SENSING AND ENERGY HARVESTING OF FLUIDIC FLOW BY
INAS NANOWIRES, CARBON NANOTUBES AND GRAPHENE

by

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Submitted in partial fulfillment of the requirements
For the degree of Doctor of Philosophy

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*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedication

To my husband, Zheng Zhou, and my parents, Meili Li, and Zehua Chen
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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Professor J. Iwan D. Alexander. He is an excellent educator. I could not have finished my Ph.D. without his guidance, encouragement, patience and support. I also would like to thank Professor Xuan P. A. Gao for letting me work in his lab. I learned a great deal from him about my project topics as well as research methods. Professor Ozan Akkus’s guidance on new ideas of my project and generous help during the experiment are appreciated. I would also like to acknowledge Professors Alexis Abramson, Liming Dai, Philip Feng, and Christian A. Zorman for the advice, wonderful collaboration and helpful discussion on my research topics. Thanks are also due to Professors Joseph M. Prahl, James S. T’ien, and Jaikrishnan R. Kadambi for their mentoring and guidance during my first several years of my Ph.D. study.

I would also like to thank all the past and present labmates for their collaboration, support, and friendship: Yng-ru Chen, Simeng Li, Xinyou Ke, Dong Liang, Richard Qiu, Yuan Tian, Chris Robert, Haixia Yu, Cheehuei Lee, Feng Du, Guodong Li, Sukrit Sucharitakul, Andrew Barnes, Chun Wong, Zhenhua Wang, Nicholas Goble, Chung Wo, David Buckmaster, Wenyi Liu, and Keliang He. Special thanks to Dong Liang, Feng Du and Chris Robert for their mentorship during my first several years in graduate school. I would also like to thank Dr. Ina Martin in the Materials for Opto/electronics Research and Education (MORE) Center at Case Western Reserve University, for her generous help and assistances.
Finally, I would like to thank my wonderful husband, Zheng Zhou, for his love, dedication, understanding, friendship and companionship; and I thank my parents for their love, inspiration, and guidance. I would not have come so far without their priceless support and love.

Last but not least, the generous financial and technical support from the Department of Energy through EE-0000275 and the Great Lakes Energy Institute are gratefully acknowledged.
Sensing and Energy Harvesting of Fluidic Flow by InAs Nanowires, Carbon Nanotubes and Graphene

Abstract

by

YING CHEN

Energy harvesting using nanoscale devices is gaining increased attention because of the interest in scavenging power from the environment and redirecting it locally to power sensors or other devices. This Ph.D. dissertation focuses on nanostructured devices based on InAs nanowires (NWs), carbon nanotubes (CNTs) and graphene. The nanostructures were fabricated and incorporated into flow channels to investigate (i): the phenomenon of flow-induced voltage generation and its mechanism, (ii): the potential for nanosensor system applications and energy harvesting. In particular, the effects of fluid flow on electrical current/potential changes on nanostructured devices with/out source-drain voltages driving the device were investigated, and the voltage generations of NW, CNT and graphene-based energy harvesters were assessed.

Indium Arsenide (InAs) nanowire (NW) and graphene field effect transistors (FETs) were incorporated into a microfluidic channel to detect the flow rate change as well as to harvest fluid flow energy for electric power generation. Discrete changes in the electric current through InAs NW FETs and graphene FETs were observed upon flow rate changes at steps of 1 ml/hr (equivalent to ~3 mm/s change...
in average linear velocity). The current also showed a sign change upon reversing flow direction. By comparing the response of device with and without a driving voltage between source-drain electrodes, it was concluded that the dominant contribution in the response was the streaming potential tuned conductance of NW/graphene. In the absence of a source-drain voltage, it was further demonstrated that ionic transport caused by the flow enabled generation of a ~mV electrical potential (or ~nA electrical current) inside the InAs NW per ml/hr increase in flow rate. This is most likely due to a charge dragging effect.

Oriented multi-walled carbon nanotube (MWCNT) arrays mounted on a silicon (Si) substrate were subjected to a stagnation-type flow configuration in a cylindrical tube. The effect of local vs. bulk flow velocity on the flow-induced voltage was examined. Pressure, shear stress and viscous energy dissipation were estimated based on the stagnation-point flow model. The tip velocity at which the flow impinges on the tips of MCWNTs in the array showed a logarithmic dependence on voltage. It was shown that the flow-induced voltage can be significantly enhanced by increasing flow velocity and/or ionic strength of the fluid. The highest flow-induced voltage measured was 52 mV, and was generated from MWCNTs aligned perpendicular to the flow in 0.2 M NaCl and tip flow velocity of 4.05×10⁻⁵ m/s.
Introduction

Introduction to InAs Nanowires, Carbon Nanotubes and Graphene
The study of nanowires (NWs), carbon nanotubes (CNTs) and graphene has become one of the most popular topics in both academia and industry for being highly promising for a variety of applications because of their excellent mechanical, electrical, thermal and optical properties. As the global energy consumption has been accelerating, as well as the disadvantages of fossil fuels, including finite resources and environmental pollution, there is a need for the research and development of clean and renewable energy alternatives. Progresses in the application of NW, CNT and graphene-related technology have been developed impressively fast and played an important role in seeking renewable energy sources. It is hoped that, with increased knowledge of nanoscale processes and nanostructure behaviors, NW, CNT and graphene-based energy harvesters and sensors will demonstrate potential in various areas, including self-powered nanosystems, analytical chemistry, and biomolecular detection.

In this dissertation, the performance of NW, CNT and graphene-based nanoscale devices for energy harvesting and flow sensing is investigated. An energy harvester itself could act as a sensor, as well as a power generator to build solely nanomaterials-based self-powered systems. These nanosystems could provide a convenient alternative to traditional power sources used to operate certain types of sensors, actuators, and microprocessor units. An energy harvester employed in system where the flow is naturally occurring, or that occurs as part of the system normal operation, could scavenge power from the environment and redirect it locally to power sensors or other devices. Such a device can provide a method of
obtaining power that could be coupled with other devices that are difficult or inefficient to power using conventional approaches. It has been shown that InAs NWs, CNTs and graphene are promising candidates for sensor applications due to their electronic transport properties. The advantages\textsuperscript{21} of these devices over other sensor technologies available today are (i): direct, real-time electrical signal transduction, and (ii): high sensitivity to fluid property changes and chemical species concentrations.

**InAs Nanowires (NWs)**

Indium arsenide (InAs)\textsuperscript{22} is a semiconductor known for its high electron mobility and narrow energy bandgap. There are several methods\textsuperscript{23} to prepare nanowires (NWs), including chemical vapor deposition (CVD), molecular beam epitaxy and electrochemical deposition. The most common technique for InAs NW synthesis is using the vapor-liquid-solid (VLS) mechanism. Here the source material is evaporated inside a tube furnace, and then carried towards the substrate by a carrier gas. Metal catalysts, gold nanoparticles, are deposited on the substrate. The source vapor dissolves in liquefied gold catalyst, and NW crystal grows once this liquid eutectic saturates. Semiconducting NWs can be used in the application of digital computing to link tiny components into extremely small circuits in the near future. Other uses of NWs are of interest in both academia and industry. For example, sensing of proteins, virus particles, and chemicals using semiconductor NWs by making NW field effect transistors (FETs). The advantages\textsuperscript{23} of NW sensors are direct electric signal outputs, real-time electrical signal transduction, label-free, and
ultrahigh sensitivity. The process of assembling large and complex NW sensing arrays at the commercial level is well established\cite{21} and NWs devices can be coupled and integrated with conventional or nanoscale electronics.

There are two different electron transfer effects associated with individual InAs NW; the surface effect and the bulk effect. Surface effect is that the properties of NW are largely influenced by the surface, especially the mobility of NW. The surface scattering is the main factor to determine the mobility due to NW’s rich surface defects and large surface to volume ratio. When the NW has an abundance of surface states and defects, the surface effect dominates. Bulk effect is the properties of NW are influenced by the whole NW since its defect free surface structure. The bulk effect dominates if InAs NW has a small electron accumulation layer, and surface state and defect densities are low. When the bulk effect dominates, the InAs NW has high electron mobility.

InAs NWs with low electron mobility (less than 100 cm$^2/(Vs)$) has a layer of the electron accumulation layer and rich surface states. The surface effect is important, and can be strongly affected by impurities. The electron accumulation layer and rich surface states contribute to high surface electron density of InAs NWs. Ideally, the gas or liquid molecules from the environment modify the surface (n-type surface states on the electron accumulation layer), make the electron density of NW
decrease, and increase the electron mobility and increase conductance of the InAs NW.

In the experiments conducted as part of this work, the NWs were immersed in a flowing liquid. The output signal was unstable and negligible due to the large signal to noise ratio. The NWs used in these experiments would be better suited to gas sensing. The change in conductance of the InAs NW in response to changing chemical vapor concentrations is a combined result of both the charge transfer and modified electron mobility effects. Surface adsorption of most chemical molecules can reduce electron density in NWs from $\sim 10^4$ to $\sim 10^3/\mu$m and greatly enhance the electron mobility (from tens to a few hundred of cm$^2/(Vs)$) simultaneously. These effects are attributed to the interactions between adsorbed molecules and the electron accumulation layer and rich surface states on the InAs NW surface. With their large surface-volume ratio, electron transport in NWs should be very sensitive to the surface condition. The carrier density $n$ in the NW can be calculated using the equation:

$$n = \frac{C_g(V_g - V_{th})}{eL}$$

(0.1)

where $C_g$ is the gate capacitance, $V_g$ is the gate voltage, $V_{th}$ is the threshold voltage, $e$ is the electron charge, and $L$ is the NW length. Since the NW conductance:

$$G_{NW} = \frac{n e \mu}{L} = \frac{C_g(V_g - V_{th})\mu}{L^2}$$

(0.2)
The mobility of carriers, $\mu$, can be estimated from the transconductance: \(^{(25)}\)

$$\frac{dG_{NW}}{dV_g} = \mu\left(\frac{C_g}{L^2}\right)$$  \hspace{1cm} (0.3)

When the NW diameter is much smaller than the gate oxide (SiO\(_2\)) thickness, $C_g$ can be approximated as:

$$C_g = \frac{2\pi\varepsilon\varepsilon_0 L}{\ln\left(\frac{2h}{r}\right)}$$  \hspace{1cm} (0.4)

where $\varepsilon$ is the relative dielectric constant of the substrate, $\varepsilon_0$ is the permittivity of free space, $h$ is the oxide layer thickness, $L$ is the channel length, and $r$ is the NW radius. The surface defect states\(^{(24)}\) are known to be critical in the formation of an electron accumulation layer on the InAs surface. The defect states in InAs can have multiple origins\(^{(24)}\), such as, an unbalanced stoichiometric ratio between In and As during the thermal evaporation of the InAs source, crystal structural defects, and incorporation of impurity atoms.

