ORIGINAL PAPER

Nanocarbon Photonics and Optoelectronics

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A Comparative Study of Field Emission From Semiconducting and Metallic Single-Walled Carbon Nanotube Planar Emitters

Victor I. Kleshch, Valentina A. Eremina, Pavel Serbun, Anton S. Orekhov, Dirk Lützenkirchen-Hecht, Elena D. Obraztsova, and Alexander N. Obraztsov*

Field electron emission from thin films composed of solely metallic or semiconducting single-walled carbon nanotubes is investigated using a scanning tip anode technique. Metallic and semiconducting nanotubes are separated by aqueous two-phase extraction. Local field emission centers observed on nanotube films of both types showed non-linear Fowler–Nordheim (FN) plots bent downwards. The curving of FN plots is much stronger for semiconducting nanotubes which is explained by their higher electrical resistance and stronger field penetration effect compared to metallic nanotubes. Particular nanotubes of both types revealed oscillations in current–voltage characteristics. The periodic oscillations indicated that the field emission current is modulated either by resonant tunnelling from confinement states in nano-objects formed by adsorbates or by the Coulomb blockade effect that can occur for emission from short carbon nanotubes.

1. Introduction

Field emission (FE) of electrons from carbon nanotubes has been thoroughly studied during the last 2 decades. It has been well established that carbon nanotubes emit electrons at relatively low electric fields, can generate stable intense currents and in general follow the standard Fowler–Nordheim (FN) mechanism of electron emission from metals.[1] However, in particular cases unusual effects have been observed in the FE from carbon nanotubes and related structures, for example electromechanical self-oscillations,[2] Coulomb blockade,[3] resonant tunnelling,[4] etc. Investigations of physical mechanisms underlying these effects attract considerable scientific and practical interest due to their possible usage for the development of novel nanoelectronic FE devices[5] as well as for the improvement of traditional vacuum electronic components.[1,6,7]

Unique electrical, optical and mechanical properties of the quasi one-dimensional single-walled carbon nanotubes (SWCNTs)[8] are of special interest for FE studies. Depending on geometrical characteristics, SWCNTs possesses either metallic or semiconducting conductivity.[9] However, SWCNT materials in most cases are composed of a mixture of different nanotubes. Several methods have been developed in order to obtain nanotubes with defined geometry.[10–12] One of the most efficient methods for the separation of metallic and semiconducting SWCNTs has been developed recently on the basis of an aqueous two-phase extraction (ATPE) technique.[13–14] Allowing production of large amounts of sorted nanotubes this method appears to be attractive for various technological applications.

In this work, we studied FE properties of macroscopic films composed solely of metallic or semiconducting SWCNTs separated by ATPE method, respectively. We found that semiconducting nanotubes show much stronger deviations from the standard FN theory than metallic samples. Moreover, some of emission sites in the SWCNTs films demonstrated unusual oscillating current behavior. Possible mechanisms responsible for the observed effects are discussed.

2. Materials and Methods

2.1. SWNCTs Samples Preparation

In this work we used SWCNTs powders supplied by OCSiAl company.[15] The average tube diameter was 1.8 nm. Purification of nanotubes from byproducts was performed by tip sonication in 2 wt.% water solution of sodium cholate for 4 h and ultracentrifugation at 22 400 g. The separation of metallic and semiconducting nanotubes was made using the ATPE

Dr. V. I. Kleshch, V. A. Eremina, Prof. A. N. Obraztsov
Department of Physics, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia
E-mail: klesch@polly.phys.msu.ru

V. A. Eremina, Dr. E. D. Obraztsova
A.M. Prokhorov General Physics Institute, RAS, 119991 Moscow, Russia

Dr. P. Serbun, Prof. D. Lützenkirchen-Hecht
Faculty of Mathematics and Natural Sciences, Physics Department, University of Wuppertal, 42119 Wuppertal, Germany

