In situ growth of nanowire on the tip of a carbon nanotube under strong electric field

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We present experimental evidence of *in situ* growth of carbon nanowires on the tip of a carbon nanotube under an applied voltage of 150 V. The grown nanowires with the well-defined geometry and diameter less than ten nanometers are structurally amorphous in nature and result in the solid carbon nanotube-nanowire junction with minimum junction size. The as-generated carbon nanotube-nanowire junction with a distinctive morphology clearly shows evidence of the bonding between the carbon atoms at the tip of carbon tube. The carbon nanotube could be used as a template for *in situ* growth of the carbonate nanowires under a strong electric field. The measured current-voltage (I-V) characteristic of the nanotube-nanowire contact shows a nonlinear relation between the current and applied bias voltage due to the saturated sp^3 bonds formed at the junction. The detected I-V behavior suggests the formation of the metal/insulator/metal structure at the nanotube-nanowire junction. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1879090]

Carbon nanotubes with unique structure, resulting in high aspect ratio, are ideal objects for producing high field-emission current density at low threshold voltage and have important application in flat panel display.[1–4] The high quality of the flat panel display relies on the reliable and durable emission field function of the carbon nanotube emitters. The most critical parameter governing the quality of the carbon nanotube emitter is the stability of the emission current density, which could be decided by the behavior of the emitter under the electric field. In fact, a carbon nanotube is a structure-dependent emitter since structural damage under an electric field could result in significant degradation in the emission property. Consequently, the quality of the nanotube emitter relies on the stability of the emitter during performance. Experimental results of individual nanotube emitters show that the nanotube emitter may have different responses to the electric field. An abrupt destruction of the nanotube, resulting from increasing the field beyond a given limit, and a gradual degradation including shortening of the emitter or damage to the outer walls of the nanotube due to high currents, have been observed for single-walled and multiwalled nanotubes, respectively.[5–10] The fluctuation of the emission current from the carbon nanotube emitters due to degradation of the emitter is predictable. However, stable emission lasting for more than two months was also measured for the emitter without any degradation.[11] The divergent results from the different groups indicate that nanotube response to the electric field is more complex and far from understood. It has been known that many factors, such as the tip morphology and atmosphere in the chamber, could affect the behavior of the carbon nanotube emitter under the electric field. Although great advances have been made in understanding the emission properties of the carbon nanotube via the experimental and theoretic studies,[12–15] a question remains about the behavior of the nanotube under a strong electric field. In present study, we dynamically demonstrate the behavior of a single carbon nanotube under a strong electric field through *in situ* transmission electron microscope (TEM) observation. We reveal that the carbon nanowire could nucleate on the tip of a carbon nanotube under a strong electric field instead of the reported damage of the outer graphite layer.

The multiwalled carbon nanotubes with a length (L) of 1–20 micron and diameter ($2R$) of 5–30 nm were synthesized by a conventional direct current discharge method. The prepared fiber consisting of the nanotubes was glued onto the nanomanipulator probe made of tungsten using silver paste, through which the electric contact was made. The distance between the probe and the ground plate counterelectrode was mechanically adjusted to about 20 micron under an optical microscope (Nikon SMZ-2B) at a magnification of 20. After the specially constructed piezodriven manipulation holder was inserted into a TEM,[16,17] the potential was increased slowly until a potential difference of 150 V was established between the probe and the grounded plate counterelectrode. Then, the probe was carefully positioned at about 500 nm away from the counterelectrode by the piezoelectric actuator.

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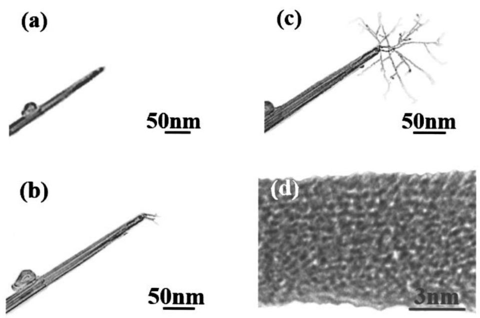

FIG. 1. Successive TEM bright-field images showing formation of the carbon nanotube-nanowire junction under strong electric field, the capped carbon nanotube (a), nucleation of the carbon nanowire at the tube tip (b), and growth of the nanowires to form the real junction, the branch characteristic of the nanowires resulted from the wire grown along the electric field near the tip. The high-resolution image of the nanowire (d) depicts the amorphous nature.

