



Short communication

Effects of adsorbates on the field emission current from carbon nanotubes

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Abstract

We report on the effects of adsorbates on the field emission properties of multiwall carbon nanotubes through current–voltage (I – V) measurements. Adsorbates were found to increase the field emission current of carbon nanotubes by as much as two orders of magnitude. At high emission current, Joule heating of the field emitting carbon nanotubes causes the emission of incandescent light and desorption of adsorbates due to heating of the field emitting carbon nanotube. We also found that electric field activated emission current jumps, probably due to the formation of enhanced tunneling configurations between adsorbate molecules and the carbon nanotube.

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Since the re-discovery of carbon nanotubes by Iijima in 1991, various potential applications of carbon nanotubes have been proposed. One of the most convincing applications is the use of carbon nanotubes as field emission electron sources on which extensive research has been carried out [1–4]. Previous results show that adsorbates on carbon nanotubes have great influence on the field emission properties of carbon nanotubes. Dean and Chalamala reported that current saturation in the high current region is a result of displacement of adsorbates from adsorbate enhanced tunneling configurations (AETC) [2]. Based on cal-

culations, Maiti et al. reported that water molecules adsorbed on carbon nanotubes tips enhance the field emission current significantly [5]. In this report, we show the effect of adsorbates on the field emission current and the influence of electric field on the re-adsorption of gas molecules on carbon nanotubes.

In order to ensure that the field emitting carbon nanotubes are mechanically and electrically anchored to the substrate, our multiwall carbon nanotube films are grown on 5 mm × 5 mm Ta (100 nm) coated silicon wafers. First, a Ni catalyst film of 20 nm thickness was deposited and patterned as a 3 mm diameter circle on the Ta coated substrate. The sample was then annealed under ammonia flow of 30 sccm at 700 °C for 10 min. A dc-plasma was generated for a few minutes to reduce the size of the catalyst islands. Finally, acetylene was

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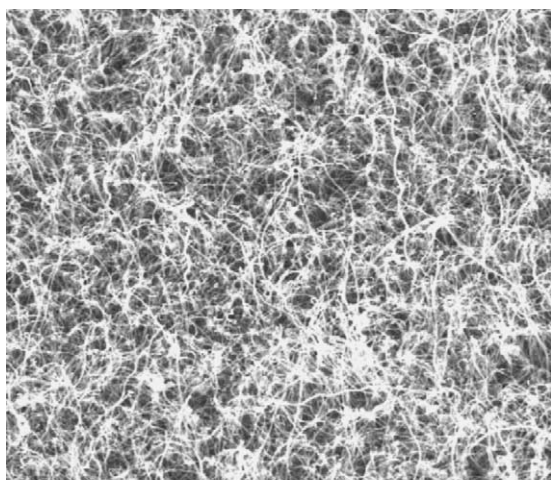
admitted at a flow rate of 30 sccm. Growth pressure was at 10 mbar. For a growth period of 30 min, an entangled MWNT film of about 5 μm thickness was obtained (Fig. 1a). Field emission measurements were carried out using a planar diode configuration with a copper plate as the cathode base and ITO coated glass as the anode. The spacing between MWNT film and the anode was 300 μm . A computer-controlled Keithley 237 source measure unit was used to perform current–voltage (I – V) measurements and current stability tests. A digital camera was used to capture the field emission

pattern. All field emission studies were done under 10^{-9} mbar vacuum environment.

Field emission studies were done at ≤ 10 μA current to limit the number of field emitting carbon nanotube sites. As reported by Nilsson et al., the field enhancement factor of a carbon nanotube thin film is exponentially distributed [6]. Thus, it is likely that at low currents, the field emission is mainly contributed by individual or a few carbon nanotubes with the highest field enhancement factor, in particular, those which are protruding above the surface (Fig. 1b). Indeed, the field emission patterns of our samples in the low current region show individual or at most a few emitting spots, indicating that field emission is dominated by a few nanotubes only. This allows us to study the effects of adsorbates on individual field emitting carbon nanotubes.

For the sample shown in Fig. 1, two light spots were observed even with naked eye at an emission current of 8 μA (600 V). The brightness of the light emission was correlated to the field emission current. We have observed stable light emission for at least 30 min. According to Purcell et al., field emission induced luminescence is due to current-induced Joule heating along the length of MWNT where the MWNT's tip is heated up to temperatures more than a thousand Kelvin by the field emission current, thereby inducing incandescent light emission [7].

