

Electrochemically Tuned Properties for Electrolyte-Free Carbon Nanotube Sheets

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Injecting high electronic charge densities can profoundly change the optical, electrical, and magnetic properties of materials. Such charge injection in bulk materials has traditionally involved either dopant intercalation or the maintained use of a contacting electrolyte. Tunable electrochemical charge injection and charge retention, in which neither volumetric intercalation of ions nor maintained electrolyte contact is needed, are demonstrated for carbon nanotube sheets in the absence of an applied field. The tunability of electrical conductivity and electron field emission in the subsequent material is presented. Application of this material to supercapacitors may extend their charge-storage times because they can retain charge after the removal of the electrolyte.

materials. High electrochemical charge injection requires the close proximity of oppositely charged ions and electronic carriers (electrons or holes) in order to mitigate repulsive Coulombic interactions. Faradaic charge injection, used for doping conducting polymers and graphite, achieves this proximity and overall charge balance by the simultaneous electrochemical insertion of ions and electronic charge within a solid. This internal ion insertion dramatically changes structure, introduces defects, and provides oppositely directed structural transformations that are hysteretic and only partially reversible during ion de-insertion. In contrast, in electrochemical non-Faradaic charge

1. Introduction

Injecting high electronic charge densities can profoundly change the optical, electrical, and magnetic properties of materials.^[1,2] Three generic methods are available for electrically inducing large changes in charge density: electrically gated charge injection in dielectric-separated electrodes,^[3] electrochemical charge injection associated with counter-ion intercalation, and electrochemical double-layer (DL) charge injection. While dielectric-based charge injection, used in field-effect transistors (FETs), provides the basis for today's electronic technology, only the latter electrochemical methods (called Faradaic and non-Faradaic, respectively) have been successfully used so far to tune the bulk properties of

injection, the counter-ions are electrostatically attracted to the injected charge of a DL and reside on the electrode surface (without intercalation into the bulk). As a result, this process can be much faster, and large structural transformation of the electrode material can be avoided. Thus, unlike Faradaic charge injection, non-Faradaic charge injection is highly reversible, which is essential for many applications. The separation between electrically injected charge carriers within the electrode and oppositely charged ions on the electrolyte side of the DL can be approximated by the Debye length, L_D , for the electrolyte if deviations from perfect charge screening in the electrode are ignored. This Debye length is given by

$$L_D = \sqrt{\frac{\epsilon\epsilon_0 kT}{2z^2 e^2 n}} \quad (1)$$

where ϵ is the dielectric constant of the electrolyte, ϵ_0 is the permittivity of free space, kT is the thermal energy, z is the ion charge in numbers of electrons, e is the charge of an electron, and n is the concentration of the electrolyte. For a concentrated electrolyte at room temperature, the Debye length is typically less than 1 nm, which is several orders of magnitude smaller than the charge separation between the gate and channel of typical FETs. However, achieving large non-Faradaic charge injection in bulk material requires a high surface-to-volume ratio for the charge-injected electrode, which for a macroscopic solid implies the existence of nanoscale porosity. Supercapacitors based on DL charge injection in nanotubes immersed in electrolytes achieve specific capacitances from tens to hundreds of Farads per gram of nanotubes, depending on the nanotube type and the electrolyte.

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While the amount of injected DL charge may be as high as 10^{-3} – 10^{-2} charge carriers per atom, changes in the electronic properties of metal electrodes are small because changes in the electronic charge density are masked by the initially large electronic charge densities of conventional metals. However, large changes in electronic and optical properties as a result of DL charge injection can be achieved using electrodes having low charge densities, such as semiconductors or nanostructured carbons that are semimetallic and have low concentrations of free charge carriers ($\sim 10^{19} \text{ cm}^{-3}$). Due to their chemical inertness and potentially high specific surface area, carbon nanotubes (CNTs) are ideal materials for accumulating large amounts of injected electrical charge and demonstrating reversible tunability in their physical properties. Non-Faradaic electrochemical charge injection in CNTs has been successfully used to provide electrochemical electromechanical actuators^[4] and liquid-ion-gated FETs.^[5] DL charge injection in nanotubes results in the bleaching of electronic transitions and corresponding changes in optical adsorption, as well as pronounced changes in the intensity and frequency of Raman lines.^[6]

