Spring 2010

Preparation of Carbon Nanotube Based Device and its Electrochemistry

Weiling Hsieh
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

---

Recommended Citation

Hsieh, Weiling, "Preparation of Carbon Nanotube Based Device and its Electrochemistry" (2010). *Master's Theses*. 3766.

DOI: <https://doi.org/10.31979/etd.ru4m-3gkm>
https://scholarworks.sjsu.edu/etd_theses/3766

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

PREPARATION OF CARBON NANOTUBE BASED DEVICE AND ITS
ELECTROCHEMISTRY

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Weiling Hsieh

May 2010

© 2010

Weiling Hsieh

ALL RIGHTS RESERVED

The Designated Thesis Committee Approves the Thesis Titled

PREPARATION OF CARBON NANOTUBE BASED DEVICE AND ITS
ELECTROCHEMISTRY

by

Weiling Hsieh

APPROVED FOR THE DEPARTMENT OF CHEMISTRY

SAN JOSE STATE UNIVERSITY

May 2010

Dr. Roger Terrill	Department of Chemistry

Dr. Joseph Pesek	Department of Chemistry

Dr. Daniel Straus	Department of Chemistry

ABSTRACT

PREPARATION OF CARBON NANOTUBE BASED DEVICE AND ITS ELECTROCHEMISTRY

by Weiling Hsieh

The purpose of this research is to develop methodologies for the exploitation of carbon nanotube thin films as chemical and electrochemical sensors. In this study we prepared thin films of carbon nanotubes (CNT) by solution casting methods and then used a novel hybrid electrochemical-conductometric method to measure the CNT film electrical conductivity as a function of electrochemical bias and stimulus. The bias between the CNT film and the contacting electrolyte and the bias between the opposite ends of the CNT film (referred to as K1 and K2) were simultaneously controlled – analogous to a transistor with an electrolyte gate. A promising motif for sensing involved a cyclic voltammetric scan of K1 and K2 but with a 10 mV_{PP}, 1 kHz AC signal summed onto the K2 potential, and thus generating a trans-film potential that was exploited, using a lock-in-amplifier detector, to monitor the CNT film conductance during the CV scan. In order to explore the chemical sensitivity of the CNT films in this setting, we examined blank electrolyte, dissolved ferrocene, and ultra-thin films of novel pyrene-modified iron(II)-terpyridine complex (Fe-tp-py) that binds to the CNT surface. Our principal finding is that this measurement method appears to discriminate between the CNT film trans-conductance and the interfacial electrochemical impedance because the iron(II)-iron(III) transition of the Fe-tp-py induced a clear change in the putative CNT film conductance that is distinct from blank or ferrocene control.

TABLE OF CONTENTS

LIST OF FIGURES	vi
LIST OF TABLES	viii
1. Introduction.....	1
1.1. Carbon Nanotubes	1
1.2. Semiconductor Properties	2
1.3. Carbon Nanotube Field-Effect-Transistor	2
1.4. Cyclic Voltammetry	7
1.5. Iron terpyridine-pyrene Fe(tpySCH ₂ -pyr) ₂ (OTF) ₂	9
1.6. Research Outline	10
2. Experimental	15
2.1. Reagents	15
2.2. Measurements	16
2.3. CNTFET Preparation.....	16
2.3.1. CNT-dispersions.....	16
2.3.2. Substrates.....	17
2.3.3. SWCNT Film Casting.....	17
2.3.4. CNTFET Preparation.....	18
2.4. Bipotentiostatic CNT-FET Characterization Experiments	18
2.4.1. DC Measurements for CNT-FET Quality Control.....	20
2.4.2. AC Measurement	24
3. Results and Discussion.....	28
3.1. CNTFET Device Characteristic.....	28
3.1.1. CNT Films Appearance	28
3.1.2. AFM Topography	30
3.1.3. Electrical Resistance of CNT Films.....	31
3.2. Bipotentiostatic Electrochemical Analysis of CNT-FETs With and Without Fe(tp-py) ₂	35
3.2.1. Device #1 in Ferrocene.....	36
3.2.3. Device #3 in Fe-tp-py	45
3.2.4. Device #4 in Fe-tp-py	48
3.2.5. Other Devices	54
4. Conclusions	54
References.....	56

LIST OF FIGURES

Figure 1. Scheme of back-gate CNTFET.	3
Figure 2. I-V curve of back-gate CNTFET similar to that illustrated above and under three constant gate voltages.	3
Figure 3. Hypothetical source-drain current versus gate voltage curve.....	4
Figure 4. (a) Cyclic potential sweep; (b) Resulting cyclic voltammogram	8
Figure 5. $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$	9
Figure 6. Cyclic voltammograms of $50\ \mu\text{M}$ $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$ at a GC electrode scanned from 0 to 1.3V with $100\ \text{mV s}^{-1}$ scan rates. ¹⁶	10
Figure 7. Experimental setup	13
Figure 8. Equivalent circuit model.....	15
Figure 9. CNTFET preparation.....	19
Figure 10. Five DC experiments setup..	21
Figure 11. Illustration of the experiment 6.	25
Figure 12. Pictures of CNT-films deposited using different dispersions: (1) DMF; (2) SDS; (3) Tween 20.....	29
Figure 13. 10 layers of CNTs-SDS dispersion deposited on substrate. Insert shows the location (dashed line) where picture was taken by a light microscope.....	30
Figure 14. Topographic images obtained inside (1) and outside (2) CNT-rings with scanning area of $8 \times 8\ \mu\text{m}^2$ using non-contact mode AFM..	31
Figure 15. (1) Picture of CNTFET device. (2) Enlarged picture at location indicated in (1).....	34
Figure 16. Four-electrode system used to perform electrical experiments.	36
Figure 17. Results of five DC experiments for device #1 immersed in $0.1\ \text{M}$ LiClO_4 acetonitrile electrolyte and a low mM concentration of ferrocene.	38

Figure 18. Experiment 6 (AC experiment) results for device #1 in (1) Ferrocene and (2) blank electrolyte solution..	39
Figure 19. Numerical derivatives of data in Figure 18-1a (black, ferrocene solution) and 2a (blank electrolyte).....	41
Figure 20. Results of five DC experiments for device #2 immersed in 0.1 M LiClO ₄ acetonitrile electrolyte and with 0.5 mM Fe-tp-py.	42
Figure 21. AC experiment 6 of device #2 in CH ₃ CN (1) and in Fe-tp-py solution (2), respectively.	44
Figure 22. Conductance of device #2 measured in (a) blank 0.1 M LiClO ₄ / CH ₃ CN electrolyte (gray), (b) spiked with Fe-tp-py (bold black), and (c) after washing the device and exchanging electrolyte with blank (black).....	46
Figure 23. Derivative conductance calculated from Figure 22.....	46
Figure 24. I-V curve of device #3 (Tween-20) using Exp 1 in blank solution. Black and gray curves indicate K1 and K2 electrodes, respectively.	47
Figure 25. I-V curve of device #3 using Exp 1 in 0.1 M LiClO ₄ acetonitrile electrolyte and with 0.5 mM Fe-tp-py.	47
Figure 26. Results of five DC experiments for device #4 immersed in 0.1 M LiClO ₄ acetonitrile electrolyte and with 0.5 mM Fe-tp-py..	49
Figure 27. Amplitudes of the Fe(II)→Fe(III) oxidation peak (baseline corrected) versus scan rate for K2 electrode of device #4..	50
Figure 28. Cyclic voltammograms of K2 electrode of device #4 performed in blank (gray), 0.5 mM Fe-tp-py (bold black), and clean CH ₃ CN (black) at 100 mV/s.	51
Figure 29. Conductance of device #4 measured in blank 0.1 M LiClO ₄ / CH ₃ CN electrolyte (gray), same electrolyte but spiked with Fe-tp-py (bold black), and after washing the device and exchanging electrolyte with blank (black).	52
Figure 30. Derivative conductance for device #4 calculated from Figure 29.....	53

LIST OF TABLES

Table 1. Compiled log resistance values for Au-contacted CNT films.	33

1. Introduction

1.1. Carbon Nanotubes

Carbon nanotubes (CNTs) have been investigated widely since they were discovered in 1990 by Iijima.¹ The structure of a carbon nanotube comprises two regions: tube and cap both made of sp² carbons. The tube may be considered as rolled-up graphene sheets that form a hollow cylinder. Both ends of the tube are often capped by a fullerene type hemisphere; the diameter and the length of a carbon nanotube can be up to several nanometers and several millimeters respectively.² There are two groups of carbon nanotubes: single-wall carbon nanotubes (SWCNTs) can be thought of a single sheet of graphene rolled up, and they are usually 1~2 nm in diameter. Multi-wall carbon nanotubes (MWCNTs) can be considered as concentric graphene sheets rolled up with sheet-sheet spacings of 0.34 nm and diameters from 2~25 nm.³ Carbon nanotubes are synthesized by mainly three methods: electrical arch discharge, laser ablation and chemical vapor deposition (CVD).⁴

Carbon nanotubes exhibit some unique and extraordinary physico-chemical and mechanical properties and are very promising for a wide variety of applications. Carbon nanotubes are very strong mechanically with a Young's modulus of about 1000 GPa (diamond = 1220 GPa). Also, they have a very high surface-to-volume ratio. In addition, they tolerate extremely high electrical current densities of nearly 10^{10} A/cm². Single-walled carbon nanotubes can be either metallic or semiconducting, depending on their diameter and exact structure. Mutli-wall carbon nanotubes are always metallic, and they have been studied for the many applications such as nanoscale circuits, flexible and

transparent conductors, supercapacitors, field emitters, and actuators. The semiconducting property and the high surface area (about $1600 \text{ m}^2 \text{ g}^{-1}$) make SWCNTs suitable for transistors and sensors because every atom on the surface is exposed to the surrounding environment.^{2,5}

1.2. Semiconductor Properties

The CNT films in this study are configured similarly to transistors, with the CNT mesh mimicking the semiconducting gate layer of the transistor. The conductivity of a semiconductor is driven by one of the following carriers: electrons and holes. A hole is a missing electron in the valence band, and the electron here refers to unbound or free electrons in the conduction band. For an intrinsic semiconductor, the number of holes always equals the number of electrons, and the intrinsic semiconductor normally has very low conductivity at the room temperature. An intrinsic semiconductor can be doped by other elements, e.g., IIIA or VA elements, and then typically becomes a p-type or n-type semiconductor, respectively. For a p-type semiconductor, the number of holes in the valence band is greater than the number of electrons, so the conductivity of a p-type semiconductor is driven by holes. On the contrary, the majority carrier in the n-type semiconductor is electrons, so the conductivity of an n-type semiconductor is driven by electrons.