A. S. Orekhov
NRC Kurchatov Institute, 123182 Moscow, Russia

Prof. A. N. Obraztsov
Department of Physics and Mathematics, University of Eastern Finland, 80101 Joensuu, Finland

DOI: 10.1002/pssb.201700268

technique.[16] For this purpose two polymers – polyethylene glycol (6 kDa) and dextran (70 kDa), and two types of surfactants – sodium dodecyl sulfate and sodium cholate in appropriate concentrations were used. It is worth noting that separation of SWCNTs with such a large average diameter by ATPE technique was demonstrated for the first time here. The purity of obtained semiconducting and metallic fractions was estimated to 98%,[16] according to optical absorbance spectra (**Figure 1**). After sorting, SWCNTs were purified from residual polymers and surfactants by adding sodium chloride and ethanol to the suspension and ultracentrifugated at 360 000 g for 15 min in order to deposit the nanotubes. Then the deposited nanotubes were ultrasonicated for several minutes. Films of SWCNTs were prepared by vacuum filtration using mixed cellulose ester (MCE) membranes. The films were transferred onto polished silicon substrates with a subsequent dissolution of MCE membranes in acetone and annealing at 230 °C to remove residual cellulose and surfactants.

Scanning electron microscopy (SEM) observations shown that the films composed of metallic and semiconducting SWCNTs have similar structure and morphology (**Figure 2**). In accordance with optical absorbance spectra (Figure 1) the films composed of nanotubes of different types had different color as it is seen on photographs in the insets of Figure 2. It should be noted that the films had a number of cracks, however, for further FE experiments flat homogeneous areas of the films were chosen for investigation.

2.2. Field Emission Experiment

FE measurements were performed using the scanning field emission microscopy technique[17,18] in an ultra-high vacuum (UHV) chamber pumped down to 5×10^{-10} Torr at room temperature. A tungsten needle-like anode with 1 μm apex radius was positioned at $z \sim 30$ μm distance above the SWCNTs film installed onto a *xyz*-stage. FE properties were measured by applying a positive voltage, U, to the anode. The initial characterization of the samples was performed by measuring

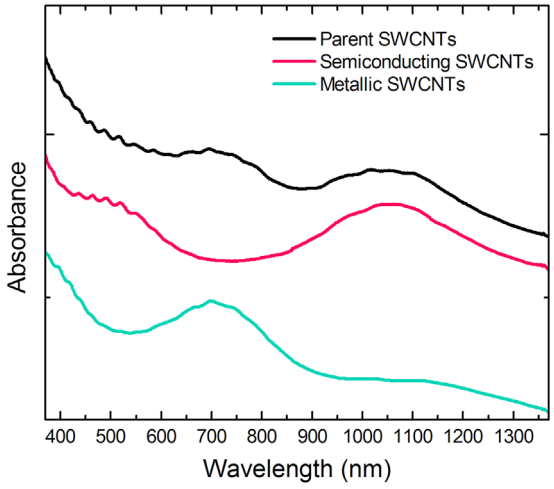

Figure 1. Optical absorbance spectra of parent SWCNTs and separated semiconducting and metallic SWCNTs.

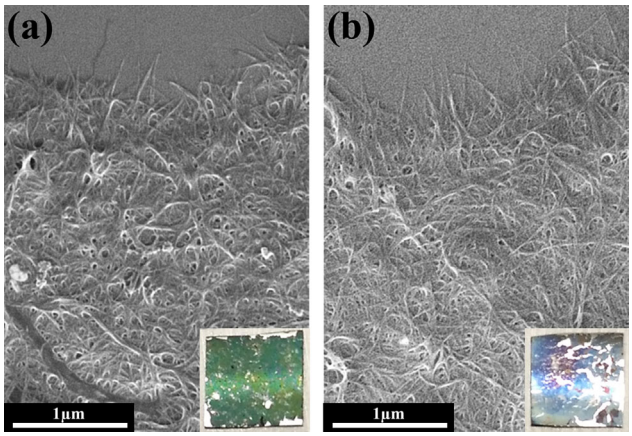

Figure 2. SEM images of (a) metallic and (b) semiconducting SWCNTs films. Insets show optical photographs of the films (green for metallic and blue for semiconducting SWCNTs) on 1×1 cm^2 Si substrates.