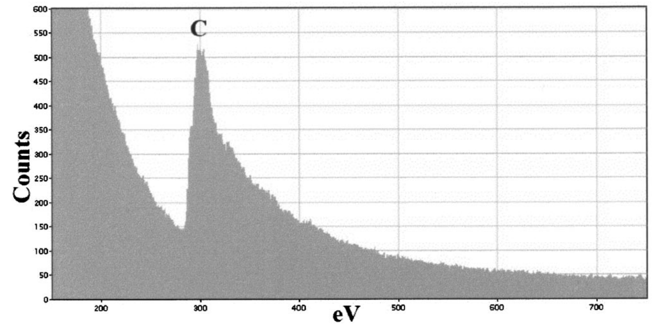

FIG. 2. Electron energy loss spectrum obtained from the nanowires in Fig. 1(d) shows the presence of carbon.

When carbon nanotubes were subjected to an electric field by applying a negative potential to the nanomanipulator probe, the protruding nanotube [Fig. 1(a)] became electrically charged and was attracted to the plate counterelectrode.[18] The electric field is most intense at the tip and has an approximately spherical shape for the capped nanotube.[19] The enhanced electric field at the tip is calculated to be about 12 V/nm by the formula for capped tubes $E_{\text{tip}}=E_0^*(0.87^*L/R+4.5)$,[20] where the uniform electric field $E_0=V/d$ is 0.3 V/nm with an interelectrode separation $d=500$ nm, the applied voltage $V=150$ V; the nanotube diameter $(2R)$ is 15 nm; the nanotube length (L) is 300 nm. *In situ* real time monitoring revealed that the tip structure reacted the foreign atoms in the chamber at a vacuum of $\sim 5\times 10^{-4}$ Pa. As shown in Fig. 1(b), the nanowires nucleate at the tip under such a strong electrical field. The nanowires grew roughly along the electrical-field gradients near the tip [Fig. 1(c)] in a similar way as the reported electron-beam-induced growth of carbon filaments and orientationally grown carbon nanotubes in sputtering or direct current plasma-enhanced hot filament chemical vapor deposition under a very strong electrical field.[21–24] A treelike morphology formed as a result of fractal growth. The nanowire growth was accelerative at a constant electrical field due to the high aspect ratio of these nanowires, and decreased as the strength of the field decreased. Thus, the growth rate can be controlled by changing the applied voltage. The diameters of the carbon nanowires are 5–10 nm and the length is more than 100 nm. The ultimate length of the nanowires could not be determined accurately due to the vibration of the very long nanowires. Figure 1(d) shows the amorphous nature of the nanowires, which may be regarded as a random stacking of carbon atoms under a strong electric field. In our experiment, very strong electrical fields were favored for foreign atoms reacting with the carbon atoms at the tip to result in *in situ* growth of the nanowires at the art-of-science level. *In situ* growth of the nanowires also resulted in the formation of the dedicated nanotube-nanowire junction with nanoscale size and clear contact geometry of two-dimensional characteristic. No fusedlike morphology, as found at the liquid metal-nanotube heterojunction, is identified to associate with this junction. The predicted diameters at the very tip of the nanowires are about 1 nm. At the tip of the nanowires, the electrical field could be as strong as 50 V/nm due to their very small diameter. In other words, formation of the nanowire may also be regarded as a failure model of the nanotube emitter, although the nanotube emitter was not destroyed structurally.

The composition of the nanowires was analyzed by an electron energy loss spectrometer. As shown in Fig. 2, only carbon was detected. The source of carbon atoms could most probably come from the residual hydrocarbons inside the TEM chamber since the morphology of the nanotube was unchanged. Hydrocarbon molecules irradiated by electron beam are polarized or ionized, and attracted by the charged nanotube. Under the electron-beam bombardment, hydrocarbons absorbed on the nanotube decomposed within a very short time and only amorphous carbon was left after volatile parts were pumped out of the chamber.[21–23,25] The electric field, mainly concentrated at the tip, introduced a potential gradient between the tip and wall. When the potential gradient is larger than the weak van der Walls force between the amorphous carbon and the nanotube's wall, the carbon atom could be driven to move along the tube to the tip as the reported mass transportation along the nanotube under an electric field and aggregated on the tip to result in growth of the nanowires.[26] Dissociation of the hydrocarbon was necessary for initializing and retaining the carbon nanowire growth. Therefore, the electron beam played an important role in this process by dissociating hydrocarbon and inducing growth of the carbon nanowires under the strong electrical field. In order to make the nanotube react with the foreign carbon atom, it is necessary to excite the valence electron transition from bonding state π to antibonding state π^* ($\sim$6 eV) for the carbon atoms of the nanotube. The electric field was strong around the tip and weak around the tube wall, which is favorable for the excitation of carbon atoms on the tip to react with the foreign atoms, resulting in nucleation of the nanowires. Consequently, a strong electric field plays a primary role in growth of the nanowires on the nanotube.

