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Field emission from multi-walled carbon nanotubes and its application to electron tubes

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Abstract. Field emission from closed and open-ended multi-walled nanotubes (MWNTs) was studied by field-emission microscopy. As an application of nanotube field emitters, we manufactured lighting elements with the structure of a triode-type vacuum tube by replacing the conventional thermionic cathodes with the MWNT field emitters. Stable electron emission, adequate luminance and long life of the tubes have been demonstrated.

Carbon nanotubes [1] have been attracting considerable attention not only because of their unique physical properties but also because of their applications in composite materials [2] and as elements of electronic devices [3–6] and nanoprobes [7]. Multi-walled nanotubes (MWNTs) [1, 8], comprising from 2 to 30 concentric graphitic layers, have outer diameters from 10 to 50 nm, and lengths more than 10 μm. On the other hand, single-walled carbon nanotubes (SWNTs) [9–11] are much thinner, being 1.0 to 1.4 nm in diameter, and of length 100 μm [12]. The high aspect ratio and the small radii of curvature at their tips are realized in carbon nanotubes. The geometric characteristic of nanotubes, together with a high chemical stability and a high mechanical strength [13, 14], is advantageous for field emitters. Indeed, field emission (FE) from an individual MWNT [3] and from assemblies of MWNTs [15, 16] has been demonstrated. Field-emission microscopy (FEM) was also performed recently for both MWNT [5] and SWNT [17]. We present here our FEM results obtained for open-ended and closed MWNTs.

Based on our study on FE from MWNTs, we have manufactured electron tubes equipped with MWNT field emitters as a cathode. The fabricated tubes (20 mm diameter, 74 mm length) are the three-electrode type, consisting of a cathode (nanotube field emitter arrays), a grid, and an anode (phosphor screen). The manufactured tubes are lighting elements, which are assembled to form a giant outdoor display. Stable electron emission, adequate luminance and long life of the tubes were obtained.

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1 Field emission microscopy of multi-walled carbon nanotubes

1.1 Preparation of nanotube emitters

Two kinds of MWNTs were used as emitters; ordinary MWNTs with closed caps, and open-ended MWNTs. The ordinary MWNTs were retrieved from the core of a cathode deposit produced by a carbon arc [18]. The open-ended MWNTs were obtained after a purification process in which graphite debris and nanoparticles were removed by oxidation with the aid of $CuCl_2$ intercalation [19]. We obtained purified MWNTs in the form of black, thin "mats" (flakes with a thickness of a few hundredths of mm). Figure 1 shows a typical TEM (transmission electron microscopy) image of an open end of a MWNT, revealing that a cap is etched off and the central cavity is exposed.

For making an electron emitter of capped MWNTs, a needle-like fragment (about 0.1 mm in diameter and 1–2 mm in length) was picked up with tweezers from the cathode deposit and was fixed on the top of a hairpin-shaped wire (tungsten or nichrome, 0.2 mm in diameter) by using carbon paste. For the purified MWNTs, a thin thread (less than 0.1 mm in width and 1–2 mm in length) with a sharp tip was cut from the mat of MWNTs by using a razor blade, and was fixed to a hairpin wire. The emitters were made of many nanotubes, thus they could be called bulk bundles. Figures 2a and 2b show the ends of the nanotube emitters made from as-obtained MWNTs and purified MWNTs, respectively.

1.2 FEM apparatus

Figure 3 shows a schematic drawing of the FEM apparatus we used. The emitter tip of the nanotubes was positioned 60 mm in front of a microchannel plate (MCP) with a phosphor screen behind. The effective diameter of the MCP was 42 mm. The working pressure of a vacuum chamber for