Potential application of the nanotube properties that have been tuned using electrochemical DL charge injection is limited by the need to maintain contact between the electrode (including both internal and external surfaces) and the electrolyte. For example, the surrounding electrolyte for the above-mentioned liquid-ion-gated FETs limits their use in gaseous state sensing because gas must first dissolve in the electrolyte before it can be detected. Consequently, device response rate and sensitivity are decreased, and detection capabilities are limited to only those gases that can effectively dissolve in the electrolyte. In conventional DL-based nanotube supercapacitors, the contacting electrolyte that separates the electrodes provides mechanisms for self-discharge, so long-term energy storage in such a supercapacitor is not possible.

With the goal of eliminating these problems, we show that the DL charge that has been injected using liquid electrolytes, and its subsequent effects, can be substantially maintained if the macroscopic CNT electrodes are removed from the electrolyte, washed, and dried. Retention of the injected charge in the dried CNT electrodes was indicated by the maintenance of the changes in physical properties and by shifts in electrochemical potential, Fermi level position, and work function (WF). This charge retention was used to tune CNT electrical conductivity and cold field electron emission in electrolyte-free electrodes.

Pioneering studies by W. N. Hansen et al.^[7,8] provide an early precedent of this phenomenon; they reported the retention of electrolyte-based DL charge in noble metal electrodes that were removed from contact with the electrolyte. Use of planar electrodes that were not nanostructured meant that only the properties of the surface layer changed and that the charge injected per unit of electrode weight was extremely low, so the tunability of bulk properties was not achieved and injected charge disappeared within minutes upon air exposure.^[7] Here, we inject charge into bulk CNT electrodes that have a very high gravimetric capacitance, and we show that the tunability of bulk properties is retained even in the absence of a contacting electrolyte. The injected charge does decay upon air exposure, due to redox reactions with components of air; the charge decay however is much faster for injected electrons than for injected holes.

2. Results and Discussion

2.1. Voltammetry

It is well known that CNTs have high electrochemical stability and provide non-Faradaic behavior in a variety of aqueous and nonaqueous electrolytes.^[9,10] Figure 1 displays typical cyclic voltammograms of single-wall CNT (SWNT) and multiwalled CNT (MWNT) sheets in 1 M NaCl aqueous solution. The cyclic voltammograms indicate nearly ideal behavior for DL charging; this is especially true for the MWNT sheets, but minor Faradaic peaks, which may be associated with oxygen-containing surface functionalities on the CNTs or on carbonaceous impurities, are present.^[9] The specific capacitance of the electrode, C , was calculated as $C = I/vm$, where I is the current at the given scan rate (v) and m is the weight of the CNT electrode. Typical values for specific capacitance were 25–30 F g^{-1} for SWNT samples and 6–10 F g^{-1} for MWNT sheets.

2.2. Retention of Potential

The retention of the DL charge for electrolyte-free CNT electrodes was investigated using the following procedure: a) electrochemically charging the CNT electrode in aqueous NaCl electrolyte to a measured potential, b) removing the CNT sheet electrode from the electrolyte and exposing it to air, c) washing the electrode in deionized water, d) drying the electrode in air, e) re-immersing the CNT electrode into the electrolyte solution, and f) measuring the electrode potential versus a reference electrode. Figure 2 presents the time-dependence (under open circuit conditions) of the CNT electrode potential in the electrolyte after electrochemical charging; following application of the washing and drying procedure, the electrode was re-immersed in the electrolytic solution and re-measured. It was observed that positively charged (hole-doped) CNT electrodes essentially retain their potential, and therefore injected DL charge, whereas the potential of the negatively charged (electron-doped) CNT electrodes is unstable in both the electrolyte and air (and it discharges substantially within several minutes in air).

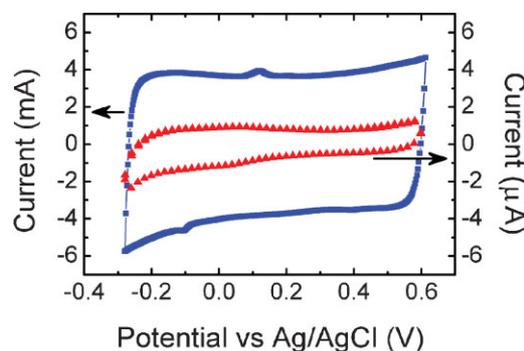


Figure 1. Typical cyclic voltammograms of a SWNT sheet electrode (squares) and a MWNT sheet electrode (triangles) in 1 M NaCl aqueous solution obtained at a scan rate of 25 mV s^{-1} . The current scales for SWNT and MWNT electrodes are provided on the left and right sides of the graph, respectively.