1.3. Carbon Nanotube Field-Effect-Transistor

The carbon nanotube field-effect-transistor (CNTFET) is a motif that has been explored recently in the scientific literature and may become one of the more important applications of semiconducting SWCNTs. The scheme of such a back-gate CNTFET is

shown in Figure 1. A carbon nanotube serves as an electron channel that connects two metal electrodes, source and drain, and these three parts are separated from a gate electrode by a dielectric layer, which is usually silicon dioxide.⁶

Figure 1. Scheme of back-gate CNTFET. Carbon nanotube bridges source (S) and drain (D) electrodes. Si back gate is separated from CNT by dielectric layer.

The amount of current flowing through the CNT channel (I_{SD}) depends on the source-drain voltage (V_{SD}) and, for suitable semiconducting CNT structures, the gate voltage (V_G). When the gate voltage is constant, a plot of I_{SD} vs. V_{SD} indicates the conductance of the CNT. Figure 2 shows source-drain current versus source-drain voltage under three constant gate voltages. The curves passing through the origin imply that the device is nearly ohmic, and the conductance (G) of the device can be calculated by the following equation: $G = I / V$, which is the slope of each line near zero V_{SD} .

Figure 2. I-V curve of back-gate CNTFET similar to that illustrated above and under three constant gate voltages. Note that the slope of each I/V curve is equal to the device CNT layer conductance. For the back-gate configuration, large voltages are needed to modulate the CNT conductance.

When the V_{SD} is kept constant, tuning the V_G can change the amount of current flowing through the CNT channel, and thus the conductance of the semiconducting SWCNT changes as well.⁶ Figure 3 shows a typical p-type CNTFET device's characteristic, in which I_{SD} is affected by applying a negative gate voltage.

Figure 3. Hypothetical source-drain current versus gate voltage curve. Under constant V_{SD} , the p-type CNTFET should exhibit elevated conductivity when the gate is negatively biased because this bias favors the migration of positively charged holes into the semiconducting CNT layer.

Since CNTs have very high surface-to-volume ratio, and all the atoms in SWCNTs are exposed to the environment, CNT-based devices have a great potential for sensing applications. The first CNT-based sensor was invented for sensing NO_2 and NH_3 by Kong *et al.*⁷ Since then, CNT-based devices have been studied widely for gas and biomolecular sensing.⁸⁻¹¹

For sensing uses, molecules adsorbed on the CNT surface act to modify the gate potential and hence can alter the conductivity of the CNT. The conductivity of a CNT is proportional to its carrier mobility and carrier density. Therefore, there are two possible reasons that the adsorbed molecules can change the conductivity of SWCNTs.⁶ First, molecules adsorbed on the SWCNTs surface may act as a scattering site and decrease the mobility of carriers in the carbon nanotubes, and hence decrease their conductivity. For

perfect CNTs, the tubular structure constrains electron transport essentially to one-dimension, and the carrier mobility is extremely high. When molecules adsorb on the CNT surface, they perturb the electronic structure of the CNT surface, so the electrons are prone to scattering. This effect is expected to be strongly mediated by charges on the adsorbed molecule that may attract or repel the electrons traveling in the CNT. This mechanism operates on both metallic and semiconducting CNTs. Second, molecules adsorbed on the SWCNTs surface may change the carrier density, and hence change the SWCNTs' conductivity. For example, when an electron transfers from the adsorbed molecules to a p-type CNT, the electron will recombine with a hole in the p-type CNT, and cause the number of holes to decrease. As a result, the carrier density of this p-type CNT is expected to decrease, and hence the conductivity of the CNT is expected to drop.

CNT-based transistors can be fabricated in different ways. First, the semiconducting part can be either a single SWCNT channel or a network of SWCNTs.¹² The single semiconducting SWCNT provides more a precise window of observation for the study of CNTFET devices because their response is mediated exclusively by a single SWCNT; however, this kind of device is extremely difficult to fabricate. The fabrication usually involves growing one SWCNT onto a silicon dioxide gate, and this single-wall carbon nanotube must also be semiconducting, not metallic. As a result, the laborious fabrication limits the utility of such single SWCNT devices for routine use.

Comparatively, the SWCNTs network is far easier to fabricate. One can simply disperse SWCNTs in a proper solution and deposit the SWCNTs dispersion on the silicon dioxide by drop casting. In most SWCNT preparations, some of the SWCNTs are metallic, and

in many cases the ratio of semiconducting to metallic SWCNTs is 2 to 1.¹² This ensures that at least some of the charge transport in a composite film will be controlled by the semiconducting SWCNTs, and therefore the overall device response may still include a substantial contribution from the semiconducting behavior of the transistor devices. Clearly, for devices made from network films of SWCNTs, many factors may influence the total conductivity of the film.

Second, the gate can be formed conventionally with an insulator film and Si or metal contact, or, as is the case in this research, it can be made by contacting the SWCNT film with an electrolyte solution. The idea of an electrolyte gate is, in part, inspired by the possibility that such an approach may enhance the efficiency of coupling gate voltage into SWCNT channels¹³ and in part by the fact that an electrolyte gate may also contain chemicals that interact with the SWCNT and therefore may impart a chemical sensitivity to the gate. When a solid gate insulator is replaced by an electrolyte, the effective distance between the gate electrode and the SWCNTs channels decreases, and hence the gate capacitance increases. For example, the metal-insulator-semiconductor gate structure in a typical field effect transistor utilizes a silicon dioxide (dielectric constant (k) = 4.5) dielectric film that is grown on the Si surface that is ca. 10 nm thick and that is then contacted with metal. In contrast, a semiconductor|electrolyte interface may have a much higher intrinsic capacitance because the electrolyte may have a very high effective dielectric, substantially exceeding that of the pure liquid (e.g. 47 in the case of acetonitrile), and which is separated from the CNT by the Helmholtz layer which is ca. 0.1 nm in thickness. In the case of the liquid electrolyte gate, the electronic coupling to

the CNT is governed by the electrical double layer, and the capacitance of which may be calculated approximately with Gouy-Chapman theory and is expected to be very high (ca. $1 \mu\text{F}\cdot\text{cm}^{-2}$) compared to that achievable with a solid dielectric. The high charge density associated with the large capacitance should improve the tuning efficiency of the gate voltage into SWCNT channels.

1.4. Cyclic Voltammetry

Cyclic Voltammetry (CV) is an important technique for electrochemical study. It is usually used for studying redox behaviors, electron transfer reactions, and adsorption processes. CV employs a three-electrode potentiostat with working, reference and auxiliary electrodes that are immersed into an electrolyte solution which contains analytes of interest. The operation of the potentiostat involves a feedback circuit in which the potential setting is applied to the working electrode using the auxiliary electrode but measured with respect to the reference electrode through which no significant amount of current passes. The potentiostat thus sets the potential of the working electrode relative to the reference electrode and measures the current flowing at the working electrode. Figure 4 shows the cyclic potential sweep and a typical cyclic voltammogram. As shown in Figure 4A, the potentiostat applies a linear potential ramp from E1 to E2 in time, and then sweeps the potential back to E1 with the same scan rate to complete a cyclic sweep. When the potentiostat applies a potential toward a positive direction, the Fermi energy level of the working electrode decreases; then electrons in the analyte will cross the electrode-solution interface and transfer to the working electrode. The analyte is oxidized in this process, and the cyclic voltammogram (Figure 4B) shows

an oxidation peak. Afterward, the potentiostat applies potential in an opposite direction, and the free electrons in the working electrode will transfer to the analyte if the Fermi energy level of the working electrode is high enough. Thus a reduction peak occurs. The detailed shape of the cyclic voltammogram may be related to the concentration and diffusion coefficient of the analyte as well as the kinetics of the electron transfer and the voltage sweep rate.

Figure 4. (a) Cyclic potential sweep; (b) Resulting cyclic voltammogram

In the work described below, the analytes are adsorbed to the CNT film, so diffusion does not come into play, but rather peak currents are related linearly to the amount of adsorbed analyte and the sweep rate. No detailed quantitative analysis of the CV response is undertaken nor is it justified as the CNT films' areas are not exactly known. Rather, the qualitative aspect of CV is correlated to the changes in CNT film conductance in an effort to relate the electrochemical events to CNT conductivity modulation.

1.5. Iron terpyridine-pyrene $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$

$\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$ (Figure 5) is a pyrene-modified iron bis-terpyridine compound. The compound contains two pyrene moieties at opposite ends of the complex. These pyrene moieties are known to adsorb to CNTs.^{14,15} Additionally, this molecule has been studied electrochemically in our lab by Lin¹⁶, and her CV results indicate that $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2^{+2}$ may adsorb to glassy carbon and CNT films from acetonitrile and that it electropolymerizes in response to the $\text{Fe}(\text{II}) \rightarrow \text{Fe}(\text{III})$ oxidation process. Electropolymerization likely occurs via cation radical forms of the pyrenyl groups.

