

were similar. The local structure can also be characterized in terms of the local symmetry of the near-neighbor bonds as expressed through local bond-order parameters (5). One of these, W_6 , is sensitive to icosahedral order, because this order parameter peaks at a value of -0.17 if the Voronoi neighbor bonds of a central particle have a perfect icosahedral surrounding (Fig. 4). The averages were close to -0.045 for all ϕ , which is an indication of moderate icosahedral order and the absence of any substantial crystalline order. The same average values have been reported for computer-simulated glasses of Lennard-Jones systems (3).

We have shown that with confocal microscopy it is possible to study structures of fluorescent colloidal model spheres in real space with high accuracy and with no essential limit to the number of particles. Contrary to some computer simulations, we found no sign of a thermodynamic phase transition underlying the glass transition. Because colloidal dispersions form equilibrium phases analogous to those of atomic systems (22), the method allows a direct three-dimensional real-space comparison with computer simulations and theory for the atomic analogs and can be easily extended to multicomponent systems (23). Furthermore, the method is not only applicable to fundamental problems in condensed-matter physics (as demonstrated above) but can also be used to study typical colloidal problems, such as gelation and aggregation (16).

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A Carbon Nanotube Field-Emission Electron Source

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A high-intensity electron gun based on field emission from a film of aligned carbon nanotubes has been made. The gun consists of a nanotube film with a 1-millimeter-diameter grid about 20 micrometers above it. Field-emission current densities of about 0.1 milliampere per square centimeter were observed for applied voltages as low as 200 volts, and current densities greater than 100 milliamperes per square centimeter have been realized at 700 volts. The gun is air-stable, easy and inexpensive to fabricate, and functions stably and reliably for long times (short-term fluctuations are on the order of 10 percent). The entire gun is only about 0.2 millimeter thick and can be produced with virtually no restrictions on its area, from less than 1 square millimeter to hundreds of square centimeters, making it suitable for flat panel display applications.

Electron guns have numerous applications in commercial devices and for industry and research. Standard electron guns used in cathode ray tubes usually utilize thermionically emitted electrons from hot tungsten wires and heated materials with low work functions. Alternatively, electron sources based on field emission from sharp tips are used for applications requiring monochromatic electron beams, as in electron microscopy and research. However, these sources typically require ultrahigh-vacuum conditions and high voltages (1). The currents are limited to several microamperes.

Carbon fibers, typically 7 μm in diameter, have also been used as electron emitters in electron guns (2, 3). Although they operate in less stringent vacuum conditions, practical applications are limited because of poor reproducibility and rapid deterioration of the tip (4). Nevertheless, these previous studies show that despite its high work function (≈ 5 eV), graphite can be used as a material for field emitters.

Consequently, the nanometric tips of carbon nanotubes (5) are very good candidates for this purpose, although the emission current of a single tube is constrained because of its very small dimensions (≈ 10

nm in diameter and ≈ 1 μm in length), as previously observed even in the case of much larger carbon fibers (10 μm in diameter). To circumvent this practical problem, one can use an array of nanotubes, where the tubes are all oriented perpendicular to a surface. Large area films of oriented nanotubes have been recently realized (6), and we have used these to construct an electron source (Fig. 1).

The emission characteristics were determined by measuring the current collected on a plate about 1 cm in front of the grid. A typical current versus voltage (I - V) curve at a residual pressure in the vacuum chamber of $\sim 10^{-6}$ torr can be compared with the Fowler-Nordheim equation for field emission (Fig. 2): $I = aE_{\text{eff}}^2 \exp(-b/E_{\text{eff}})$, where a and b are constants that depend on the electronic work function of the surface and only slightly on the electric-field strength at the emitting surface $E_{\text{eff}} = \gamma E_0$ (7), where $E_0 = V/d$ is the average uniform field and d is the distance from the nanotube surface to the grid. The sharp tips and the geometry of the emitting surface cause the electric fields at the tips to be amplified by a factor γ compared with E_0 . For standard field emitting tips, γ is on the order of 10 (7). The electron energy distributions have been measured with an energy analyzer, and we find (for low emission currents) that they are narrow, consistent with field emission, and contain usually one, but sometimes several, peaks with widths between 0.15 and 0.2

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eV in a range of about 1 eV.

Plotting $\log(I/V^2)$ versus $1/V$ (Fig. 2, inset) yields a straight line in agreement with the Fowler-Nordheim equation, confirming that the current is indeed the result of field emission. We also verified that the voltage needed to draw a given emission current is inversely proportional to d , again in agreement with field emission. From an analysis of the I - V curve with the Fowler-Nordheim equation, we find that $\gamma \approx 1300$ for this particular electron emitter, although its value more typically falls between 500 and 800 (assuming that the graphite work function of 5 eV applies). Hence, γ can be as much as a factor of 100 greater than its value for conventional field emitting tips.

