Field-Emission-Induced Luminescence from Carbon Nanotubes

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We report on the observation of luminescence during electron field emission on singlewall and multiwall carbon nanotubes. Spectra acquired at different emitted currents, as well as the dependence of the luminescence intensity with the current, show that the light emission is not due to blackbody radiation or to current-induced heating. In fact, our results suggest that the light emission is caused by electron transitions between different electronic levels participating in the field emission. [S0031-9007(98)06854-9]

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There has been a lot of interest recently in the use of carbon nanotubes as electron field emitters. Both singlewall [1,2] (SWNT) and multiwall [3–7] (MWNT) nanotubes, as single emitters [3,7] or assembled in films [1,4–7], have been used in field emission experiments, and were shown to provide high currents at relatively low operation voltages with good stability. However, little is known yet about the emission mechanism. Most authors conclude that carbon nanotubes are metallic emitters [1,4,6], essentially because the I-V characteristics seem to follow the Fowler-Nordheim law [8]. By performing field emission studies over a large current range, we, however, observed systematic deviations from the Fowler-Nordheim model at high emitted currents [7]. Additionally, recent experimental evidence strongly suggests that the electrons are not emitted from a metallic continuum as in usual metallic emitters, but from localized states at the tip [9]. We report here on an additional clue to the understanding of the emission, as well as an unforeseen path for potential applications, which is provided by the fact that the nanotubes emit light during field emission.

We observed luminescence during electron field emission on SWNT and MWNT films as well as on single MWNT emitters. The films were realized by drawing a colloidal suspension of nanotubes through a 0.2 μm pore silica filter, and by transferring this film on a teflon-coated metal surface. Single MWNT were mounted on a supporting gold wire that was electrolytically etched to a $\sim$250 nm radius tip, with the tubes being held onto the tip by van der Waals forces. For field emission, a 3 mm diameter cylindrical counterelectrode was placed at a distance of 1 mm for single MWNTs and 125 μm for the films. The measurements were carried out in a vacuum chamber at pressures below 10^{-7} mbar. We alternatively detected the luminescence with three detectors located outside the chamber: (i) a Si photodiode, (ii) a CCD camera, and (iii) a spectrometer equipped with a CCD detector with a detection range between 1.1 and 3.1 eV, and a collection solid angle (with our experimental setup) of $\sim$0.001.

Figures 1(a) and 1(d) show a view of the experimental setup for single MWNT and film emitter characterization, respectively, as seen by the CCD camera located outside the chamber. The gold tip supporting the single MWNT, as well as the counterelectrode, is easily visible in Fig. 1(a). The same camera, carefully isolated from surrounding light sources, was used for recording the images of Figs. 1(b) and 1(c), where the emitted current was 0.1 and 0.2 mA, respectively. The images show that light is emitted from the vicinity of the apex of the gold tip, and that the emitted intensity increased with the emitted current (the acquisition time for the two images was identical). Similarly, Fig. 1(d) shows the metallic plate supporting a MWNT film (located on the bottom side of the plate) and the counterelectrode. The image of Fig. 1(e) was recorded just after the one of Fig. 1(d), with a 900 V potential difference applied between the MWNT film and the counterelectrode. The emitted current density was $\sim$2 mA cm^{-2}, and the image shows clearly light emission coming from the vicinity of the film. Figure 1(f) displays a composite view obtained by adding the optical and luminescence images of Figs. 1(d) and 1(e). The composite image reveals that the luminescence is not homogenous on the emitter surface, as intensity variations are detected, but that it is strictly confined to the portion of the film that directly faces the counterelectrode. No light emission was detected without applied potential, and the intensity decreased very rapidly with decreasing voltage. The emitted light intensity closely followed the variations in emitted current (not shown here).

To further investigate this phenomenon, we analyzed the spectral repartition of the emitted light for single MWNTs. Figure 2(a) shows typical spectra acquired on