InAs NWs with high electron mobility (100-1000 cm\(^2\)/(Vs) or more) and a high quality crystal structure do not have an electron accumulation layer or surface states (defects). These kind of NWs are promising candidates for chemical and flow sensors. The fluid flow rate change presumably does not induce electron transfer between the NW and liquid, but does induce a streaming potential gating of the
NW. Liquid molecules change the conductance ($\Delta G_{NW}$) of NWs because of the streaming potential ($\Delta V_{str}$) induced by the flowing liquid.

\[
\Delta G_{NW} = f(\Delta V_{str}) = f(\Delta v) = f\left[\Delta V_g (\Delta \phi_s)\right]
\]  

(0.5)

where $v$ is the flow rate, $V_g$ is the gate voltage, and $\phi_s$ is the surface potential. It is not necessary to consider modified electron mobility effects on NW surface by the liquid molecules, due to its flawless or defect free surface structure. The electron accumulation takes place within the entire NW because of its small diameter. The bulk effect dominates in this case. The conductance change of NW ($\Delta G_{NW}$) induced by the streaming potential change ($\Delta V_{str}$) was calculated as following.

Using InAs NW as an example, the streaming potential from the Si/SiO$_2$ substrate is described as:

\[
\Delta V_{str} = \frac{\varepsilon\varepsilon_0\zeta R}{\eta e(C + \lambda)\mu} \Delta v
\]  

(0.6)

where $v$ is the flow rate, $C$ is the ionic strength, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant of the electrolyte solution, $\zeta$ is the zeta potential of the ionic double layer, $R$ is the hydraulic flow resistance estimated from Poiseuille’s law, $\eta$ is the viscosity of the electrolyte solution, $e$ is the electron charge, $\lambda$ is the offset concentration that generated from the background concentration of ions, and $\mu$ is the effective ionic mobility of the electrolyte.
solution.\textsuperscript{27,28} $\Delta V_{\text{str}}$ is the potential difference between NW and the reference electrode on the Si/SiO\textsubscript{2} substrate. The difference can be expressed as:

\[
\Delta V_{\text{str}} = \Delta V_g(\Delta \phi_s)
\]  
(0.7)

The flow-induced voltage is $\Delta V_{\text{str}}$, which is the equivalent gate voltage ($\Delta V_g$) applied by changing the NW’s surface potential $\Delta \phi_s = \Delta V_g(\Delta \phi_s)$. The relationship between $\Delta V_g(\Delta \phi_s)$ and $\Delta G_{NW}$ can be obtained from a $I_{sd}$-$V_g$ curve or $I_{sd}$-$t$ (by changing the gate voltage $V_g$) curve. Using the $I_{sd}$-$V_g$ curve (Fig. 0.1) and the equality $G_{NW} = I_{sd} / V_{sd}$, the relationship between $\Delta V_{\text{str}}$ and $\Delta G_{NW}$ can be obtained.
Figure 0.1 Response of an InAs nanowire field effect transistor’s source-drain current ($I_{sd}$) to changes in water gate voltage $V_g$ at source-drain voltage of 10 mV.
Carbon Nanotubes (CNTs)

There are three commonly used techniques for preparing carbon nanotubes (CNTs): (i) arc-discharge; (ii) laser ablation technique and (iii) chemical vapor deposition (CVD).\textsuperscript{29,30} The arc-discharge method was one of the earliest reported techniques for CNT growth.\textsuperscript{30,31} Two carbon electrodes are used as the carbon source. With a high voltage applied to the carbon electrodes, the inert gas (helium) in the vacuum chamber is ionized to plasma to stimulate evaporation of the carbon source. The carbon vapor is then transported and deposited on the negative electrode to form CNTs. For the laser ablation technique,\textsuperscript{30} the carbon source is evaporated in a furnace by a high power laser, and then transported \textit{via} an inert gas and deposited onto a substrate. A temperature between 3000-4000 °C is required to evaporate carbon source during the process of the arc-discharge and laser-ablation. For preparing CNTs by CVD,\textsuperscript{30} a tube furnace is heated up to a temperature of 550-1000 °C to convert the carbon source (typically methane, acetylene or ethylene) into reactive species. The reactive species are reacted with catalysts of Ni, Fe or Co on the cold substrate, and formed the CNTs. This method requires a lower temperature than arc-discharge and laser ablation. It scales well and is an efficient way to make vertically aligned multi-walled carbon nanotubes (MWCNTs) (Fig. 0.2) by controlling the growth process. Aligned or patterned CNTs, like vertically aligned MWNTs (VA–MWNTs) (Fig. 0.2) reported in Dai’s group\textsuperscript{32} are highly desirable for most device-related and energy-related applications because of their well-defined high surface area and tube spacing, as well as good electrical and
mechanical properties. Other methods for CNTs growth are pyrolysis of hydrocarbons,\textsuperscript{32-35} pyrolysis of carbon monoxide,\textsuperscript{33,36} and plasma-enhanced CVD.\textsuperscript{37}
Figure 0.2 Scanning electron microscope image of vertically aligned multi-walled carbon nanotubes
Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are two types of CNTs which belong to the fullerene family.\textsuperscript{30} The discovery of MWNTs by Iijima\textsuperscript{7,31} and the SWNTs by Benning et al.\textsuperscript{38} opened the possibility for making smart devices based on nanoscale materials, including actuators,\textsuperscript{39-41} sensors,\textsuperscript{42,43} and power generators.\textsuperscript{44} A SWCNT\textsuperscript{30} is ideally a one-atom thick graphene rolled up into a seamless cylinder with the diameter of nanometers scale.\textsuperscript{45} MWCNTs consist of multiple concentric cylindrical layers of graphene with a common central axis. CNTs have strong and stiff structures due to the C-C bond and seamless hexagonal network. CNTs have unique electrical properties, either metallic or semiconducting, depending on the tube chirality of the tube (i.e., the chirality, defined in terms of a chiral vector $\mathbf{c} = n\mathbf{a}_1 + m\mathbf{a}_2$ where $n$ and $m$ are integers and the $\mathbf{a}_i$ are lattice vectors in the hexagonal lattice, and a chiral angle $\theta = \arccos(\mathbf{a}_1 \cdot \mathbf{c})$ that defines the degree of twisting of the rolled sheet).\textsuperscript{46}

The idea that ambient energy can be collected (or scavenged) and converted into usable power for nanoscale devices without batteries or an external power source is gaining more and more attention.\textsuperscript{47} The generation of electrical current by CNTs\textsuperscript{7} in a flowing ionic fluid has potential for medical and energy-scavenging applications – such as powering implantable devices. Semiconducting CNTs have a high electron mobility, which makes good candidates for use as nanoscale sensors.\textsuperscript{48} Kong et al.\textsuperscript{43} built a SWCNT chemical gas sensor for the detection of NO$_2$ and NH$_3$. Carbon nanotubes can also be used as biosensors\textsuperscript{49} with a range of
potential applications in drug discovery, biohazard screening, disease screening, and real-time electrical detection of proteins or DNA.

Graphene

Graphene is a one-atom thick layer of the mineral graphite. Graphene can be synthesized in a number of ways. Chemical vapor deposition (CVD) is a popular method. It has the advantage of allowing for large scale production of graphene films. The CVD techniques include thermal CVD, plasma enhanced CVD and thermal decomposition on SiC and other substrates. Plasma enhanced CVD provides graphene at a lower temperature (650 °C) compared to thermal CVD (1000 °C). In addition to that, plasma enhanced CVD has the advantage of a short deposition time (less than 5 minutes).

Exfoliation and cleavage is another method for preparing graphene. Mechanical exfoliation is a process where layers are peeled from a highly oriented pyrolytic graphite (HOPG) sheet using a scotch tape. Among the challenges of this method are controlling the number and maintaining the structure of graphene layers during the process, and scaling it for mass production. Another method is synthesis of graphene oxide by oxidation of graphite and followed by reduction process. The reduction process is chemical reduction or thermal reduction.
Graphene is a planar monolayer of C-C atoms arranged into a two-dimensional (2D) honeycomb lattice.\textsuperscript{62-64} It has a high electron mobility of 250,000 cm\textsuperscript{2}/Vs at room temperature,\textsuperscript{15-17} a thermal conductivity of 5000 W/m,\textsuperscript{13} a large theoretical specific surface area of 2600 m\textsuperscript{2}/g, and high mechanical strength of 130 GPa to super stiffness with a Young’s modulus up to 1 TPa.\textsuperscript{14} There are plenty of potential applications for this material due to its unique structure and superior properties. These include gas/liquid (chemical or bio) detection, high strength composites, energy conversion systems of solar cells and fuel cells, and energy storage devices of supercapacitors and lithium ion batteries.\textsuperscript{14,59,65-67}

Due to the increase of world energy consumption, as well as the disadvantages of fossil fuels, energy harvesting options have become attractive. Energy harvesting utilizes sources such as wind, solar etc., can occur on a variety of scales. Nano and carbon materials can be used as small scale ‘passive’ power sources, or/and small flow sensors. In this Ph.D. dissertation, energy harvesting and sensing of fluidic flow by InAs NWs, MWCNTs, and graphene were investigated.

In Chapter 1, single and multiple InAs NWs were incorporated into a microfluidic channel to detect the flow rate change as well as to harvest fluid flow energy for electric power generation. The InAs NW(s) was parallel to the flow direction and was laid down horizontally onto a micro-fluid channel with a dimension of 200 μm × 500 μm. The synthesis, alignment, fabrication, characterization and performance of the InAs NWs field effect transistor were discussed in this chapter.
In Chapter 2, oriented MWCNT arrays perpendicular mounted on a Si substrate were subjected to a stagnation-type flow configuration in a cylindrical tube. The flow direction was the same as the growth direction of MWCNTs. The bundled MWCNTs samples have a dimension of centimeter scale. The amplified energy harvesting effects at different flow conditions were investigated by increasing the number of MWCNTs (bundled-MWCNTs) and using stagnation-type flow configuration.

In Chapter 3, graphene samples were laid down on a microfluidic channel and the flowing liquid was parallel onto the graphene surface. The current changes of graphene can be observed in response to flow rates, flow directions and pH under an applied source-drain voltage. In the absence of source-drain voltage, the ionic flow could enable the generation of electrical potential on graphene. The application as power scavenged from a flowing liquid could be used to fabricate self-powered graphene-based systems.

Some InAs NWs were provided by Dong Liang, Yuan Tian and Guodong Li in Dr. Xuan Gao’s group to make comparison with my NW samples during the experiments. MWCNTs samples were provided by Feng Du in Dr. Liming Dai’s group. Graphene samples used in the experiments were provided by Cheehuei Li in Dr. Xuan Gao’s group.
REFERENCES


Chapter 1

Sensing and Energy Harvesting of Fluidic Flow Using InAs Nanowires
ABSTRACT

Indium Arsenide (InAs) nanowire (NW) field effect transistors (FETs) were incorporated into a microfluidic channel to detect the flow rate change as well as to harvest fluid flow energy for electric power generation. Discrete changes in the electric current through InAs NW FETs were observed upon flow rate changes at steps of 1 ml/hr (equivalent to ~3 mm/s change in average linear velocity). The current also showed a sign change upon reversing flow direction. By comparing the response of device with and without a driving voltage between source-drain electrodes, it was concluded that the dominant contribution in the response was the streaming potential tuned conductance of NW. In the absence of source-drain voltage, it was further demonstrated that the ionic flow could enable generation of a ~mV electrical potential (or ~nA electrical current) inside the InAs NW per ml/hr increase of flow rate, most likely due to a charge dragging effect.

