Title
Synthesis and Characterization of One-Dimensional Nanomaterials for Thermoelectrics and Gas Sensors

Permalink
https://escholarship.org/uc/item/9sw331x3

Author
Zhang, Miluo

Publication Date
2014

Peer reviewed|Thesis/dissertation
Synthesis and Characterization of One-Dimensional Nanomaterials for Thermoelectrics and Gas Sensors

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Miluo Zhang

March 2014

Dissertation Committee:

Dr. Nosang V. Myung, Chairperson
Dr. Ashok Mulchandani
Dr. Phillip N. Christopher
The Dissertation of Miluo Zhang is approved:

________________________________________

________________________________________

________________________________________

__________________________________________
Committee Chairperson

University of California, Riverside
ABSTRACT OF THE DISSERTATION

Synthesis and Characterization of One-Dimensional Nanomaterials for Thermoelectrics and Gas Sensors

by

Miluo Zhang

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, March 2014
Dr. Nosang V. Myung, Chairperson

One-dimensional nanostructures, such as nanowires and nanotubes have attract intensive interest in various applications including gas sensors and thermoelectrics, due to their unique size-dependent electrical, thermal transport and mechanical properties. Miniature and portable gas sensors are of great importance in detecting gaseous molecules for environmental pollution analysis, homeland security, industrial emission control and outer space exploration. Thermoelectric energy converters, which generate electricity by harvesting waste thermal energy, can improve the efficiency of environmentally-friendly and renewable energy generation. The overall objective of this work is to engineer one-dimensional nanostructures using various techniques such as electrospinning and electrochemical routes for thermoelectric and gas sensor applications.

Electrospinning and galvanic displacement reaction were combining to synthesize ultra-long metal chalcogenide nanofibers with controlled dimensions, morphologies, and
compositions. The structure, electrical and thermoelectric properties were systematically examined to understand relationships between nanofiber structures and their resulting thermoelectric performance.

In addition to thermoelectrics, high performance nano gas sensor were realized by either surface functionalizing CNTs with various Te morphologies or contacting the CNT with various electrodes for different types of electrical contacts (i.e. ohmic and Schottky contacts). An understanding of the underlying fundamental sensing mechanism was investigated to fabricate a high-performance gas sensor array.
TABLE OF CONTENTS

CHAPTER 1 ........................................................................................................................................ 1
INTRODUCTION: NANOSTRUCTURED THERMOELECTRICS AND GAS SENSORS .......................................................... 1

1.1 Nanostructured Thermoelectrics ................................................................................................. 1
   1.1.1 An Overview of Thermoelectrics ......................................................................................... 1
   1.1.2 Efficiency of Thermoelectrics ............................................................................................ 3
   1.1.3 Interdependence of Thermoelectric Parameters ................................................................. 4
   1.1.4 Thermoelectric Materials .................................................................................................. 8
   1.1.5 Fundamental Physics for Electrical Transport in Thermoelectric Materials .................. 8
   1.1.6 Recent Development of Thermoelectric Materials with Improved ZTs .......................... 17

1.2 Nanostructured Gas sensors ........................................................................................................ 26
   1.2.1 An Overview of Gas Sensors ............................................................................................ 26
   1.2.2 Gas Sensing Mechanism ................................................................................................... 29
   1.2.3 Carbon Nanotubes ........................................................................................................... 31

1.3 Research Objectives .................................................................................................................... 35

1.4 Thesis Organization ..................................................................................................................... 37

1.5 References .................................................................................................................................. 38

CHAPTER 2 ........................................................................................................................................ 74
THERMOELECTRIC PROPERTIES OF ULTRA-LONG LEAD SELENIDE HOLLOW NANOFIBERS .................................................. 74

2.1 Abstract ...................................................................................................................................... 74
2.2 Introduction .................................................................................................................. 75
2.3 Experimental .................................................................................................................. 78
2.4 Results and Discussion ................................................................................................. 81
2.5 Conclusions ................................................................................................................... 95
2.6 References ..................................................................................................................... 97