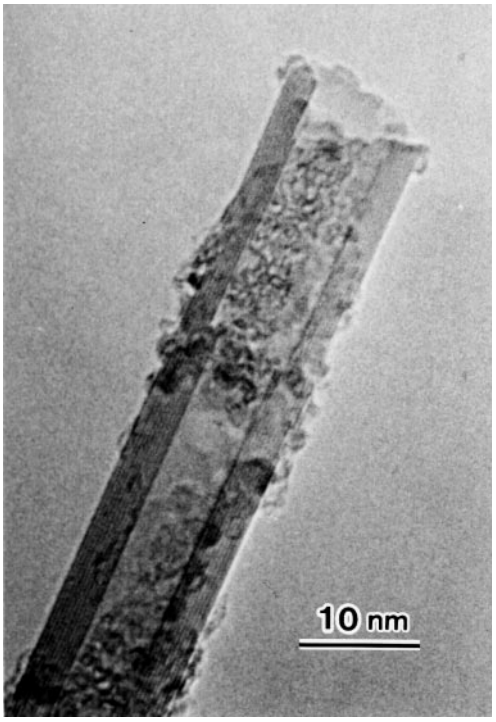

Fig. 1. TEM image of an open end of a MWNT. The cap of the nanotube was etched off in a purification process including oxidation