voltage maps $U(x, y)$, that is the voltage dependence on x-y coordinates for the constant current value. During anode scanning over the sample surface at a fixed inter-electrode distance the FE current was kept constant by a proportional–integral–derivative (PID) regulation of the applied voltage. Further experiments consisted in the measurements of current–voltage, $I(U)$, characteristics for individual emission sites revealed on $U(x, y)$ maps.

3. Results

The films composed of semiconducting and metallic SWCNTs demonstrated similar $U(x, y)$ maps consisting of randomly distributed emission sites with an average size of about 50 μm as exemplarily shown in **Figure 3**a. The individual emission sites with symmetric circular shapes were selected in the $U(x, y)$ map (as indicated by an arrow in Figure 3a) and $I(U)$ characteristics were measured from their central parts. In total 15 different emission sites were studied up to now.

Typically the initial $I(U)$ dependence was not stable and demonstrated sudden current jumps, high noise level and hysteresis (see sweeps 1–3 in Figure 3b). However, after increase

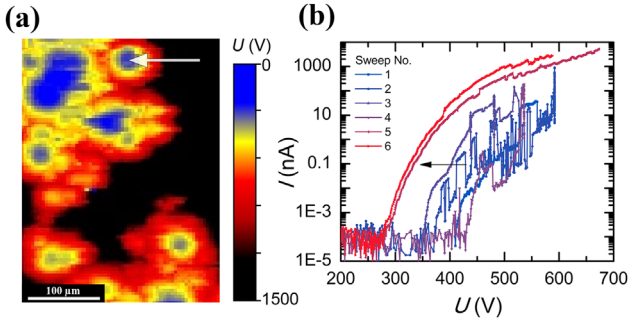

Figure 3. (a) A typical voltage map $U(x, y)$ of semiconducting SWCNTs film obtained at constant FE current of 0.1 nA and inter-electrode distance of 30 μm. (b) The current–voltage dependencies measured for an individual emission site indicated by the white arrow in panel (a).

of the FE current to several μA, $I(U)$ curves usually shifted to lower voltages and became much more stable and reproducible (see sweeps 5–6 in Figure 3b). After such a high-current treatment the threshold voltage (for 1 pA) of most emission sites was in the range of 300–400 V for both types of the SWCNTs films. **Figure 4** shows the current–voltage characteristics for different individual emission sites plotted in FN coordinates, that is as a dependence of $\mathrm{Ln}(I/U^2)$ versus $1/U$. Semiconducting nanotubes showed non-linear FN plots bent downwards, usually referred as "saturated" current–voltage characteristics (Figure 4b). Metallic nanotubes had more linear FN plots at low currents, often with abrupt drops of the current in the microampere range (Figure 4a).

Some of the emission sites on both types of the films demonstrated another distinctive behavior in the form of oscillating $I(U)$ dependencies. After intense emission with currents above 1 μA, the current started to oscillate during reduction of the voltage, as it is shown in **Figure 5**a for one of emission site on a metallic SWCNTs film. The oscillations continued to be reproducible and independent on the dc voltage sweeping rate (Figure 5b). Similar oscillating behavior was found also for several emission sites on semiconducting SWCNTs film (see Figure 5c, d). The dependencies of the 1st order derivative of the current, $\mathrm{d}I/\mathrm{d}U$, versus voltage, U, (Figure 5e, f) showed that the oscillations were quite regu lar with period, ΔU, in the range from 20 to 100 V for different emission sites. Once observed, the oscillations were fairly stable below 100 nA and usually disappeared at currents higher than 1 μA.