Figure 5. $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$

Figure 6, reproduced from Lin, shows the cyclic voltammogram of $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$ molecules at a GC electrode.¹⁶ The anodic peak potential (E_{PA}) is 0.927 V and the cathodic peak potential (E_{PC}) is 0.886 V. The peak splitting of 41 mV implies that the reaction between $\text{Fe}(\text{II})$ / $\text{Fe}(\text{III})$ is reversible. The relationship between peak current

(i_p) and scan rate indicates that the complex is immobilized onto the electrode surface.

Other experiments showed that the peak current grows with anodic scan numbers beyond reasonable monolayer coverages, which implies that polymerization occurs during the anodic reaction and likely through the pyrene moiety.

Figure 6. Cyclic voltammograms of 50 μM $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$ at a GC electrode scanned from 0 to 1.3V with 100 mV s^{-1} scan rates.¹⁶

The studies detailed in this Thesis also employ $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$ but are focused on the relation between the electrochemical oxidation of Fe(II) to Fe(III) and the resulting conductance changes of the CNTFETs to which they are adsorbed or polymerized.

1.6. Research Outline

As noted above, the goal of this research is to study how the oxidation of Fe(II) to Fe(III) in $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$ films changes the conductance of simple

electrochemical CNTFETs prepared with SWCNT mesh films drop cast onto glass substrates. Specifically, we have developed methods to prepare solution cast films of SWCNTs and then to configure them as CNTFETs that are modified with ultra-thin films of $\text{Fe}(\text{tpySCH}_2\text{-pyr})_2(\text{OTF})_2$. Our results indicate that the Fe(II)/(III) oxidation increases the conductance of the CNTFETs based on the data detailed below.

The first part of this project involved the preparation of CNTFETs. This involved fabricating very thin SWCNT films on glass that had adequate conductivity. We employed a very simple solution drop casting method to make the films using SWCNT dispersions in a variety of solvents. Three different SWCNT dispersions were prepared and deposited onto two differently modified glass substrates. The three dispersions used were SWCNTs dissolved in N, N- dimethylformamide (DMF), aqueous sodium dodecyl sulfate (SDS) and aqueous Tween-20® nonionic surfactant. The substrates were bare and aminopropyltriethoxysilane (APTES) treated glasses. Hexamethyldisilazane treated glass was tested preliminarily but rejected due to apparently extremely poor SWCNT film adhesion.

After the deposition, the formed CNT films were characterized by light microscopy and atomic force microscopy (AFM). The resistance of the CNTFETs was measured in air for acquiring preliminary results of their electrical properties.

The second part was to explore the relationship between the $\text{Fe(II)} \leftrightarrow \text{Fe(III)}$ inter-conversion and the conductance of the CNT layer. This latter measurement constitutes a principal experimental challenge undertaken in this Thesis. The details of this novel measurement are described and revisited in sections below so the following is

an introduction only. Briefly, the measurement of CNT-FET performance as a function of the $\text{Fe(II)} \leftrightarrow \text{Fe(III)}$ inter-conversion was achieved by using a bipotentiostat to simultaneously sweep the gate (i.e. electrochemical) potential while applying a low-amplitude but high-frequency AC source-drain excitation. The resulting AC current was then monitored with a lock-in amplifier and appears to be characteristic of the Fe(II/III) oxidation state as manifested in the CNT layer conductance. In the electrical engineering lexicon, what we have generated is a transistor with a very modest SD conductance modulation and a very leaky gate. The combined DC sweep / AC excitation method helps us to resolve gate leakage (redox currents) from source-drain (through-CNT) currents. From a binary logic device perspective, this accommodation would be regressive at best given the performance of Si-based transistors, but from the chemical sensor perspective, the properties of CNT-based sensors of this type may be well worth the detection effort. The general qualities of the CNT – high surface to volume ratio, stability, ease of surface modification etc. may make them highly desirable as direct electrical transducers of interfacial chemical events.

In the experiments detailed below, a matrix of CNTFET devices was prepared, and each CNTFET was tested in the bipotentiostat configurations as shown in Figure 7. The coupling between gate potential and SD conductance was then systematically investigated with five DC and one AC experiments. In each experiment, a CV scan (i.e. a gate voltage sweep) was performed while the source and drain electrodes were subjected to a bias voltage of some kind. The V_{SD} biases used were: a) sweeps matching the gate sweep, b) 20 mV DC biases and c) 1 kHz, 10 mV_{pp} AC functions. The aggregate of these

approaches allowed us to examine over a range of possible conditions the impact of gate potential on CNT film conductance. By performing the DC experiments both at positive and negative SD bias we could crudely assess the symmetry of the CNT film across the electrolyte-exposed active region. Lastly, the AC experiment was expected to most dramatically differentiate between gate leakage and SD conductance modulation, and specifically that was dependent on the Fe(II)/Fe(III) redox process.

Figure 7. Experimental setup. Network of SWCNTs bridges source (S) and drain (D) electrodes in CNTFET device. Device connects to bipotentiostat. $V_{K1} - V_{K2} = V_{SD}$

Figure 7 shows the experimental setup. The bipotentiostat connects to auxiliary, reference, and the two working electrodes (K1 and K2, also termed source and drain). The bipotentiostat electronics permit the independent control of the potentials of the two working electrodes relative to the solution gate. In the experiments described below, K1

and K2 at times have equal potentials and are sometimes biased with respect to one-another. The bipotentiostat performs scans by sweeping potentials on working electrodes. If there is no bias potential between two working electrodes, there is no driving force for trans-film currents and all current may be ascribed to current that flows through the CNT|electrolyte interface, and this is called gate current (I_G) or gate leakage. When the bipotentiostat applies different potentials on the K1 and K2 electrodes, the resulting trans-film bias voltage (ΔV_{SD}) drives a current from source to drain, and this current is called I_{SD} . The overall setting can be crudely modeled using the equivalent circuit shown in Figure 8. In this circuit the mainly ohmic resistance of the CNT film is indicated as a series of resistances, and the electrochemical impedance of the CNT|electrolyte interface is indicated as a parallel combination of resistance and capacitance. It should be kept in mind that the magnitude of the charge transfer resistances (R_{CT}), i.e. those that lead to gate leakage, are strongly dependent on the presence of redox active entities on the CNT surfaces or in the solution, and the gate potential particularly with respect to its proximity to the $E^{0'}$ value for the redox species in question. This point is crucial to understanding the overall response in experiments described below. The CNT|solution interface is a terminating capacitance (i.e. $R_{CT} \rightarrow \infty$) unless a redox reaction is occurring, in which case this resistance is a complex function that in general finds a minimum value near $E^{0'}$ for the redox species in the solution phase. On the other hand, the source-drain current is the current flowing through the CNT film; therefore, according to Ohm's Law, under a constant potential bias, the amount of current flowing through the CNT films is proportional to the conductance of the CNT film. Hence, to the extent that the SD bias is

orthogonal to the gate bias, either in magnitude or frequency, the bipotentiostatic approach that we employ appears to offer a modality in which we can monitor the CNT film conductance changes during interfacial redox processes occurring there. Some experiments aimed at separating R_{CT} and R_{CNT} will be described below.

Figure 8. Equivalent circuit model. R_s = solution resistance corresponding to the resistance of the electrolyte. R_{CT} = charge transfer resistance and corresponds to the kinetic limitations of the electron transfers between redox molecules in the electrolyte or adsorbed onto the CNTs. C_{dl} = double layer capacitance and is governed by the electrolyte | CNT interface. R_{CNT} = CNT resistance. This important quantity corresponds to the ability of the CNT assembly to transport electrons from source to drain and is modulated by the gate (i.e. RE/CE potential) and the presence of charges adsorbed onto the CNTs.

2. Experimental

2.1. Reagents

Iron terpyridine-pyrene compounds were synthesized by Dr. Daniel Straus and Victoria Johnson at San Jose State University. Single-wall carbon nanotubes (~1.1 nm outside diameter, 5~30 μm length, 90% purity by weight) were purchased from

Cheaptubes.com, and were used as received. Aminopropyltriethoxysilane (APTES), acetonitrile (HPLC grade), lithium perchlorate, toluene, and Tween-20 were purchased from Aldrich (St. Louis, MO). N, N- Dimethylformamide (DMF) and sodium dodecyl sulfate (SDS) were purchased from Mallinckrodt Chemical (Hazelwood, MO).

2.2. Measurements

An Agilent (Palo Alto, CA) 5500 Atomic Force Microscope (AFM) was performed in non-contact mode to investigate the surface of SWNT films. A Hewlett Packard (HP, Palo Alto, CA) 34401A multimeter and an EG&G Princeton Applied Research (Princeton, NJ) Potentiostat Model 273 were used to measure the electrical resistance of SWNT films, where the former showed the resistance values, the latter provided current versus potential (I-V) curves.

Electrochemical measurements were performed by computer-controlled bipotentiostat (Pine Research Instrumentation, Grove City, PA) employing locally written software. The electrochemical system had two working electrodes (source and drain), one auxiliary electrode (platinum wire) and one reference electrode (silver wire). The measurements were performed at room temperature in a home-made silicon cell. In AC experiments, the bipotentiostat was connected to a sum device of local construction, a HP 3324A Synthesized Function Generator as well as a Stanford Research Systems (Sunnyvale, CA) SR530 Lock-in Amplifier.

2.3. CNTFET Preparation

2.3.1. CNT-dispersions

As received SWCNTs were dispersed in three solutions as follows: 2 mg of CNTs

in 10 mL pure DMF, 3.5 mg of CNTs in 10 mL of 1% aqueous SDS, and 3.8 mg of CNTs in 10 mL of 1% aqueous Tween-20. The dispersions were then sonicated for 5 minutes for DMF, and 6 hr for SDS and Tween-20.

