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Enhanced Electron Field Emission from Carbon Nanotubes Irradiated by Energetic *C* Ions

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The field emission performance and structure of the vertically aligned multi-walled carbon nanotube arrays irradiated by energetic *C* ion with average energy of 40 keV have been investigated. During energetic *C* ion irradiation, the curves of emission current density versus the applied field of samples shift firstly to low applied fields when the irradiation doses are less than 9.6×10^{16} cm^{-2}, and further increase of dose makes the curves reversing to a high applied field, which shows that high dose irradiation in carbon nanotube arrays makes their field emission performance worse. After energetic ion irradiation with a dose of 9.6×10^{16} cm^{-2}, the turn-on electric field and the threshold electric field of samples decreased from 0.80 and 1.13 V/μm to 0.67 and 0.98 V/μm respectively. Structural analysis of scanning electron microscopy, transmission electron microscopy and Raman spectroscopy indicates that the amorphous carbon nanowire/carbon nanotube hetero nano-structures have been fabricated in the *C* ion irradiated carbon nanotubes. The enhancement of electron field emission is due to the formation of amorphous carbon nanowires at the tip of carbon nanotube arrays, which is an electron emitting material with low work function.

Keywords: Carbon Nanotube, Nanowire, Ion Irradiation, Field Emission.

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1. INTRODUCTION

Carbon nanotubes (CNTs) have attracted great enthusiasm among the researchers, since they were found firstly by lijima in 1991.[1] Due to their unique physical and chemical properties, CNTs have lots of potential applications in many important fields, such as nano-electronic device, super-strength materials, energy storages, electron emitters and opto-sensors. Among their applications, because of their high-aspect ratio, excellent electrical and mechanical property, CNT is a potential candidate as the next-generation field electron emitters. The first report about the field emission characteristics of a single multi-walled CNT was conducted by Rinzler et al. in 1995.[2] And in the passed nearly ten years, field emission investigation has become one of the hot subjects in CNTs world. However, the relatively high work function of CNTs limits its ability to emit electrons. So there is a need to enhance the field emission properties of CNTs further by reducing their work function and improving their structure.

Recently, Smith's group pointed out that the carbon vertically aligned nanotube arrays (CNTAs) emitters would have maximum efficiency when the intertube separation was three times to the CNT height.[3] Furthermore, post-treatment of as-grown CNTs like nanocoating modification[4–5] and plasma treatment,[6–8] have been proven to be effective methods to enhance the field emission property. Gohel et al.[6] reported that they got a lower turn-on field of 1 V/μm (E_{on}, which is an applied field at the current density of 10 μA/cm^2) and higher field emission current of CNTs by the better structure and reduced work function after N_2 plasma treatment. And the similar process conducted by hydrogen, oxygen and rare gas plasma were also reported.[7–10] Some reports[11, 12] pointed out that the doped CNTs with metal elements (for example, argentum and caesium) also could get better field emission performance, because the metal element doping could enhance the electronic density of states near the Fermi level of CNTs and make field emission easier. So, there are many works have been done to enhance the field emission property of CNTs.

The energetic ion irradiation technique has superior controllability of the ion species, incident energy, irradiation

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dose and beam current, which is an effective tool for precise machining. In this paper, we investigate the electron field emission enhancement from carbon nanotubes irradiated by energetic *C* ions. We think the improvement of the field emission (FE) characteristics of CNTs is due to the fabrication of amorphous carbon nanowire/CNT hetero nanostructures at the tip of CNTs.

2. EXPERIMENTAL DETAILS

Multi-walled Carbon nanotube arrays (MW-CNTAs) were synthesized on (100) silicon substrates by a thermal chemical vapor deposition (TCVD) at 750 °C for 30 minutes. In this procedure, a Fe thin film with a thickness of 5 nm was used as a catalyst, and the mixing of hydrogen and acetylene with a H_2/C_2H_2 flow rate ratio of 6.9:1 was used as a reactive source. Energetic *C* ion irradiation was carried out by MEVVA ion implanter. The incidence angle of the ions was about 45°, and the average energy of *C* ions was about 40 keV. The irradiation doses were 5.6×10^{16}, 9.6×10^{16}, 2.3×10^{17}, 3.4×10^{17} and 5.6×10^{17} cm^{-2} respectively, which were calculated by a TRIM simulation program. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to characterize the structures of as-grown and the irradiated CNTs. Field emission measurement was carried out in a bipolar measurement equipment with a base pressure of 1×10^{-7} Pa at room temperature.