4. Discussion

The observed stabilization of FE after high-current measurements (Figure 3b) is a typical behavior for carbon nanotubes.[19] At currents above 1 μA the emitting apex of a nanotube can be strongly heated up to 2000 K by the Joule effect,[20] which resulted in thermal desorption of volatile molecules and weakly coupled chemical residuals used during nanotubes purification and sorting. Typically after such high current cleaning procedure the FN plots of SWCNTs became stable and follow linear dependence in agreement with the FN theory.[19] However, in our experiments semiconducting nanotubes showed pronounced

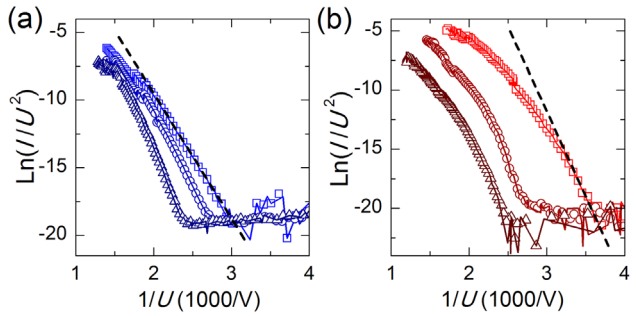

Figure 4. Local current–voltage characteristics in FN coordinates of different individual emission sites for (a) metallic and (b) semiconducting SWCNTs films. The dashed lines are introduced to guide the eye.

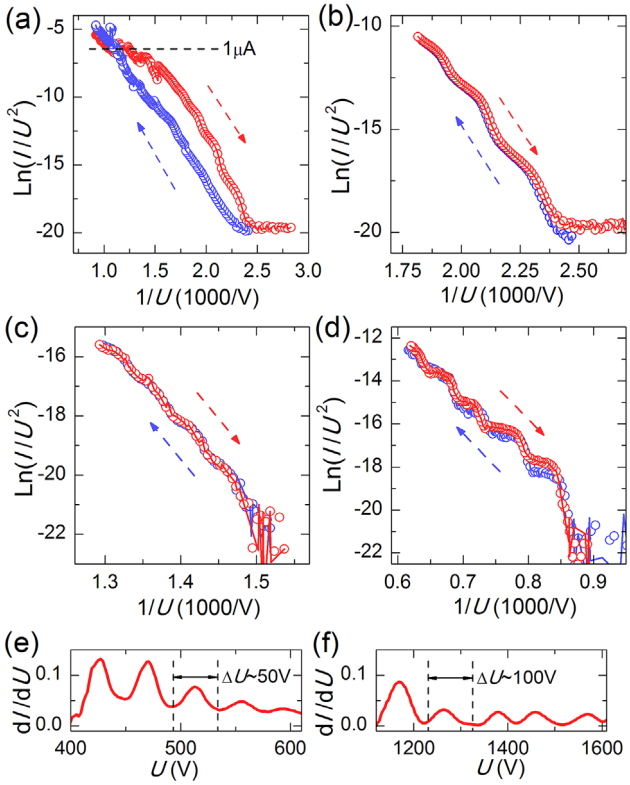

Figure 5. (a) Hysteresis of FN plot for the emission site on the film composed of metallic SWCNTs showing oscillating behavior during the voltage down sweep. (b) Subsequent reproducibly oscillating FN plot for the same emission site. (c–d) Examples of oscillating FN plots for two different emission sites on the film of semiconducting SWCNTs. (e) and (f) present dependencies of $\mathrm{d}I/\mathrm{d}U$ versus U for the current–voltage characteristics presented in (b) and (d), respectively. The dashed arrows show the voltage sweep direction.

