

## Field emission patterns from multiwall carbon nanotubes with a cone-shaped tip

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Electron emission from multiwall carbon nanotubes (CNTs) with a cone-shaped tip, on the apex of which five pentagons are present, has been studied by field emission microscopy (FEM). Two types of FEM patterns were observed: one is a well-defined “pentagon” pattern that is typically observed for ordinal multiwall CNTs though the number of pentagons is five in the case of cone-shaped CNTs, and the other is a “dim” pattern that is usually observed for single-wall CNTs. Appearance voltages of the respective patterns and transmission electron microscopy study of the cone-shaped CNTs suggest that the pentagon patterns originate from CNTs with apex radii larger than approximately 2 nm while the dim patterns originate from those with the smaller apex radii.

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Carbon nanotubes (CNTs) possess various unique properties such as a needlelike shape with nanometer-size diameter, high mechanical strength, chemical stability, and high electrical conductivity, which are advantages as field emitters.<sup>1–3</sup> Application of CNTs to electron emitters in field emission displays,<sup>4–6</sup> cold electron sources in electron microscopes<sup>7</sup> and x-ray tubes,<sup>8,9</sup> and so on is now attracting considerable attention. Field emission microscopy (FEM) has been employed to reveal the electron emission properties of cold cathodes including CNTs.<sup>10–12</sup>

It has so far been reported that FEM patterns of multiwall CNTs with closed caps show clear pentagonal rings<sup>11</sup> while those of single-wall CNTs do not show pentagonal rings but dim (blurred) patterns.<sup>12</sup> The origin was not so far clarified, but we shed some light to this issue by using multiwall CNTs with cone-shaped tips<sup>13</sup> with various radii of curvature.

In this letter, it is reported that cone-shaped multiwall CNTs give two different types of FEM patterns (“pentagon” and “dim” patterns) as well as different threshold voltages, depending on the radius of curvature of a cone tip. The origin of the two different types of FEM patterns of CNTs is discussed on the basis of the radius of curvature of the tip.

Cone-shaped CNTs were produced by rf-plasma heating of graphite in argon gas.<sup>13</sup> The cone-shaped CNTs are multiwalled, and the diameter of a cylinder part is approximately 10 nm, as revealed by transmission electron microscopy (TEM) images in Fig. 1. A structure model of the tip of a cone-shaped CNT is shown in Fig. 2. The cone angle is 19.2°, indicating the presence of five pentagons at the apex. CNT emitters for FEM were fixed on a metal base by the two methods as follows. In the first method, a bundle of CNTs was attached to a filament (0.15 mm in diameter) of tungsten (W) by using adhesive paste. In the second method, by using

electrophoresis, a single CNT or a small bundle of CNTs was adhered to the tip of a W needle (0.15 mm in diameter) which was spot welded to a W filament. FEM experiments were carried out in an ultrahigh vacuum ( $10^{-7}$  Pa). The CNT emitter can be heated to about 1300 K by resistive heating of the W filament. This heating process in high vacuum is important to clean the surfaces of CNTs. A microchannel plate with a phosphor screen for observation of FEM images was placed at about 30 mm in front the CNT emitter. The effective diameter of the observation screen was 42 mm. The electrical potential applied to the nanotubes emitter relative

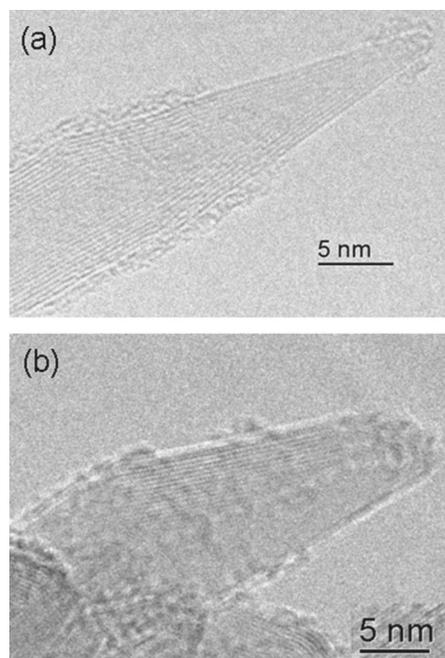


FIG. 1. TEM pictures of tips of cone-shaped CNTs with different curvatures. (a) Sharp tip (radius of curvature  $\approx 1$  nm) and (b) dull tip (radius of curvature  $\approx 4$  nm).