KEYWORDS: Sensor, Flow, Energy conversion, Nanowire, Indium arsenide
INTRODUCTION

Electrical detection of chemical and biological species using novel nanomaterial devices, such as nanowire (NW) and carbon nanotube (CNT) field effect transistors (FETs), has attracted significant attention during the past decade. This is because the nanomaterial devices can act as real-time and ultrasensitive biological and chemical sensors. Advances in micro- and nano-fabrication techniques have made micro- or nano-fluidics more accessible experimentally. A number of theoretical and experimental studies of the interaction between flow and nanostructure/substrate have demonstrated that a net conductance and surface potential difference can be generated in nano-structures in the presence of fluid flow.

Previously studied nanoscale flow sensors are mostly based on CNT, graphene, or silicon nanowire (Si-NW). For semiconductor NWs, small bandgap III-V compounds such as InAs seem to be another promising candidate as a sensing material due to their high electronic transport performance. The InAs NW could be sensitive to surface potential changes caused by molecule adsorption on the surface or ionic flow in the environment. There appears to be no reports of InAs NW’s flow sensing properties to date aside from the work discussed here. Furthermore, there has been significant interest in using nanodevices to convert fluid flow energy into electricity. But whether an ionic flow environment can indeed generate an electrical current or voltage in nanomaterials still remains controversial. In this work it is shown that FETs of either individual or multiple
parallel aligned InAs NWs can be used to locally sense the flow of an ionic liquid with different directions, flow rates, and pH via the streaming potential modulated conductance effect. Significantly, it is also found that current could be generated in an InAs NW FET by fluid flow even without any electrical voltage driving the device. This opens up the possibility of exploiting fluid flow for electric power generation or self-powered nanoelectronics.
EXPERIMENTAL, RESULTS AND DISCUSSION

Different InAs NW morphologies were created by varying the growth conditions, in particular the hydrogen gas partial pressure, the chamber pressure, source/wafer temperature, growth time, and the thickness of the catalyst layer. In this experiment, InAs NWs were grown on Si (100) substrates in a custom built vapor deposition system via the vapor-liquid-solid (VLS) mechanism with 40 nm commercial Au nanoparticles (Ted. Pella, Inc.) as the catalyst. A high temperature tube furnace (Lindberg Blue M) was used to control the evaporation temperature of the InAs powder source (Alfa Aesar) and the growth temperature at the Si substrate. To functionalize the growth substrate with Au nanoparticles, the substrates were treated with poly-L-lysine (Ted. Pella, Inc.) for 8.5 minutes and covered with 40 nm Au catalyst solution (The Au catalyst solution was diluted 1:6 by volume in deionized water (DI-water) from as received Au nanoparticle solution) for 5 minutes successively. The Au nanoparticle functionalized Si substrate was placed at a distance of 13.5 cm from the source. A maximum flow rate of 100 sccm (standard cubic centimeters per minute) Ar and H₂ (10 %) mixture carrier gas was introduced after the system was pumped down to the base pressure of 8 mTorr. When the temperature of the furnace was increased to 660 °C, the flow rate was decreased to 4 sccm. The pressure was kept at 1.5 Torr for 5 minutes and then changed to 100 mTorr. InAs NWs were grown under these conditions for 3 h with growth substrate at ~480 °C. An optical image of InAs NWs on growth substrate is shown in Fig. 1.1.
Figure 1.1 Optical image of InAs nanowires (NWs)
NW FET micro-fabrication process\textsuperscript{44} includes transferring NWs from growth wafer to a new Si/SiO\textsubscript{2} substrate, and patterning a micron-scale circuit on top of the NWs by photolithography and metal deposition. This kind of NW FET device has a back gate Si electrode insulated by a layer of SiO\textsubscript{2} from the source and drain electrodes. The source and drain electrodes are connected to a semiconducting NW. The NW FET can also have a water gate electrode insulated by a layer of DI-water.

There are many methods\textsuperscript{44} to remove the NWs from the growth wafer. The most common ones are drop casting NW solution from sonication and lubricant-assisted mechanical transfer methods. For the sonication, a small piece of the growth wafer is cut and sonicated into ethanol solution for 3 seconds at a low sonication rate. Higher sonication rate or longer sonication time results in nanoparticles and broken NWs. The NWs in ethanol solution are dispersed onto a clean Si/SiO\textsubscript{2} substrate (Fig. 1.2). The procedure requires many repetitions to reach the desired high density of NWs. It is difficult to remove the solvent residue and control the direction of NWs during transfer.
Figure 1.2 Transfer InAs NWs on the Si/SiO$_2$ substrate by sonication

(a) low density
Figure 1.2 Transfer InAs NWs on the Si/SiO$_2$ substrate by sonication

(b) high density
Figure 1.2 Transfer InAs NWs on the Si/SiO$_2$ substrate by sonication

(c) high density with water residue
To transfer randomly oriented NWs from the growth wafer onto a Si/SiO$_2$ substrate with desired density and alignment for device fabrication, a lubricant assisted contact printing transfer was adopted.$^{45}$ The donor (NW growth wafer) substrate was cut into the desired dimension, and then gently brought into contact on the receiver substrate (Si with 300 nm thick SiO$_2$ on surface), pushed with a constant velocity of ~20 mm/min by the pressure of a mounted weight at ~15 g/cm$^2$ (Fig. 1.3). An octane and mineral oil (2:1, v: v) mixture was used as a lubricant during the transfer process.$^{45}$ The donor substrate and the weights were then gently removed and the receiver substrate was rinsed well in octane and DI-water. The NWs aligned on a clean Si/SiO$_2$ substrate are shown in Fig. 1.4.
Figure 1.3 The process of transferring NWs on the Si/SiO$_2$ substrate by lubricant transfer
Figure 1.4 Transfer InAs NWs on the Si/SiO$_2$ substrate by lubricant transfer

(a) short NWs
Figure 1.4 Transfer InAs NWs on the Si/SiO₂ substrate by lubricant transfer

(b) long NWs
Photolithography\textsuperscript{44} was used to pattern the electrode arrays for NW FETs. The photoresist LOR3A was spin coated onto the Si/SiO\textsubscript{2} substrate (which has NWs) at 4000 rpm for 40 seconds. The substrate was then heated at 190 °C for 5 minutes. The photoresist S1805 was spin coated onto the substrate at 4000 rpm for 40 seconds, and then baked at 115 °C for 3 minutes. The exposure time during the photolithography was 2.5 seconds by UV light passing through the mask (Fig. 1.5) using a mask aligner (Fig. 1.6). The substrate was then developed in CD-26 for 1 minute. After UV light and by lifting of using DI-water, the area without photoresist on the substrate was lifted off (Fig. 1.7).

The mask pattern (Fig. 1.5) was designed\textsuperscript{44,46} for chemical and/or bio-sensing experiments. The NW FET devices and electrodes patterns are in the middle of the substrate, with the metal contact pads at the edges. This design allows solution to be passed through the NW FETs by a microfluidic channel to keep metal contact pads dry for electrical measurements.
Figure 1.5 (a) Optical microscope image of photo mask pattern; (b) Schematic of the central electrodes patterns
Figure 1.6 Photo of mask aligner (provided by MORE center @ CWRU)
Figure 1.7 Schematic of photolithography process
A 60 nm thick Ni was deposited as electrodes by electron beam (E-beam) evaporation (Fig. 1.8) after photolithography. In addition, 30 nm thick Al₂O₃ was E-beam evaporated onto Ni electrodes to avoid current leakage in the fluid. The effectiveness of the Al₂O₃ passivation was confirmed by measuring leakage current in water between electrodes without the NW.
Figure 1.8 Photo of an Angstrom Engineering Evovac physical vapor deposition chamber (provided by MORE center @ CWRU)
Wire bonder (Fig. 1.9) was required to connect the electrodes and on chip golden pad to measure the conductivity and current of NW devices. Electrical characteristics of NW devices were tested by measuring source-drain current vs. source-drain voltage, and source-drain current vs. back gate voltage ($V_g$) at a constant source-drain voltage by probe station (Fig. 1.10 (a)) (The Micromanipulator Co., Inc) at room temperature. The $I$-$V$ characteristic (Fig. 1.10 (b)) shows a linear characteristic which indicates Ohmic contact behavior. The back gate ($V_g$) was swept from zero to the lower limit (-10 V), then to the upper limit (+10 V), then back to zero (Fig. 1.10 (c)). Fig. 1.10 (d) shows that the current passing from source to drain was modulated by voltages applied to the top gate electrode (water gate). The larger the transconductance, or slope of these curves, the better for sensing applications. One of the major challenges of NW FET sensors to date is that the electrical characteristics vary greatly from device to device. The other challenge is that NW devices are easily broken when immersed in a solvent under high applied voltages (Fig. 1.11 (e)). Optical images of the single and multiple NWs FET devices are shown in Fig. 1.11.
Figure 1.9 Photos of wire bonder (provided by MORE center @ CWRU)
Figure 1.10 (a) Photo of probe station (provided by MORE center @ CWRU)
Figure 1.10 (b) $I-V$ characteristic of NW FET
Figure 1.10 (c) Relationship of current ($I_{sd}$) and back gate voltage ($V_g$) of NW FET

($V_{sd} = 10$ mV)
Figure 1.10 (d) Relationship of current ($I_{sd}$) and water gate voltage ($V_{g}$) of NW FET ($V_{sd}$=10 mV)
**Figure 1.11** Optical images of the single and multiple NWs FET devices.

(a) a single NW FET device
Figure 1.11 Optical images of the single and multiple NWs FET devices.

(b) multiple NWs FET devices (short NWs by sonicated method)
Figure 1.11 Optical images of the single and multiple NWs FET devices.

(c) multiple NWs FET devices (short NWs by lubricant transfer)
Figure 1.11 Optical images of the single and multiple NWs FET devices.

(d) multiple NWs FET devices (long NWs by lubricant transfer)
**Figure 1.11** Optical images of the single and multiple NWs FET devices.