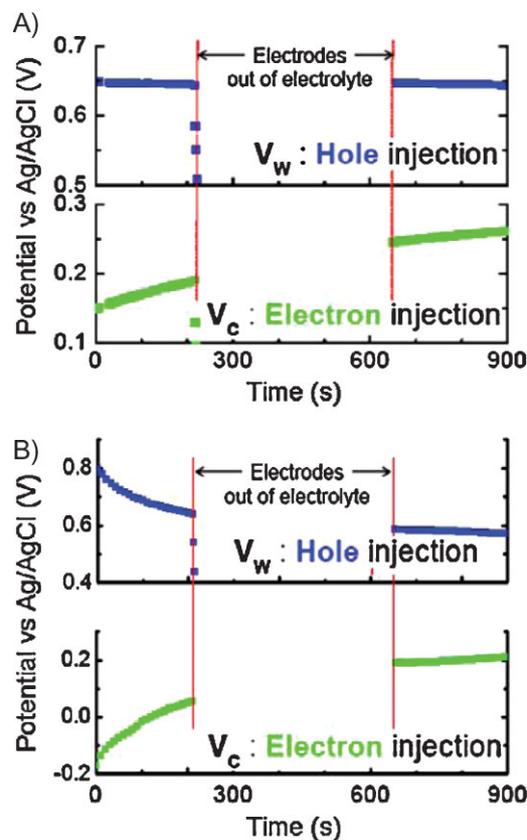


Figure 2. Time-dependence of the potential of the electrode before and after moving it from the 1 M NaCl electrolyte to air and after subsequent re-immersion in the electrolyte for A) SWNT and B) MWNT sheet electrodes. The electrodes were measured under open circuit conditions from time zero (after charging), so the potential changes in the electrolyte reflect parasitic redox processes for this electrolyte. The measured electrode potentials of both positive and negative electrode indicate that non-Faradaically injected charge is partially retained even when the electrodes are removed from the electrolyte and placed in air.

The observed difference in behavior of the hole- and electron-doped CNT electrodes may be explained in terms of DL-induced work function changes. The WF of a DL-charged electrode depends linearly on the electrode potential, exhibiting a slope of 1, and is independent of the electrode material.^[7] Hole-doped (positively charged) CNT electrodes have high WFs, which means that they do not rapidly oxidize in the presence of oxygen. On the other hand, electron-doped (negatively charged) electrodes have substantially lower WFs, so redox reactions can rapidly occur in air.

The degree of long-term charge retention, and the corresponding changes in WF, was demonstrated in air for a hole-doped MWNT sheet electrode using Kelvin probe microscopy. A detailed description of Kelvin probe microscopy, also referred to as electric force microscopy, is provided elsewhere.^[10] In brief, Kelvin probe microscopy enables the mapping of the contact potential difference (CPD) between a conducting sample and a conducting probe. Since the CPD equals the difference between the WFs of the sample and probe, this method allows spatial mapping of the work function of the conducting sample. Since the roughness of the

sample surface is a critical parameter for scanning probe microscopy techniques, densified aligned MWNT sheet electrodes having relatively well-defined surfaces were used for this study. Figure 3 provides CPD images of a MWNT sheet electrode in air taken at different times after its removal from the electrolyte. These images show that the WF of the MWNT sheet is very uniform both before electrochemical charging and during air exposure after charging.

The average CPD value for an uncharged sample, $CPD_0 = 50$ mV, was measured independently using the same probe. Using this value and the reported WF value for pristine MWNTs ($\varphi_0 = 5.3$ eV),^[11] we calculated the WF using the relationship $WF = \varphi_0 + e(CPD_0 - CPD)$, where e is again the electron charge. Figure 3E presents the observed dependence of the average CPD value and the corresponding dependence of the WF on amount of time the sample was exposed to air. A relatively slow discharge process (several hours) is observed for the hole-doped CNT electrode.