A carbon nanowire and nanotube with armchair tip are good conductors. The current-voltage (I-V) behaviors of the nanotube and nanotube-nanowire junction were characterized, respectively, by moving the counterelectrode to touch them under TEM inspection.[16] A Keithley 480 picoampere meter was used for measuring the current with picoampere sensitivity. The Nanofactory™ SU100 controller system provided the applied voltage up to 50 V. The current was averaged for up to 2 s at each voltage value and total 500 current values were measured for the used voltage range. Figure 3(a) is a dc electric measurement of the nanotube before growth

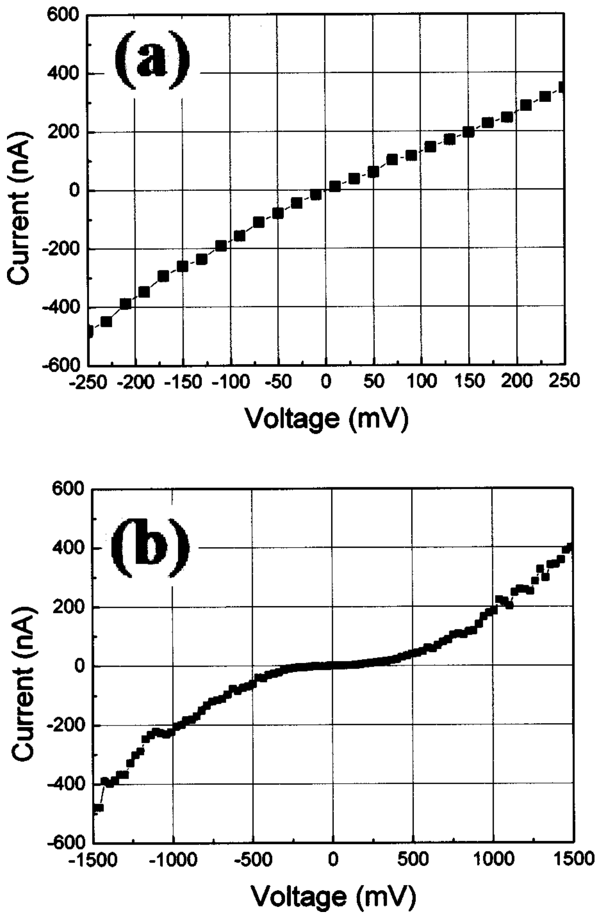

FIG. 3. The measured *I-V* characteristics of the carbon nanotube (a) and the nanotube-nanowire junction (b) show linear and nonlinear relations between the current and applied bias voltage.

of the nanowires. The linear response between the current and applied voltage coincides with Ohmic characteristic. However, the nonlinear relationship between the current and the applied bias voltage is demonstrated in the dc measurement, as shown in Fig. 3(b), of the nanotube-nanowire junction. This *I-V* curve coincides with the tunneling in the symmetric barrier. The rapid increase in current happens above a threshold voltage of 0.3 V. In this case, the junction seems to act as a potential barrier for electron transportation through the junction. A possible explanation of the junction may rely on sp^3 bonds formed at the junction. Each carbon atom on the nanotube bonded with three neighboring carbon atoms to form the unsaturated sp^2 bonds. When the carbon atoms on the tip of the nanotube reacted with the foreign carbon, there would be one more atom bounded to the atoms on the tip. Therefore, the number of neighboring atoms increased to four, which resulted in the unsaturated sp^2 bonds replaced by the saturated sp^3 bonds. The junction with sp^3-bonds behaves as an insulator.

In summary, we have experimentally demonstrated *in situ* growth of carbon nanowires on the tip of carbon nanotube under an electric field. The produced carbon nanotube-nanowire junction with very high resolution at the selectable position and minimum structural damage of the tip structure is difficult to fabricate otherwise using a conventional contact making method. The measured electric property of the nanotune-nanowire junction showed a nonlinear response between the current and applied bias voltage. The carbon nanotube-nanowire junction with the dimension subtly reduced down to nanoscale may enable the development of a number of applications in nanodevice engineering. Also, the substantial extension of the nanotube-nanowire junction technology to nanomaterials may result in important advances toward fully nanotube or nanowire-based electronics and devices.

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