The solubility of SWCNTs is governed differently in the different solvents. DMF is a good solvent for SWCNTs. Presumably the amide groups of the DMF can bond to the carboxylate defect sites on the surface of SWCNTs and hence debundle and solvate them adequately.¹⁷ On the other hand, SWCNTs can also be dispersed into aqueous surfactant solutions. We used two common surfactants, SDS and Tween-20. In this case the dispersion is more likely mediated by the hydrophobic interactions between the surfactant and the graphene CNT surface.¹⁸

2.3.2. Substrates

Glass substrates used were cut from microscope slides. The APTES treated substrates were prepared by immersing the clean glass substrates in 2% APTES (in toluene) overnight, and the process was done in a N₂-purged glove bag.

2.3.3. SWCNT Film Casting

To cast thin films of SWCNTs, about 7 μ L of CNT-SDS dispersion was pipetted onto the glass substrates while the substrate was held at ~ 70 °C on the heated surface of a hot plate. This practice increased the rate of solvent evaporation, which was important since in many cases our SWCNT films were made from multiple droplet depositions. The substrates were then rinsed with pure water to remove SDS, and then dried by nitrogen gas; thus a layer of SWCNTs formed on each substrate. This process was repeated until the desired number of layers was achieved.¹⁹ Tween-20 films were cast at

a higher temperature ($\sim 120\text{ }^{\circ}\text{C}$) and substrates were not rinsed between each deposition because the provided temperature was higher than the boiling point of Tween-20 ($100\text{ }^{\circ}\text{C}$), and the surfactant was presumed to be removed by heating alone. The Tween-20 SWCNT films were rinsed following the final SWCNT layer. For casting films from DMF solution, the temperature of the hot plate was $\sim 180\text{ }^{\circ}\text{C}$, which was also higher than the boiling point of DMF ($153\text{ }^{\circ}\text{C}$). After the deposition, the DMF-substrates were heated at $200\text{ }^{\circ}\text{C}$ for 1hr to further remove the residual DMF solvent.

2.3.4. CNTFET Preparation

The preparation of CNTFETs is illustrated in Figure 9. After the deposition of CNTs dispersions (Figure 9-2), a wire (diameter = 0.1 mm) was fixed onto the CNT films as a mask (Figure 9-3). Then the substrates were put into a conventional thermal evaporator (base pressure ca. $1 \times 10^{-5}\text{ T}$) to coat chromium (2 nm) and gold (50 nm) layers (Figure 9-4). After the gold layers were formed, two copper wires were connected to the gold layers by silver painting for future connection to the bipotentiostat, as shown in Figure 9-5. Then a layer of insulating green paint was sprayed on the substrates (Figure 9-6), and the substrates were put in an oven and heated overnight. Finally, the wire mask was removed, thus allowing some portions of CNT films to be exposed to the environments (Figure 9-7).

2.4. Bipotentiostatic CNT-FET Characterization Experiments

Since our approach to electrochemical CNT-FET characterization is a novel one, and coupled to a novel CNT-FET construction, it is important to thoroughly describe the

Figure 9. CNTFET preparation. Substrate (1) was coated a layer of CNT film (2). Then a metal wire was used as mask (3), and substrate was then coated with gold layer (4). Two copper wires connected to gold layer (5), and then an insulating layer was sprayed on the device (6). CNT-FET was prepared after taking off the mask (7).

experiments used to validate the CNT-FETs and their performance in terms of sensitivity to the Fe(II/III) transition. Therefore, in the following section validation experiments and their results will be described in a general way, but deferring a detailed description of the key AC results pertaining to the CNTFET performance to the results section.

Opposite ends of the CNT-films were connected to the bipotentiostat K1 and K2 working electrode leads via the copper wires as illustrated in Figure 9-5. Each CNTFET

device was then subjected to the five DC (Fig. 10) and one AC (Fig. 11) experiments as indicated below.

2.4.1. DC Measurements for CNT-FET Quality Control

The five DC experiments are illustrated in Figure 10. Experiments 1 and 2 (Fig. 10-1 and 2) involved sweeping one or the other working electrodes between 0 and 1 V while the opposite one is kept at zero volts. This experiment generates large V_{SD} biases that are intended to characterize the current-voltage response of the CNT film. Because this experiment was done in the electrochemical setting, i.e., with electrolyte contact to the CNT film, some electrochemical background current naturally contributes to the overall current – or in other words, some gate leakage is summed into the I/V curve. The responses were used to screen the devices for asymmetry and non-ohmic behavior, i.e., to evaluate whether for any reason the opposite biases result in substantially different responses or if the I/V curves deviated greatly from linearity. In our thinking, asymmetry would most likely result from large inhomogeneity in the CNT film from one side to the other, leading to large asymmetry in the gate leakage, or possibly from Schottky or other rectifying interfaces elsewhere in the structure, e.g., between the metal coating and the CNT film. Both of these effects would detract from subsequent analyses, but fortunately none of the CNTFETs investigated exhibited dramatic asymmetry in these experiments. As noted, the resulting I-V curves characterize I_{SD} versus V_{SD} and show the average electrical conductance of the CNT film. Inevitably in this setting the gate potential will vary with respect to position across the CNT film with one end held at 0 V versus reference and the other end sweeping from 0 to 1 V and back. An ideal device with zero

Figure 10. Five DC experiments setup. K1 and K2 electrode potential indicated by black and grey color, respectively. In (1) and (2), one of the electrodes sweeps while the other is kept zero. In (3), both electrodes sweep identically. In (4) and (5), two electrodes sweep at the same time scale with constant bias voltage of 20 mV.

contribution from gate current is expected to show an ohmic response; in which case the response would be two straight lines representing K1 and K2 electrodes and each of which will cross the origin. All CNT films exhibited slightly upwardly curving responses in these experiments. This is not surprising given the large current densities that may have been operative within the CNT films. Junctions between CNTs or CNTs themselves might be expected to deviate slightly from ohmic behavior under large biases because potentially high power densities may exist within the devices. Since in subsequent experiments the SD biases were kept small (i.e. ± 20 mV for Experiments 4 and 5 or ± 10 mV for Experiment 6) and well within the Ohmic region of the above, no further investigation of this phenomenon was undertaken.

In experiment 3 (Fig. 10-3), two working electrodes are swept identically in time and with zero SD bias. Because there is zero SD bias, there is, to a good approximation, zero SD current. Therefore, the resulting I-V curves consisted entirely of “gate leakage” current – that is, current that flows from solution redox entities into the CNT film and thus were typical cyclic voltammograms. Since there were two working electrodes being swept, the resulting cyclic voltammogram had two current responses. A perfect device would have two identical working electrodes, corresponding roughly to the left and right sides of the CNT film, and hence two current responses should be identical inasmuch as the CNT films are perfectly uniform. The results displayed in Figures 17-3(a), 20-3(a) and 25-3(a) were typical of the broad range of films tested and showed sometimes substantial quantitative differences between K1 and K2, but qualitatively the curves were always similar. This suggests that the CNT films had significant non-uniformity within

the insulated gap. We believe that although these results indicate that our structures were not ideal, they nonetheless retain the qualities needed for the analyses below – namely good SD conductivity and reasonable film uniformity.

Experiments 4 and 5 (Figure 10-4 and 10-5) involve two working electrodes (source and drain) being swept together but maintaining a small, i.e. 20 mV, DC potential difference between them. In experiment 4, $\Delta V(K2-K1)$ was +20 mV and in experiment 5, it was -20 mV. In other words, the gate voltage V_G is swept while maintaining a constant source-drain bias voltage (V_{SD}) of 20 mV. In the limit of zero gate current, i.e. zero electrochemical current, it would be possible to derive the CNT film conductance versus gate potential by subtracting the source and drain currents. However, none of the results indicated that the gate currents were small enough to neglect. Another way to think of this experiment is that it sweeps the average gate bias while holding a small SD bias which attempts to separate SD and gate currents; however, because the source and drain are at different potentials and therefore experience different amounts of gate current leakage, the Δi_{SD} contains contributions from both SD and gate currents. The success of this approach depends on the magnitude of the difference between the gate currents corresponding to the 20 mV and the source-drain currents generated by the 20 mV bias. In the case where substantial gate currents do flow, the gate currents of one of the two working electrodes should slightly lead the other. Consequently, the source-drain current (I_{SD}) that is obtained by subtracting two current values should have a component that is roughly equal to a derivative of the gate current as manifests in a dynamic I_{SD} vs. V_G scan. Significant, asymmetry was observed when comparing experiments 4 and 5 results

across a range of devices. For example, in Figures 17, 19 and 25, the differences between panels illustrate that it is generally not equivalent to have K2 positive of K1 and vice-versa. In Figure 17 4b and 5b, the oxidation of ferrocene, a reversible diffusing redox probe, illustrates that experiments 4b and 5b generate a quasi-derivative to the experiment 3a or conventional CV response. This result is eminently logical given the small ΔV maintained during the sweep, which upon subtraction yields a small Δi versus voltage response. This experiment also shows that the DC bias imposed does not significantly separate the gate response from the source-drain response. If this were the case, then the K2-K1 response would *not* show a large sensitivity to the ferrocene oxidation and reduction since this process *only* generates gate current, i.e. the ferrocene oxidation only changes R_{CT} . Consequently, more attention will be paid to experiment 6 results since these appear to generate a response more reflective of R_{CNT} (*vide infra*).

2.4.2. AC Measurement

Experiment 6 is illustrated in Figure 11. In this experiment, the source electrode (K1) is swept with a ramp (E1) in the same way as described in Figure 10-3. This ramp is then summed with a 10 mV_{PP}, 1 kHz AC signal and applied to the drain electrode (K2).

K1 DC signals: The current response from the K1 electrode is then monitored at the output of the potentiostat and digitally signal averaged over many cycles of the kHz signal for each recorded point in such a way as to generate a DC average response. The resulting DC current response from the K1 electrode is recorded and plotted as I versus V_g . **K2 AC signals:** The potential applied to K2 potential fluctuates around the K1 potential at a high frequency (Figure 11a) and thus has a hybrid DC and AC excitation.