The retention of the DL charge and the CNT electrode potential under an inert atmosphere, together with the high specific capacitance of the CNT sheets, suggests that CNT sheets might be used as dry-state charge-storage supercapacitors. This would involve removal of the electrolyte from the supercapacitor after the electrodes have been DL charge injected, thereby eliminating electrolyte-based redox processes, which result in supercapacitor discharge. Subsequent filling of the supercapacitor with inert gas would eliminate the possibility of air-associated charge-discharge processes. Charge could likely be stored in such supercapacitors for many years; as needed, the electrolyte could be re-introduced into the supercapacitor, which could then be discharged, releasing electrical energy.

2.3. Tuning and Retention of the Conductivity of Electrolyte-Free CNT Sheets

Retention of DL charge in CNT electrodes was also confirmed by the retention of increased electrical conductivity, which resulted from the charge injection. Figure 4B shows the observed tunability of the four-point electrical conductivity as a function of injected charge per carbon atom for a SWNT sheet immersed in 1 M NaCl aqueous solution. It is seen that the four-probe electrical conductivity increases about an order of magnitude upon injecting 0.008 holes per carbon atom.

These results can be compared with those for conducting polymers (such as polyacetylene) that are doped by intercalation. Pristine polyacetylene film is a large-bandgap insulator before doping, but it exhibits semiconducting behavior at intermediate doping levels (0.1% to a few percent) and metallic behavior at high doping levels (>6%, which results in a conductivity of $\sigma \sim 10^4$ S cm^{-1}). The amount of DL charge injection into the SWNT sheets is similar to that of the intermediately doped polyacetylene films, and they have comparable electrical conductivities.^[12,13]

The zero-charge-injection state in Figure 4B is defined as the state of SWNTs in air before DL charge injection. However, the position of the conductivity minimum indicates that about 0.001 holes per carbon exist in the SWNTs sample before charge