(e) a broken NW FET
Fig. 1.12 shows the experiment set-up of InAs NW FETs integrated in a microchip, where the NW devices were laid down horizontally on the Si/SiO$_2$ substrate and covered by a polydimethylsiloxane (PDMS) flow channel. The main parts of source and drain electrodes$^{16,36,47}$ were packaged and covered by the PDMS layer that reduces exposure of electrodes to water. The flow of the liquid through the PDMS microfluidic channel was controlled by a syringe pump (New Era Pump Systems, Inc.). In the flow sensing experiments, typically, a 10 mV D.C. voltage was applied to the source and drain electrodes. The source-drain current $I_{sd}$ was converted to a voltage by a current amplifier (Stanford Research, model SR570) and recorded using a National Instrument data acquisition card and BNC terminal box.
**Figure 1.12** Experimental set-up of InAs NW transistor devices enclosed in microfluidic flow channel for flow sensing and power harvesting.
The two curves in Fig. 1.13 show the relationship between time and conductance of a FET with a single InAs NW. The NW is contained in a 2 μm long channel. The results show the relationship for different flow directions and rates \( v \) of DI-water at a source-drain voltage \( V_{sd}=10 \text{ mV} \). The flow direction was the same as (opposite to) the source-drain current flow direction for the top or black (bottom or red) trace. Generally, once the flow velocity was set to change by a sudden change of pump rate, a gradual rise or drop of conductance followed by a stable steady state reading was observed in the InAs NW’s conductance response, as shown in the top left schematic of Fig. 1.13. In Fig. 1.13, the black arrows mark the steady state regime after a flow rate change and the NW conductance stabilizes. The 1-2 minute transient period was attributed to the time required for the fluid flow to reach steady state in the system. It was also observed that the flow direction affected the sign of the conductance change. With increasing \( v \), the conductance increased when the source-drain current was in the same direction as the flow and decreased if it was oppositely directed. This InAs NW FET device had a clear step-wise response and showed reliability and reversibility at least over the two hours of experiment period. In addition, as a good candidate for a flow sensor, the current signal response time of the InAs NW FET was about 10 seconds after \( v \) was changed. Similar sensing data from another device can be found in the Appendix (Fig. S 1).
Figure 1.13 Effect of flow directions and rates $v$ on the conductance of a single InAs NW FET with source-drain voltage $V_{sd}=10 \text{ mV}$ in DI-water. The black (red) curve corresponds to flow direction same as (opposite to) the current flow. The inset on the right shows a dark field optical image of a single InAs NW device connected to electrodes. The top left inset shows a schematic of device’s response to flow rate change.
In prior flow sensing experiments with CNT, Si-NW and graphene, the device’s response was attributed to a fluid flow induced streaming potential effect.\textsuperscript{21,36} When the Si/SiO\textsubscript{2} substrate is in contact with liquid solutions with a pH value greater than the isoelectric point (\textasciitilde{2}-3) of SiO\textsubscript{2}, the substrate surface becomes negatively charged due to the deprotonation of the silanol groups [SiOH(s): SiO\textsuperscript{−}(s) + H\textsuperscript{+}(aq)].\textsuperscript{21} With flowing liquid, the excess counter ions in the electrical double layer (EDL) at the surface of the SiO\textsubscript{2} substrate are swept downstream by the pressure-driven flow. This generates a steaming potential $\Delta V_{str}$ which offsets the water gate (or reference electrode) voltage and thus shifts the surface potential of InAs NW (Fig. 1.14 (a)).\textsuperscript{21} Since the sign of the generated streaming potential reversed upon the reversal of fluid flow direction, an opposite change of current (or conductance) in NW FET was expected at opposite flow directions as shown schematically at the bottom of Fig. 1.14 (a). This was consistent with the experimental observation here.

According to the electrokinetic theory of streaming potentials based on the Smoluchowski equation, the steaming potential is a function of flow rate ($v$) and ionic concentration ($C$) and given by:\textsuperscript{22,34-36}

$$\Delta V_{str} = \frac{\varepsilon_0 \varepsilon_r \zeta R}{\eta e (C + \lambda) \mu} \Delta v \quad (1.1)$$

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant of the electrolyte solution, $\zeta$ is the zeta potential of the ionic double layer, $R$ is the hydraulic flow resistance estimated from Poiseuille’s law, $\eta$ is the viscosity of the electrolyte solution\textsuperscript{35}, $e$ is the electron charge, $\lambda$ is the offset concentration that
generated from the background concentration of ions, and $\mu$ is the effective ionic mobility of the electrolyte solution.\textsuperscript{34,36} According to equation (1.1), the streaming potential is proportional to $v$. In Fig. 1.14 (b), the source-drain current $I_{sd}$ against flow rate for data in Fig. 1.13 is plotted. A linear dependence between the current and flow rate was observed for both flow directions. According to the streaming potential mechanism for nanoelectronic FET flow sensing, the streaming potential adjusted the surface potential of NW which modulated the conductance of NW through the field gating effect. Note that, using pH as another independent control of NW’s surface potential, it was experimentally confirmed that the InAs NW FET investigated here showed clear response to surface potential change (Fig. 1.15). The flow rate induced surface potential change $\Delta \phi$ at the surface of InAs NW is quantified as follows. The current change in the sensing experiment is compared to the relationship between the device’s current and the water gate voltage $V_g$ (or reference electrode voltage) in Fig. 1.14 (c) and to the corresponding potential change $\Delta \phi$ seen on the right-hand axis in Fig. 1.14 (b). Based on this analysis, it is found that every ml/hr change in flow rate causes a $\Delta \phi$ or streaming potential change of $\Delta V_{str} \sim 10$ mV. Using the cross-section area (500 $\mu$m $\times$ 200 $\mu$m) to estimate the average flow velocity, this led to an estimate of $\Delta V_{str} / \Delta v \sim 3.5$ mV/(mm/s). This was very close to the value obtained in Si-NW flow sensors at comparable ionic strength ($\mu$M).\textsuperscript{21}
Figure 1.14 (a) Schematic illustration of fluid flow generated streaming potential. The generated streaming potential between the reference electrode and the NW FET changed sign as the flow direction reversed.
Figure 1.14 (b) Plot of InAs NW FET’s current (left axis) and equivalent surface potential change Δφ (right axis) vs. flow rate for experiment in Fig. 1.13.
Figure 1.14 (c) Response of InAs NW FET’s source-drain current to changes in water gate voltage $V_g$ at source-drain voltage of 10 mV. Linear fitting of $I_{sd}$ vs. $V_g$ yielded conversion factor of 0.45 nA/mV for the calculation of $\Delta \varphi$ in (b).
Figure 1.15 Effect of the potassium phosphate buffer solutions with different pH values on a single InAs NW FET ($V_{sd}=10$ mV). The decrease of current at higher pH is consistent with that the InAs NW is n-type and the high pH value leads to more negatively charged NW surface and a negative shift of surface potential.
While the InAs NW FET flow sensor investigated here behaves consistently with other nanoscale FET flow sensors studied in the past, the question whether nanomaterials or devices can indeed be used to harvest electrical power from fluid flow remains to be answered. In bundles of CNTs with macroscopic dimensions (~mm), the flow of liquid can generate voltage on order of mV along the flow direction.

However, such an effect may also be caused by the streaming potential developed over the macroscopic length and not related to carrier transport in CNT per se. In graphene devices immersed in hydrochloric acid (HCl), the flow of HCl solution was also found to generate more than 10 mV voltage. But such an effect was explained alternatively by the interaction of electrode and ionic water. Therefore, it remains unclear if fluid flow can cause carriers in nanomaterial to generate a voltage or current via any intrinsic mechanism. Here it is found that water flow can indeed induce power generation in InAs NW FETs (~ 1 nA or mV every mm/s flow rate increase). It is proposed that an intrinsic dragging effect is responsible for the observed phenomenon.

Fig. 1.16 illustrates the source-drain current through a second InAs NW device in response to flow rate changes without any external source-drain voltage to drive the NW (the set-up is sketched as inset). This measurement was in contrast to the sensing experiment, where nonzero $V_{sd}$ was applied. Here, although the flow rate change induced a streaming potential change $\Delta V_{str}$, $\Delta V_{str}$ was not expected to cause any current flowing through the NW since $\Delta V_{str}$ influenced only the conductance of NW which converted to a current change only if a finite $V_{sd}$ was applied. Without
any source-drain voltage applied on the NW, it is clearly seen that there is an approximate ~1 nA step-wise increase of current through the NW for every ml/hr increase of flow of DI-water. The generated current also reverses direction when the flow changes direction. A control experiment on a device without NW between the electrodes did not show any measurable current over a similar range of water flow rate. This attests to the good isolation of electrodes from water in the device and proves that the flow induced current in Fig. 1.16 came from the InAs NW. Using the measured NW resistance of ~1 MOhms, the equivalent electrical voltage generated inside NW was estimated to be ~1 mV for every ml/hr increase of flow rate (corresponding to ~ pico-Watt power). In the literature, there are mainly two mechanisms for such flow induced voltage/current generation in material. The first one is pulsating asymmetric ratcheting,\textsuperscript{29,41} in which fluctuating Coulombic field of the liquid (caused by shear stress) imbalances local charge neutrality of ionic fluid, provides stochastic asymmetric potential which moves with flow, and drags free carriers to induce voltage. It is proposed\textsuperscript{29,41} that a fluctuating Coulombic potential arises due to local imbalances in charge neutrality of the ionic fluid. The unidirectional nature of the flow provides a bias that can be thought of as the deformation of the transient accumulation of charges. The pulsating asymmetric ratcheting resulted voltage is:\textsuperscript{29,41}

\[
V \approx V_0 \left( \frac{1 - \exp[-av]}{\exp[-bv]} \right) \quad (1.2)
\]
where $V_0$, $a$, $b$ are the constants and $v$ is the flow velocity. Equation (1.2) predicts a sublinear relation between induced voltage and flow velocity. This appears to disagree with data in Fig. 1.16 where quasi-linear dependence is seen.

Another possible explanation\textsuperscript{26} is that voltage generation arises due to a phonon wind that drags free carriers in InAs NW. That is the transfer of momentum from the flowing liquid molecules to the acoustic phonons as the phonon quasi-momentum, which in turn drags free electrons in the NW. In this model, the voltage has a linear relationship to the flow velocity and liquid viscosity. The velocity dependence expected in the carrier drag mechanism seems to be in agreement with the observation here.
**Figure 1.16** Fluid flow generated current through an InAs NW at different flow rates and directions without any source-drain voltage applied on the NW. The inset shows a schematic of experimental circuit.
In addition to studying single InAs NW devices, the possibility of scaling up the InAs NW FET flow sensor by preparing NW thin film FETs with multiple parallel InAs NWs between the electrodes using repeated contact printing transfers to increase the number and density of NWs between electrodes was also explored. Such a multi-NW device may provide longer life-time and better statistical performance characteristics compared to a single NW device. The initial work showed that multi-InAs NW device (with ~6 NWs in each FET) still responded to flow rate in a similar fashion to the single NW device after repeated contact printing transfers, as shown in Fig. 1.17. Compared to the single NW device in Fig. 1.13, not only did the absolute value of conductance increase in the multi-NW device, the flow induced the conductance change at a given flow rate was also amplified by 3-4 times, due to the larger number of NWs between electrodes. Further work is being performed to test if such multi-NW devices can be exploited to generate larger current and power in the power generation configuration without any source-drain bias. A key to a nanosystem is how nanogenerator or nanosensor could provide high output voltage and power. In this regard, multiple parallel aligned NWs device has the potential to yield much greater power than the single NW device as the internal resistance of the device reduces. It is also noted that the initial result on the flow rate sensing by multi-NW device presented here appears to show larger conductance fluctuations than individual NW devices. These fluctuations may be related to the low frequency 1/f noise in NW devices. In the future, it will be essential to determine how such fluctuations change from single NW device to
multi-NW device since they are intimately tied to the signal-to-noise ratio in sensing applications or the output power stability in the energy harvesting.
Figure 1.17 Sensing response over the flow rates and direction changes of DI-water for a FET device with multiple (~6) horizontally aligned InAs NWs between the electrodes. The source-drain voltage is 10 mV. The inset shows a dark field optical image of multiple horizontally aligned InAs NWs connected on electrodes.
In conclusion, InAs NW FETs were demonstrated to show a linear response to the changing flow rate of water in a microfluidic channel. The observed fluid flow sensing effect is attributed to the streaming potential of a flowing ionic liquid. Besides, fluid flow is found to induce electrical current through InAs NW FET even in the absence of a source-drain voltage. To the best of our knowledge, this is the first time a NW-based electronic device is shown to convert energy from fluid flow into electricity. It is expected that the demonstrated InAs NW-based sensors and energy harvesters for liquid flow may find uses in applications ranging from analytical chemistry, biomolecular detection to self-powered nanosystems.
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Chapter 2

Flow-induced Voltage on Multi-walled Carbon Nanotubes
ABSTRACT

Oriented multi-walled carbon nanotube (MWCNT) arrays mounted on a silicon (Si) substrate were subjected to a stagnation-type flow configuration in a cylindrical tube. The effect of local vs. bulk flow velocity on the flow-induced voltage was examined. Pressure, shear stress and viscous energy dissipation were estimated based on the stagnation-point flow model. The tip velocity at which the flow impinges on the tips of MCWNTs in the array showed a logarithmic dependence on voltage, confirming earlier results. It was shown that the flow-induced voltage can be significantly enhanced by increasing flow velocity and/or ionic strength of the fluid. The highest flow-induced voltage measured was 52 mV, (21 times higher than the highest voltage reported to date for single-walled carbon nanotube) and was generated from MWCNTs aligned perpendicular to the flow in 0.2 M NaCl and tip flow velocity of $4.05 \times 10^{-5}$ m/s.