curving of the FN plots comparing to metallic nanotubes (Figure 4). Possible reasons which are usually considered in order to explain such deviations from FN law include: the presence of adsorbed molecules, the influence of high apex curvature, space charge effects, localized surface electron states, contact resistance, etc.[1] However, in our comparative study semiconducting and metallic nanotubes had similar geometries and were measured using identical experimental conditions. Therefore, it is straightforward to assume that the changes in FE current–voltage characteristics are caused by the difference in type of conductivity of the nanotubes. First, semiconducting nanotubes have higher electrical resistance and during emission larger voltage drops can occur inside them which can cause pronounced saturation-like deviation from the classical FN behavior.[21] Moreover, the saturation behavior which is usually observed for semiconducting tip emitters[22,23] can be also explained by the formation of a highly resistive region (depletion zone) at the emitter apexes due to the penetration of the electric field.[24] The depletion zone limits the tunnelling current and results in nonlinear FN plots. Calculations show that penetration of the electric field is also possible in SWCNTs at the apex region.[25] In our case we used nanotubes with quite a large

average diameter of 1.8 nm. Since the field penetration may be more efficient for wider nanotubes it can be one of the reasons why saturation effects are rarely observed for FE from clean SWCNTs.

Approximately 25% of the studied emission sites of both the metallic and semiconducting films showed oscillating behavior of the current–voltage characteristics (Figure 5). The periodic nature of the oscillations is clearly demonstrated by the current derivatives (Figure 5e,f), evidencing that the emission occurs from a single SWCNT rather than from several different nanotubes or their bundles. It is unlikely that a high dispersion of geometrical and electronic properties of nanotubes in the film can lead to the observed regular dependence in FE characteristics.

We suppose that the origin of the oscillations for an individual nanotube is connected with a modified FE mechanism which is different from a standard FN tunneling through a single energy barrier formed at the nanotube apex. Various resonant tunnelling mechanisms from confinement states in nanocarbon emitters are usually considered in order to explain experimentally observed deviations from FN theory and, particularly, non-monotonic FN plots.[5] However, taking into account the periodic character of the current oscillations, another probable explanation is the Coulomb blockade (CB) of FE which was considered theoretically in Ref. [26]. It has been shown that for a nanoscale emitter (e.g., a nanotube) weakly coupled to a cathode the FE current increases in a step-like fashion due to single-electron charging. As a result the current-voltage characteristic of the emitter reveals current oscillations known as the Coulomb staircase. The weak coupling between the emitter and cathode, required for CB realization, in our samples could be provided by the presence of poorly conducting residual surfactants at the contact of an emitting nanotube and the rest of the film. It should be noted that CB-modulated emission with similar oscillating $I(U)$ curves have been observed recently for SWCNTs[3] and nanocarbon clusters[27] grown in situ during FE experiment. Similarly to the present work CB was also observed at room temperature with the oscillations period of tens of volts and the maximum CB-modulated current of about 1 μA. The disappearance of the CB staircase at high currents as well as the sudden current drops observed in our experiments can be explained by a combination of Joule heating and high electric field at the emitting SWCNT apex. It is worth noting that both of the discussed mechanisms of periodic behavior, that is resonant tunneling and CB, are possible in our experiments and may come either from short nanotubes or from nano-objects which are readily formed on surfaces with adsorbates.

5. Conclusions

The ATPE method was used to separate semiconducting and metallic SWCNTs with purity up to 98% estimated from optical absorbance spectra. The films composed of sorted SWCNTs were studied by scanning anode FE techniques. Stabilization of local current–voltage characteristics was observed after emission at currents above 1 μA which was explained by thermal desorption of adsorbates induced by heating of the nanotube by the Joule effect. After stabilization, both types of the samples demonstrated saturation-like deviations from FN plots. Stronger saturation observed for semiconducting nanotubes was explained by their higher electrical resistance and by possible penetration of the electric field to the apexes of nanotubes with a large average diameter of 1.8 nm. Approximately 25% of the emission sites on the studied nanotube films demonstrated oscillating current-voltage characteristics with periods in the range of 20–100 V. The periodicity of the oscillations gives evidence that resonant tunneling or Coulomb blockade effect occurred during FE from short carbon nanotubes or nano-objects formed by adsorbates.

Acknowledgement

The work was supported by RSF project 15-12-30041.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous two-phase extraction, field emission, single-walled carbon nanotubes

Received: June 2, 2017
Revised: August 30, 2017
Published online: October 5, 2017

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