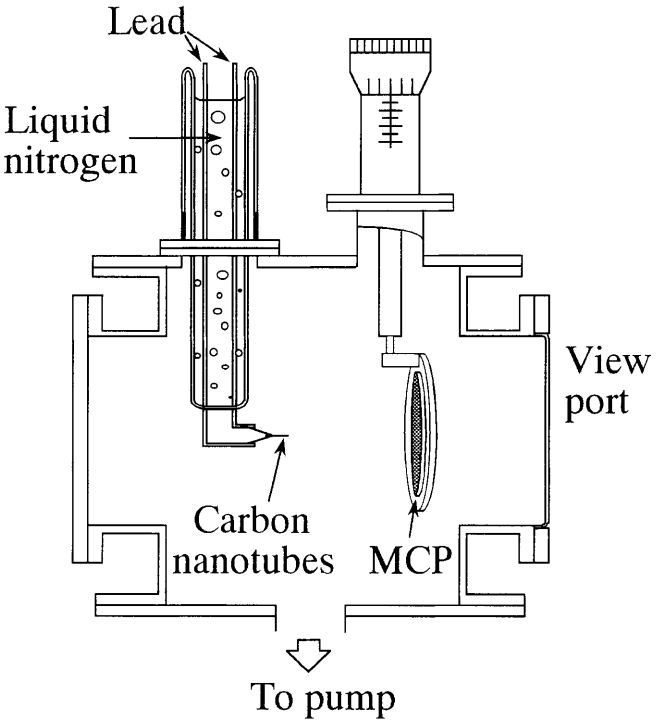

Fig. 3. Schematic of the FEM apparatus used

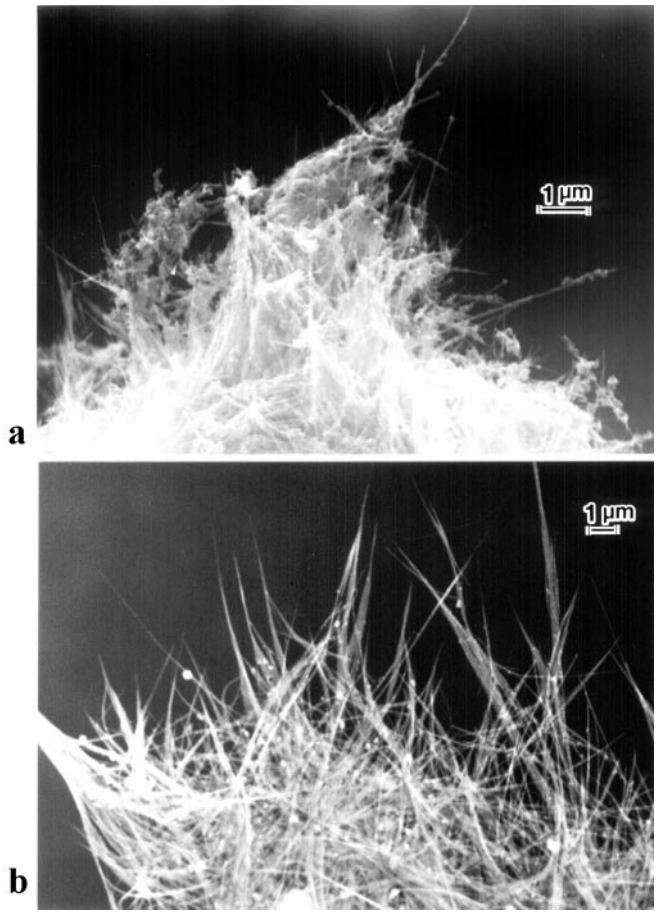

Fig. 2a,b. Scanning electron micrographs of the ends of MWNT emitters. **a** As-obtained MWNTs (capped). **b** Purified MWNTs (open-ended). Many separated MWNTs are extruding from the bulk bundles

FEM was typically 2×10^{-9} Torr. The emitter tip was cooled by liquid nitrogen. Emission patterns were recorded with a charge-coupled device (CCD) camera (Hamamatsu C5985, 756×483 pixels, 8 bits).

For measuring current from a restricted region of an emitter, another FEM apparatus was used, in which a 1-mm probe hole was positioned 30 mm from the nanotube tip. A gimbal (tilt adjustment) device holding the emitter enabled us to bring a selected region to the hole. The working pressure of the second FEM chamber was typically 3×10^{-8} Torr.

1.3 Electron emission and emission patterns

Emission patterns could be observed when the negative electric potential applied to a tip against the grounded anode (a front face of the MCP) was larger than about 400–500 V for close-capped MWNTs and about 300 V for open MWNTs. Figures 4a and 4b show emission patterns from capped MWNTs at two different tip voltages, $V_T = -440$ and -480 V, respectively. In the pattern at the lower voltage (Fig. 4a), one bright spot is observed (a faint spot is also found next to it). We have no idea of the magnification of the pattern at present, but later we will show that the bright spot originates from a single MWNT. At this lower voltage the electric field on the end of the MWNT, which extrudes most prominently from the other tubes, is strong enough to cause field emission. The increase in the tip voltage brings forth more bright spots as shown in Fig. 4b. Since many individual MWNTs extrude from the end of the bulk bundle, it is expected that under a higher applied potential, several MWNTs other than those observed in Fig. 4a could emit electrons.

Figure 5 shows a typical emission pattern from an open MWNT. A small, dark hole surrounded by an annular bright