Figure 11. Illustration of the experiment 6. Black and grey color represents the potential, current, and the response of K1 and K2 electrode, respectively. Relationship of E1 and E2 (Fig. A) provides a constant source-drain bias potential

If one wishes to express it in this way, one can consider the two signals as differing greatly in frequency and amplitude: the DC ramp is at about 0.05 Hz and the AC excitation at 1000 Hz; the “DC” ramp has an amplitude of about 1 V and the AC excitation is at 0.01 V. Examined in this way, one can see that at any moment there is an AC bias between K1 and K2 of ± 10 mV, but that averaged over any given millisecond, a single AC cycle, this bias is zero. In experiment 6, the K2 current is converted to a voltage by the bipotentiostat and this signal goes into the input of the lock-in-amplifier (LIA). Since the LIA is referenced to the same function generator that generates the SD bias, it measures exclusively the 1 kHz AC component of the K2 current originating from the AC signal imposed onto K2 and flowing both to K1 and to some extent into the solution or ‘gate’. The LIA also rejects all other frequencies including the low-frequency DC signals from the slow potential ramp. It is hypothesized that since the SD bias is oscillating at 1 kHz, the LIA response may therefore be considered approximately proportional to the SD currents. This neglects currents that flow through solution from K1 to K2, so experiments 1-6 are essentially phenomenological tests of the hypothesis. The following approximate definition (which neglects currents that may flow through the gate) of the CNT conductance is used and allows us to experimentally test the suitability of the approximation:

$$G_{CNT} = \frac{i_{SD}}{\Delta V_{SD}} \approx G \equiv \frac{i_{AC}}{V_{AC}} = \frac{V_{K2} g_{K2} g_{LIA}}{10mV(pp)}$$

G_{CNT} = putative CNT film conductance (amps/volt)

G = overall AC conductance

V_{K2} = bipotentiostat current signal (volts)

g_{K2} = potentiostat current gain (amps/volt)

g_{LIA} = lock-in gain

A test of this relation was made in the ferrocene control experiments detailed in the AC experiments in Figure 18 and 19. In this experiment the K1 DC response (Figure 18-1b) is nearly identical to the conventional CV response seen in Figure 17-3a. This confirms that the current recorded on the DC channel of the source electrode K1 is simply the current flowing through the CNT-solution interface, i.e. through R_{CT} , as a function of V_G , the gate potential.¹ Since in this experiment K1 and K2 potentials are swept simultaneously, the resulting DC and AC responses share common time and DC potential axes. Accordingly the AC response is plotted against the DC “gate” potential. Figure 18-1a illustrates that the AC response is only slightly responsive to the ferrocene oxidation, which indicates a degree of success in validating the approximation that AC response may be considered to be proportional to G_{CNT} , and orthogonal to R_{CT} . This is of course in contrast to the differential DC experiments 4 and 5, wherein Δi signals contained a very large derivative-like signal remnant from the ferrocene oxidation waves and hence clearly did not separate SD and gate currents effectively. However, the AC channel of experiment 6 had only a small oscillation characteristic of the CV response. This oscillation is more clearly evident in Figure 19 which shows the derivative of G_{CNT} with respect to gate potential dG_{CNT} / dV_G . This derivative format appears to defeat the

---

¹ As noted above, sweeping the potential across $E^{0'}$ generates an oscillation in R_{CT} wherein R_{CT} is a minimum near $E^{0'}$. Thus, the plot of i versus V_g resembles a typical cyclic voltammogram of the K1 electrode

original intent of establishing an orthogonal measurement of G_{CNT} in the presence of changing R_{CT} , but appears to play an interesting role in elucidating surface redox reactions as we will describe below. We must note that the qualitative rejection of the cyclic voltammetric signal by the AC measurement does not prove that the AC signal is exclusively comprised of CNT-based source drain currents, i.e. it does not prove that $i_{\text{AC}} \propto G_{\text{CNT}}$, but it is entirely consistent with this hypothesis.

3. Results and Discussion

3.1. CNTFET Device Characteristic

3.1.1. CNT Films Appearance

Figure 12 shows pictures of the CNT-films deposited using DMF, SDS and Tween-20 dispersions with different numbers of depositions on bare glass substrates. The CNT-DMF dispersion formed the thickest and most uniform CNT-films. CNT-SDS dispersions tended to yield films with most of the CNTs on the periphery and thus presented CNT-rings and had low uniformity. CNT films made from Tween-20 dispersions can barely be seen even after 15 depositions. The relative amount of CNTs deposited from these solutions was a result of the solubility of the CNTs in each solution. The low solubility of CNTs in general is a function of their tendency to aggregate which makes them insoluble in most solutions. DMF and aqueous SDS are two commonly used solvents that effectively de-bundle and dissolve most CNTs, and thus they were chosen in this research. The reason that Tween-20 was chosen in this research is that its boiling point is only 100 °C. We hypothesized that CNT films deposited from Tween-20 solutions could be made and the Tween-20 surfactant removed by simply heating the

films above the Tween-20 boiling point. In this case, the substrate would not need to be rinsed with pure water following each deposition to remove the residual surfactant, and thus more CNTs would remain on the substrate. Tween-20, however, did not disperse CNTs well; the color of CNTs-Tween-20 dispersion was light; on the contrary, CNTs-DMF and CNTs-SDS dispersions were a dark black color. Also, CNT films deposited from Tween-20 dispersions still required rinsing with water after the last deposition step because residual Tween-20 was still evident on the substrates.

Figure 12. Pictures of CNT-films deposited using different dispersions: (1) DMF; (2) SDS; (3) Tween 20.

The CNT film formed from 10 depositions of SDS dispersed CNT was observed under a light microscope to see if substantial amounts of CNTs remained inside the CNT-rings. Figure 13 is an optical micrograph of this film. The diagram in the upper left indicates the location where the image was taken. The picture shows that most of the CNTs were on the periphery, and that very little CNT material seems to exist inside the rings. This film was then further studied using atomic force microscopy.

Figure 13. 10 layers of CNTs-SDS dispersion deposited on substrate. Insert shows the location (dashed line) where picture was taken by a light microscope.

3.1.2. AFM Topography

The 10x SDS film imaged in Figure 13 was further studied using non-contact mode AFM. The topographic images shown were obtained from: a) (Figure 14-1) an apparently clean area inside the ring of deposited CNTs (i.e. not on one of the thick rings) and b) (Figure 14-2) well outside the ring to show the response from clean glass. This latter image serves as a clean flat glass reference surface. The scanning areas were $8 \times 8 \mu\text{m}^2$. The root mean square roughness of two areas was measured by the AFM software. Two main differences were observed in these images. Firstly, the RMS roughness obtained from inside the ring is 25.5 nm, and is about 64 times greater than that obtained outside the ring, just 0.4 nm. Secondly, the height scale of the AFM images is also greatly different - 244.8 nm inside and just 2.5 nm outside on the reference glass. The images were ambiguous as to the source of the roughness – no CNT bundles could be clearly resolved, but given the large differences in surface texture, it is safe to say that there was a substantial amount of material, likely CNTs, inside the ring-like periphery of the film.

Figure 14. Topographic images obtained inside (1) and outside (2) CNT-rings with scanning area of $8 \times 8 \mu\text{m}^2$ using non-contact mode AFM. Root mean square roughness inside and outside the ring is 25.5 nm and 0.4 nm, respectively.

3.1.3. Electrical Resistance of CNT Films

The resistance of each Au-contacted CNT film was measured with a high-impedance multi-meter. The results provide a preliminary evaluation of each device. Table 1 shows the log-resistances of each CNT film prepared for this study. Overall, CNT films made from DMF dispersions had the lowest resistances, followed by SDS and Tween-20 dispersions. The devices made from Tween-20 CNT dispersions presented higher and unstable resistances and in the case of the 5-layer films were beyond the resistance capability of the measuring instrument. This may have been caused by an insufficient amount of CNTs deposited on the substrate, or too much residual surfactant left on the substrate. The devices were made on both bare glass and APTES treated glass. The careful APTES modification leaves a monolayer of silane-coupled aminopropyl groups on the glass surface electrostatically interact with the numerous carboxyl defect groups known to exist on the surface of SWCNTs. Hence, APTES treated glass is

believed to enhance the adhesion and uniformity of SWCNT films cast onto glass from solution, for example in studies wherein APTES treated glass was used to fabricate carbon nanotube transistors.¹⁹⁻²² In Table 1, the logarithm of each device resistance is recorded because of the wide range of values observed for the film resistance. The difference in magnitude between the bare and APTES treated glass is shown in the rightmost column in order to illustrate the impact that this treatment has on the film resistances. For most SDS and Tween-20 dispersions, APTES appears to lower the device resistances relative to bare glass. This seems to be especially important for Tween-20 dispersions which yield films that are 3 to 5 orders of magnitude more conductive on APTES treated glass. DMF dispersions showed the opposite behavior, and on average yielded films that were about one order of magnitude more resistive on APTES treated glass substrates. The substantial amount of scatter in overall magnitude makes it difficult to generalize regarding which dispersions may yield the most conductive films. The Tween-20 APTES device used for electrochemical experiments, though originally quite conductive, evidently failed shortly after immersion in solution however, suggesting that these films may tend to lose continuity when immersed in water or acetonitrile. Also, direct comparison between SDS and DMF-deposited films is not really appropriate either because the SDS-deposited films listed in Table had been modified as follows. The edges of the film, i.e. the thick peripheral ring of CNT deposit, had been removed where it would otherwise have bridged the gap between the Au contacts. This was done to improve the uniformity of the CNT film within the measured gap in this case and was an innovation undertaken later in the experimental process and

Table 1. Compiled log resistance values for Au-contacted CNT films.

