Development of Carbon Nanotube Field-Effect-Transistor (CNT-FET) biosensor with a point-of-care device for water quality analysis in terms of water-borne bacteria.

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Abstract

This study aspires to create an unconventional and alternative device capable of analysing water in a point-of-care perspective. The main objective is to assess, using a personal computer, the amount of water-borne bacteria present in a given water sample. The base device is a field-effect-transistor in which the channel is a single walled carbon-nanotube network, this network shows a p-type like semiconductor behaviour.
Each device was manufactured in five steps. Firstly, a microfabrication step in which the basis of the device was assembled. Secondly, a dielectrophoretic deposition step in which the carbon-nanotube network was deposited. Thirdly, a functionalization step in which a specific antibody is adsorbed on to the carbon-nanotubes. Fourthly, *E. Coli* bacteria from the string DH5α were applied in different but known concentrations to different devices. Lastly, the characterization of these devices was done by obtaining the Id-Vd and Id-Vg curves of the field-effect-transistors using a semiconductor parameter analyser.
After the data was collected and analysed a calibration curve was obtained, capable of correlating the drain-current of the transistor with the *E. Coli* concentration, this curve is essential to the proper working of the point-of-care device.
This study overviews the principles of working of the single walled carbon-nanotube field-effect-transistors as well as methods to improve their reproducibility of results. The point-of-care device is a rudimentary picoameter, capable of reading the devices drain-currents (pA), this picoameter is connected to a computer via an Arduino board and a MATLAB software. No paragraph breaks.
Keywords: SWCNT, FET, CNT-FET, *E. Coli*, Schottky Barriers, Direct charge transfer, CNT dispersions, dielectrophoretic deposition of CNTs.

1. Introduction

The potential of water to transport microbial pathogens to great numbers of people, causing subsequent illness, is well documented in countries at all levels of economic development (1,2). This study presents a way to fabricate and calibrate a point of care biosensor capable of detecting *E. coli* bacteria in water. Over the past decade, electrical detection of biological species using novel nanostructure-based devices has attracted significant attention for chemical, genomics, biomedical diagnostics, and environmental applications(3). The use of nanostructured devices in biological sensors in place of conventional sensing technologies has advantages of high sensitivity, low energy consumption and potentially highly miniaturized integration. Therefore, in this study the biosensor used is a carbon nanotube field effect transistor. A common CNT-FET biosensor includes the structure of a three-electrode transistor. The drain and source electrodes are interdigitated and are connected by a semiconductor channel, which in this case is a carbon nanotube random network, furthermore the gate electrode modulates conductance of this channel (46). The structure of a typical CNT-FET device is illustrated in Figure 1.

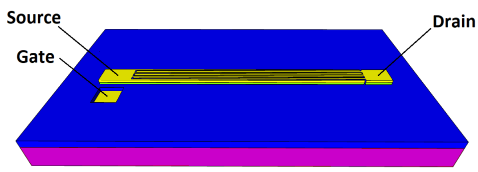

Figure 1 - Picture illustrating a back-gated CNT-FET for bio sensing application. In between the two interdigitated electrodes (Source and Drain) lies a network CNTs. The

square pad is the gate electrode which connects to the Si layer below in order to apply the gate voltage through-out the channel. The FETs used in this study were provided by INESC-MN and have the same appearance as the one shown.

2. Principles of Working

As stated before carbon nanotube field effect transistors have the typical structure display of a three-electrode transistor. The drain and source electrodes are connected by the semiconductor channel, which in this case is a carbon nanotube random network, furthermore the gate electrode modulates conductance of this channel (4,5,7). There is not yet a consensus about the primary method of conductance change within the channel, two different mechanisms to modulate the current within the channel have been proposed in literature (5,8,9).

2.1. Schottky barrier modification

Schottky Barriers are generally formed when a semiconductor is brought into direct contact with a metal due to the mismatch of the work functions of the metal and the CNT (5,10,11). A charge transfer occurs at the interface which results in the bending of the conduction and valence bands. Such bending generates a charge depletion (potential barrier) that opposes further charge transfer, Figure 2. This potential barrier (Schottky Barrier) can be modulated by the Gate Voltage of the device or by adsorption of molecules on top of the CNT-network that locally change the electric field thus changing the the Schottky barriers width, allowing or prohibiting current flow between Source and Drain.