KEYWORDS: Flow-induced voltage, Multi-walled carbon nanotubes
INTRODUCTION

Multi-walled and metallic single-walled carbon nanotubes (MWCNTs, SWCNTs) have been reported to generate voltage in the presence of fluid flow and could act as flow sensors, nanoelectronics and energy harvesters.\textsuperscript{1,2,3} There are several different mechanisms explaining the voltage generation phenomenon. One explanation\textsuperscript{4} is that voltage generation occurs due to a phonon wind that drags free carriers in the CNT. Persson et. al\textsuperscript{5} have invoked a frictional stick-slip to explain the observed phenomenon of flow-induced voltages in SWCNT. It was shown by Ghosh\textsuperscript{6} that induced friction which is predicted to exist from the fluctuation-dissipation theorem, flow-induced drag (where Doppler shifted and aberrated photonic fluctuations), and reduction of induced friction at high flow speeds are theoretical mechanisms of the induced voltage. Ref.\textsuperscript{7} demonstrated that interactions between the water dipole chains and charge carriers in a tube can result in a charge redistribution in a SWCNT. This causes a voltage difference between the two ends of the tube by molecular dynamics. Another proposed mechanism\textsuperscript{8} is “pulsating asymmetric ratcheting”. It is proposed that a fluctuating Coulombic potential arises due to local imbalances in charge neutrality of the ionic fluid. The unidirectional nature of the flow provides a bias that can be thought of as the deformation of the transient accumulation of charge. This results in asymmetric fluctuating potential.

The mechanism of pulsating asymmetric ratcheting can be modeled as a Gaussian white noise driven potential fluctuation, governed\textsuperscript{2,3} by equation (2.1) and (2.2)
\[
\begin{align*}
\dot{j} &= j_0 \left\{ 1 - e^{\frac{\gamma \lambda^2 \Delta}{Q U_m}} \right\} \\
\varphi(x) &= \left[ \frac{(\gamma)}{(Q)} \right] \int_{0}^{x} \left[ \frac{1}{U'(y)} \right] dy
\end{align*}
\] (2.1, 2.2)

here \( \lambda \) is the period of the pulsating ratchet, \( Q \) is the strength of the fluctuating coulombic potential, \( \gamma \) is the frictional coefficient for the carriers in nanotube, \( U_m \) is the maximum of the ratchet potential and \( \Delta \) is an asymmetry parameter.

The nonlinear voltage dependence of an individual nanotube in a specific fluid can be expressed by small degrees of asymmetry \( (\Delta) \) in terms of the parameters \( V_0, a \) and \( b \). That is

\[ V \cong V_0 \left\{ \frac{1 - \exp[-au]}{\exp[-bu]} \right\} \] (2.3)

here \( V_0, a, b \) are constants.

Voltage generation in MWCNT arrays was investigated as a function of bulk flow velocity \( (v_0) \), local (CNT tip) flow velocity \( (u) \) and the ionic strength of the
flowing solution. In addition, effects of pressure, shear stress and viscous dissipation on voltage generation were estimated using a stagnation-point flow model. The MWCNT configuration under investigation was one in which the MWCNT deposited on a silicon (Si) substrate and the tubes were oriented perpendicular to the substrate. The voltage generated by the interaction of the flow with the MWCNT array showed a logarithmic dependence on tip velocity ($u$) (i.e. the flow velocity in the vicinity of the MWCNT tips) as proposed earlier in Ref.$^2$. 
EXPERIMENTAL

The carbon nanotubes used in this study were prepared by pyrolysis\textsuperscript{2} of metal-organic complexes and metal catalyzed reactions. The process produced MWCNTs aligned perpendicular to the Si substrate. The MWCNTs have the diameter of 50 nm, length of 50 µm, the gap of 100-200 nm and the density of $2 \times 10^9$ per cm\textsuperscript{2}.

Fig. 2.1 is a schematic that shows the orientation of the MWCNTs with respect to the bulk flow. The circuit was made by connecting two opposite edges of the arrays. The bulk velocity and voltage signals were recorded using a data logger (DATAQ, DI-158U). There was no voltage signals if flow direction perpendicular to the MWCNTs.
Figure 2.1 Schematic of the multi-walled carbon nanotubes (MWCNTs) orientation with respect to the bulk flow.
The stagnation-point flow model is depicted in Fig. 2.2. The stagnation-point is at the origin \((x=0)\). \(u\) and \(v\) are the \(x\) and \(y\) components of velocity, which are given by

\[
\begin{align*}
  u &= BxF'(\eta), \quad v = -\sqrt{B\nu}F'(\eta) \\
\end{align*}
\]

(2.4)

where \(B = \frac{v_0}{L}, \quad \eta = y\sqrt{B/\nu}\), \(v_0\) is the magnitude of bulk flow velocity, \(\nu\) is the kinematic viscosity and

\[
F'''' + FF'' + (1 - F'^2) = 0
\]

(2.5)

with

\[
F(0) = F'(0) = F'(\infty) - 1 = 0
\]

(2.6)

and \(F''(0) = 1.232588\) (Ref.\(^9\)). Flow velocity at any point can be calculated by stagnation-point model. The tip velocities \((u)\) were calculated at \(y = 50 \mu m\) since the length of MWCNTs is 50 µm. The bulk velocities \((v_0)\) had the range from 0.001 to 0.1 m/s, which means the tip velocities \((u)\) ranging from \(5.83 \times 10^{-8}\) to \(4.05 \times 10^{-5}\) m/s.
Figure 2.2 Configuration of stagnation-point flow model
The flow pressure at any point can be obtained and is given (see Fig. 2.3) by

$$\frac{p(x, \eta) - p_0}{\rho} = -\frac{1}{2} B^2 x^2 - \frac{1}{2} B \nu F^2 - B \nu F'$$  \hspace{1cm} (2.7)$$

where $p_0$ is the stagnation-pressure at the origin ($x = 0$).

Fig. 2.3 shows that the pressure difference of stagnation-point pressure to tip pressure increases quadratically with increasing the distance along from the center of the substrate to the edge. The pressure differences increase with increasing flow velocities.
Figure 2.3 The dependence of distance along from the center of the substrate and pressure difference (stagnation-point pressure and tip pressure) with respect to tip velocities in DI-water
The pressure gradients in the direction parallel (in $x$ direction) and normal (in $y$ direction) to the substrate are expressed as below:

\[
\frac{\partial p}{\partial x} = -\rho B^2 x \quad \text{(2.8)}
\]

\[
\frac{\partial p}{\partial y} = -\rho B \sqrt{B \nu} (F F' + F'') = O(\sqrt{\nu}) \quad \text{(2.9)}
\]

The shear stress ($\tau$) acting on the MWCNTs array is

\[
\tau = \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \quad \text{(2.10)}
\]

where $\mu$ is the dynamic viscosity. $\tau$ (see Fig. 2.4) at stagnation-point is

\[
\tau = \mu B x F''(0) \sqrt{\frac{B}{\nu}} \quad \text{(2.11)}
\]

Fig. 2.4 shows that $\tau$ increases linearly with increasing the distance along from the center of the substrate to the edge. $\tau$ increases with increasing flow velocity.
Figure 2.4 The dependence of distance along from the center of the substrate and shear stress ($\tau$) with respect to tip velocities in DI-water.
The equation of energy in terms of the transport properties for Newtonian fluids

(For rectangular coordinate):

\[
\rho C_p \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = k \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] + 2\mu \left\{ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 \right\} + \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 \]

(2.12)

\[
\rho \frac{DU}{Dt} = -\nabla \cdot q - p \nabla \cdot v - (\tau : \nabla v) \quad (2.13)
\]

Rate of gain of internal energy per unit volume equals to the rate of internal energy input by conduction per unit volume plus reversible rate of internal energy increase per unit volume by compression and plus irreversible rate of internal energy increase per unit volume by viscous dissipation.

The energy generation due to viscous dissipation (\(\varepsilon_{\text{diss}}\)) is found from

\[
\varepsilon_{\text{diss}} = \tau : \nabla v = \tau_{xx} \left( \frac{\partial u}{\partial x} \right) + \tau_{yy} \left( \frac{\partial v}{\partial y} \right) + \tau_{xy} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \]

(2.14)

or

\[
\varepsilon_{\text{diss}} = \tau : \nabla v \approx \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 \]

(2.15)

The dependence of \(\varepsilon_{\text{diss}}\) and the distance along from the center of the substrate with respect to tip velocities \(u\) in deionized water (DI-water) is shown in Fig. 2.5. \(\varepsilon_{\text{diss}}\) increases quadratically with increasing the distance. \(\varepsilon_{\text{diss}}\) increases
with increasing flow velocity. Fig. 2.6 shows $\varepsilon_{diss}$ increases quadratically with increasing $\tau$. 
Figure 2.5 The dependence of distance along from the center of the substrate and $\varepsilon_{diss}$ with respect to tip velocities in DI-water.
Figure 2.6 The relationship between $\varepsilon_{diss}$ and $\tau$ in DI-water
RESULTS AND DISCUSSION