Glass	Dispersion	Layers	Log (R/ Ω)	Glass	Dispersion	Layers	Log (R/ Ω)	Difference
Bare	SDS	5	6.46	APTES	SDS	5	1.70	-4.76
		10	3.70			10 ^(d)	3.65	-0.05
		15	3.69			15	3.08	-0.61
		20	2.90			20	2.95	0.05
	DMF	1	2.48		DMF	1	3.98	1.50
		3	1.85			3	3.08	1.23
		5	2.00			5	3.11	1.11
		10 ^(b)	2.48			10	2.11	-0.36
		15	2.11			15 ^(a)	2.95	0.84
	Tween 20	5	>7.5		Tween 20	5	1.48	
		10	6.36			10 ^(c)	3.15	-3.22
		15	6.54			15	1.60	-4.94

Tables on left and right contrast results for bare and APTES treated glass. Logarithm of resistance for each slide was calculated, and difference is shown in last column. (a), (b), (c), and (d) are device #1, #2, #3, and #4 used for experiments shown in Figure 16, 19, 23, and 25, respectively. Note that for SDS deposited films, CNT peripheral ring material was removed before Au contact coating to reduce current flow through this thick layer.

so was not done for the other films.

The resistance of each slide was measured again after the green paint was applied over the wire mask. The results in general were that the CNT film resistances tended to increase by 2~3 times after the green paint was applied. This may have been caused by paint that partially coated the CNT film in the gap and in this region tended to separate the CNTs and interrupt the films' electrical continuity. Figure 15 -1 shows a CNTFET device, and Figure 15-2 shows an enlarged picture at the location indicated in Figure 15-1. The picture shows how the green paint directly contacts a portion of the CNT film underneath the wire.

Figure 15. (1) Picture of CNTFET device. (2) Enlarged picture at location indicated in (1). Black color indicates CNTs, and gray color indicates insulting green painting.

It is believed that the insulating green paint penetrated into the CNT-films and reduced the CNT-CNT connectivity in this region thereby increasing the resistance

locally (i.e. along the contact edge). On the other hand, if insufficient green paint is applied, gold will be exposed to the environment and will interfere with later electrochemical experiments. In addition, if paint dries on the surface of the CNT-films in the electrode gap, it will decrease the exposed area of CNT-films, and thus decrease the sensing ability of the CNTFET. In this research, the green paint insulating step cannot be controlled well, so other materials may be needed to replace it in the future.

3.2. Bipotentiostatic Electrochemical Analysis of CNT-FETs With and Without Fe(tp-py)₂

Electrochemical experiments were performed in 0.1 M LiClO₄/acetonitrile electrolyte and using a bipotentiostat. The bipotentiostat connects to four electrodes: reference, auxiliary, and two working electrodes. The reference and auxiliary electrodes are immersed in the electrolyte solution. The two working electrodes (K1 and K2) connect to source and drain, as shown in Figure 16. The K1 and K2 working electrodes connect to opposite ends of the CNT-films exposed to the electrolyte solution.

The CNTFETs were connected to the bipotentiostat for electrical measurements. Each device was tested using the five DC and one AC experiments described above. Experiments were done in four different settings: i. blank – i.e. with clean electrolyte only; ii. diffusing redox molecule control – in this case ferrocene² (Fc) added to the electrolyte; iii. experiments wherein 0.5 mM Fe-tp-py⁺² was in solution; and iv. experiments following the above wherein the Fe-tp-py⁺² that has irreversibly adsorbed or

---

² Experiments were performed over the potential range wherein ferrocene undergoes a reversible one-electron redox reaction and shows two obvious cyclic voltammetric peaks at about E°' ~ 0.5 V. Ferrocene was chosen because it undergoes a facile and reversible one-electron oxidation at a moderate potential and is not expected to interact to any substantial degree with the CNT's. Ferrocene is a standard in electrochemical analyses.

Figure 16. Four-electrode system used to perform electrical experiments. Reference and Auxiliary immerse into electrolyte solution. Two ends of exposed CNT-films represent two working electrodes.

polymerized onto the CNT mesh is interrogated without Fe-tp-py^{+2} in the solution. This last experiment is simply conducted following iii. where potential cycling with 0.5 mM Fe-tp-py^{+2} in solution but following an exchange of electrolyte.

3.2.1. Device #1 in Ferrocene

Figure 17 shows the results of device #1 measured in 0.1 M $\text{LiClO}_4/\text{acetonitrile}$ electrolyte and a low mM concentration of ferrocene with a scan rate of 100 mV/s. Device #1 was made using 15 serial castings from CNT-DMF dispersion and deposited on an APTES treated glass substrate. Figures 17-1 and 17-2 show the results of experiment 1 and 2. The first two DC experiments are used to examine the electrical performance of the device and also the symmetry of the two working electrodes. Figures

17-1 and 17-2 show that the conductance of the CNT film is symmetric, yielding a conductance of 105 μS , and 106 μS for the two configurations respectively. Figure 17-3 (experiment 3) shows a typical cyclic voltammogram of Fc, in which the oxidation peak is at 0.56 V and the reduction peak is at 0.38 V vs. Ag QRE. The two working electrodes still show excellent symmetry since the difference between currents at the two electrodes is less than 3 μA (17-3b). Figures 17-4 and 17-5 show experiments 4 and 5, in which two electrodes were swept while maintaining a bias potential of 20 mV. Figures 17-4b and 17-5b show the differences in the current response between K1 and K2. The K2-K1 (or K1-K2) plots are reminiscent of derivative cyclic voltammograms. This result means that such a DC bias sweep experiment may actually exaggerate the influence of redox currents when plotted as difference currents. This experiment is repeated for all films below, but according to this initial result it is believed that it is unlikely to be representative of exclusively source-drain currents (I_{SD}) and hence is not the appropriate mode for monitoring FET-like modulations in CNT film behavior.

Following the five DC experiments, the device was then measured using the AC experiment (Exp 6) in which the bipotentiostat was connected to an AC function generator and a lock-in-amplifier as described above. These results are shown in Figure 18. The 18-1b, black, lower plots show the DC response from the K1 electrode, and the gray upper plots (18-1a) show the AC response from the LIA coupled to the K2 electrode. Figure 18-1b is clearly similar to a typical cyclic voltammogram illustrating that the AC perturbation is not strongly coupled into this response. Figure 18-1a has only a small oscillation tracking the substantial DC voltammetric peak, indicating that

Figure 17. Results of five DC experiments for device #1 immersed in 0.1 M LiClO₄ acetonitrile electrolyte and a low mM concentration of ferrocene. Device #1: CNTs-DMF dispersion deposited on APTES treated glass (15 serial drop castings). Each figure is current vs. potential. Black and gray colors indicate K1 and K2 electrodes, respectively. 3(A), 4(A), and 5(A) are the original results obtained from bipotentiostat, and 3(B), 4(B), and 5(B) are the electrical current differences ($i_{K1} - i_{K2}$) between source and drain. Experiments 1 and 2 show acceptable symmetry, and gate leakage is seen as a small electrochemical current superimposed on the sloping source-drain current. In experiment 3, K1 and K2 almost overlap, and the difference is less than 3 μ A. In experiments 4 and 5, electrodes K1 and K2 have a +20 mV bias respectively. The difference currents show a predominantly derivative-like cyclic voltammogram and thus fail to enhance source-drain contributions relative to gate currents.

Figure 18. Experiment 6 (AC experiment) results for device #1 in (1) Ferrocene and (2) blank electrolyte solution. Gray lines (a) are the lock-in amplifier AC response from the K2 electrode. Black lines (b) are the DC current response of the K1 electrode; These responses are intended to reflect the average CNT film conductance as a function of gate voltage and hence their ordinate scale is labeled conductance and is in arbitrary units. Arrows indicate the corresponding voltage scan directions.

whatever electrical pathway this current is following, it is not strongly related to the redox current taking place at the CNT|solution interface. The blank response in Figure 18-2 is made to a slightly more extreme potential limit (1.3 V vs Ag QRE) and shows a monotonic curve to higher conductance in the AC response (18-2a) and an unremarkable DC blank response in 18-2b. The 18-1a response is in strong support of the hypothesis

that the AC response may be a way to measure the CNT film electrical conductance independently of the interfacial redox processes that may be occurring at the CNT|solution interface. In other words, this experiment appears to separate the current flowing through the solution-CNT interface (in the DC part b) and the conductance of the CNT-films (in the AC part a).

Figure 19 shows a derivative plot of the outgoing sweeps in Figure 18-1a (black) and 18-2a (gray). In this representation the similarities between these two experiments are clear. The small oscillation due to the Ferrocene oxidation is now clearly resolved as a derivative peak in the black trace, but aside from this oscillation, the overall shape of the derivative curves are quite similar for blank and Fc controls. We do not suggest that this derivative format is a better metric of the CNT film electrical properties – in fact it seems to reverse this and to re-elucidate the redox processes at the film.

3.2.2. Device #2 in Fe-tp-py

Figure 20 shows results of five DC experiments for device #2 measured in 0.1 M LiClO₄/acetonitrile electrolyte and with 0.5 mM Fe-tp-py. Device #2 was made using ten serial castings from CNTs-DMF dispersion deposited onto a bare glass substrate. Both Figures 20-1 and 20-2 show substantial curvature, indicating that the device is not Ohmic, but instead is quite a bit more highly conductive at high bias and with an average conductance of about 220 μ S, and differ from K1 to K2 by about $\pm 10\%$ hence that two working electrodes are not identical. Note that the overall average conductance of this device is approximately twice that of Device #1 measured above. The cyclic voltammograms, and their differences obtained from Figures 20-3a, 4a and 5a show scant

Figure 19. Numerical derivatives of data in Figure 18-1a (black, ferrocene solution) and 2a (blank electrolyte). In this presentation, the gate leakage current due to ferrocene oxidation near 0.4V is strongly enhanced and the overall response is clearly a superposition of the source-drain curve (gray) and the ferrocene-mediated gate response (black).

evidence of Fe-tp-py^{+2} despite its presence in the solution at 0.5 mM throughout. Only a slight remnant of a reduction peak seems to appear as a dip below the axis as the scans reverse and cross the abscissa near 1.0 V. No new conclusions are drawn from the difference currents in 20-3b,4b and 5b, and they still appear to be unsuitable for obtaining the currents flowing through the CNT-films.