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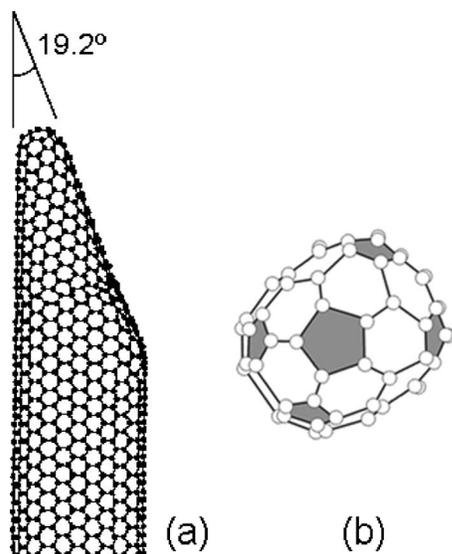


FIG. 2. Structure model of the tip of a cone-shaped CNT: (a) side view and (b) top view. Five pentagons are present at the apex of the cone.

to the screen was in a range from  $-0.2$  to  $-2$  kV. FEM images were recorded with a charge-coupled device camera.

The cone-shaped CNTs gave two types of FEM patterns: one is the dim (blurred) pattern and the other is the pentagon pattern consisting of clear pentagon rings, as shown, respectively, in Figs. 3(a) and 3(b). The latter type is typically observed for multiwall CNTs, though the number of pentagonal rings is different from the ordinary multiwall CNTs, i.e., five pentagons are clearly observed for the cone-shaped CNTs while six pentagons are found for the ordinary multiwall CNTs produced by arc-discharge technique.<sup>11</sup> Interference fringes of electron waves emanating from each pentagon are also observed in boundary regions between the neighboring pentagons, as has been found in the ordinary multiwall CNTs.<sup>11,14,15</sup>

On the other hand, the dim pattern is similar to that observed for single-wall CNTs.<sup>12</sup> Dean and Chalamala pointed out that the FEM patterns from single-wall CNTs resemble scanning tunneling microscope images of  $C_{60}$  fullerenes,<sup>12</sup> suggesting that the pattern reflects the local density of states of electrons on the tip of single-wall CNTs. The emitter voltage required to observe this pattern ( $-0.4$  kV) was lower than that for the pentagon pattern ( $-2.0$  kV), indicating that the radius of the apex curvature giving the dim pattern was smaller than that giving the pentagon pattern. The dim patterns were more frequently observed than the pentagon ones: the ratio of occurrence of the two patterns was about 3.5:1.

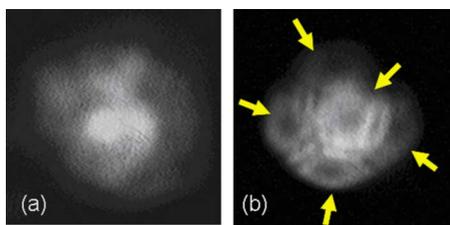


FIG. 3. (Color online) Two types of FEM patterns obtained from cone-shaped CNTs: (a) "dim" pattern and (b) "pentagon" pattern. Arrows show pentagon images.

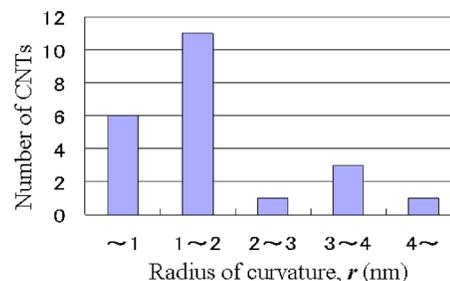


FIG. 4. (Color online) Histogram of tip radii of cone-shaped CNTs.

Since the CNT emitters used in the present experiment were bundles of CNTs and plenty of CNT tips were protruding in random orientations, it was impossible to find and identify the CNT tips which gave FEM patterns by TEM. So, attempts to make one-to-one correlation between FEM and TEM measurements on individual CNTs were abandoned. Instead, using as-grown CNTs before gluing on W filaments, tip structures of cone-shaped CNTs were examined by TEM. Careful measurement of tip radii of 22 CNTs suggested that the radii of cone tips are classified into two groups: one has a small radius of curvature, as shown in Fig. 1(a), and the other has a large radius, as shown in Fig. 1(b). Figure 4 shows a histogram of the radii of curvature, exhibiting clearly two peaks at about 1.5 and 3.5 nm. Assuming the boundary of the two groups being located at 2 nm, the average radii of curvature are calculated to be 1.3 nm for the small radius group and 3.3 nm for the large radius one.

The electric field strength  $E$  appearing on the tip surface is inversely proportional to the tip radius  $r$ , i.e.,  $E \propto V/r$ , where  $V$  represents the electric voltage applied to the emitter. Since the strength of  $E$  required for observable electron tunneling is expected to be the same even for different tip radii, the voltage necessary for observing an FEM pattern should be inversely proportional to the tip radius. The threshold voltage for the pentagon patterns was 1.22 kV on average, while that for the dim patterns was 0.56 kV on average. The ratio of the threshold voltages ( $1.22$  kV/ $0.56$  kV  $\approx 2.2$ ) was fairly in good agreement with the ratio of radii ( $3.3$  nm/ $1.3$  nm  $\approx 2.5$ ).