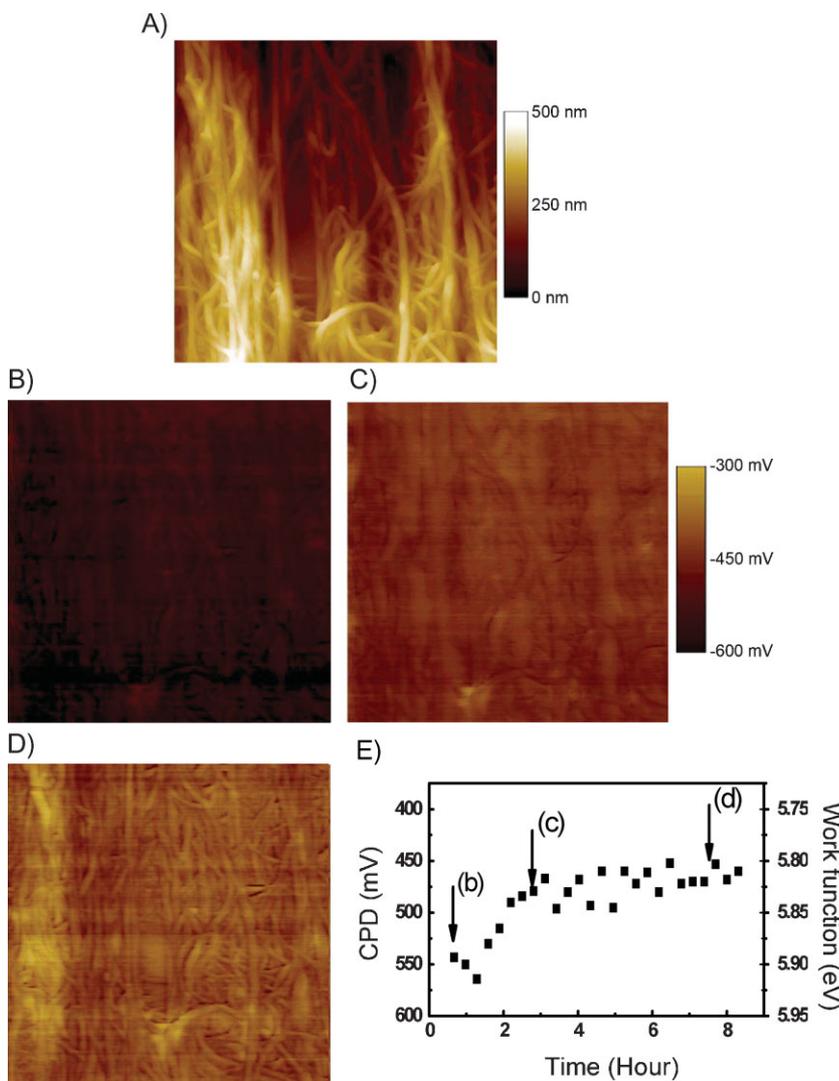


Figure 3. A) Typical AFM image of the topography of the MWNT aligned sheet electrode. CPD measured B) 40, C) 150, and D) 420 min after removing the electrode from 1 M NaCl aqueous solution and exposing it to air. E) The observed time-dependence of the average CPD value and the WF. The labels, b, c, and d, indicate when the measurements for B, C, and D were obtained.

injection. The origin of this pre-existing hole concentration has been discussed extensively elsewhere.^[14–16] While we cannot identify the nature of the dopant here (i.e., oxygen or other compound), this method clearly indicates the amount of pre-existing charge carriers. The initial curve is slightly different from curves obtained after several successive cycles, which might reflect a slight capacitance increase with increased cycling due to increased SWNT wetting by the electrolyte.

Figure 4C presents the electrical conductivity data of the hole-doped SWNT electrode as a function of time when the DL charge injected electrode is exposed to different environments under different conditions. While the electrical conductivity decreased slowly, it remained much higher than the conductivity of the pristine state. The observed slow decrease in electrical conductivity for the CNT electrode in air agrees with the decreasing WF and electrode potential, which were discussed above. The discharge

mechanism for the hole-injected electrodes in air is not presently understood; however, the conductivity decrease in vacuum was likely a result of the partial removal of water molecules, which solvate the ions on the CNT surface that provide the counter-charge to the injected holes.

After removing the DL charge injected MWNT sheet electrodes from the electrolyte, the electrical conductivity shows essentially the same type of behavior as that of the SWNT sheets. However, the fractional change in MWNT sheet electrical conductivity upon DL charge injection is much lower than that of the SWNT sheets because MWNT sheets comprise predominantly metallic CNTs having higher conductivity and higher carrier concentration than the CNTs of SWNT sheets.

2.4. Tuning of Electron Field Emission for Electrolyte-Free CNT cathodes

DL charge retention in the absence of the electrolyte is promising for various applications of CNTs. Tuning the work function of CNTs is of special practical interest. It has previously been shown that electrochemical tuning of the WF of Pt, Pd, Rh, Ag, and some other metals can increase catalytic activity by over two orders of magnitude. This effect, known as non-Faradaic electrochemical modification of catalytic activity (NEMCA), has been extensively discussed in the literature.^[17] Another phenomenon that is very sensitive to the WF value of a material is electron field emission. CNTs are known to act as exceptional electron field emission cold cathodes because they can provide high spatial and temporal coherence, high current densities, low operation voltages, and high stability.^[18] They are already used as cold cathodes for numerous applications, such as field emission displays, cathodoluminescent lamps,

and X-ray sources.

Cold electron field emission is a quantum mechanical phenomenon in which the electrons tunnel through the triangular potential barrier created by an external electric field, rather than going over it. In the case of metals, the field emission density of the current is given by the Fowler–Nordheim law.^[19]

$$I_{FE} = A(F^2/\varphi) \cdot \exp(-B \cdot \varphi^3/2/F) \quad (2)$$

where A and B are appropriate constants, F is a local electric field near the emitter, and φ is the WF of the emitter. The local electric field can be expressed as $F = \beta V$, where β is the field enhancement factor and V is the bias voltage. It is seen from Equation 2 that the field emission current depends dramatically on the value of the WF of the emitting material. The WF for