3. RESULTS AND DISCUSSION

Energetic ion irradiation can induce defect creation (substitution, interstitial and vacancies creation), doping, and re-crystallization in target materials, which can cause the transformation of composition and phase structure in the material. In our work, the irradiation effects mainly locate at the tip of CNTs because of the defined incidence angle and one dimension structure. Figure 1 shows the SEM pictures for as-prepared CNTAs and CNTAs irradiated by different dose of energetic *C* ions. The cross-section images nearby the top reveal that the straight tubular structure of CNTAs has been bent gradually along with the irradiation. When the irradiation dose comes to 5.6×10^{17} cm^{-2}, the individual nanotube-structure has disappeared completely (seen in Fig. 1(d)). And the top-view images show that the top morphology of CNTAs changed not obviously when the irradiation dose is less than 9.6×10^{16} cm^{-2}. When the dose is larger than 9.6×10^{16} cm^{-2}, the structural change becomes evident. At the dose of 2.3×10^{17} cm^{-2}, the individual tubular structure on the top of the CNTAs begins to adhere with each other. When the dose is increased to 5.6×10^{17} cm^{-2}, the top area of CNTAs is damaged seriously and the individual nanostructure is almost replaced by adhesion structure (seen in Fig. 1(h)).

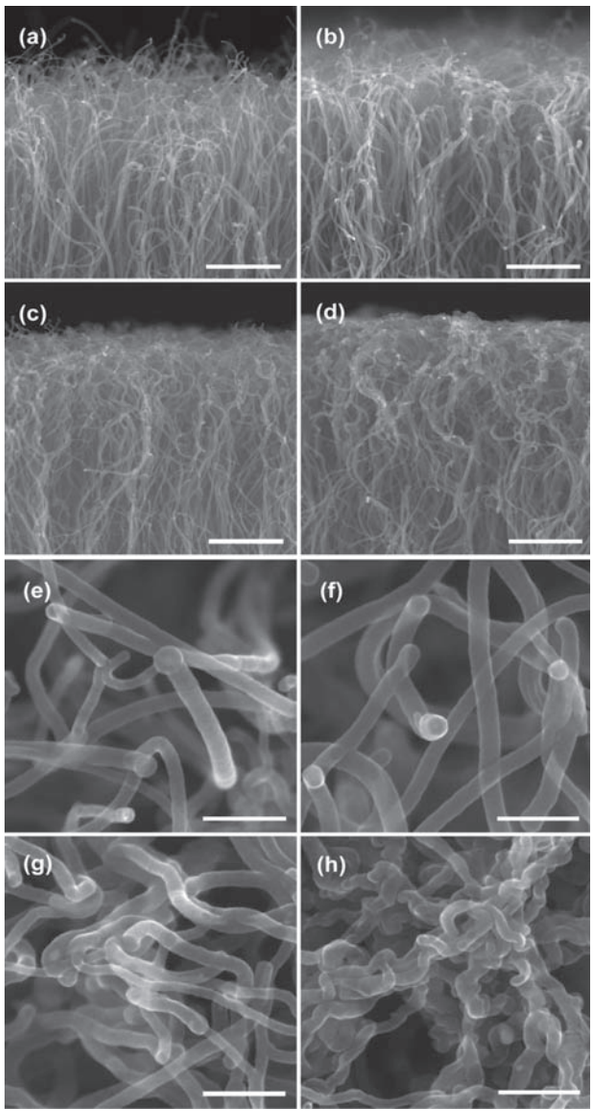

Fig. 1. SEM pictures of CNTAs irradiated by different doses. (a–d) The side views. Scale bar is 1 μm. (e–h) The top views. Scale bar is 150 nm. Corresponding irradiation dose from (a, e) to (d, h) is 0, 9.6×10^{16}, 2.3×10^{17}, and 5.6×10^{17} cm^{-2}, respectively.