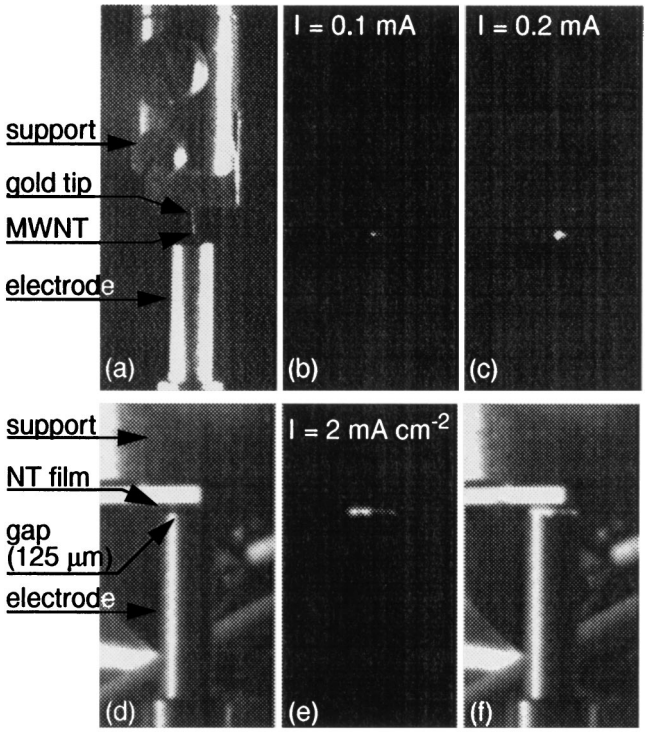

FIG. 1. (a),(d) Optical images of the experimental setup for field emission; (b),(c),(e), and (f) corresponding field-emission-induced luminescence images for (a)–(c) a single multiwall nanotube and (d)–(f) a multiwall carbon nanotube film. The emitted current during the acquisition of images (b) and (c) was 0.1 and 0.2 mA, respectively, with the same acquisition time (2.5 s). The emitted current density during the acquisition of image (e) was 2 mA cm^2. Image (f) is a composite image obtained by adding images (e) and (f). The images (a)–(c) and (d)–(e), respectively, were sequentially recorded with the same, near-infrared sensitive, CCD camera.

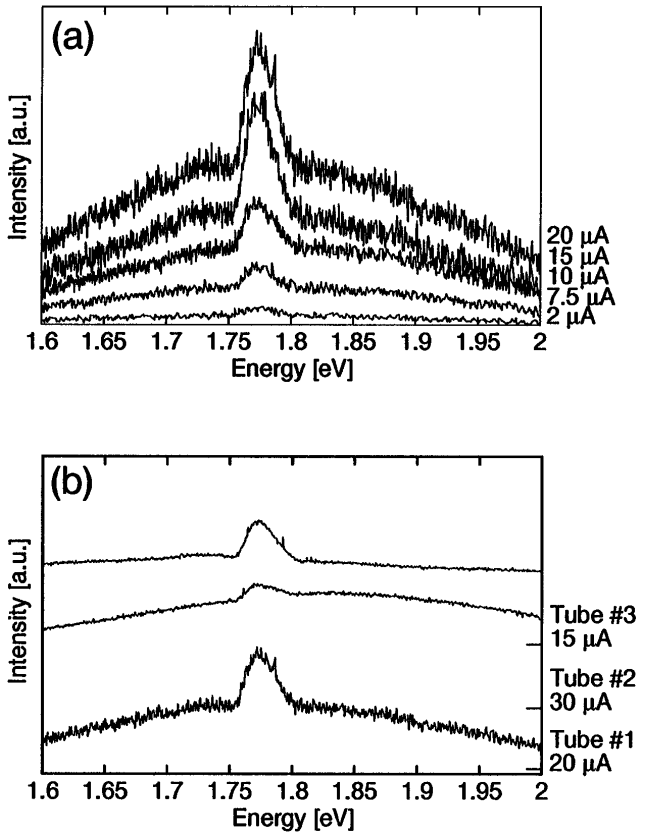

FIG. 2. Spectra of field-emission-induced luminescence. (a) Variation of the spectrum with the emitted current for the same MWNT (emitted currents were 2, 7.5, 10, 15, and 20 μA, respectively, corresponding to applied voltages between 275 and 415 V); (b) spectra of three different MWNT for the emitted current of 20, 30, and 15 μA. The applied potential was in the 400 V range.

the same tube at different emitted currents. Two superposed peaks were detected, with an intensity maximum at around 1.8 eV and extending from 1.5 to 2.1 eV. No emission was recorded in the remaining sensitivity range of the CCD detector. The spectra can be described with very good accuracy as a sum of two Gaussian functions, with peak energies, widths, and relative intensities that varied with experimental conditions. The full width at half maximum (FWHM) values in the case of Fig. 2(a) were 0.34 eV and 22 meV for the broad and the narrow Gaussians, respectively, with an integrated intensity ratio of typically 20. The position of the narrow Gaussian remained very stable for one acquisition (and from one day) to the next, and peaked at 1.774 eV. This was not the case for the broad Gaussian, which is shifted by 5 meV between the two current extrema of Fig. 2(a), and where variations of ± 25 meV were detected from one day to the next.