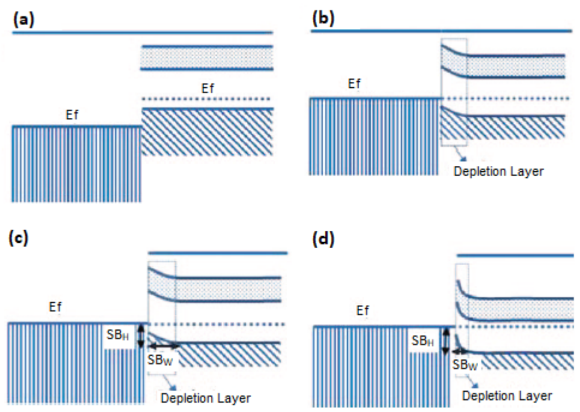

Figure 2 - Scheme illustrating the formation of Schottky barriers (SB). The CNT has been schematized as a p-type since oxygen from the environment can dope the CNT with holes. In this case, the Fermi level of the CNT is close to the valence band. When the CNT and the metal contact are brought together (a), the Fermi level of both materials will try to equilibrate by flowing charge carriers between them (b). That results in a bending of the bands forming a depletion layer which gives place to the generation of Schottky barriers that inhibit the charge carrier transport.

The width of the Schottky barrier can be modulated by the gate voltage as one can see in (c) and (d), the height of the barrier in more dependant on temperature.(5)

2.2. Direct charge transfer to CNT network

Direct charge transfer to CNT network refers to the charge carrier recombination or formation phenomena that occurs when a certain molecule adsorbs on a semiconductor with a certain charge carrier density. When this adsorption occurs on the CNT-network (p-type) with electron-donating molecules a recombination occurs (electrons from the adsorbed molecule recombine with the holes of the semiconductor). When this adsorption occurs on the CNT-network (p-type) with electron-withdrawing molecules a formation of charge carriers within the semiconductor happens (free electrons from the CNT-network are withdrawn and new holes are formed). Certain molecules have been proven to interact weakly with minimal charge transfer to CNTs while others have demonstrated noticeable charge transfer (7). All atoms of single-walled carbon nanotubes (SWCNTs) reside at the surface which means that direct-charge transfer can be a major form of conductance change within the channel of the CNT-FET.

3. Characterization and Results

In this study a total of 69 CNT-FETs were manufactured, these sensors were tested using 7 different *E. Coli* concentrations, Table 1.

Table 1 - *E. Coli* concentrations used and number of CNT-FETs allocated to each concentration.

Allocated CNT-FETs	2 μL Volume
9	200 UFC/2 μL
10	100 UFC/2 μL
10	50 UFC/2 μL
10	25 UFC/2 μL
10	12,5 UFC/2 μL
10	6 UFC/2 μL
10	3 UFC/2 μL

The CNT-FETs used in this study were characterized using an Agilent 4155C Semiconductor Parameter Analyser machine at the University of Aveiro. This machine does a DC sweep from -5V to 5V on the Gate Voltage for a certain bias Source-Drain Voltage, the Source-Drain Volatges used were 0V, 0.5V, 1V, 1.5V and 2V. Each measurement records the drain-current in the CNT-FET for a certain combination of Vds and Vg. The end result of the characterization of the sensors was the scatter plot in Figure 3.

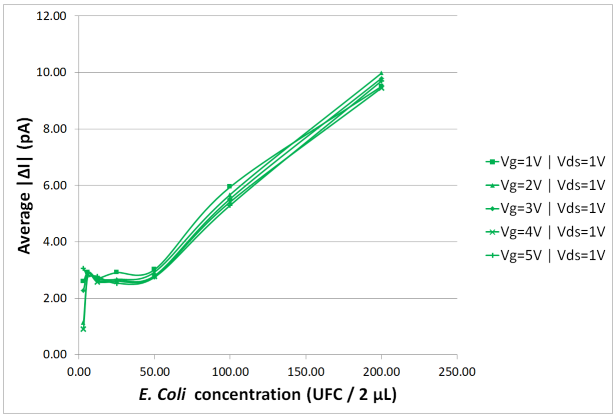

Figure 3 - Scatter plot using a Source-Drain Voltage of 1.5V with Gate voltages between 1V and 5V.