Figure 21 shows the AC mode results for device #2 measured first in blank 0.1 M

Figure 20. Results of five DC experiments for device #2 immersed in 0.1 M LiClO₄ acetonitrile electrolyte and with 0.5 mM Fe-tp-py. Device #2: CNTs-DMF dispersion deposited on bare glass (10 castings). Each figure is current vs. potential. Black and gray colors indicate K1 and K2 electrodes, respectively. 3(A), 4(A), and 5(A) are the original results obtained from bipotentiostat, and 3(B), 4(B), and 5(B) are the electrical current differences ($i_{K1} - i_{K2}$) between source and drain. Experiments 1 and 2 show good symmetry between two electrodes. Experiment 3 shows that K1 and K2 do not exactly overlap, especially at high gate potential. Experiments 4 and 5 show substantial asymmetry in responses of K1 and K2 resulting from the 20 mV biases illustrating a large impact due to redox-related gate currents as was seen above.

LiClO₄ acetonitrile (21-1, left) and with the addition of 0.5 mM Fe-tp-py solution (21-2, right). The DC responses from 21-1b (blank) and 21-2b (Fe-tp-py) are not highly informative. The main difference is the cathodic peak that projects below the voltage abscissa on the return sweep in 21-2b and which may indicate the reduction of some Fe-tp-py³⁺ species generated on the anodic vertex. This is consistent with some interfacial Fe-tp-py(2+/3+) redox activity but is by no means conclusive. The AC responses from 21-1a (blank) and 21-2a (Fe-tp-py) are somewhat compelling however.

Interestingly, the overall magnitude of the AC response is lowered in the presence of the Fe-tp-py (2a) relative to blank. The blank response has a broad peak shape and a small oscillation near 1.0V, but the Fe-tp-py (2a) response has a clear and reversible sigmoid that traces out a possible redox transition centered on about 0.9 V vs. Ag QRE. Of course, this AC mode is not particularly sensitive to redox activity; hence this sigmoidal signature in 2a may therefore be a reflection of this redox process as it manifests in the CNT film conductance. This implies that the oxidation of Fe(II) in Fe-tp-py molecules may increase the conductance of the CNT-films.

Following these measurements in CH₃CN / Fe-tp-py solution, device #2 was washed with clean CH₃CN and then measured in fresh electrolyte solution with no Fe-tp-py molecules. Figure 22 shows the AC conductance sweeps of device #2 measured in blank electrolyte (a, gray), Fe-tp-py (b, bold black), and in blank electrolyte following a rinse (c, black). The result clearly shows that the bold black curve and the black curve have a nearly identical sigmoidal pattern. This implies that the Fe-tp-py molecules were immobilized on the surface of CNT-films, and that this immobilized Fe-tp-py²⁺, when

Figure 21. AC experiment 6 of device #2 in CH_3CN (1) and in Fe-tp-py solution (2), respectively. Black color (B) represents DC response (current) of K1 electrodes; Gray color (A) represents AC response from K2 electrodes.

oxidized to Fe-tp-py³⁺ elevated the CNT film conductance, and that this was not coupled to solution phase Fe-tp-py²⁺, nor was it coupled to a thick film of Fe-tp-py²⁺ that would otherwise have yielded significant Faradaic currents in the DC voltammetric responses in Figure 20. It is similarly compelling to ascribe the shift in conductance seen in 22b and c to an Fe(2+/3+) oxidation when we examine the derivative conductance plotted in Figure 23. These peaks are clearly reminiscent of voltammetric oxidations. The integral response therefore would be proportional to the amount of the Fe(3+) form. The above is strong circumstantial evidence that in these cases the AC response is tracking some component of the CNT film conductance that is proportional to the Fe(3+) content of a putative Fe-tp-py adsorbed film.

3.2.3. Device #3 in Fe-tp-py

A series of experiments were performed on device #3. Device #3 was made using ten serial castings from a CNT-Tween dispersion and on APTES treated glass. This device exhibited a strong asymmetry in experiment 1 in blank electrolyte. It survived experiments one through six in blank electrolyte, but the current response from K2 was lost upon introduction of 0.5 mM Fe-tp-py solution. Figures 24 and 25 show the I-V curve of device #3 measured using DC experiment 1 in blank and 0.5 mM Fe-tp-py solution, respectively. The black curve and gray curve represent the K1 and K2 electrodes, respectively. In Figure 25, the K1 electrode seems to show a pair of redox peaks in the cyclic voltammogram, but by that time the K2 electrode had become completely discontinuous. This device had a high initial resistance (~9 μ S) and the loss of the K2 response was suggestive of a possible loss of CNTs to solution which may be

Figure 22. Conductance of device #2 measured in (a) blank 0.1 M $\text{LiClO}_4 / \text{CH}_3\text{CN}$ electrolyte (gray), (b) spiked with Fe-tp-py (bold black), and (c) after washing the device and exchanging electrolyte with blank (black). Note that gate voltages were swept from 0 to 1.3 V at 0.1 V/s.

Figure 23. Derivative conductance calculated from Figure 22. Gray scan shows irregular blank baseline. Bold black and black scans illustrate persistence of response in Fe-tp-py free electrolyte.

Figure 24. I-V curve of device #3 (Tween-20) using Exp 1 in blank solution. Black and gray curves indicate K1 and K2 electrodes, respectively.

Figure 25. I-V curve of device #3 using Exp 1 in 0.1 M LiClO_4 acetonitrile electrolyte and with 0.5 mM Fe-tp-py. Black and gray curves represent K1 and K2 electrodes. Continuity with electrode K2 was lost for this film indicating possible solubility of Tween-CNT dispersions.

idiosyncratic of the Tween dispersions which tended to yield low amounts of CNT material on the substrates. Therefore, Tween 20 dispersions appear to be unsuitable for generating CNT films.

3.2.4. Device #4 in Fe-tp-py

Device #4 was made using ten serial castings from a CNTs-SDS dispersion deposited on APTES treated glass. Figure 26 shows DC results for device #4 performed in 0.5 mM Fe-tp-py solution and with a scan rate of 100 mV/s. The plots of I_{SD} vs. V_{SD} in Figures 26-1 and 26-2 show upward curvature and a small amount of hysteresis – therefore, the device is not perfectly ohmic. The conductances of the K1 and K2 electrodes are approximately 140 and 120 μS , respectively.

In the DC voltammetric experiments (Figures 26-3 to 26-5), the K2 electrode clearly shows two redox couple peaks near 0.25 V and more clearly near 0.9 V vs Ag QRE. The latter, clearer couple is attributed to the Fe-tp-py^{2+/3+} oxidation. The K1 electrode, however, shows only a hint of the Fe-tp-py peaks. This large difference therefore actually exaggerates the redox response in the difference plots 3b, 4b and 5b. The redox peak splitting, ΔE_p , was calculated from the K2 electrode response in Figure 26-3 to be 87 mV. This splitting is larger than that observed for Fe-tp-py films adsorbed to glassy carbon (Figure 6, ca. 45 mV). This implies that the response is either due to diffusing species or that there is a significant kinetic barrier to the electron transfer.

To better understand this response, a scan rate study was performed in 0.5 mM Fe-tp-py solution and at $\nu = 100, 200, 300, 500$, and 1000 mV/s. Figure 27 shows

Figure 26. Results of five DC experiments for device #4 immersed in 0.1 M LiClO₄ acetonitrile electrolyte and with 0.5 mM Fe-tp-py. Device #4: CNTs-SDS dispersion deposited on APTES treated glass for 10 times. Black and gray colors indicate K1 and K2 electrodes, respectively. 3(A), 4(A), and 5(A) are the original results obtained from bipotentiostat, and 3(B), 4(B), and 5(B) is the difference between two electrodes. Experiment 1 and 2 show good symmetry between two electrodes. Experiment 3 shows that K2 electrode had clearly evident Fe-tp-py peaks, but K1 did not. Experiments 4 and 5 reflect this substantial asymmetry and still prominently exhibit the K2 redox peaks. For this reason the differences (B) do not isolate CNT-FET conductance.

that $i_p = 0.0663 v^{0.75}$ where i_p = baseline subtracted peak voltammetric current and v = scan rate / mV/s. In theory and according to the *Randles-Sevcik equation*, if redox analyte is transported to the electrode surface by diffusion, then the peak current will be proportional to $v^{0.5}$. On the other hand, the *Laviron equation* predicts that if an analyte is immobilized on the surface of the working electrode, then i_p will be proportional to scan rate (v^1). The result obtained from Figure 27, $i_p \propto v^{0.75}$ implies that the response may either be due to a mixture of both adsorbed and diffusing species, or possibly due to a purely adsorbed component but one that presented a substantial kinetic barrier to redox reaction. For comparison, a purely adsorbed film of Fe-tp-py on glassy carbon yielded a

Figure 27. Amplitudes of the Fe(II)→Fe(III) oxidation peak (baseline corrected) versus scan rate for K2 electrode of device #4. Experiments were performed in 0.5 mM Fe-tp-py solution.

similar plot wherein i_p was shown to be proportional to $v^{1.00}$ indicating that at least under those conditions it is possible kinetically for an Fe-tp-py film to behave ideally according to the Laviron equation.¹⁶ Since a diffusing species cannot give an exponent greater than 0.5, it must be assumed that at least some of the response from Device #4 was due to immobilized Fe-tp-py.

Figure 28 contrasts the experiment 3 cyclic voltammetric response of the K2 electrode first in CH₃CN as blank, then with 0.5 mM of Fe-tp-py solution, and finally following a rinse and in clean CH₃CN electrolyte.

Figure 28. Cyclic voltammograms of K2 electrode of device #4 performed in blank (gray), 0.5 mM Fe-tp-py (bold black), and clean CH₃CN (black) at 100 mV/s.