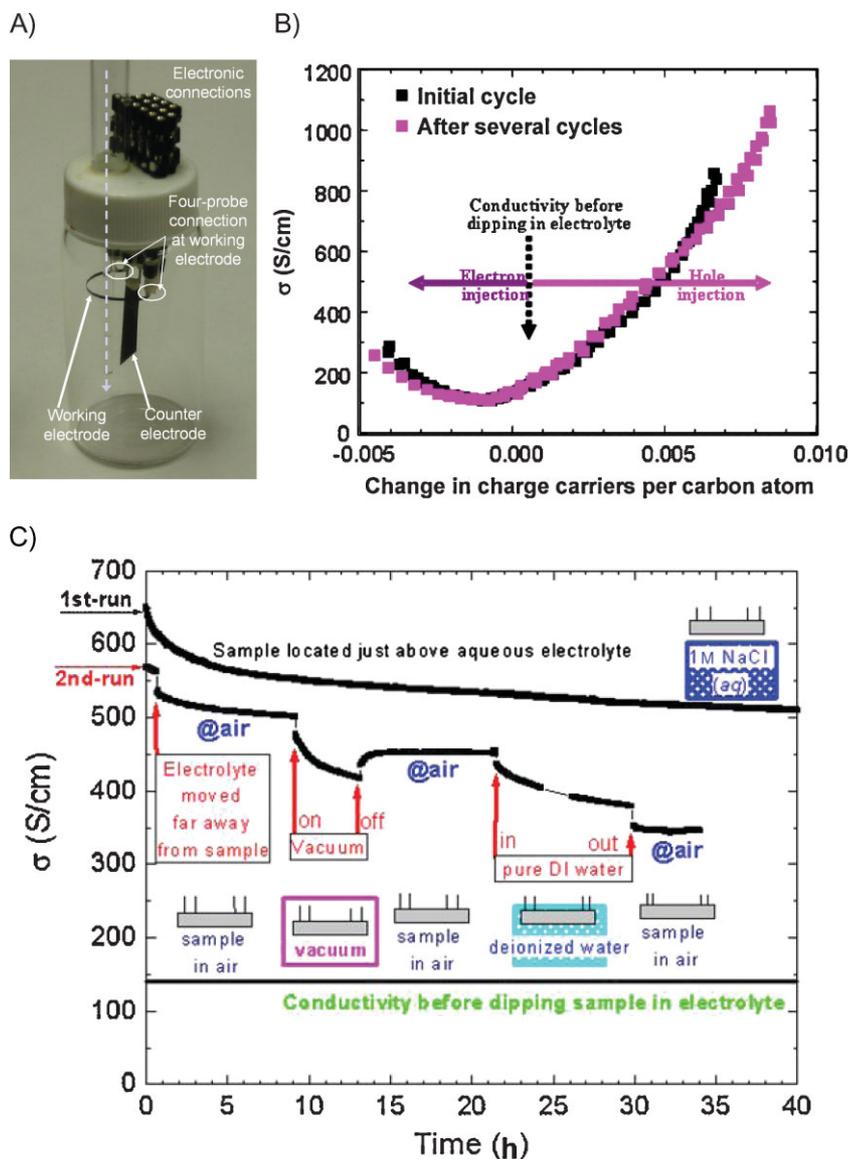


Figure 4. Charge injection and associated tunability of the electrical conductivity in wet and dry states for a SWNT sheet. A) Photograph of the experimental electrochemical cell using a small-area SWNT sheet working electrode and a large-area SWNT sheet counter electrode. B) The dependence of the four-point electrical conductivity (σ) upon the amount of injected charge (per carbon atom) for the SWNT sheet in 1 M NaCl aqueous electrolyte. C) First run: Electrical conductivity versus time when a DL charge-injected SWNT sheet is removed from the electrolyte and held in air just above the electrolyte for 40 h. Second run: Electrical conductivity versus time when a DL charge-injected SWNT sheet is dried in air for 8 h, exposed to vacuum for 4 h, exposed to air again for 8 h, washed in deionized (DI) water for 8 h, and then dried in air for 6 h.

different types of CNTs is usually in the range of 4.5–5.5 eV.^[20] To enhance the field emission of CNTs, this value can be irreversibly lowered either by alkali-metal film deposition^[21] or by intercalation.^[22] However, when the resulting material is coated with Cs or intercalated with an electron donor, it is unstable in air due to oxidation of the CNTs.