Since the average | ΔI | values for the lower concentrations showed an irregular behaviour. One decided to construct the calibration curve of the sensors using only the higher concentrations, from 50 UFC / 2μL to 200 UFC / 2μL. The calibartion curve obtained after a Log normalization followed by a simple linear regression is shown in Figure 4. The equation which describes this calibration curve was further implemented in a point-of-care device.

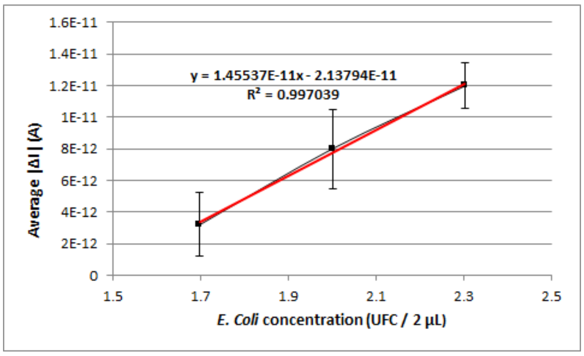

Figure 4 - Scatter-plot of the normalized values, the linear regression, calibration curve equation and R2 test value.

The calibration curve equation.

$$[E.Coli] = 10 \frac{(\mid \Delta I \mid + 2.13794 * 10^{-11})}{1.45537 * 10^{-11}}$$

4. Device Implementation

The point-of-care device can divided into two parts. A signal amplification circuit part, which used a Op-Amp with an extremely low input bias current and a 10GΩ resistor. And, a Arduino board and MATLAB part. In the first part (signal amplifying circuit) the Drain-currents of the CNT-FET were converted to a voltage and amplified to the mV range. In the second part (Arduino board and MATLAB) a simple script was written to measure the output voltage of the amplifying circuit using an arduino board, this script also included the calibration curve equation thus allowing one to obtain the *E. Coli* concentration as a function of the read values with the Arduino board.

5. Conclusions

CNT-FETs are, in fact, very powerful tools for biosensing applications, and, in this study it was concluded that CNT-FETs can be used to assess water quality in a point-of-care perspective, detecting *E. Coli* concentrations as low as 50 bacteria in 2μL of water.

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References

1. Pandey PK, Kass PH, Soupir ML, Biswas S, Singh VP. Contamination of water resources by pathogenic bacteria. 2014;1–16.

2. Taylor P, Bradford SA, Morales VL, Zhang W, Ronald W, Packman AI, et al. Critical Reviews in Environmental Science and Technology Transport and Fate of Microbial Pathogens in Agricultural Settings. 2013;(December 2014):37–41.

3. Hu P, Zhang J, Li L, Wang Z, Estrela P. Carbon Nanostructure-Based Field-Effect Transistors for Label-Free Chemical/Biological Sensors. 2010;5133–59.

4. Molaie M. Field effect transistor nanobiosensors : State-of-the-art and key challenges as point of care testing devices. 2016;3(2):69–82.

5. Pujadó MP. Carbon Nanotubes as Platforms for Biosensors with Electrochemical and Electronic Transduction.

6. Yang D, Wang L, Zhao Q, Li S. Fabrication Of Single-Walled Carbon Nanotubes (SWNTs) Field-Effect Transistor (FET) Biosensor. 2010;(Bmei):1482–5.

7. Ali Javey JK. Carbon Nanotube Electronics.

8. Heller I, Janssens AM, Ma J, Minot ED, Lemay SG, Dekker C. Identifying the Mechanism of Biosensing with Carbon Nanotube Transistors. 2008;28–32.

9. Chen J, Klinke C, Afzali A, Avouris P, Heights Y. Air-Stable Chemical Doping of Carbon Nanotube Transistors. 2003;10606(2000):137–8.

10. Jiménez D, Cartoixà X, Miranda E, Suñé J, Chaves F a, Roche S. A simple drain current model for Schottky-barrier carbon nanotube field effect transistors. Nanotechnology. 2007;18(41):419001.

11. Dang T, Anghel L, Leveugle R. CNTFET basics and simulation. Int Conf Des Test Integr Syst Nanoscale Technol 2006 DTIS 2006 [Internet]. 2006;28–33. Available from: http://ieeexplore.ieee.org/xpl/login.jsp?tp=&arnumber=1708731&url=http://ieeexplore.ieee.org/iel5/11202/36064/01708731

1. Pandey PK, Kass PH, Soupir ML, Biswas S, Singh VP. Contamination of water resources by pathogenic bacteria. 2014;1–16.