In order to further understand the structural changes of the *C* ions irradiated CNTs (CI-CNTs). High-resolution transmission electron microscopy (HRTEM) was used to determine the crystalline structure of the CI-CNTs. Figure 2 shows the HRTEM images of the CNTs irradiated by energetic *C* ions at the dose of 9.6×10^{16} cm^{-2}. The magnified Figures (b–d) are correspond to the location of 1, 2 and 3 in Figure (a), and they depict the tip, neck and bottom of the CI-CNTs respectively. As shown in the images (Figs. (b–d)), the structure at the top of the CI-CNTs is amorphous, and at the bottom of the CI-CNTs is still well tubulose structures with multi-layered graphite. These indicate that amorphous carbon nanowire/CNT hetero nanostructures have been fabricated in the CI-CNTs.

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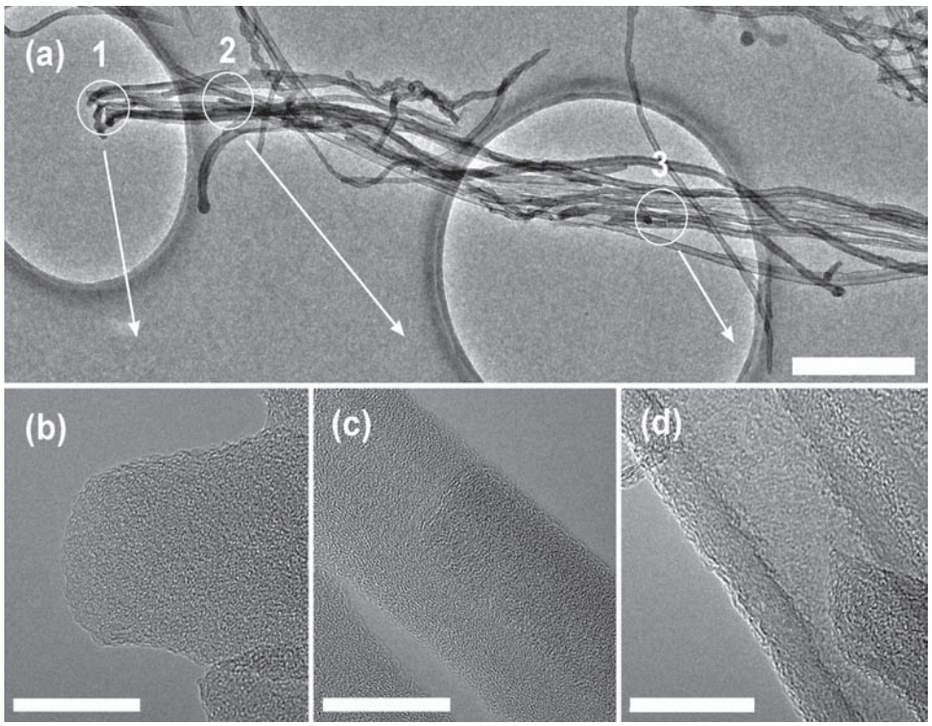

Fig. 2. TEM pictures of CNTs irradiated at the dose of 9.6×10^{16} cm^{-2}. (a) Whole section of the CNTs. Scale bar is 0.5 μm. (b–d) Magnified TEM pictures corresponding to the location of 1, 2, 3 in Figure (a). Scale bar is 20 nm.

XPS was also used to analyze the chemical bonds of C. Figure 3 shows XPS spectra of C1*s* peak from the CI-CNTs at the dose of 5.6×10^{16} and 9.6×10^{16} cm^{-2} respectively. From the figures, we can see that the C1*s* peak has a wide distribution, and is asymmetrical, which indicate that the C1*s* bound is not a single state. The C1*s* peak (Fig. 3(a)) was fitted with three components centered at 284, 285.1 and 288 eV respectively through the program of XPS PEAK. These three components correspond to the sp,^{2} sp^3 hybrid peak of C1*s* and the organic carbon adsorbed, respectively.[13, 14] The binding energy of sp^2 and sp^3 hybrid is shifted to 284.5 and 285.2 eV with the increased irradiation dose (Fig. 3(b)), which indicates that the hybrid form of the shell electron has been changed during the irradiation. Calculation shows that with the increase of the irradiation dose, the content of sp^2 is decreased and more sp^3 bond is formed. When the irradiation dose increases from 5.6×10^{16} ion/cm^{-2} to 9.6×10^{16} ion/cm^{-2}, the content of sp^2 is decreased from 67% to 29%, and the content of sp^3 bond increases from 28% to 65% at the same time. Thus, the amorphous carbon fiber/CNTs composite structure has been fabricated and the content of amorphous carbon fiber is increased with the increase of the *C* ions irradiation dose.