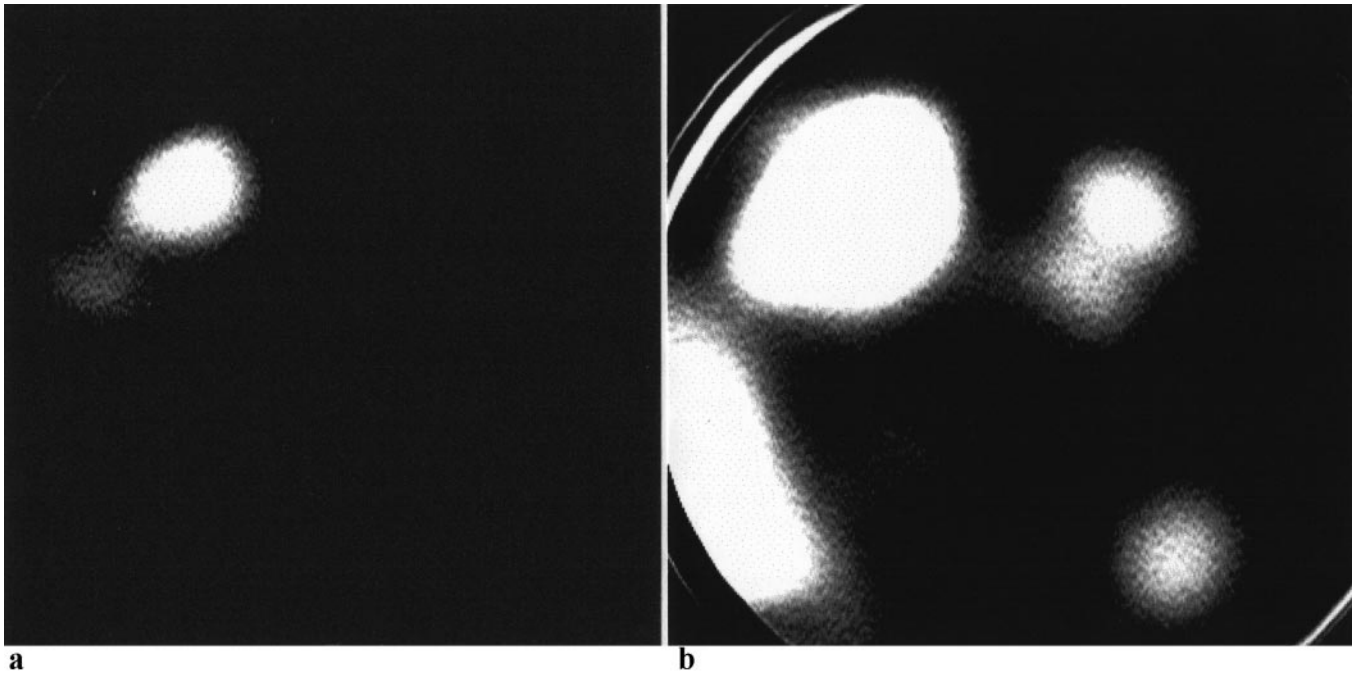

Fig. 4a,b. Field-emission patterns from capped MWNTs. The tip voltage (V_T) is **a** −440 V, **b** −480 V

Fig. 5. Field-emission pattern from an open MWNT. $V_T = -220$ V

region is observed. A black hole (i.e., a region where no electrons are emitted) corresponds to an exposed cavity of a MWNT. For ordinary capped MWNTs (not purified), this peculiar pattern was not observed (Fig. 4).

Diameters of inner black spots observed for open-ended MWNTs were 2 to 3.5 mm on the screen. Since the actual inner diameters of MWNTs are typically 5 to 10 nm, the approximate magnification of our FEM is reckoned to be 0.4×10^6. Applying the same value of magnification to the field-emission patterns of capped MWNTs (Fig. 4), we obtain 15–25 nm as the tip diameters of extrusions. The estimated diameters coincide with the typical diameters of MWNTs, indicating that all spots observed in Fig. 4 are from individual MWNTs.

Rinzler et al. [3] claimed FE from a linear carbon chain that had been unraveled from a graphene edge of an open MWNT. Contrary to their proposition, no sharp contrast corresponding to the atomic chain was observed in the present emission patterns. Electron emission seems to occur from the circular edges of graphene sheets of the open MWNT.

The current of electrons emitted from a single MWNT was measured using the 1-mm probe hole in the phosphor screen. Figure 6 shows a time trace of the probe current for an open MWNT at a fixed V_T of 600 V. The current was relatively stable though step-like changes were frequently observed. Current versus voltage characteristics were measured for both the purified (i.e., open-ended) and the raw (i.e., closed) MWNTs as shown in Fig. 7a. Data points of the capped nanotube are marked by solid circles, and those of the open nanotube by open circles. The open-ended nanotube begins to emit electrons at a lower voltage than the capped one. This is because of the absence of graphite debris and nanoparticles for the purified MWNTs and also because of the sharp edges of the etched tubes. These two factors work to make the effective electric field on the tube tips stronger. The Fowler–Nordheim (F–N) plots shown in Fig. 7b give straight lines in a region of low emission, whereas a declining of the slopes is found in a higher current region for both the open and capped nanotubes. The slope of the F–N plots for the open MWNT is gentle compared with that for the capped one.