The dependence of induced voltage in perpendicularly aligned MWCNTs on tip velocity ($u$) and ionic strength is shown in Fig. 2.7. A flow-induced voltage of 43 mV was generated from DI-water at a relatively low flow velocity of $1.49 \times 10^{-5}$ m/s. This is roughly 21 times higher than the highest voltage reported to date for single-walled carbon nanotubes (SWCNTs). A flow-induced voltage of 52 mV was generated from an aqueous solution of 0.2 M NaCl at a relatively low flow velocity of $4.05 \times 10^{-5}$ m/s. This is roughly 1.2 times higher than the highest voltage generated from DI-water, confirming that the ionic strength of the flowing liquid affects flow-induced voltage, as predicted by the “pulsating asymmetric ratcheting” mechanism. The shear-flow past the nanotube surface provided the unidirectional bias (fluctuating). Fluctuating imbalanced the local charge neutrality of ionic fluid, and provided stochastic asymmetric potential which moving with flow and dragging free carriers to induce voltage.$^{3,5,8}$
Figure 2.7 The relationship between flow-induced voltages and tip velocities in NaCl solution with different concentrations.
As seen in Fig. 2.7 and Tab. 2.1, the DI-water line generally generated the lowest voltage. A rapid increase in the flow-induced voltage at as NaCl concentration was increased from 0. At higher concentrations, the rate at which the voltage increased with increasing NaCl concentration slowed down. The 0.2 M NaCl curve had the highest slope, indicating that at this concentration the voltage change was most sensitive to a change in velocity. For 0.4 and 1 M NaCl, the voltage change was relatively insensitive to a change in flow velocity because of the saturation effect. The flow-induced voltages dependence on tip velocities ($u$) and bulk velocities ($v_0$) are shown in Figs. 2.8 and 2.9, respectively for DI-water. The curves were fit to equation (2.3). The results were consistent with a “pulsating asymmetric ratcheting” proposed for SWCNTs.$^2$
**Table 2.1** Relationship between the ionic strength of the flowing liquid and the slope of voltage-generation curve and velocity sensitivity of multi-walled carbon nanotubes

<table>
<thead>
<tr>
<th>Solution</th>
<th>H₂O</th>
<th>NaCl 0.1 M</th>
<th>NaCl 0.2 M</th>
<th>NaCl 0.4 M</th>
<th>NaCl 1 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>4.70</td>
<td>3.53</td>
<td>5.21</td>
<td>2.56</td>
<td>0.2283</td>
</tr>
<tr>
<td>Velocity sensitivity (mV)</td>
<td>38.47</td>
<td>28.25</td>
<td>39.64</td>
<td>17.8</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Figure 2.8 Flow-induced voltages dependence on the tip velocities in DI-water

\[ V \approx V_0 \left( \frac{1 - \exp[-au]}{\exp[-bu]} \right) \]

\( (V_0 = 50 \text{ mV}, \ a = 232200, \ b = -14900) \)
Figure 2.9 Flow-induced voltages dependence on the bulk flow velocities in DI-water ($V_0 = 23.8832$ mV, $a = 99.1902$, $b = 12.1675$)
REFERENCES


CHAPTER 3

Sensing and Energy Harvesting of Fluidic Flow Using Graphene
ABSTRACT

Graphene field effect transistors (FETs) were incorporated into microfluidic channels. These FETs can locally sense changes in conductance and electrostatic potential induced by the flow of an ionic liquid. It was demonstrated that graphene FET’s conductance and electrostatic potential changed in response to changes in flow rates, flow directions, pH, and water gate voltages under an applied source-drain voltage. In the absence of source-drain voltage, it was further demonstrated that the ionic flow could enable the generation of electrical potential on the graphene FETs. Specific application as power scavenged from a flowing liquid could be used to fabricate self-powered graphene-based systems. Quantitative analysis suggested that, with an applied source-drain voltage, the current change was dominated by a consequence of the streaming potential generation. Without source-drain voltage, the potential change of graphene was most likely due to a charge dragging effect.

KEYWORDS: Sensor, Flow, Energy conversion, Graphene
INTRODUCTION

Nanowire (NW) or carbon nanotube (CNT) field effect transistors (FETs) are one of the most promising candidates for label free sensors\textsuperscript{1-4} because NW and CNT have small diameters and high aspect ratios, however; the control of the diameter of NW or CNT is still a major challenge.\textsuperscript{5,6} Graphene holds several important advantages over other nanoscale materials, such as NW or CNT. First, graphene has a two dimensional (2 D) structure and every atom is exposed on its surface. The electrical properties of graphene are sensitive to the change of the charge environment induced by the reaction or adsorption of ions on the graphene surface. Therefore, graphene is a promising material for highly sensitive chemical and biological sensor.\textsuperscript{7,8} Second, it is relatively easier to fabricate graphene into any desired shape and size relative to NW or CNT. Last but not the least, the robust nature of C-C bonds in graphene makes it chemically and mechanically stable, enabling a broad range of potential device applications.\textsuperscript{9-14}

Graphene, as a single atom layer of carbon atoms, has already shown the potential for electronics and biosensing applications.\textsuperscript{15,16} However, graphene is ultrasensitive to the underlying substrate and surface chemistry, which can alter charge transport properties of pristine graphene.\textsuperscript{17} In an ideal case of grounded graphene, its charge neutrality point (CNP) is located at zero back or water gate voltage ($V_g$). However, most of the graphene based FETs show initial p-doping (CNP is positioned at positive $V_g$) and hysteresis in ambient conditions. The doping of graphene can be caused either by adsorbates on top or underneath the graphene surface.\textsuperscript{17-19}
Depending on the nature of the dopant or the electrochemical environment, the initial doping can be either p or n, which introduces a shift of the graphene CNP to positive or negative gate voltages, respectively. Different dopings (p or n) have been shown in following experiments to illustrate different doping effects by varying electrochemical environments. That is the different offset gate voltage applied on graphene FET through streaming potential generation. According to the streaming potential mechanism for nanoelectronic FET flow sensing, the streaming potential adjusts the surface potential of graphene which modulates the conductance of graphene through the field gating effect. The effective gate voltage applied on the graphene FET would be changed by flow rate whenever a fixed gate voltage was applied. Using the buffer solutions with different pH values as another independent control of graphene’s surface potential, it was experimentally confirmed that the graphene FET showed clear response to surface potential change. Therefore, graphene FETs can be used to locally sense the flow of a liquid with different directions, flow rates, and pH via the streaming potential modulated conductance effect. It was also found that the current could be generated in the graphene by fluid flow even without any electrical voltage driving the device. This opens up the possibility of exploiting fluid flow for electric power generation or self-powered nanoelectronics. In the near future, a three dimensional (3 D) energy harvester using graphene and other nano- (bio-) structures could be potential built.
EXPERIMENTAL

Graphene films were synthesized by chemical vapor deposition (CVD) (Fig. 3.1) on copper (Cu) foil using methane (CH$_4$) and hydrogen (H$_2$). Base pressure check, leak rate check (pressure/time) were required before the experiment. Leak check was carried out by opening all connections, and dropping acetone on the area of inspection. If there is a leakage, the gauge pressure will increase. The mass flow controllers (MFCs) was calibrated through getting the relationship between the gauge pressure and gas flow rate from MFCs. H$_2$ was used to make sure there was no O$_2$ in the furnace tube. The CH$_4$ was the source material for graphene growth. Graphene film could be obtained by reorganizing carbon atoms in CH$_4$.

A sample of copper (1.5 cm × 4-5 cm) was carefully cut using scissors. The copper foil was hold and flattened using two glass slides. Both sides of the copper foil was cleaned using acetone, ethanol and compressed air. The copper foil was slowly put into the center of the chamber using tweezers. The tube chamber was pumped down to the range of 13-18 mTorr. The H$_2$ gas was turned on and the furnace temperature was set to 1000 °C. The CH$_4$ was turned on after the furnace temperature reaching 1000 °C. The whole system was kept running for 30 minutes followed by 1 hour cooling down by setting the temperature to zero in the tube furnace. After cooling down, the CH$_4$, H$_2$ and the pump valves were turned off, and the copper foil could be picked up onto a sample dish by opening the furnace tube.
Figure 3.1 Schematic diagram of the graphene chemical vapor deposition (CVD) growth process
The next step was to transfer the graphene film onto a 300 nm SiO₂/Si substrate. The 300 nm SiO₂/Si substrate was exposed on UV light at 110 °C for 10 minutes. A thin layer of polymethyl methacrylate (PMMA) was spin coated on the copper foil (which has graphene on it) at 2000-4000 rpm for 40 seconds. The copper foil was dried in air for 2 hours, and then the copper foil was dissolved in 1 M FeCl₃ for 30 minutes. The graphene was scooped by the Si/SiO₂ substrate in deionized water (DI-water) 3 times to clean the PMMA and transfer the graphene film onto the Si/SiO₂ substrate. The Si/SiO₂ substrate with graphene film was baked at 150 °C for 15 minutes under vacuum, and acetone and isopropyl alcohol (IPA) were used to remove PMMA for 30 minutes after cooling down. The graphene sample was dried by blowing compressed air. An optical image of centimeter scale single layer graphene film with low level defects transferred onto a 300 nm SiO₂/Si substrate is shown in Fig. 3.2. Photolithography followed by electron beam (E-beam) evaporator deposition was used to pattern electrodes (Ni, 60 nm) on the top surface of the transferred graphene film (3 mm × 4 mm). The main parts of the metal contacts were passivated using Al₂O₃. The I-V characteristic (Fig. 3.3) showed a linear characteristic at room temperature, indicating Ohmic contact behavior. The experimental set-up is shown in Fig. 3.4. The graphene FET was laid down on the Si/SiO₂ substrate and covered by a polydimethylsiloxane (PDMS) microfluidic channel. The flowing liquid passing through the PDMS flow channel was controlled by a syringe pump (New Era Pump Systems, Inc.). A 10 mV D.C. voltage was applied to the source and drain electrodes. The source-drain current $I_{sd}$ was converted to a voltage by a current amplifier (Stanford Research, model...
SR570) and recorded using a National Instrument data acquisition card and BNC terminal box. The flow rate ($v$) was between 1 and 8 ml/h during the test.
Figure 3.2 Optical image of centimeter scale single layer graphene film with low level defects transferred onto a 300 nm SiO$_2$/Si substrate
Figure 3.3 The I-V curve of graphene field effect transistor (FET)
Figure 3.4 Experimental set-up of graphene transistor devices enclosed in microfluidic flow channel for flow sensing and power harvesting
RESULTS AND DISCUSSION

The two curves in Fig. 3.5 show the relationship between time and current of a graphene FET in the 2 μm long channel at different flow directions and rates $v$ of DI-water at a source-drain voltage $V_{sd}=10$ mV. The flow directions are the same as (and opposite to) the source-drain current flow direction as seen in the Fig. 3.5 (a) and Fig. 3.5 (b), respectively. It was observed that the flow direction affected the sign of the conductance change of graphene FET. With increasing $v$, the conductance increased when the source-drain current was in the same direction as the flow and decreased if it was oppositely directed. This graphene FET device also had a clear step-wise response to $v$ and showed reliability and reversibility at least over one day of experiment period. In addition to that, as a good candidate for a flow sensor, the current signal response time of the graphene FET was approximately 10 seconds after $v$ was changed.
Figure 3.5 (a) Effect of flow directions and rates $\nu$ on the current of a graphene FET with source-drain voltage $V_{sd}=10$ mV in DI-water. The flow direction is the same as the current flow.
Figure 3.5 (b) Effect of flow directions and rates $v$ on the current of a graphene FET with source-drain voltage $V_{sd}=10$ mV in DI-water. The flow direction is opposite to the current flow.
With flowing liquid, the excess counter ions on graphene are swept downstream by the pressure-driven flow, generating steaming potential. According to the electrokinetic theory of streaming potentials based on the Smoluchowski equation, the steaming potential is a function of flow rate ($v$) and ionic concentration ($C$) and governed by:\textsuperscript{7,14,20,21}

$$\Delta V_{str} = \frac{\varepsilon_0 \varepsilon_r \zeta R}{\eta e (C + \lambda) \mu} \Delta v$$ \hspace{1cm} (3.1)