Figure 4 present the Raman spectra from the pristine sample and the samples irradiated with the dose of 9.6×10^{16} and 5.6×10^{17} cm^{-2}, respectively. The D peak (1330 cm^{-1}) is associated with vibration of carbon atoms with disordered graphite, such as defects, dangling bonds in plane terminations and grain boundaries. The G peak (1590 cm^{-1}) corresponds to an E_{2g} mode of graphite, which is relevant to vibration of the sp^2–bonded carbon atoms in a two-dimensional hexagonal lattice.[15] The area integrated intensity ratio I_D/I_G from Lorentzian function fitted Raman spectra of the as-prepared CNTs and the irradiated CNTs at the dose of 9.6×10^{16} and 5.6×10^{17} cm^{-2} is 2.9, 3.5 and 5.1 respectively. This implies that the degree of disorder and defect concentration is increased with the *C* ion irradiation dose, which is consistent with that of TEM images.

Figure 5(a) shows the curves of emission current density versus the applied field (*J–E*) of the MW-CNTAs irradiated by energetic *C* ions at the different doses and the inset is the corresponding Fowler–Nordheim (*F–N*) plots. From Figure 5(a), we can see that *J–E* curves of samples shift firstly to the low applied field, and show a gradually improved field emission characteristic when the irradiation dose increase from 0 to 9.6×10^{16} cm^{-2}. However, further increase of dose makes *J–E* curves reversing to the high applied field, which shows that high dose irradiation in MW-CNTAs makes their field emission performance worse. After energetic ion irradiation with a dose of 9.6×10^{16} cm^{-2}, the turn-on electric field (E_{on}) and threshold electric field (E_{th}, which is an applied field at current density of 10 mA/cm^2) of samples decrease from 0.80 and 1.13 V/μm to 0.67 and 0.98 Vμm

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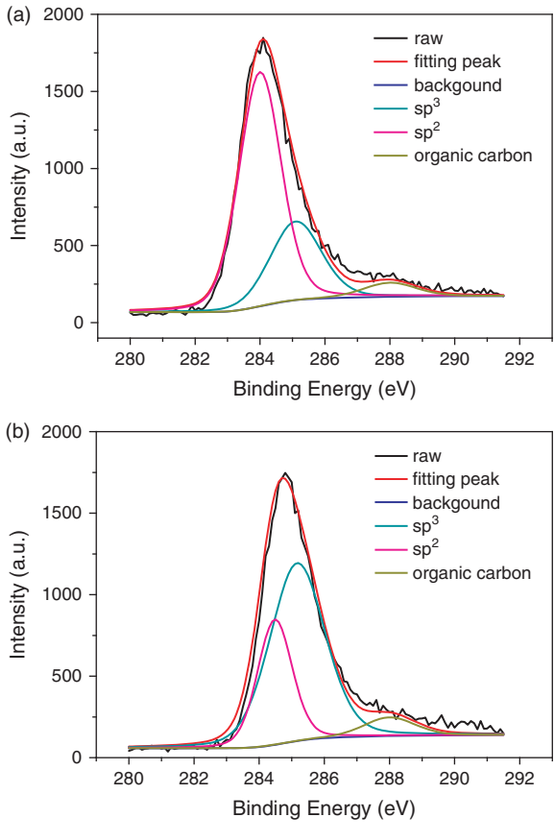

Fig. 3. XPS spectra of C1s peaks of CNTAs irradiated at different doses. (a) Irradiated at the dose of 5.6×10^{16} cm^{-2}. (b) Irradiated at the dose of 9.6×10^{16} cm^{-2}.