According to the F–N equation for field emission [20], the slope is proportional to $-\phi^{3/2}/\beta$, where ϕ is the work function of the emitter and β is a proportionality factor relating the applied voltage V and the effective electric field E_{eff} on the tip ($\beta = E_{\text{eff}}/V$). For an isolated tip with a shape of a hemi-

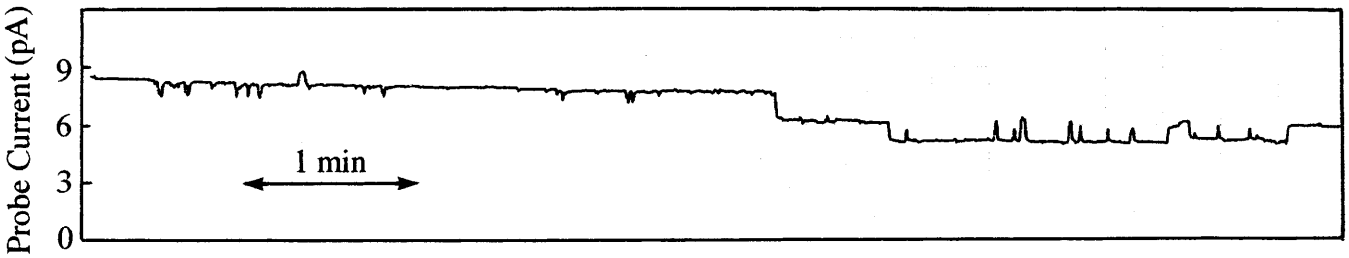

Fig. 6. Time trace of a probe current (I_p) from an open MWNT. The current was measured with the probe hole of 1 mm diameter. The tip voltage was fixed at −600 V

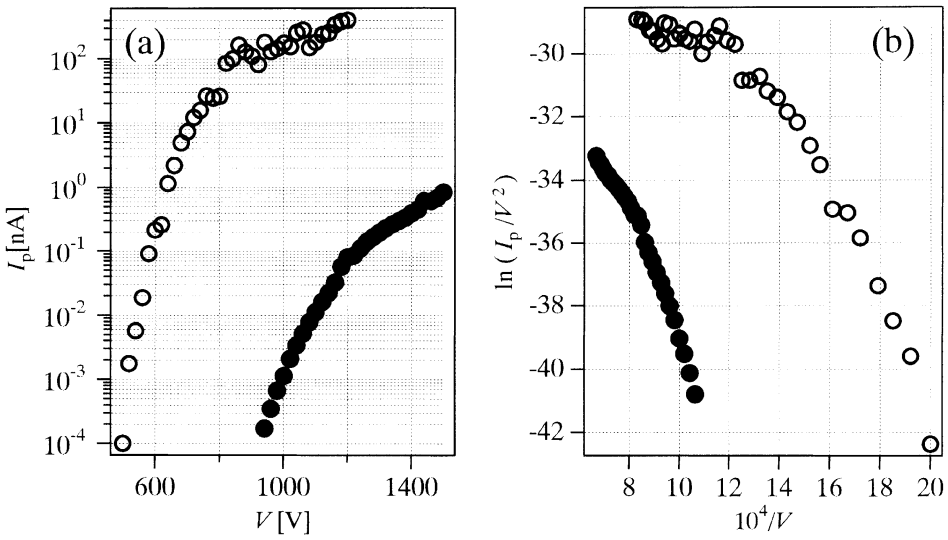

Fig. 7. a Current versus voltage characteristics and **b** F–N plots of a capped (●) and an open MWNT (○). Current (I_p) was measured with the 1 mm probe hole

sphere on an orthogonal cone, the factor is well approximated by $1/(5r)$, where r is the radius of curvature of the tip. The smaller value of the F–N slope for the open tube is caused by the larger β factor ($\approx 1 \times 10^7\ \mathrm{m}^{-1}$) than that for the capped one ($\approx 2 \times 10^6\ \mathrm{m}^{-1}$) because the E_{eff} on the tip of an open nanotube is larger than that on the round tip of a capped one at the same applied voltage. The difference in work functions between the basal plane and the edge plane of graphite might be another reason. However, the precise values of work functions depending on the crystallographic surfaces of graphite are not known.