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant of the electrolyte solution, $\zeta$ is the zeta potential of the ionic double layer, $R$ is the hydraulic flow resistance estimated from Poiseuille’s law, $\eta$ is the viscosity of the electrolyte solution,\textsuperscript{21} $e$ is the electron charge, $\lambda$ is the offset concentration that generated from the background concentration of ions, and $\mu$ is the effective ionic mobility of the electrolyte solution.\textsuperscript{7,14} The steaming potential $\Delta V_{str}$ offsets the water gate (or reference electrode) voltage and thus shifts the surface potential of graphene (Fig. 3.6).\textsuperscript{22} Since the sign of the generated streaming potential reversed upon the reversal of fluid flow direction, an opposite change of current (or conductance) in graphene FET was expected at opposite flow directions as shown schematically at the bottom of Fig. 3.6. This was consistent with the experimental observation here. According to equation (3.1), the streaming potential is proportional to $v$. A linear dependence between the current and flow rate was observed for both flow directions.
Since the streaming potential is mainly influenced by the three parameters, including the flow rate, the ionic strength of the fluid and the zeta potential of the substrate, the device can be used for sensing any one of the three quantities when the other two were known.\textsuperscript{7} The streaming potential was proportional to the zeta potential ($\zeta$) of the substrate. The zeta potentials of Si/SiO$_2$ substrate in DI-water were reported to be about -75 mV.\textsuperscript{23,24} The zeta potential $\zeta$ of a substrate has a logarithmic dependence on the ionic concentration $C$ and is approximately given by,\textsuperscript{7,25}

\begin{equation}
\zeta = a \log(C + \lambda)
\end{equation}

where $a$ is the constant, $\lambda$ is the background concentration of ions. The substrate of the microfluidic channel plays an important role on the streaming potential and the sensitivity of the graphene FET for flow velocity sensing.\textsuperscript{7}
**Figure 3.6** Schematic illustration of fluid flow generated streaming potential. The slope of the generated streaming potential between the reference electrode and the graphene FET changes sign as the flow direction reverses.
Fig. 3.7 illustrates the source-drain current through a second graphene device in response to flow rate changes without any external source-drain voltage to drive the graphene. This measurement was in contrast to the sensing experiment, where nonzero $V_{sd}$ was applied. Here, although the flow rate change induces a streaming potential change $\Delta V_{str}$, $\Delta V_{str}$ is not expected to cause any current flowing through the graphene since $\Delta V_{str}$ influences only the conductance of graphene which converts to a current change only if a finite $V_{sd}$ is applied. A control experiment on a device without graphene between the electrodes did not show any measurable current over a similar range of water flow rate. This attests to the good isolation of electrodes from water in the device and proves that the flow induced current in Fig. 3.7 came from the graphene. In the literature, there are mainly two mechanisms for such flow induced voltage/current generation. The first mechanism is pulsating asymmetric ratcheting,\textsuperscript{26,27} in which fluctuating Coulombic field of the liquid caused by shear stress imbalances local charge neutrality of ionic fluid, provides stochastic asymmetric potential which moves with flow, and drags free carriers to induce voltage. It is proposed\textsuperscript{26,27} that a fluctuating Coulombic potential arises due to local imbalances in charge neutrality of the ionic fluid. The unidirectional nature of the flow provides a bias that can be thought of as the deformation of the transient accumulation of charges. The pulsating asymmetric ratcheting resulted voltage is:\textsuperscript{26,27}

$$V \approx V_0 \left( \frac{1 - \exp[-av]}{\exp[-bv]} \right)$$

(3.3)
where $V_0$, $a$, $b$ are the constants and $v$ is the flow velocity.

Equation (3.3) predicts a sublinear relation between induced voltage and flow velocity. This appears to disagree with data in Fig. 3.7 where quasi-linear dependence is observed.

Another possible explanation$^{28}$ is that voltage generation arises due to a phonon wind that drags free carriers. That is the transfer of momentum from the flowing liquid molecules to the acoustic phonons as the phonon quasi-momentum, which in turn drags free electrons in the graphene. In this model, the voltage has a linear relationship to the flow velocity and liquid viscosity. The velocity dependence expected in the carrier drag mechanism seems to be in agreement with the observation here.
Figure 3.7 Fluid flow generated current through a graphene at different flow rates without any source-drain voltage applied on the graphene.
The conductance of n-type (p-type) graphene increases with decreasing (increasing) pH of the buffer solutions (in Figs. 3.8 (a) and (b)). That makes the graphene a candidate for pH sensor. The increase (decrease) of current at lower pH is consistent with that the n-type (p-type) graphene and the low pH value leads to more positively (negatively) charged graphene surface and a positive (negative) shift of surface potential.

It was difficult to determine the property of ions (positive or negative) on a graphene surface when it was immersed in the aqueous solution. Whether ions on the graphene surface were positive or negative (p-type or n-type) can be detected through pH sensing. Using pH was an independent control of graphene’s surface potential, it was experimentally confirmed that the graphene FET investigated here showed clear response to surface potential change. The steaming potential $\Delta V_{str}$, (by changing pH value of the buffer solution) offsetted the water gate (or reference electrode) voltage, and consequently shifted the surface potential of graphene.
Figure 3.8 (a) Effect of the potassium phosphate buffer solutions with different pH values on p-type graphene FETs ($V_{sd}=10$ mV)
Figure 3.8 (b) Effect of the potassium phosphate buffer solutions with different pH values on n-type graphene FETs ($V_{sd}=10$ mV)
In the literature, the Dirac point (the charge neutrality point) of graphene FET at a solution shifts with the change of the pH, flow velocity and ionic strength, etc.\textsuperscript{7} Variations in water gate across the Dirac point demonstrated both n- and p-type recording could be achieved with the same device simply by offsetting the water gate voltage.\textsuperscript{13} In DI-water, p-type and n-type graphene samples were found in experiments. There are mainly two reasons for this phenomena. One reason is that generated streaming potential in the flowing liquid is a function of the water gate voltage. The Dirac point of graphene FET shifts with the change of the water gate voltage. The other reason is from different structures and growth conditions of graphene. Two different graphene samples are shown in Fig. 3.9. The p-type graphene FET and ambipolar electric field effect characteristics are shown in Fig. 3.9 (a). P-type graphene has positive charges on its surface. Fig. 3.9 (b) is shown for n-type graphene FET, which means negative charges are on graphene surface.

The different graphene FETs showed the different Dirac point at the same conditions during the experiment. A possible explanation of the instability is due to charged impurities such as defects underlying SiO\textsubscript{2} or Si. Charged impurity scattering is a major subject in the graphene technology.\textsuperscript{29,30} These uncontrollable charged impurities may lead to the Dirac point instability.\textsuperscript{5} Another reason is the 2D structure of the graphene devices differs significantly, in terms of active detection area and surface topography or roughness, versus 1D nanowire FETs.\textsuperscript{13} The reduction of the defects in graphene,\textsuperscript{31,32} the optimization of the growth and transfer
conditions,\textsuperscript{33,34} and the choice of the substrates\textsuperscript{35} with reduced roughness and chemical reactivity could further enhance the performance of graphene FETs.\textsuperscript{36}
Figure 3.9 (a) DI-water gating effect of p-type graphene FET
Figure 3.9 (b) DI-water gating effect of n-type graphene FET
In conclusion, due to the unique ability to sense minute changes in their immediate environments, graphene FETs can be used as probes of electrochemical phenomena in flowing liquids. The sensitivity of electrical transport in graphene FETs to the flow rate, flow direction and pH buffers can be explained by streaming potential, the variation of the local electrochemical potential of the liquid next to graphene. It is expected that the demonstrated graphene-based label-free sensors for liquid flow and ionic strength will find applications ranging from analytical chemistry to biomolecular detection. As energy harvesters, graphene and other nanomaterials could be used as basic elements to build 3 D structures for power generation. Multiple advantages of graphene including higher mechanical strength, high output current signal comparing to nanowire and carbon nanotube, and the ability to fabricate large surface area single layer films of graphene on an industrial scale, should promote the rapid development of such sensors and energy harvesters.
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CONCLUSIONS

In this dissertation, mechanisms on flow sensing and energy harvesting were investigated. The streaming potential tuned conductance of nano- and carbon materials facilitated by a gating effect is the main mechanism for flow sensing. Flow-induce voltage generation on InAs NWs, MWCNTs and graphene is due to a charge dragging effect. With the applied source-drain voltages, the charge dragging effect contributes about 10% of the induced voltage produced by the streaming potential.

Two different flow patterns, stagnation-type flow configuration and the flow parallel to the device surface are each worth trying on nano- and carbon material devices. Each flow has its own advantages and disadvantages with respect to inducing voltage generation. Stagnation-type flow configurations are easier to employ as a large scale (bundled) energy harvester. However, it is difficult for flowing liquid to enter the inside of the devices. For flow parallel to the device surface, the flowing liquid can contact every surface of a single or bundled devices. However, it is required to design the flow channel specifically for the large scale devices in this flow model.

The sensitivity of InAs NW, $\Delta V_{\text{str}} / \Delta v \sim 3.5$ mV/ (mm/s), is very close to the value obtained in Si NW flow sensors at comparable ionic strength in literature. A 40-50 mV voltage can be harvested from bundled multiple MWCNTs (the number
of MWCNTs is around $10^9$. This is the highest observed voltage generation compared to InAs NWs and graphene due to the high numbers of MWCNTs. Bundled InAs NWs also have the advantages of increasing the absolute value of conductance and the conductance change at a given flow rate is amplified by 3-4 times compared to single NW device. The long time stability, long life-time and reproducibility of multiple and bundled devices have the potential to build 3 D macro-structured energy harvesters for much greater power generation as the internal resistance of the devices is reduced.

These experiments used a forced flow generated by a pump. In this sense of course, more energy is supplied to the pump than is harvested by the device. For energy harvesting applications, the nano or carbon devices could be employed in systems where the flow is either naturally occurring or is part of the normal system operation. Simulated blood flow is another option for future experiments to investigate the possibility of powering implantable devices for medical and energy related applications.
APPENDIX

APPENDIX A: Flow sensing from another InAs nanowire device

Figure S 1 Effect of flow directions and rates $v$ on the current of a single InAs nanowire (NW) field effect transistor (FET) that is different from the device discussed in the main text. A source-drain voltage $V_{sd}=10$ mV was applied. The flowing liquid is DI-water. The black (red) curve corresponds to flow direction same as (opposite to) the current flow.
APPENDIX B: ZnO nanowires growth by chemical vapor deposition

There are two major growth methods of growing ZnO nanowires (NWs) by chemical vapor deposition (CVD). One of them is using elemental Zn powder and the carrier gas is a mixture of Ar and O₂. The other method is carbon reduction method. The source material contains a mixture of ZnO powder and carbon powder and the gases are O₂ and Ar. The carbon reduction method was the method being used during the experiments in this work.