Here, we show that it is possible to tune the field emission of SWNT cathode sheets by changing the WF through electrochemical double-layer charge injection and subsequent removal of the electrode from the electrolyte. A SWNT sheet was electro-

chemically charged in 1 M NaCl aqueous electrolyte and washed in deionized water for a minute to remove excess salt. The SWNT electrode was then placed in vacuum where the field emission current was measured as a function of applied voltage. Figure 5A shows field emission current versus voltage for a pristine sheet and for negatively and positively charged sheets. Figure 5B shows the current–voltage plot using Fowler–Nordheim coordinates ($\ln(I_{FE}/V^2)$ versus $1/V$). The linear dependence of all three curves in Fowler–Nordheim coordinates suggests that the field emission process can be relatively well described by Fowler–Nordheim theory. However, deviations from the straight-line Fowler–Nordheim behavior appear at high field emission currents for the hole-doped sheet. This effect is not observed for undoped and electron-doped (i.e., n-type) CNT sheets, suggesting that the high-field instability for the hole-doped sheets might arise from field-induced ejection of Cl^- counter-ions.

The changes of field emission as a function of charge injection were consistent with changes of the WF determined independently using Kelvin probe microscopy and Equation 2. However, up to 5% error in the determination of WFs was routinely observed due to CNT discharge during washes with deionized water (see Fig. 4C). In order to confirm the effect of DL charge retention, we measured field emission current versus applied voltage for negatively and positively charged CNT cathodes, and then we exposed these CNT sheet cathodes to air for various time periods and again measured field emission properties. Figure 5C and D shows current–voltage plots for negatively and positively charged CNT cathodes after partial discharge of the CNT cathodes in ambient air. According to the presented data, we may conclude that negatively charged CNT cathodes show almost complete loss of the properties caused by DL charge injection in less than a day; meanwhile, positively charged sheets show a degree of DL charge retention in ambient air for about 3 days.

3. Conclusions

This work shows that high DL charge densities injected into CNT sheets can be largely retained in the absence of contacting electrolyte, which means that the properties arising from DL charge injection can be utilized without the continued use of electrolyte after the charge injection. Since the initial charge injection depends upon having an electrolyte, where ionic charges in the DL of the electrolyte compensate the electronic charges on the CNTs, this may seem impossible; however, precedents of such

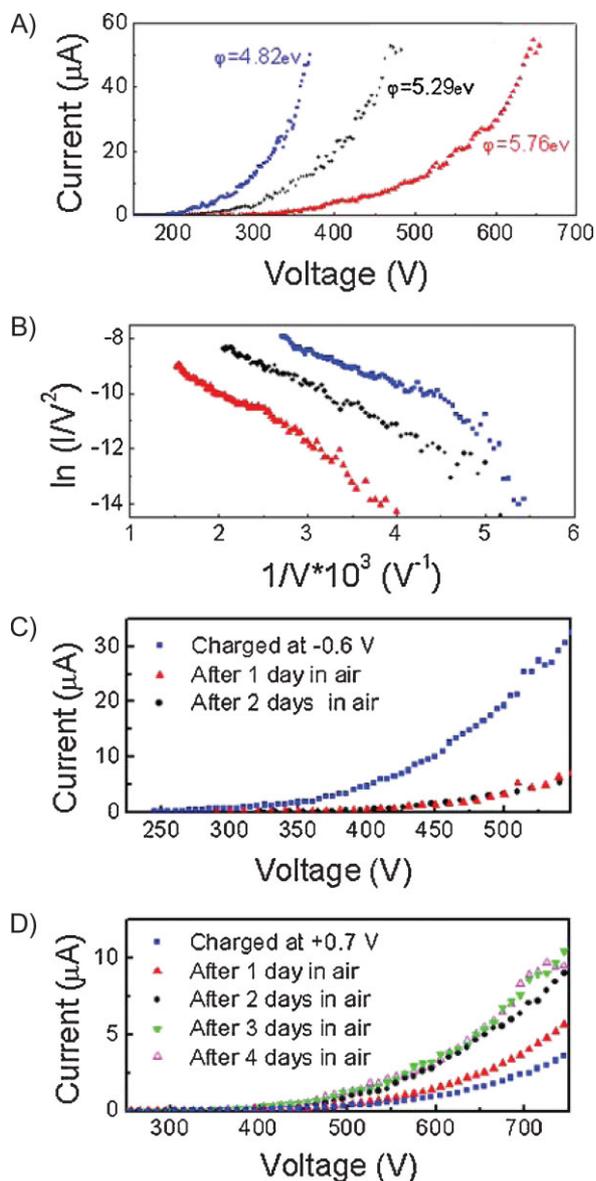


Figure 5. A) Field emission current versus voltage for pristine (■), negatively charged (▲) and positively charged (●) SWNT sheets. B) Fowler–Nordheim plot for the results in A. C) Field emission current versus voltage for a SWNT sheet after it was charged to -0.6 V versus Ag/AgCl and after air exposure for 1 and 2 days. D) Field emission current versus voltage curves for a SWNT sheet after it was charged to $+0.7$ V versus Ag/AgCl and after air exposure for 1–4 days.