Joule heating provides a means to desorb adsorbates from nanotubes so that we can compare I – V measurements of nanotubes with and without adsorbates. For the sample shown in Fig. 1, a field emission current of 8 μA (600 V) was extracted to desorb adsorbates before a voltage sweep (300–420 V) was performed on the clean nanotubes. Under an applied voltage of 420 V, the field emission current of clean nanotubes increased from the initial value of ~ 10 nA to about 450 nA in 3 min. After that, the field emission current fluctuated around a mean of 450 nA, indicating that field emission is now through AETC. A voltage sweep (300–420 V) was again performed on the adsorbate-covered nanotubes. As a result, we find that adsorbates enhanced the field emission current by two orders of magnitude. The I – V measurement with and without adsorbates is shown in Fig. 2a. In both cases, the Fowler–Nordheim plot shows straight lines that are parallel to each other. This suggests that the field enhancement factor and work function of both cases remain the same. The increase in



(a)



(b)

Fig. 1. (a) SEM micrograph of entangled MWNT film at 45° tilted view. Horizontal field size = 20 μm , (b) SEM micrograph of entangled MWNT film at 85° tilted view. Horizontal field size = 20 μm .

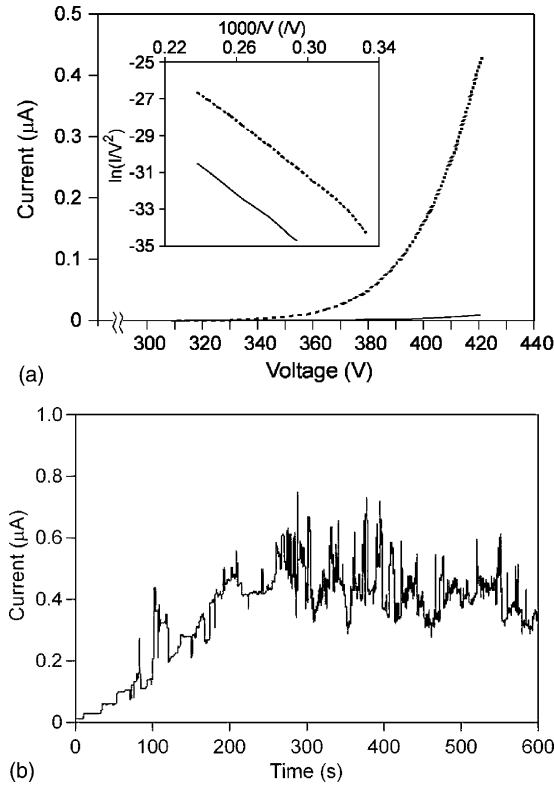


Fig. 2. (a) I - V characteristic with (broken line) and without (continuous line) adsorbates. Inset shows the corresponding F-N plots. (b) Field emission current stability at 420 V. Initially, field emission is from clean nanotubes. After 200 s, field emission is predominantly through adsorbate-enhanced tunneling states.

field emission current is probably due to enhanced tunneling probability due to the presence of adsorbates. Furthermore, as shown in Fig. 2b, the emission current of clean nanotubes shows lower frequency and magnitude of fluctuation compared to the emission current of nanotubes with adsorbates.

In order to further reveal the effect of adsorbate dynamics on the field emission current, we performed closed I - V sweeps from 300 to 600 to 300 V as shown in Fig. 3. Sweeps 1, 2 and 3 are a series of continuous sweeps. Each closed sweep took about 2 s. In sweep 1, it is clear that the I - V characteristics of the up and down sweeps show hysteresis. Initially, in the 300–420 V region (cf. Fig. 2a), emission current is through the AETC. In this region, adsorbates are firmly bonded to the nanotubes. In the 420–560 V region, field emission current fluctuation is observed. This may be due to two reasons. First, current fluctuation may be

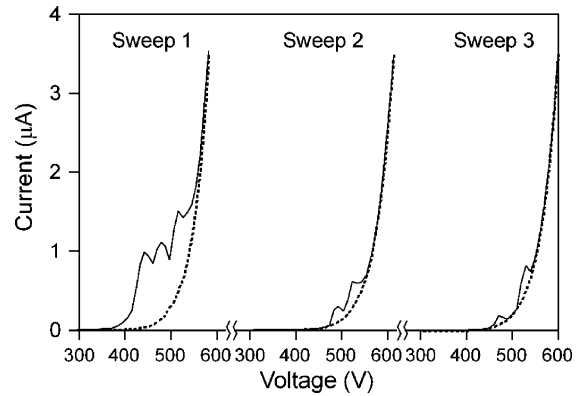


Fig. 3. Continuous closed sweeps of 300–600–300 V. Continuous line: forward sweep, broken line: reverse sweep.

due to the increased mobility of adsorbates as the nanotube temperature is higher as a result of Joule heating. Adsorbates gain higher and higher mobility from the increasing nanotube temperature until they are desorbed from the nanotubes. Second, it may be due to the increased electric field at the nanotube tip attracting adsorbates towards it which then reside on the tip, but no strong bonds could be formed before they were desorbed. These caused disturbances to the field emission current in this region. Finally, in the 560–600–300 V region, adsorbates have already been desorbed. I - V measurements show typical Fowler–Nordheim behavior. Sweeps 2 and 3 show the I - V measurements of subsequent sweeps after the first sweep. It is important to note that the I - V measurements of both sweeps show no discrepancy between up and down sweeps, except in 450–550 V region. This is attributed to the electric field attracting adsorbate species to reside on the clean CNT, but before a strong bond is formed, adsorbates were desorbed due to increasing nanotubes temperature.