2 Nanotube field emitters in electron tubes

Nanotubes used for manufacturing cathode ray tubes (CRTs) were those grown on the end of the cathode of a carbon arc. Cylindrical deposits (about 6 mm in diameter) containing nanotubes were sliced into thin disks with thickness 0.5–1.0 mm by a rotating diamond cutter. Each sliced disk was glued to a stainless steel plate (5 by 5 mm, 0.15 mm in thickness) by using silver paste, one basal face of the disk being attached to the plate and the other basal face being free. After baking of the glued disks at 450–500 °C in air to cure the paste, the outer hard shells of the deposit were removed, leaving only the fibrous core with diameter 2–3 mm consisting of MWNTs.

Thus-prepared MWNT emitters were installed in electron tubes as their cathodes by substituting for conventional hot cathodes. The electron tubes we employed for examining the performance of our nanotube field emitters are CRT lighting elements (kinds of light bulbs), which are used practically as giant outdoor displays. All the parts other than cathodes are the same as those routinely used for manufacturing the lighting elements in a factory [21, 22].

Figure 8 shows the structure of a lighting element equipped with MWNT field emitters. Nanotube field emitters are covered with a grid electrode which controls emission of electrons from nanotubes. The spacing between nanotube tips and the grid is 0.5–1 mm in the present experimental manufacture. The phosphor screen, being an anode, is printed on the inner surface of a front glass and backed by an aluminum film (100 to 150 nm in thickness) to give electrical conductivity and also to reflect fluorescent light in the forward direction (the aluminum film acts as a mirror). After sealing the vacuum tube, getter material was flashed to attain a high vacuum of the order of 10^{-8} Torr.

The nanotube cathode is grounded (0 V), and the control grid is biased to a positive voltage (in a range from 0.5 to 1.0 kV) to render the electric field on the nanotube tips strong enough to extract electrons. The grid voltage can be decreased to a few hundred volts by reducing the separation between the nanotube tips and the grid to about 0.1 mm, as has been demonstrated by de Heer et al. [4] A high voltage (typically 10 kV) is applied to the anode so as to accelerate electrons which excite the phosphor screen to emit visible light. Figure 9 shows the total current emitted from a nanotube cathode as a function of voltage applied to the control

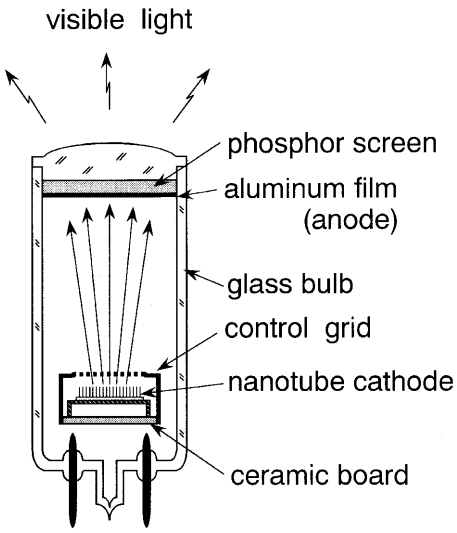

Fig. 8. Schematic drawing of a longitudinal cross section of a CRT fluorescent display with a field-emission cathode made of carbon nanotubes. The front glass forms a convex lens to condense emitted light in the forward direction

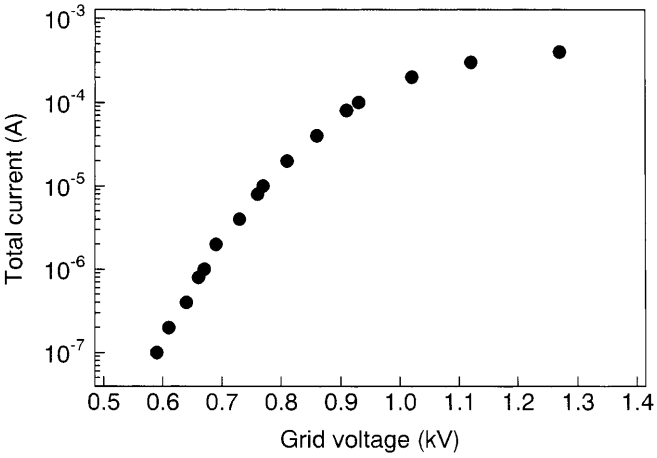

Fig. 9. Total emission current from a nanotube field-emission cathode as a function of voltage applied to the grid. About 60% of the total current passes through the grid and strikes the anode

grid. About 60% of the emission current passes through the grid and strikes the anode.

