

Helium Detection via Field Ionization from Carbon Nanotubes

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ABSTRACT

A novel, high-efficiency detector for neutral atoms such as helium is described. The design uses multiwalled carbon nanotubes (MWNTs), grown by chemical vapor deposition on a steel support wire. Application of a positive bias to the MWNTs generates electric fields sufficient to field-ionize passing gas-phase atoms. Under ultrahigh vacuum conditions, the detector was demonstrated to be capable of ionising and detecting even helium gas, the element with the highest ionization potential.

With the highest ionization energy of any element, conventional detection efficiencies for gaseous helium can be as poor as one part per million.¹ Despite this limitation, the unrivaled sensitivity offered by helium atom beams as probes of surface structure has driven their continual development.² Most recently, construction of optical elements for helium makes the tantalizing goal of an atom beam microscope technically feasible.^{3,4} However, progress is currently limited by low signals and the lack of a spatially resolved helium detector. Recent developments have aimed to improve helium signal by boosting source intensity.^{5–7} Here, we describe a superior approach: direct improvement of helium detection. We use the strong electric fields generated at the tips of positively biased carbon nanotubes⁸ (CNTs) to field-ionize helium atoms and demonstrate that CNTs could be used for high efficiency, spatially resolved helium detection over large areas. Such a detector could revolutionize atom-beam techniques, improving signal by several orders of magnitude and making feasible a host of spatially resolved experiments that have previously been limited by poor signal quality.

Field emission properties of CNTs have recently attracted a great deal of research interest, driven primarily by the wide range of potential commercial applications such as bright electron sources⁹ and flat panel displays.¹⁰ Owing to their extremely sharp radii, even a relatively moderate *negative*

voltage at the nanotube tip is sufficient to cause field emission of electrons.^{11,12} Application of a *positive* voltage to a sharp (typically metal) tip, on the other hand, has long been used in field ionization microscopy,¹³ where the strong electric fields generated at the tip are sufficient to strip electrons even from helium. Previous attempts to use this effect for gas detection, however, have been limited by the extremely small size of the ionization region.¹⁴ Recent progress in the fabrication of large-scale sparse arrays of carbon nanotubes¹⁵ offers the possibility of circumventing this problem, by providing a large number of individual field ionization sites that could cover several square millimeters at minimal expense.

For the experiments detailed here, carbon nanotubes were grown by catalytic decomposition of acetylene on an etched stainless steel wire (grade 316, 0.25 mm diameter) and under a slight applied potential. The support wire was constructed in an inverted ‘T’ configuration, spot-welded from 0.25 mm diameter tungsten wire and supported by the legs of a standard electron microscopy filament assembly. During nanotube growth, the tip was heated resistively by passing current through the tungsten wire. The end of the ‘T’ piece, where nanotube growth was concentrated, was left intentionally blunt, typically 20–30 microns radius, such that field emission or ionization direct from the wire would not occur during experiments. Growth of CNTs under these conditions is described in detail elsewhere and produces a large number of densely packed, multiwalled CNTs growing perpendicular to their substrate.¹⁶ Scanning electron microscopy (SEM)

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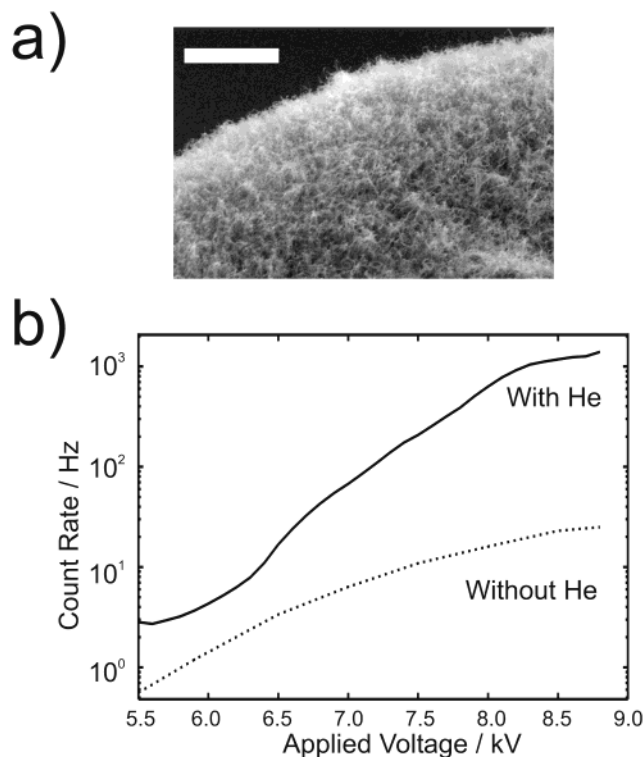


Figure 1. (a) SEM of the carbon nanotubes used for helium detection. The scalebar is 5 microns. (b) Field ionization of helium from carbon nanotubes. The upper trace indicates the time-averaged detection current as a function of voltage applied to the CNT-coated wire. The dotted line indicates the “background” ion current, measured in the absence of admitted helium.

analysis indicated that the nanotubes have lengths of up to $2\ \mu\text{m}$ and radii around 50 nm (Figure 1a).