ZnO NWs were grown on Si/SiO₂ substrates in a custom built CVD system via the vapor-liquid-solid (VLS) mechanism. The experimental set-up is shown in Fig. S 2. A mixture of ZnO powder and carbon powder acted as source material and was put in the middle of the furnace. The source material was heated in the furnace at a low pressure. The source material evaporated and flowed with the carrier gases of Ar and O₂. The vapor flowed down the quartz tube to a substrate of Si/SiO₂ wafer seeded with Au nanoparticles. Governed by the VLS mechanism, the source vapor dissolved on the Au catalyst to form a eutectic mixture. The mixture shifted into a different region of the eutectic phase diagram where the source material becomes solid, as more source vapor dissolved onto the Au. This resulted in the source material precipitating out of the Au-source mixture to form a crystal. As the process continues, the crystal extended in one direction, and formed a NW as the Au nanoparticle stayed on the tip of the wire.
Different wire morphologies were created by varying the growth conditions, specifically the oxygen partial pressure, the chamber pressure, source/wafer temperature, growth time, and the thickness of the catalyst layer, etc. Optimal growth conditions were found as following:

A clean Si/SiO₂ wafer was cut to 1.5 cm × 3.5 cm, sonicated in acetone, and rinsed by ethanol and DI-water. Then a layer of poly-L-lysine was coated on the substrate for 8.5 minutes. The wafer was rinsed by DI-water and air blown dry. A solution of spherical catalytic Au nanoparticles with a diameter of 40 nm was coated on to the substrate for 5 minutes, rinsed by DI-water, and then the wafer was air blown dried. The Si/SiO₂ substrate was placed 11-13 cm downstream in a 1 inch diameter Lindberg Blue tube furnace with the source material in a 1:1 weight ratio (0.1 g each), and placed at the center of the tube furnace (Fig. S 2). The quartz tube was pumped down to 0.1 Torr and then heated up to 1050 °C. The mixed gas flow of 25 sccm Ar and 8 sccm O₂ was turned on when the furnace reached the desired temperature. The total pressure in furnace tube was adjusted to 2.3 Torr. Growth time of NWs was around 1 hour. A table summarizing the results of several of the experiments in different parameters is shown on Tab. S 3. Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs were shown in Fig. S 4.
Figure S 2 Schematic diagram of the ZnO nanowire (NW) chemical vapor deposition (CVD) growth process
Table S 3  Summary of ZnO nanowires (NWs) growth under different growth conditions

<table>
<thead>
<tr>
<th>Chip</th>
<th>poly-L-lysin (min)</th>
<th>Au (nm; min)</th>
<th>Temperature (°C)</th>
<th>Pressure (Torr)</th>
<th>Gas Flow Ar/O₂ (sccm)</th>
<th>Time (min)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>8.5</td>
<td>10; 5</td>
<td>950</td>
<td>0.1; 2.6</td>
<td>25:100</td>
<td>30</td>
<td>Flakes (Amorphous crystal growths)</td>
</tr>
<tr>
<td>Si</td>
<td>4</td>
<td>10; 3</td>
<td>1050</td>
<td>0.1; 2.6</td>
<td>25:100</td>
<td>45</td>
<td>Several NWs;</td>
</tr>
<tr>
<td>Si</td>
<td>4</td>
<td>10; 3</td>
<td>1050</td>
<td>0.1; 2.3</td>
<td>25:20</td>
<td>60</td>
<td>Small and short NWs on the edge of flakes (Sparse growth)</td>
</tr>
<tr>
<td>Si</td>
<td>4</td>
<td>10; 3</td>
<td>950</td>
<td>0.1; 2.3</td>
<td>25:20</td>
<td>45</td>
<td>Nanostructure growth</td>
</tr>
<tr>
<td>Si</td>
<td>8.5</td>
<td>40; 5</td>
<td>1050</td>
<td>0.1; 2.3</td>
<td>25:80</td>
<td>45</td>
<td>Small and short NWs; Sparse growth</td>
</tr>
<tr>
<td>Si</td>
<td>8.5</td>
<td>40; 5</td>
<td>1050</td>
<td>0.38; 2.2</td>
<td>25:60</td>
<td>60</td>
<td>Small and short NWs; Sparse growth and small flakes</td>
</tr>
<tr>
<td>SiO₂</td>
<td>8.5</td>
<td>40; 5</td>
<td>1050</td>
<td>0.1; 2.3</td>
<td>25:80</td>
<td>60</td>
<td>Dense and short nanowires</td>
</tr>
<tr>
<td>SiO₂</td>
<td>8.5</td>
<td>40; 5</td>
<td>1050</td>
<td>0.1; 2.3</td>
<td>25:1</td>
<td>60</td>
<td>NW particles</td>
</tr>
<tr>
<td>SiO₂</td>
<td>8.5</td>
<td>40; 5</td>
<td>1050</td>
<td>0.1; 2.2</td>
<td>25:5</td>
<td>60</td>
<td>NW particles/wires</td>
</tr>
</tbody>
</table>
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (a) OM image of no NW growth (only Au catalyst)
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (b) OM image of flakes (amorphous crystal growths)
**Figure S 4** Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (c) OM image of flakes with several NWs (amorphous crystal growths)
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (d) OM image of NW clusters and particles
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (e) OM image of small and short NWs
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (f) OM image of long NWs with sparse growth
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (g) OM image of long NWs with dense growth
**Figure S 4** Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (h) OM image of longer NW with higher density
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (i) SEM image of NWs clusters
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (j) SEM image of NW ribbons
**Figure S 4** Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (k) SEM image of long NWs with low density
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (l) SEM image of long NWs with high density.
Figure S 4 Optical microscopic (OM) images and scanning electron microscope (SEM) images of grown ZnO NWs. (m) SEM image of single NW with high quality
APPENDIX C: Matlab program for calculating tip flow velocity of Multi-walled carbon nanotubes (MWCNTs)

- function [s,t,N]=solveequation(h, L,thr)
  - u=1;v=0;t=1;
  - while abs(u-v)>thr
    - clear N;
    - clear y1;
    - clear y2;
    - clear y3;
    - N=round(L*t/h+1);
    - y1=zeros(N,1);
    - y2=zeros(N,1);
    - y3=zeros(N,1);
    - y1(1,1)=0;
    - y2(1,1)=0;
    - y3(1,1)=1.232588;
    - for i=2:N
      - y1(i,1)=y1(i-1,1)+h*y2(i-1,1);
      - y2(i,1)=y2(i-1,1)+h*y3(i-1,1);
      - y3(i,1)=y3(i-1,1)+h*(-1-y1(i-1,1)*y3(i-1,1)+y2(i-1,1)*y2(i-1,1));
    - end
Technically, the velocities of different directions on every position of MWCNTs can be obtained.
APPENDIX D: Matlab program for fitting the experimental data into the mathematic equation

```matlab
>> u=1.0e-
007*[0.0027;0.0077;0.0192;0.0226;0.0272;0.0692;0.1050;0.1310;0.1510]

u =

1.0e-007 *

0.0027
0.0077
0.0192
0.0226
0.0272
0.0692
0.1050
0.1310
0.1510

>>

V=[4.1600;10.1200;18.5100;22.1960;24.1300;30.4900;33.7800;39.8700;42.6300]

V =
```
<table>
<thead>
<tr>
<th>u</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1600</td>
<td>10.1200</td>
</tr>
<tr>
<td>10.1200</td>
<td>18.5100</td>
</tr>
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<td>18.5100</td>
<td>22.1960</td>
</tr>
<tr>
<td>22.1960</td>
<td>24.1300</td>
</tr>
<tr>
<td>24.1300</td>
<td>30.4900</td>
</tr>
<tr>
<td>30.4900</td>
<td>33.7800</td>
</tr>
<tr>
<td>33.7800</td>
<td>39.8700</td>
</tr>
<tr>
<td>39.8700</td>
<td>42.6300</td>
</tr>
</tbody>
</table>

```matlab
>> myfunc=inline('beta(1)*(1-exp(-beta(2)*u))./exp(-beta(3)*u)','beta','u')
```

```matlab
myfunc =

    Inline function:
    myfunc(beta,u) = beta(1)*(1-exp(-beta(2)*u))./exp(-beta(3)*u)
```

```matlab
>> beta=nlinfit(u,V,myfunc,[10000000,10000000,10000000]);
```

Warning: The Jacobian at the solution is ill-conditioned, and some model parameters may not be estimated well (they are not identifiable).

Use caution in making predictions.

> In nlinfit at 223
beta =

1.0e+007 *

0.0045  0.0221  -9.1423

>> t=0:1e-010:max(u);  (t means from 0 to the max of u, at the interval of 1e-010,z means V, and use same my function to calculate the z(t), and then plot the figure use the t-z points and u-V points to make the figure more pretty and accurate)

>> z=beta(1)*(1-exp(-beta(2)*t))./exp(-beta(3)*t);

>> plot(t,z,u,V,'.')
APPENDIX E: Instruments and uncertainty analysis of the experiment on flow-induced voltage from Multi-walled carbon nanotubes (MWCNTs)

Cole-Parmer flow meter (volumetric, water, differential pressure, 0 to 5 L/min):

±2 %

Masterflex™ pump drive economy drive, AC input 90-130 V: ±0.25 %

Economy Series Locking-Jaw Slide Caliper: ±0.0015” (0.04 mm)

Uncertainty Analysis

\[
V \approx V_0 \left\{ \frac{1 - \exp[-au]}{\exp[-bu]} \right\}
\]

\(V_0, a, b\) are the constants.

\[V = V(u)\]

\[
\frac{U_u^2}{v^2} = \left( \frac{u \partial v}{v \partial u} \right)^2 \left( \frac{U_u}{u} \right)^2
\]

\[
\frac{U_u^2}{v^2} = \left( \frac{u \ e^{-au}}{1 - e^{-au} + b} \right)^2 \left( \frac{U_u}{u} \right)^2
\]

\[
\left( \frac{U_u}{u} \right)^2 \leq \pm 2\%
\]
APPENDIX F: Figure of kinematic viscosity vs. the density of NaCl solution

Figure S 5 Figure of kinematic viscosity vs. the density of NaCl solution
APPENDIX G: Preparation of the potassium phosphate buffer solutions with different pH values³

Prepare the potassium phosphate buffer solution with pH=7:
2.1 ml, 100 mM monobasic K phosphate (KH₂PO₄) and 2.9 ml, 100 mM dibasic K phosphate (K₂HPO₄) were mixed together and diluted 10 times in DI-water.

Prepare the potassium phosphate buffer solution with pH=4.5 (10 mM monobasic K phosphate (KH₂PO₄)):
K phosphate (KH₂PO₄) monobasic powder (molecular weight × 100 mM × volume) was dissolved in DI-water to make 100 mM monobasic K phosphate (KH₂PO₄), and then diluted 10 times in DI-water.

Prepare the potassium phosphate buffer solution with pH=8.4 (10 mM dibasic K phosphate (K₂HPO₄)):
K phosphate (K₂HPO₄) dibasic powder (molecular weight × 100 mM × volume) was dissolved in DI-water to make 100 mM dibasic K phosphate (K₂HPO₄), and then diluted 10 times in DI-water.
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Chapter 2


Chapter 3


Appendix