The manufactured CRTs underwent a "knock" treatment (intentionally applying a high voltage, for example, 30 kV, to remove origins of discharge) and an "aging" process. The nanotube cathode sustained stable electron emissions without any noticeable diminution in current for long-term operation of over 2000 h (See below, for a test of lifetime). The robust and stable nanotube emitters contrast strongly with the delicate and sensitive metal emitters such as tungsten and molybdenum tips. For the metal field emitters, an ultrahigh vacuum condition (10^{-10} Torr) is essential to sustain field emission. In contrast to metal emitters, it is quite surprising that the carbon nanotube emitters operate stably even in a moderate vacuum condition (no need for ultrahigh vacuum). This reliable operation is probably due to the chemical inertness and mechanical strength of carbon nanotubes.

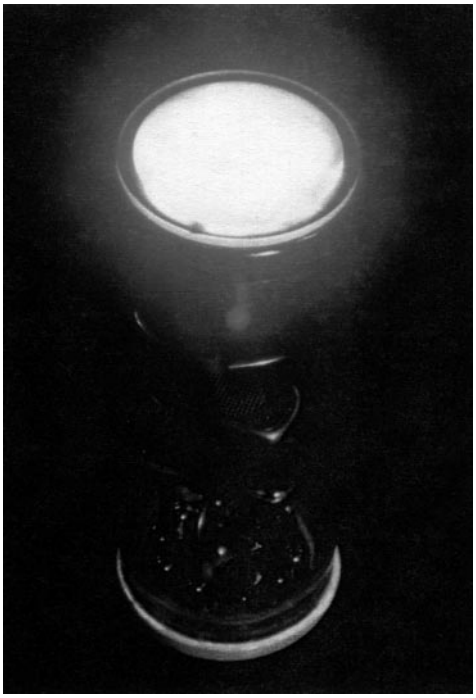

Fig. 10. CRT fluorescent display emitting visible light. The anode current and voltage are 200 μA and 10 kV, respectively

Figure 10 shows a CRT lighting element with nanotube field emitters under operation, emitting red light. Colors of the emitted light depend on phosphors printed on the anode, viz., ZnS:Cu, Al for green, Y_2O_3:Eu for red, and ZnS:Ag for blue. The luminance of the phosphor screens measured on the axis of the CRTs with an anode current of 200 μA is 6.3×10^4 cd/m^2 for green, 2.3×10^4 cd/m^2 for red, and 1.5×10^4 cd/m^2 for blue, which is twice as intense as that of conventional thermionic CRT lighting elements commercially available now [21, 22]. The emitted light is brilliant and stable enough to be used practically for giant outdoor displays. One of the fabricated field-emission CRTs is now undergoing a test of its lifetime under a dc driving condition; the electron emission is still continuing without any diminution since the test began more than three months ago, suggesting a life time of over 10 000 h.

3 Concluding remarks

We succeeded for the first time in installing carbon nanotubes in vacuum tubes as field emitters. Field-emission vacuum tubes are energy-saving compared with thermionic ones because no heating is necessary to emit electrons. Moreover, carbon nanotubes are made from only carbon and are free from any precious and/or hazardous elements. Therefore, carbon nanotube field emitters are environmentally friendly as well as economical. The lighting elements presented here would be the first practical products utilizing carbon nanotubes on an industrial scale.

Electron beams from field emitters have distinct advantages over thermionic emitters; small energy-spread, high current density, and high coherency. These properties enables us to produce finely focused electron beams with higher

brightness. The present success in manufacturing CRTs with MWNT field emitters would be a milestone toward materialization of ultrahigh quality color CRT displays, bright flat-panel displays, high-brightness electron guns for electron microscopes, and so on.

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