Field ionization experiments were conducted under ultra-high vacuum conditions. Both the sample and chamber were baked ($120\ \text{°C}$) prior to experiments, giving a base pressure of 5×10^{-10} mbar. After baking, the sample was held at a $+7.5\ \text{kV}$ for several hours in order to remove adsorbed species such as water from the sample. Helium (Messer, 99.999% purity) was admitted through a leak valve to a pressure of 4×10^{-5} mbar. A positive voltage was then applied to the sample and the ionization current was collected at the grounded face of a channel electron multiplier (CEM), approximately 20 mm distant.

Helium detection via field ionization from CNTs is demonstrated in Figure 1. The upper trace indicates that the ion current detected by the CEM increased rapidly with increasing positive voltage applied to the sample. A dotted black line indicates the background counts, i.e., the current detected in the absence of helium gas. Note the logarithmic scale. At the highest applied voltage, the helium count rate is 2 orders of magnitude more than the background, demonstrating unambiguous detection of helium and illustrating a favorable signal-to-noise ratio. The strong voltage dependence of Figure 1 is consistent with previous observations of metallic field ionization tips and derives from a rapid increase in tunneling probability for electrons tunneling from impinging He atoms to the tip.¹³ Its precise power-law nature depends on the form of the electronic density of states of

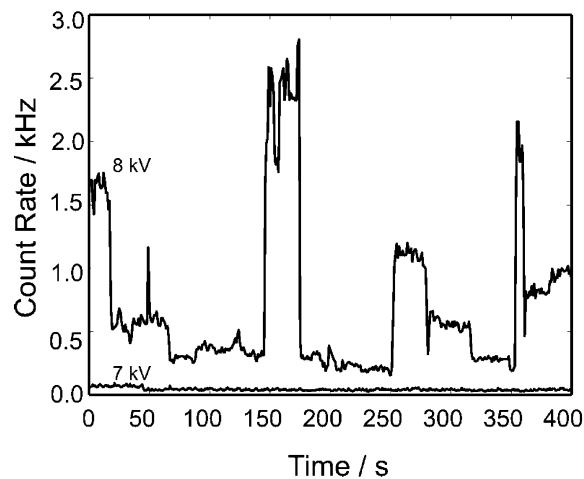


Figure 2. Helium ion current measured at the CEM under a constant helium pressure of 4×10^{-5} mbar and tip voltage of 7 kV (lower) and 8 kV (upper).

the tip, and the average count rate here is proportional to the sixteenth power of the voltage. Further data (not shown) taken at different helium pressures also indicate an approximately linear dependence of count rate on helium pressure, which is useful in terms of fabricating a practicable detector.

By assuming ideal-gas kinetics we can calculate the impingement rate of helium atoms on the nanotube-coated wire. Given that the ionization probability is of the order of 100% and is not observed to be a function of the incident helium atom velocity,¹⁴ we estimate the effective size of the ionization region to be only a few square nanometers. We therefore conclude that only a tiny fraction of CNTs are field emitting, most likely because their dense packing smoothes the electric equipotentials and only those nanotubes protruding significantly above their neighbors can enhance the electric field sufficiently for field ionization to occur – a conclusion confirmed by SEM observation of the sample.

At the highest applied voltages, the detected ion current is relatively unstable. Figure 2 illustrates the instability by presenting two detection currents, taken while the sample was held at constant potentials of $+7\ \text{kV}$ and $+8\ \text{kV}$. Both traces exhibit noise and step-changes in the detected current; however, the range of the step changes appears to increase substantially at higher applied voltages, where the current often alters by up to an order of magnitude within a sampling period (1s). Once again, the scale of the changes observed suggests that the recorded current is not the averaged signal of many CNTs but results from only a small number of ionization sites. Similar instabilities have been observed during field emission of electrons but are generally attributed to changes caused by migration and desorption of molecular adsorbates.^{17,18} A molecular adsorbate can enhance field emission by altering the local work function or by acting as a sharp protrusion on a CNT tip, thereby increasing the local electric field strength.¹⁸ Migration of adsorbates to and from prominent positions can then cause fluctuations in the electric field and hence in the emission current. In a similar manner, field ionization of helium would be affected by migration

