (a). (c) The proposed model for (b).

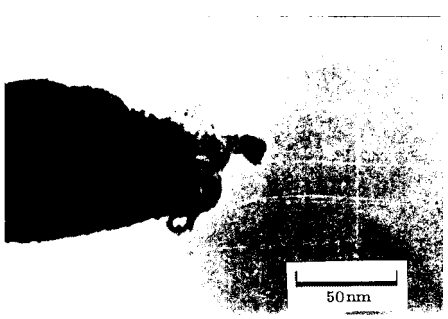


Fig.3. TEM image of a SWCNT bundle.

Figure 3 shows a TEM image of SWCNTs assembled on a tungsten tip. The left part is the tungsten tip while the right is the SWCNT, whose top has a radius curvature of approximately 5nm, further confirming that what was observed was actually a bundle formed by SWCNT agglomeration.

In order to determine the constituent components of the residual gas in the vacuum chamber when the sample was under heat treatment, we also carried out a mass spectroscopy analysis using a quadrupole mass spectrometer. The result on a tungsten tip is shown in Fig.4. Figure 4(a) shows the background mass spectrum of the system at 5.7×10^{-7}Pa, and Fig.4(b) shows the mass spectrum of the residual gas at the highest pressure (5.6×10^{-6}Pa) under 820°C sample heating.

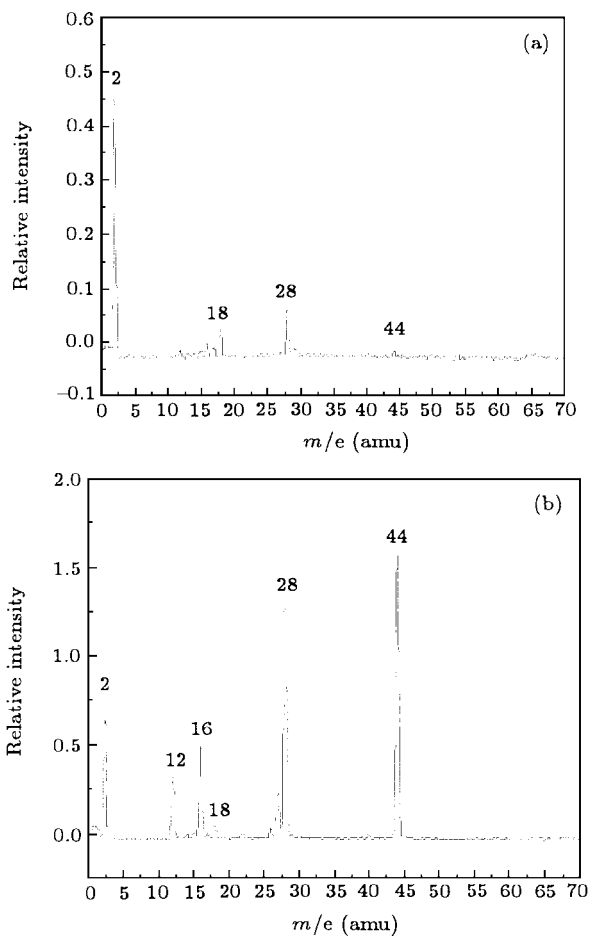


Fig.4. The mass spectra of the residual gas at different heating temperatures: (a) room temperature; (b) 820°C.

Field evaporation is known to be fairly effective in removing adsorbates. If the field strength is sufficiently high, even the intrinsic atoms on samples being observed can be evaporated. For instance, it is

by means of field evaporation that the perfect FIM image of a single tungsten crystal has been achieved. However, the electric field strength for the occurrence of field evaporation of carbon atoms is as high as 1433MV/cm.[21] Thus the end of SWCNTs cannot be rid of amorphous carbon atoms by applying a high field only; heat treatment is indispensable to the removal of these carbon atoms. In our present experiment, when the voltage was raised sufficiently high, SWCNTs collapsed and then field evaporation images of tungsten emerged. However, in our previous experiments, the FEM images of SWCNT samples underwent obvious changes under heat treatment, and FEM images with atomic resolution of individual SWCNTs were even achieved.[17,18]

After observing the FIM image in Fig.1, we gave the sample a further heating and the FIM image shown in Fig.5 was obtained. In Fig.5, circle '1' corresponds to the circle in Fig.1, while circle '3' is considered to be an image of the end of a newly exposed SWCNT. Figure 4 can help us to understand how heating cleans the SWCNT ends. In Fig.4(a), the H_2 peak is the principal peak, and the peaks of N_2, H_2O, CO_2, etc, also exist. It can be seen in Figs.4(a) and (b) that heating of tungsten results in the enhancement of CO (28amu) and CO_2 (44amu) peaks. While in Fig.4(b), peaks of 16 amu and 12 amu are also enhanced considerably, which could not be a result of fragments of CO and CO_2 molecules. It is known that oxygen and carbon atoms exist among the grains in polycrystalline tungsten. As the tungsten filament is heated, the grains grow in size and oxygen and carbon atoms are released into vacuum. Besides generating CO and CO_2, they also impose decoration upon SWCNT ends. For instance, oxygen atoms could react with amorphous carbon atoms on the ends, and the latter will leave the SWCNT in the form of CO or CO_2. Therefore SWCNT ends are exposed and circle '3' shown in Fig.5 results. An in-depth investigation is now underway into the heat treatment influence at higher temperatures on FIM images of SWCNT bundles.

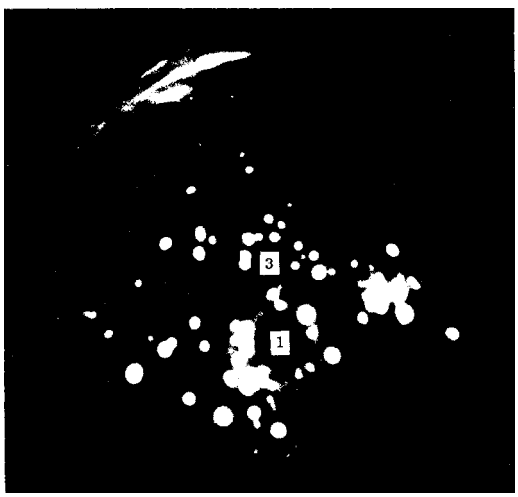


Fig.5. FIM image of the SWCNT after further heat treatment.

4. Conclusion

FIM, which is a tool for surface analysis with atomic resolution, has been used to study the atomic structure of SWCNT ends. With helium as the imaging gas, the open ends of SWCNTs were observed. Under heat treatment, oxygen and carbon atoms released from the tungsten filament imposed decoration upon SWCNT ends and removed amorphous carbon from them.

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