From the histogram of Fig. 4, furthermore, the ratio of population of the sharp tips to that of the dull tips is counted to be 3.4:1. This population ratio coincides with the occurrence ratio of the two types of FEM patterns (i.e., 3.5:1).

These considerations concerning the threshold voltages and the occurrence ratio of the two types of FEM patterns lead to the conclusion that the pentagon patterns originate from CNTs with apex radii larger than approximately 2 nm, while the dim patterns originate from those with the smaller apex radii. This finding is consistent with the previous FEM studies for ordinal multiwall and single-wall CNTs. The diameters of ordinal multiwall CNTs are in a range from about 5 to 50 nm, and those of single-wall CNTs are in a range from about 1 to 2 nm. The radii of their caps are half of their diameters. The present result combined with the previous reports<sup>11,12</sup> indicates that the separation between adjacent pentagons on a CNT cap defines the types of FEM patterns. Since the pentagon-pentagon separation  $s_{p-p}$  is roughly the same as the radius of tip curvature,<sup>16</sup> the  $s_{p-p}$  which differentiates the patterns is approximately 2 nm.

According to the argument on the spatial resolution of FEM,<sup>17,18</sup> resolutions of 0.2 and 0.35 nm are possible for

emitters with tip radii of 1 and 4 nm, respectively. The resolution of our FEM images from sharp tips ( $r \approx 1$  nm) approaches the atomic scale, but is not enough to resolve individual atoms on the CNT caps. Electron emission intensity in FEM depends on the two principal factors: one is the local field strength (tunneling probability) and the other is the local electron density of states at the Fermi level. When the tip radius is small, say  $r \lesssim 2$  nm, CNT caps have a round shape as a whole similar to  $C_{60}$  and  $C_{70}$  fullerene cages, indicating that the electric field may appear evenly over the pentagon and hexagon sites on the caps. Therefore, FEM images of CNTs with small tip radii arguably reflect the surface electronic states of the CNT caps, as discussed by Dean and Chalamala.<sup>12</sup>

When the tip radius is large, say  $r \gtrsim 2$  nm, on the other hand, the separations between the adjacent pentagons  $s_{p-p}$  are also large, which makes the topological character of the pentagons strikingly clear; geometrical strain in a curved hexagon sheet is concentrated to the pentagons, so the pentagon sites extrude like vertices of a polyhedron as has been illustrated in literature.<sup>11,19</sup> Electric field at the local protrusions is higher than that in the other flat regions on the CNT cap, and thus tunneling probability of electrons at the pentagon sites is higher than that at the other flat hexagon regions. Therefore, it is considered that the electrons are preferentially emitted from pentagons on a CNT cap. High density of electronic states around the pentagons, which is predicted by electronic structure calculation,<sup>20</sup> may be a partial reason for the preferential electron emission around the pentagons. Since the  $s_{p-p}$  for the large tip radii ( $r \gtrsim 2$  nm) is well within the reach of FEM resolution, the preferential emission from locally protruding pentagons makes them clearly visible. If an eigenstate of electrons is distributed over adjacent pentagons, electrons even though being emitted from different pentagons are coherent and interfere with each other and thus interference fringes are formed between the adjacent pentagons.

FEM and TEM studies of cone-shaped multiwall CNTs revealed that the “pentagon” patterns originate from CNTs with apex radii larger than approximately 2 nm while the “dim” patterns originate from those with smaller apex radii. The conclusion is consistent with the previous reports on ordinal multiwall and single-wall CNTs, and the present study clarifies the origin of difference between the two kinds of FEM patterns; i.e., distances between the adjacent penta-

gons on the CNT caps play an important role in the appearance of well-defined pentagon patterns.

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<sup>16</sup>A closed tip (i. e., a curved graphene) of a CNT is considered as a part of a fullerene cage. When twelve pentagons are evenly distributed over a fullerene cage similar to  $C_{60}$  which has icosahedral symmetry,  $s_{p-p}$  is approximately equal to the edge length ( $L_e$ ) of the icosahedron since pentagons are located at positions corresponding to vertices of the icosahedron. For the icosahedron with the length  $r$  from its center to vertices,  $L_e = (\sqrt{1+\tau^2}/2)r \approx 0.951r$ , where  $\tau$  is the golden ratio  $[(\sqrt{5}+1)/2]$ , indicating  $L_e$  is nearly equal to  $r$ . Therefore,  $s_{p-p}$  is on average approximated to a radius of curvature of a closed graphene cage (in this case, radius of curvature of a CNT cap).

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