In Fig. 4, we show the influence of the electric field on the formation of AETC. I - V measurements for clean nanotubes and nanotubes with adsorbates as shown in Fig. 2a were first collected as reference. We define the re-adsorption time as the time taken for the field emission current for clean nanotubes to recover back to the range of adsorbate-enhanced field emission current. The voltage was first swept up to 600 V ($\sim 8 \mu\text{A}$) to desorb adsorbates, and a series of three closed sweeps (300–420–300 V) with different time intervals between each sweep were performed to

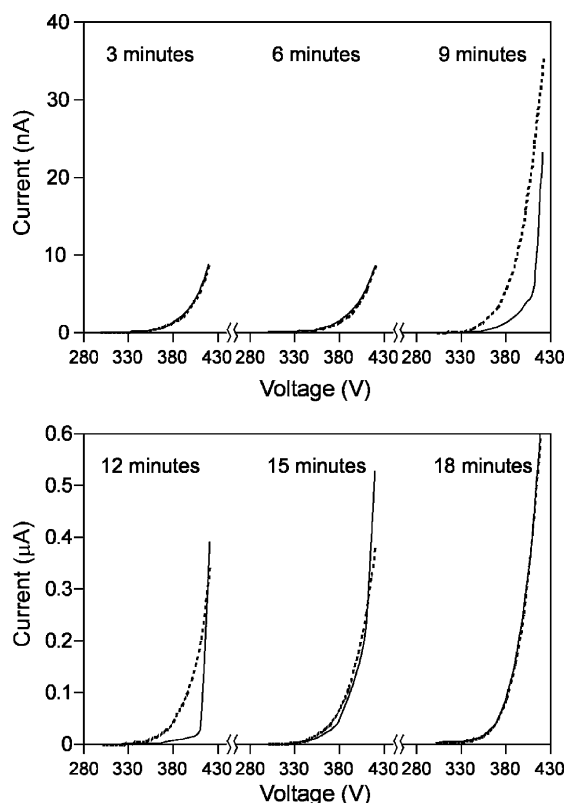


Fig. 4. Series of sweeps at intervals of 3 min. Measurement time per closed sweep is about 2 s. Continuous line: forward sweep, broken line: reverse sweep.

monitor the current changes. The time intervals between sweeps are 1, 3 and 60 min. As shown in Fig. 4, the first sudden current increase happens during the third sweep for the series with time intervals of 1 (not shown) and 3 min. On the other hand, for the 60 min time interval series (not shown), the first drastic current increase does not happen until the midst of the first sweep, indicating that no adsorbate-enhanced tunneling states are formed despite the long interval. Subsequent sweeps caused the second drastic increase of current to the range of adsorbate-enhanced field emission current as shown in Fig. 4. The first drastic current jump increased the current by 2–3 times while the second drastic current jump increased the current by two orders of magnitude. Further subsequent sweeps slightly increased the current and smoothed the I - V curve.

From the experiment above, we observed that (1) drastic current increase occurs during voltage sweep-

ing, implying that the formation of AETC happens during the sweep; (2) adsorbate re-adsorption time depends strongly on the frequency of voltage sweeping. Based on the observations, it is believed that during the forward sweep, emission electron caused surface gas molecule desorption from the ITO-coated glass. At the same time, the strong electric field at the tip of a carbon nanotube attracts the adsorbate molecules towards it to form AETC and thus increase the emission current. Another possibility is that the strong electric at the nanotube tip initiates the diffusion of adsorbates close by towards the tip and finally form AETC there.

Finally, it is obvious that the electric field can initiate the formation of AETC, which results the enhancement of tunneling probability, and thus increase the field emission current significantly. Furthermore, based on the observations, we propose that the adsorbate species which enhance the field emission should be molecules that exhibit strong dipole moment in an electric field. Further studies will be conducted to confirm this assumption.

As a conclusion, we observed light emission from carbon nanotubes resulting from Joule heating at high field emission current of about a few μA per nanotube. Furthermore, adsorbates enhance field emission current by two orders of magnitude before they were desorbed at high emission current region due to Joule heating. Finally, we observed that the electric field initiate the significant step-like jumps of field emission current which are believed to be due to the formation of adsorbate enhanced-tunneling configurations between adsorbates and field emitting carbon nanotubes.

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