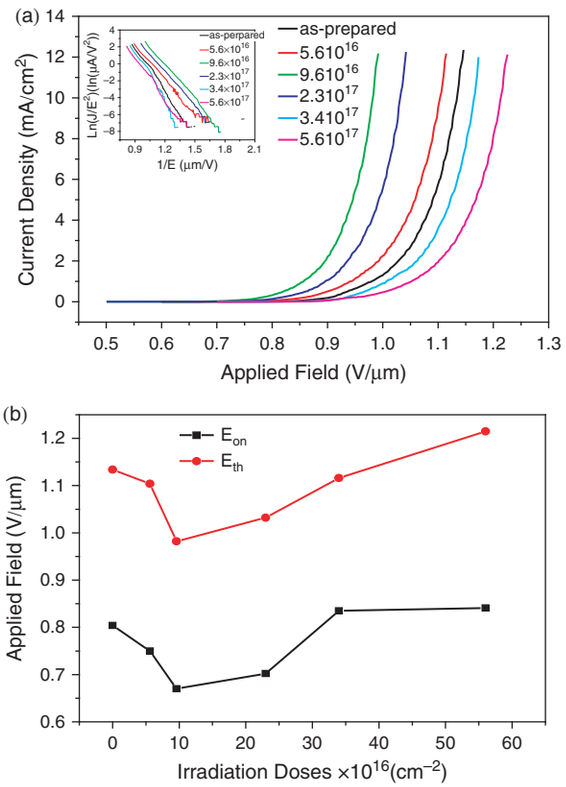

Fig. 5. Field emission characteristics of original and *C* ion irradiated CNTAs. (a) *J–E* curves of CNTAs irradiated by *C* ions at different doses. (b) Diversification of E_{on} and E_{th} with *C* ion doses.

respectively. The *F–N* plots of the CI-CNT arrays show an approximately linear relationship between ln (J/E^2) and $1/E$ in the high applied field area, which further demonstrate that emission electrons in the *J–E* curves are induced by the applied field. E_{on} and E_{th} are important parameters for an electron emitter. Figure 5(b) shows the E_{on} and E_{th} of the MW-CNTAs irradiated with different *C* ion doses. From the picture, it can be seen that the E_{on} and E_{th} of the CI-CNT arrays first gradually decrease with the increase of ion dose from 0 to 9.6×10^{16} cm^{-2} and then increase with a further increase of ion dose. The minimum E_{on} and E_{th} of the CI-CNTs arrays irradiated at the dose of 9.6×10^{16} cm^{-2} are 0.67 and 0.98 V/μ, respectively, which are lower than those of the as-grown CNT arrays (E_{on}, 0.80 and E_{th}, 1.13 Vμm). Thus, the experimental data shows that the FE property of CNTs arrays can be substantially improved, and the best processing condition is at the irradiation dose of 9.6×10^{16} cm^{-2}.

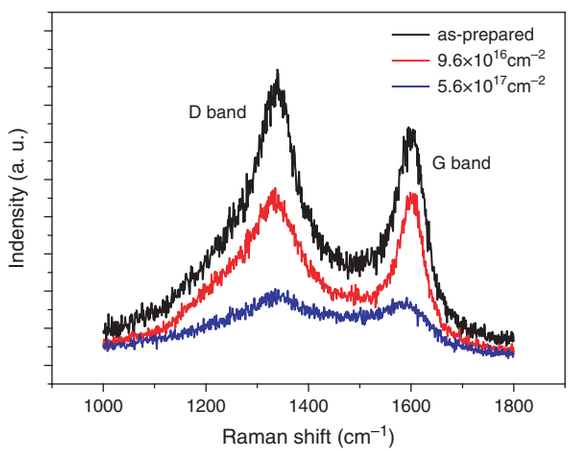

Fig. 4. Raman spectra of as-prepared CNTAs and *C* ions irradiated CNTAs with the dose of 9.6×10^{16} and 5.6×10^{17} cm^{-2}.

When energetic particles, such as electron or ion, hit the target, different mechanisms of damage creation can work, depending on the target material and the particle characteristics. The mechanisms can be the kinetic energy transfer, electronic excitations, ionization, etc. For CNTs irradiated by energetic ions, the most important mechanism is the knock-on atom displacements due to kinetic energy transfer. Electronic excitations and ionization effects seem to be relatively less because of the high thermal and electrical conductivity of graphite shells.[16] In our work, because of the self-ion irradiation, there is no other element introduced into the samples during the processing. So, we think the

improved field emission characteristic of the CNT arrays is due to the change of the graphite structure in CNTAs.