Similar findings were observed on other tubes. Spectra from three different tubes are compared in Fig. 2(b). The emitted current was in the 20 μA range, corresponding to applied voltages around 400 V. Intriguingly, the position and width of the narrow Gaussian remained nearly constant from one tube to the next. As for the broad Gaussian contribution, we observed peak intensities and widths varying between 1.73 and 1.83 eV and between 0.3 and 1 eV, respectively. Finally, for SWNT films, light was emitted at higher energies as compared with MWNTs, but their behavior was otherwise readily comparable to those of their multiwalled counterparts.

There have been a few previous studies on light emission during electron field emission [10–15]. In some cases, light spots were observed on the anode [10,11] and were caused by the interaction of electron beams coming from the emitter with the electrode. The voltage used during these experiments was in all cases fairly high (from 2.5 up to 130 kV), and the greatest part of the emitted light, usually labeled as "transition" radiation [10], corresponded to element-specific x-ray emission due to inner shell ionizations by the penetrating electrons and consequent filling of the vacancies by outer shell electrons. The remaining part was incandescent radiation following electron-beam induced heating of the cathode and/or anode [10].

In the 1970s, Hurley and Dooley [12–14] and later Latham and Wilson [15] studied the spectra of the light emission from the cathode of field emission setups. Although their spectral resolution was rather crude (~20 nm, against ~0.5 nm in our case), it allowed them to draw some conclusions on the nature of the light emission.

Hurley and Dooley used plane copper [12,13] and other metallic cathodes [14], and found that the spectrum was composed of one or several sharp peaks between 2.1–2.5 eV with a tail sometimes extending into the infrared. The shape of the spectra did not significantly vary with the emitted current [12]. The experimental findings suggest that the light emission was caused by electroluminescence produced by the action of the electric field on semiconducting inclusions on the cathode surface (e.g., Cu_2O, which is a p-type semiconductor with a room-temperature band gap in the range 1.94–2.14 eV, for the copper cathodes). Electron-hole pairs were created by the ionization of atoms by the acceleration of conduction electrons, and light was emitted following electron-hole pairs recombination.

As for Latham and Wilson [15], they performed studies on etched carbon fibers. The luminescence was composed of two peaks at 2.17 and 2.48 eV with a low-energy tail extending down to 1.55 eV. The authors concluded that the luminescence was due to electron-hole recombinations in amorphous carbon pockets.

In our case, the applied voltages (typically 400 V) were definitely too low to provoke anode luminescence through x-ray emission and/or incandescence. The fact that the light emission is observed only in the presence of a finite electron emission current shows, furthermore, that the luminescence was directly linked to the emitted current, as opposed to the more usual, field induced luminescence where ionization occurs through field accelerated electrons [16].

There has been one report of observed luminescence on opened nanotubes [3], but it was attributed to an incandescence of carbon chains at the tip of the tube provoked by resistive heating. The above results, however, strongly suggest that the light emission is directly coupled to the field emission. The narrowness of the luminescence lines and the very small shifts with varying emitted current (<5 meV) show that we are not in the presence of current-induced heating effects. The observed spectra, furthermore, correspond neither to a black-body curve nor to any obvious discharge spectra. The shape of the spectra indicates rather that we are observing the consequences of electron transition between different electronic levels. In fact, theoretical calculations [9,17] supported by scanning tunneling microscopy measurements [17] show that the local density of states at the tip presents sharp localized states with well-defined energy bands. We thus suggest that the luminescence is due to electronic transitions between energy levels at the tip that are participating in the field emission.

To further support our interpretation, we consider the dependence of the total intensity with the field emitted current. In Fig. 3, we report the variation of the total emitted light intensity I_p as measured for one single MWNT, taken as the area below the spectrum, as a function of the emitted current, I_e. The luminescence intensity follows a power law $I_p \propto I_e^{\alpha}$, as can be seen in Fig. 3 where the solid line is a power law fit of the experimental data. The exponent amounts in the case of Fig. 3 to $\alpha = 1.4 \pm 0.2$.