The large field amplification factors of the nanotubes are related to the geometry of the tube terminations. As shown by Iijima *et al.* (8), the terminations have a variety of structures and are often conical with 20° opening angles, with radii of curvature at the tips that may be <1 nm. The density of emitting tips is estimated to be on the order of 10^5 cm^{-2} . Because this is only a small fraction of the nanotube density ($\sim 10^8 \text{ cm}^{-2}$) [figure 1 of (6)], only those tubes with particularly sharp tips that are favorably situated on the film emit efficiently.

The device functions as a diode: under a reverse bias, there is no detectable current (9). The nanotube-produced electron beams (with energies ≈ 400 eV) were deflected with radii on the order of 1 cm in magnetic fields of $B \approx 10$ G. The deflections correspond to charge carriers with the free electronic mass, verifying that the current is indeed carried by electrons and not by ions, whose deflections would be at least 100 times smaller.

Several electron emitters have been constructed with comparable emission characteristics, within a factor of about 3 of

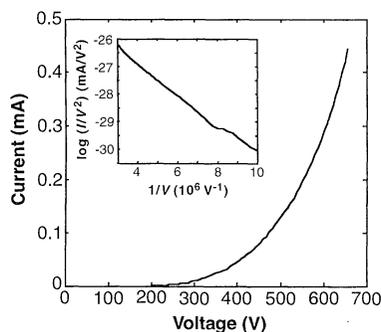


Fig. 2. Current versus voltage plot of a nanotube-film field emission source (emitting area = 1 mm^2). (Inset) Fowler-Nordheim plot. The linearity of this curve indicates that the emission of the electron source agrees with the properties expected for field emission.

each other. The electron beam was stable for long times (Fig. 3), even without feedback stabilization (with feedback, the stability was excellent). This stability is remarkable, considering the exponential dependence of the current on the applied field. During 48 hours of continuous operation at $30 \mu\text{A mm}^{-2}$, current drifts on the order of $\pm 5\%$ were observed, but the average current did not degrade.

No degradation was observed for most of the devices during the course of our investigations, even after the guns had been repeatedly removed from and reintroduced into the vacuum chamber. However, for large applied voltages (>1000 V), discharges were observed that caused deterioration, which manifested itself as a decrease in the emission current and larger fluctuations.

We also succeeded in extracting very weak emission currents (on the order of microamperes) from an unprocessed deposit of tube containing arc material. The voltages required to observe any emission were very high (>1 kV), resulting in discharges

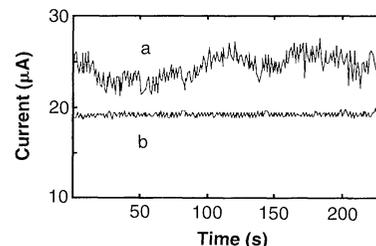


Fig. 3. Emittted current as a function of time. The fluctuations are of the order of 10% (curve a) but can be easily reduced to at least 2% (curve b) with a simple feedback system between the emitted current and the applied voltage.

and unstable operation. No detectable emission was found from carbon black films. Hence, we conclude that aligned nanotubes are required to produce high field emission currents at low voltages.

For practical purposes only, we kept the dimensions of our electron guns rather small, but upscaling is immediately possible because the nanotube films can be made arbitrarily large: ours were typically 2 cm in diameter. With higher transmitting grids (that is, on the order of 90%) and by using the full surface of one of these films, currents on the order of 500 mA should be possible. We are confident that further improvements in stability and maximum currents can be obtained by optimizing the film production and using better construction methods.

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Fig. 1. Schematic diagram of the electron source. The emitting surface is a β -aligned carbon nanotube film (a) at room temperature, with nanotubes oriented perpendicular to, and anchored on, a polytetrafluoroethylene (PTFE) substrate. The films were produced as described in (6). Carbon nanotubes were formed in the deposit of a high-intensity carbon arc in a He atmosphere following the method of Ebbesen and Ajayan (10). The deposit was extracted and ultrasonically dispersed in spectroscopic-grade ethanol. The resulting carbon nanotube suspension was partially purified, after which the liquid was drawn through a ceramic filter, producing a film on the filter surface. This film was pressed against a PTFE sheet, whereby the nanotube film was transferred to the PTFE. This procedure yielded dense, aligned nanotube films. Typically the tubes were 10 ± 5 nm in diameter and about $1 \mu\text{m}$ long (11). A perforated mica sheet (b) with a thickness $d \approx 20 \mu\text{m}$ and a 1-mm-diameter hole was bonded to the nanotube film. The hole was covered with a 3-mm-diameter, 50% transmitting, 200-mesh electron microscopy copper grid (c). Applying a voltage to the carbon nanotube film produced an electron beam that passed through the grid and was detected at the anode.