According to the *F–N* equation[17]:

$$J(E) = A(\beta E)^2/\varphi \exp(-B\varphi^{3/2}/\beta E) \quad (1)$$

where J is the current density, A and B are constants, β is the field e nhancement factor, E is the applied electric field and φ is the work function of emitter. The FE property is mainly depended on the work function and field enhancement factor. In our experiment, we thought the formation of amorphous carbon nanowires with a low work function at the tip of CNTAs should be responsible for the improvement of FE property. In order to understand the enhancement of field emission properties, the work function of samples was measured by the ultraviolet photoelectron spectrometer (UPS). The results show that work functions of as-prepared CNT arrays and the CI-CNT arrays with the dose of 9.6×10^{16} and 5.6×10^{17} cm^{-2} are 4.8, 4.71 and 4.67 eV respectively, and demonstrate that the amorphization of carbon nanostructures induces the decrease of work function of the emitters. However, one question will be proposed, why the FE property of CI-CNT arrays with lower work function is worse than that of as-grown CNTAs when the irradiation dose is 5.6×10^{17} cm^{-2}. Here, we divide the process into two steps: first, little change for the morphology of CNTAs and the formation of carbon nanowires are brought to CNTs when the irradiation dose is less than 9.6×10^{16} cm^{-2}, as shown in Figure 1(f), second, further high dose irradiation induce a much change on the tip morphology, in which the individual CNTs is disappeared and carbon nano-net is formed at the tip of CNTAs. In the first step, the defect density in CNTs increase with the increase of irradiation dose and amorphous carbon nanowires are gradually synthesized at the top of CNTs, which have been proven by Raman spectra (seen in Fig. 4) and TEM images (seen in Fig. 2). During the synthesis of the amorphous carbon nanowires, the amount of vacancy-related defects at the tip of CNTs is gradually increased due to ion irradiation and enhances the emission current.[18] And much previous study show that the FE properties of CNTs are enhanced by the increased density of state of the valence band of CNTs near the Fermi level, which can be caused by the generation of defects in CNTs.[19–21] On the other hand, the field enhancement factor β is related with the tip microstructure (such as the shape and aspect ratio) and conductivity of emitting materials. The formation of amorphous carbon nanostructure changes the conductivity of carbon nanomaterials, and induces the increase of the field enhancement factor. Then, the formation of amorphous carbon nanowire/CNT hetero nano-structures in CNTs will be responsible for the enhancement of the FE property, and the lower work function of the amorphous structure is the dominate factor in this stage.

However, when the irradiation dose is larger than 9.6×10^{16} cm^{-2}, the tip morphology of the irradiated CNTAs is damaged seriously, as shown in Figures 1(g–h). The carbon net-work structure in the tip of CNTAs will replace individual tubulose structure, which reduces the number of emission sites of CNTAs and the field enhancement factor of emitters. Although the lower work function can be obtained in the irradiated CNTs. The field enhancement factor will play a dominate role in the second step. According to the *F–N* Eq. (1) combine with the *F–N* plots (insert of Fig. 5(a)), the corresponding field enhancement factor of the as-grown CNTs and irradiated CNTs with the dose of 9.6×10^{16} and 5.6×10^{17} cm^{-2} are 4640, 5023 and 4318, respectively. Therefore, a higher irradiation dose will induce the formation of bad morphology at the tip of CNTs, and make the FE property of CNTs degrading.

4. CONCLUSIONS

Field emission characteristic and structure change of MW-CNTAs irradiated by energetic *C* ions have been investigated. The lower E_{on} and E_{th}, 0.67 and 0.98 V/μ, have been obtained when the *C* ion irradiation dose is 9.6×10^{16} cm^{-2}. The *C* ion irradiation induced defects and the fabrication of amorphous carbon nanowires with decreased work function from 4.8 to 4.67 eV at the tip of CNTAs will be responsible for the enhancement of FE characteristics. However, excessive ion irradiation will introduce serious damage to the morphology of CNTAs, which can deteriorate the FE property by the decreased field enhancement factor, from 4640 to 4318. Self-ion irradiation method has been proven to be an effective technology for the improvement of FE property of CNTs.

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