phenomena involving the retention of injected charge can be found in early work on charge injection in noble metal sheets and catalyst particles.^[7,8,17]

It is physically possible to retain the effects of DL charge injection after the electrolyte is removed because electrolyte removal does not involve removing the ionic counter-charges to the electronic charges of the CNT. In fact, even after extensive washing and extended dynamic pumping in vacuum, the counter-charges were maintained on the CNT surfaces. Although this aspect is not investigated here, the retention of solvent molecules

(water in the present examples) as solvating species for ions might also be maintained even when long periods of dynamic vacuum are involved. Hence, DL charge injection in CNTs acts like intercalation-based charge injection in CNT bundles (as well as intercalation-based charge injection in solid conducting polymers and graphite); in all cases, maintenance of electrolyte contact is not needed to maintain charge injection. However, the benefit of using DL charge injection (rather than intercalation of a solid material) is the fast rate and highly reversible nature of DL charge injection and the elimination of potentially problematic gross structural changes. To meet the needs of applications, a combination of DL and intercalation-based charge injection may also be possible.

In air, injected DL charge decays, as it does for DL charge injected electrodes in an electrolyte, even in the absence of air. As expected from the results for other charge injected materials, such as conducting polymer and graphitic intercalation complexes, such charge degradation in air is fastest for electron-doped CNT sheets.

This present demonstration, which shows that effects of electrolyte-based DL charge injection can be largely maintained in the absence of contacting electrolyte, is of significant importance to various applications. The characterized tunability of the electrical conductivity and work function, as well as the corresponding tuning of CNT cold electrode field emission are particularly relevant for cold X-ray sources, displays, and other applications. Among a host of other possible applications, a method for providing CNT supercapacitors having an inherently indefinitely long storage time in the charged state is conceptually demonstrated using the observed properties of DL charge injected sheets.

4. Experimental

Charge retention, along with retention of charge-induced property changes, was demonstrated for both SWNT and MWNT sheets. SWNT sheets were made by a filtration method [23] using CNTs produced using the high-pressure carbon monoxide (HiPco) route [24], and then annealed at temperatures up to 950 °C to remove surfactant and other pyrolyzable contaminants. A small piece of SWNT sheet (typically 2–3 cm in length, 0.5 mm in width, 40 μ m in thickness) having four electrical connections for four-probe electrical conductivity measurement, formed the working electrode, and a larger piece of SWNT sheet (approximately ten times that of the working electrode) was adopted as the counter electrode. Aligned transparent MWNT sheets were prepared by solid-state drawing from CNT forests [25]. As-drawn MWNT sheets were placed on glass substrates patterned with four gold strip electrodes and densified using acetone. The alignment of MWNT bundles in the sheets was perpendicular to two of the gold strip electrodes and parallel to the other two.

The electrolyte was an aqueous solution of 1 M NaCl (from Aldrich). Electrochemical experiments were carried out using a CHI 660 Electrochemical Workstation (CH Instruments, TX, USA) or a EG&G PAR 273A potentiostat (AMETEK Princeton Applied Research, TN, USA) with a Ag/AgCl reference electrode. After charging, the sheet electrodes were removed from the electrolyte, washed in deionized water to remove the salt from the surface, and dried in air. Kelvin probe microscopy images were taken using a NT-MDT Solver PRO-M atomic force microscope (NT-MTD, Zelenograd, Moscow). Doped silicon probes were used to take topographic and surface potential profiles.

Field emission properties of the CNT cathodes were studied in a high-vacuum chamber (10^{-7} Torr, 1 Torr = 133.32 Pa) utilizing a Keithley 237 source-measurements unit (Keithley Instruments, Inc., OH, USA). A polished tungsten plate was used as the anode. An interelectrode distance of 300 μ m was used for all experiments.

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