We can compare the dependence outlined in Fig. 3 with theoretical predictions, by using the simple model presented in Fig. 4. The tube body is represented by a metallic Fermi sea with Fermi energy E_F, which is a good approximation since recent electrical measurements on single MWNTs have shown that they are essentially metallic conductors at room temperature [18,19]. The distribution of the localized states at the nanotube tip is simplified to a two level system, with the main emitting level located at an energy E_1 below or just above the Fermi energy, and a deep level, located at an energy $E_2 > E_1$. When an electron is emitted from the main level, it is replaced by an electron from the tube body, which tunnels into the localized state through the thin potential barrier at the tip-body interface. Note that the difference in energy between emitted and replacement electrons provokes a tip heating or cooling (Nottingham effect), depending on the position of the Fermi level [20,21]. In the case of emission from the deep level, the replacement electron can come either from the Fermi sea after tunneling, or from the main level, which may induce the emission of a photon (see Fig. 4). From the Fowler-Nordheim model, the transition probability $D(E)$ for an electron of energy E below the top of the surface barrier with a given applied field just above the emitter surface F is $D(E) = \exp[-4/3(2m/\hbar^2)^{1/2}E^{3/2}/eF]$ [8]. Since in the frame of our model $I_e \propto D(E_1)$ and $I_p \propto D(E_2)$, one can estimate the dependence of $D(E_2)$ versus $D(E_1)$ from the above equation as $D(E_2) = D(E_1)^{\alpha}$ with $\alpha = (E_2/E_1)^{3/2}$. If

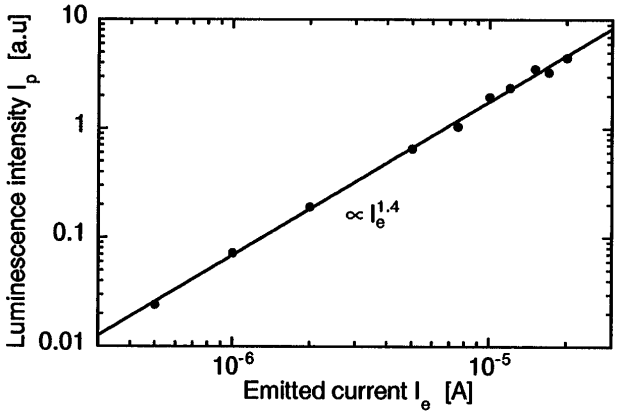

FIG. 3. Variation of the total emitted intensity (taken as the area below the spectrum) as a function of emitted current. The solid line is a power law fit of the experimental data and yields an exponent of 1.4 ± 0.2.

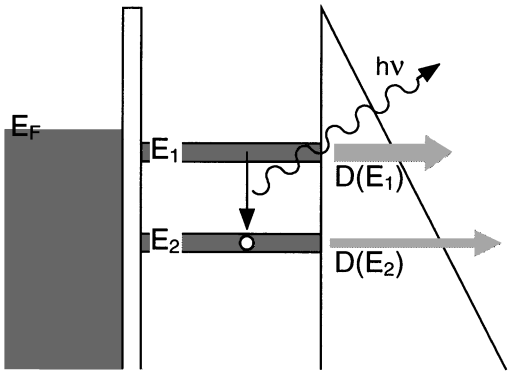

FIG. 4. Schematics of the two-level model for field-emission-induced luminescence. The main emitting level, located at an energy E_1 below or just above the Fermi energy, E_F, shows a transmission probability $D(E_1)$. The deep level, located at an energy $E_2 > E_1$ has a corresponding transmission probability $D(E_2) \ll D(E_1)$.

we take $E_1 = E_F = 5$ eV [22], we obtain exponents of $\alpha = 1.51$, 1.58, and 1.65 for energy differences $\Delta E = E_1 - E_2 = 1.6$, 1.8, and 2.0 eV, respectively, which is in reasonably good agreement with the experimental results of Fig. 3. The fact that the measured exponent is low as compared to the simulated ones may come from several effects. First, it is known that an increase in voltage can induce a down-shifting of the levels on nonmetallic tips, and thus a smaller-than-expected increase of the emitted current with the voltage [20]. Second, the energy of the main emitting level may not correspond to the Fermi level, as we assumed above. If the level is located 0.5 eV below the Fermi level, the exponents drop by $\sim$0.07. Finally, it is worth noticing that the above findings do not depend on the ratio of emitted photons to emitted electrons from the deep level.

From the detection efficiency of our spectrometer assembly and collected solid angle, we estimate that one emitted photon corresponds to at least 10^6 field emitted electrons. Although the greatest part of the emitted current arises from occupied states with a large density of states at the tip located near the Fermi level, other, more deeply located electronic levels will also contribute to the field emission. In this case, the emitted electron will be replaced either by an electron from the semimetallic tube body with an energy comparable to the level energy, or by a tip electron from the main emitting state. Clearly, the second alternative may provoke the emission of a photon. Even if the tunneling probability for electrons from deep states is several orders of magnitude lower than for the main emitting state, it will be readily sufficient to provoke the observed light intensities.

Additional studies are under way to determine the exact origin of the two luminescence lines. It seems, however, that carbon nanotubes have unveiled yet another puzzling aspect of their fascinating properties.

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