The blank curve (Figure 28, gray line) exhibited no peaks near 0.9V, but the Fe-tp-py solution (bold black line) gave a strong 0.9V peak. The fact that a persistent and clear

0.9V peak persisted following the rinse and exchange for blank electrolyte (Figure 28, thin black curve) is strong evidence that the Fe-tp-py molecules were immobilized on the surface of the CNT-film. This result is clearly consistent with those obtained previously on glassy carbon. In this case it was shown that redox cycling of the Fe-tp-py^{2+/3+} at glassy carbon led to an immobilized film of Fe-tp-py that retained a clear voltammetric response.¹⁶

Figure 29 shows the corresponding AC responses of device #4 in blank (gray), 0.5 mM Fe-tp-py solution (bold black), and then in clean CH₃CN electrolyte (black) after the device was rinsed.

Figure 29. Conductance of device #4 measured in blank 0.1 M LiClO₄ / CH₃CN electrolyte (gray), same electrolyte but spiked with Fe-tp-py (bold black), and after washing the device and exchanging electrolyte with blank (black). Note that gate voltages were swept from 0 to 1.3 V at 0.1 V/s.

The blank response gray line is a gentle S-curve and at about 20% lower average conductance than the latter two. Both the Fe-tp-py and the rinsed film responses have a similar overall shape but with an abrupt rise in conductance centered near 0.9 V and very similar to the responses observed for device #2 (Figure 22). Again, the sigmoidal rise that appears upon introduction of Fe-tp-py solution is retained following a rinse and replacement of clean electrolyte. Also similarly, the derivative responses have a compelling resemblance to a redox peak as illustrated in Figure 30 at the corresponding gate voltages of 0.88 and 0.95 V. The gray blank curve does exhibit a broad downward going peak near 1.06 V.

Figure 30. Derivative conductance for device #4 calculated from Figure 29. Gray scan shows blank baseline. Bold black and black scans illustrate persistence of response in Fe-tp-py free electrolyte

3.2.5. Other Devices

In addition to those described above, six additional devices were measured in 0.5 mM Fe-tp-py solution as well; two of them were made using the CNT-SDS dispersion, and the others using a CNT-DMF dispersion. None of these devices showed Fe-tp-py peaks similar to those obtained in Figure 26-3 to 26-5. The reason for this inconsistency is unclear but it seems likely that it may be related to the morphology of the CNT films.

4. Conclusions

In this research, rudimentary electrolyte contacted CNT-FETs were fabricated, modified with a pyrenyl iron terpyridine complex, and analyzed using a novel AC coupled bipotentiostatic method. A modest increase in the CNT film conductance was observed as a result of the electrochemical oxidation of adsorbed Fe-tp-py films. The fact that the Fe(II)→Fe(III) transition correlated to a rise in CNT film conductivity is consistent with a n-type semiconductor contribution that gains electron density because the additional positive charge on the surface could potentially attract additional electron density into the CNT film analogously to how a positive gate bias on a n-type depletion-mode FET channel will turn on the SD channel. The AC experiment appears to have successfully separated the current that goes through the solution-CNT interface from that goes through the CNT-films. Both the devices made by CNTs-SDS and CNTs-DMF dispersions showed a clear increase of conductance when the Fe(II) of Fe-tp-py was oxidized to Fe(III) and a clear decrease of conductance when Fe(III) was reduced to Fe(II). The derivative plots of Δ conductance versus corresponding gate voltage showed obvious peaks at the electrochemical potential corresponding to the Fe(II-III) oxidation

and lend further qualitative support to the hypothesis that the CNT film conductivity is positively impacted by the oxidation of the Fe-tp-py film from Fe^{2+} to Fe^{3+} . This approach is a promising avenue for the design of CNT-based sensors and points to the fact that redox-coupled CNT film conductance modulation may be a possible sensing modality.

Clearly however the CNT-FETs fabrication needs to be improved. The resistivity of the drop cast films varied dramatically from experiment-to-experiment and the optical and topographic images obtained from AFM showed substantial inhomogeneity in the layers. Also, many devices showed poor symmetry between two working electrodes. This is probably a result of uneven CNT film distributions. Of the nine CNT-FET devices fabricated, only one exhibited clear voltammetric redox peaks when in contact with a 0.5 mM Fe-tp-py solution, though at least two additional Fe-tp-py redox films could be identified based on their signature modulation of the AC conductance response.

Many of these problems may be related to a highly uneven CNT film morphology. This may be partly caused by residual surfactant which was not washed out well, residual metal catalyst remaining in the CNTs samples as supplied, or a poor casting method. Clearly the adoption of a spin-casting method would be an improvement. Also, the crude aerosol paint insulator was not controlled well, and in many cases the paint appeared to penetrate the CNT-films and substantially decrease their conductance. An alternate insulator layer such as vapor deposited SiO_2 would obviate the problem of paint flowing under the mask. The combination of smoother CNT films and no compromise to

the CNT-FET conductivity due to paint intrusion should significantly improve the device performance.

References

1. S.Iijima Helical microtubules of graphitic carbon. *Nature*. **1991**, 354, 56.
2. Hoenlein, W.; Kreupl, F.; Duesberg, G. S.; Graham, A. P.; Liebau, M.; Seidel, R.; Unger, E. Carbon nanotubes for microelectronics: status and future prospects. *Mater. Sci. Eng. C*. **2003**, 23, 663-669.
3. Zhao, Q.; Gan, Z.; Zhuang, Q. Electrochemical Sensors Based on Carbon Nanotubes. *Electroanal*. **2002**, 14, 1609-1613.
4. Rivas, G. A.; Rubianes, M. D.; Rodrigues, M. C.; Ferreyra, N. F.; Luque, G. L.; Pedano, M. L.; Miscoria, S. A.; Parrado, C. Carbon nanotubes for electrochemical biosensing. *Talanta*. **2007**, 74, 291-307.
5. Merkoci, A.; Pumera, M.; Llopis, X.; Perez, B.; Valle, M.; Alegret, S. New materials for electrochemical sensing VI: Carbon nanotubes. *Trend. Anal. Chem*. **2005**, 24, 826-838.
6. Gruner, G. Carbon nanotube transistors for biosensing applications. *Anal. Bioanal. Chem*. **2006**, 384, 322-335.
7. Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. Nanotube Molecular Wires as Chemical Sensors. *Science*. **2000**, 287, 622-625.
8. Besteman, K.; Lee, J.; Wiertz, F. G. M.; Heering, H. A.; Dekker, C. Enzyme-Coated Carbon Nanotubes as Single-Molecule Biosensors. *Nano. Lett*. **2003**, 3, 727-730.
9. Curreli, M.; Zhang, R.; Ishikawa, F. N.; Chang, H.; Cote, R. J.; Zhou, C.; Thompson, M. E. Real-Time, Label-Free Detection of Biological Entities Using Nanowire-Based FETs. *IEEE T NANOTECHNOL* **2008**, 7 (6), 651-667.
10. Villamizar, R. A.; Maroto, A.; Ruis, F. X.; Inza, I.; Figueras, M. J. Fast detection of Salmonella Infantis with carbon nanotube field effect transistors. *BIOSENS BIOELECTRON* **2008**, 24, 279-283.
11. Star, A.; Gabriel, J. P.; Bradley, K.; Gruner, G. Electronic Detection of Specific Protein Binding Using Nanotube FET Devices. *Nano. Lett*. **2003**, 3, 459-463.

12. Kim, S. N.; Rusling, J. F.; Papadimitrakopoulos, F. Carbon Nanotubes for Electronic and Electrochemical Detection of Biomolecules. *Adv. Mater.* **2007**, *19*, 3214-3228.
13. Chen, C.; Zhang, Y. Review on Optimization Methods of Carbon Nanotube Field-Effect Transistors. *The Open Nanoscience Journal* **2007**, *1*, 13-18.
14. Dai, H. Carbon Nanotubes: Synthesis, Integration, and Properties. *Acc. Chem. Res.* **2002**, *35*, 1035-1044.
15. Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. Noncovalent Sidewall Functionalization of Single-Walled Carbon Nanotubes for Protein Immobilization. *J. Am. Chem. Soc.* **2010**, *123*, 3838-3839.
16. Lin, H. Electrochemistry of Pyrenyl Iron Terpyridines on Glassy Carbon, Gold and CNT. Master San Jose State University, 2008.
17. Lee, K.; Lee, J.; Dong, K.; Ju, B. Gas sensing properties of single-wall carbon nanotubes dispersed with dimethylformamide. *Sensor. Actuator. B.* **2008**, *135*, 214-218.
18. Rastogi, R.; Kaushal, R.; Tripathi, S. K.; Sharma, A. L.; Kaur, I.; Bharadwaj, L. M. Comparative study of carbon nanotube dispersion using surfactants. *J. Colloid. Interf. Sci.* **2008**, *328*, 421-428.
19. Lay, D. M.; Novak, J. P.; Snow, E. S. Simple Route to Large-Scale Ordered Arrays of Liquid-Deposited Carbon Nanotubes. *Nano. Lett.* **2004**, *4*, 603-606.
20. Auvray, S.; Derycke, V.; Goffman, M.; Filoramo, A.; Jost, O.; Bourgoin, J. Chemical Optimization of Self-Assembled Carbon Nanotube Transistors. *Nano. Lett.* **2005**, *5*, 451-455.
21. LeMieux, M. C.; Roberts, M.; Barman, S.; Jin, Y. W.; Kim, J. M.; Bao, Z. Self-Sorted, Aligned Nanotube Networks for Thin-Film Transistors. *Science*. **2008**, *321*, 101-104.
22. Ko, H.; Tsukruk, V. V. Liquid-Crystalline Processing of Highly Oriented Carbon Nanotube Arrays for Thin-Film Transistors. *Nano. Lett.* **2006**, *6*, 1443-1448.