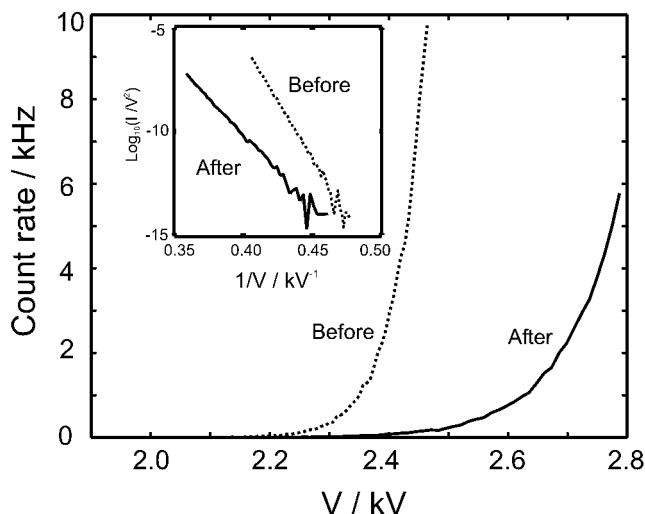


Figure 3. Field emission characteristics of the nanotube-coated steel wire before and after field ionization trials and (inset) the same data in a Fowler–Nordheim plot.¹⁷

of adsorbates on a CNT tip and could account for the observed fluctuations in ionization current. However, such a mechanism here is surprising, given the sample cleaning procedure outlined above, and further experiments are being conducted to clarify this point.

The sample's field emission characteristics were also investigated by applying a negative bias (typically 1–3 kV) to the sample before and after field ionization experiments. Emission currents (I) as a function of tip voltage (V) detected at the CEM are plotted in Figure 3. Fowler–Nordheim plots (inset) of $\log(I/V^2)$ vs $1/V$ are linear, indicating that emission is governed by electronic tunneling from a CNT with metallic conduction characteristics.^{11,19–21} Following the analysis of, for example, Bonard et al.¹² and taking an approximate work-function of 5 eV for CNTs,²⁰ the maximum field magnitude was fitted as 1.70 V/nm for the first data set of Figure 3, which we calculate to be a field enhancement of 100 over the field generated by the bare iron wire alone. For comparison, the optimal imaging field for He ionization used in field ionization microscopy¹³ is ~ 44 V/nm, far higher than the field magnitudes used in either Figure 1 or Figure 3 and evidently far higher than the field magnitude required for the onset of He ionization. The comparison suggests that successful and practicable helium detection in a CNT detector is possible well below the fields that might be expected from the literature, although it is clear that increasing the applied field beyond the range used here will increase the detected ion count further.

In contrast to pre-ionization trends, the post-ionization data in Figure 3 has an increased field amplification factor (i.e., a decreased slope in the Fowler–Nordheim data) but also an increased turn-on voltage. These changes in emission characteristics, which appear to be irreversible, are difficult to reconcile with the reversible ‘switching’ behavior observed in Figure 2 and most likely derive from a distinct mechanism. We believe the net effect to arise from a series of abrupt, irreversible events which occur whenever a new maximum voltage is applied but which diminish rapidly with time. To

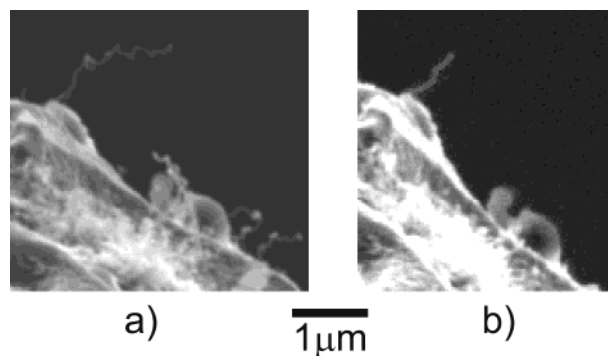


Figure 4. Scanning electron micrograph of a nanotube-coated steel support (a) before and (b) after field ionization trials.

understand the effect further, SEM images of the same region of a CNT-coated sample were taken before and after helium ionization trials: the images are presented in Figure 4. (Note that the sample illustrated is not that used for the data presented in previous figures and has a very low CNT number density.) Figure 4a illustrates a small number of CNTs grown on a microscopically rough steel substrate. Comparison between Figure 4a and Figure 4b indicates that field ionization results in occasional snapping or complete removal of a nanotube from its support. An isolated nanotube, visible in the top left of both images, has broken-off, while other CNTs, to the bottom right, have been removed completely. The top left CNT appears to have snapped at a kink site, suggesting that degradation occurs through mechanical failure at a point of crystallographic weakness. Alternative explanations²² for CNT degradation, for example, through Ohmic heating or via ion bombardment, are inappropriate here. Only small currents were passed through CNTs and their positive potential would repel most ionized species. We believe that the removal of mechanically weak CNTs accounts for the long-term changes observed in the Fowler–Nordheim plots of Figure 3. After a brief ‘break-in’ period, when most weak CNTs are removed, the sample could be used as a stable detector.

We have demonstrated detection of neutral atoms via field ionization from carbon nanotubes. By extending this work to arrays of well-separated, isolated nanotubes,¹⁵ improvements are possible in terms of the detected ion current as well as providing spatial sensitivity. Further experiments are planned to demonstrate this concept.

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