2. Taylor P, Bradford SA, Morales VL, Zhang W, Ronald W, Packman AI, et al. Critical Reviews in Environmental Science and Technology Transport and Fate of Microbial Pathogens in Agricultural Settings. 2013;(December 2014):37–41.

3. Hu P, Zhang J, Li L, Wang Z, Estrela P. Carbon Nanostructure-Based Field-Effect Transistors for Label-Free Chemical/Biological Sensors. 2010;5133–59.

4. Molaie M. Field effect transistor nanobiosensors : State-of-the-art and key challenges

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5. Pujadó MP. Carbon Nanotubes as Platforms for Biosensors with Electrochemical and Electronic Transduction.

6. Yang D, Wang L, Zhao Q, Li S. Fabrication Of Single-Walled Carbon Nanotubes (SWNTs) Field-Effect Transistor (FET) Biosensor. 2010;(Bmei):1482–5.

7. Ali Javey JK. Carbon Nanotube Electronics.

8. Heller I, Janssens AM, Ma J, Minot ED, Lemay SG, Dekker C. Identifying the Mechanism of Biosensing with Carbon Nanotube Transistors. 2008;28–32.

9. Chen J, Klinke C, Afzali A, Avouris P, Heights Y. Air-Stable Chemical Doping of Carbon Nanotube Transistors. 2003;10606(2000):137–8.

10. Jiménez D, Cartoixà X, Miranda E, Suñé J, Chaves F a, Roche S. A simple drain current model for Schottky-barrier carbon nanotube field effect transistors. Nanotechnology. 2007;18(41):419001.

11. Dang T, Anghel L, Leveugle R. CNTFET basics and simulation. Int Conf Des Test Integr Syst Nanoscale Technol 2006 DTIS 2006 [Internet]. 2006;28–33. Available from: http://ieeexplore.ieee.org/xpl/login.jsp?tp=&arnumber=1708731&url=http://ieeexplore.ieee.org/iel5/11202/36064/01708731

1. Pandey PK, Kass PH, Soupir ML, Biswas S, Singh VP. Contamination of water resources by pathogenic bacteria. 2014;1–16.

2. Taylor P, Bradford SA, Morales VL, Zhang W, Ronald W, Packman AI, et al. Critical Reviews in Environmental Science and Technology Transport and Fate of Microbial Pathogens in Agricultural Settings. 2013;(December 2014):37–41.

3. Hu P, Zhang J, Li L, Wang Z, Estrela P. Carbon Nanostructure-Based Field-Effect Transistors for Label-Free Chemical/Biological Sensors. 2010;5133–59.

4. Molaie M. Field effect transistor nanobiosensors : State-of-the-art and key challenges as point of care testing devices. 2016;3(2):69–82.

5. Pujadó MP. Carbon Nanotubes as Platforms for Biosensors with Electrochemical and Electronic Transduction.

6. Yang D, Wang L, Zhao Q, Li S. Fabrication Of Single-Walled Carbon Nanotubes (SWNTs) Field-Effect Transistor (FET) Biosensor. 2010;(Bmei):1482–5.

7. Ali Javey JK. Carbon Nanotube Electronics.

8. Heller I, Janssens AM, Ma J, Minot ED, Lemay SG, Dekker C. Identifying the Mechanism of Biosensing with Carbon Nanotube Transistors. 2008;28–32.

9. Chen J, Klinke C, Afzali A, Avouris P, Heights Y. Air-Stable Chemical Doping of

Carbon Nanotube Transistors. 2003;10606(2000):137–8.

10. Jiménez D, Cartoixà X, Miranda E, Suñé J, Chaves F a, Roche S. A simple drain current model for Schottky-barrier carbon nanotube field effect transistors. Nanotechnology. 2007;18(41):419001.

11. Dang T, Anghel L, Leveugle R. CNTFET basics and simulation. Int Conf Des Test Integr Syst Nanoscale Technol 2006 DTIS 2006 [Internet]. 2006;28–33. Available from: http://ieeexplore.ieee.org/xpl/login.jsp?tp=&arnumber=1708731&url=http://ieeexplore.ieee.org/iel5/11202/36064/01708731