CHAPTER 3 ......................................................................................................................... 115
THERMOELECTRIC PROPERTIES OF ULTRA-LONG LEAD TELLURIDE HOLLOW NANOFIBERS .......................................................................................................................... 115
3.1 Abstract .......................................................................................................................... 115
3.2 Introduction .................................................................................................................... 116
3.3 Experimental .................................................................................................................. 120
3.4 Results and Discussion ................................................................................................. 121
3.5 Conclusions ................................................................................................................... 128
3.6 References ..................................................................................................................... 130

CHAPTER 4 ......................................................................................................................... 140
THERMOELECTRIC PROPERTIES OF ULTRA-LONG SILVER ANTIMONY LEAD TELLURIDE HOLLOW NANOFIBERS ......................................................................................... 140
4.1 Abstract .......................................................................................................................... 140
4.2 Introduction .................................................................................................................... 140
4.3 Experimental .................................................................................................................. 144
4.4 Results and Discussion ................................................................................................. 146
4.5 Conclusions ................................................................................................................... 154
4.6 References ..................................................................................................................... 156
CHAPTER 5

A HYDROGEN GAS SENSOR BASED ON PALLADIUM/SINGLE-WALLED CARBON NANOTUBE BACK-TO-BACK SCHOTTKY CONTACT

5.1 Abstract .................................................................................................................. 170
5.2 Introduction ............................................................................................................. 171
5.3 Experimental .......................................................................................................... 174
5.4 Results and Discussion .......................................................................................... 176
5.5 Conclusions ........................................................................................................... 187
5.6 References ............................................................................................................. 188

CHAPTER 6

A NITROGEN DIOXIDE GAS SENSOR BASED ON TELLURIUM/SINGLE-WALLED CARBON NANOTUBE HYBRID NANOSTRUCTURES

6.1 Abstract .................................................................................................................. 202
6.2 Introduction ............................................................................................................. 203
6.3 Experimental .......................................................................................................... 205
6.4 Results and Discussion .......................................................................................... 208
6.5 Conclusions ........................................................................................................... 217
6.6 References ............................................................................................................. 219

CHAPTER 7

CONCLUSIONS ............................................................................................................. 234
**FIGURE LIST**

**Figure 1.1** Various energy conversion applications of thermoelectric devices. ..... 49

**Figure 1.2** A generic diagram of a thermoelectric unit. Red denotes hotter temperature, and blue denotes colder temperatures. ......................... 50

**Figure 1.3** Practical thermoelectric module that consists of several unit legs connected electrically in series and thermally in parallel. .................. 51

**Figure 1.4** Thermoelectric power generation efficiency (grey area) versus $T_H$. Efficiency for conventional mechanical engines as well as the Carnot limit are shown. ..................................................................................... 52

**Figure 1.5** Interdependence of the Seebeck coefficient ($S$), electrical conductivity ($\sigma$), and thermal conductivity ($\kappa$). .................................................. 53

**Figure 1.6** Thermoelectric performance ($zT$) of the state-of-art commercial (a) n-type and (b) p-type thermoelectric materials as function of temperature ........................................................................................................ 54

**Figure 1.7** The Fermi-Dirac distribution function $f_{0E}$ (solid line) and its first-order derivative $df_{0E}/dE$ (dotted line) ................................................. 55

**Figure 1.8** Density of states of 3D, 2D, and 1D semiconductors. .................. 56

**Figure 1.9** Normalized carrier concentration as a function of $\eta$ at temperature of 300 K ......................................................................................... 57

**Figure 1.10** Seebeck coefficient as a function of $\eta$ at temperature of 300 K for 1D, 2D, and 3D semiconductors ......................................................... 58

**Figure 1.11** DOS (blue line) and electrons density distribution (yellow area) in the...
conduction band of (a) bulk Si, (b) 2 nm Si nanowire, and (c) 5 nm Si nanowire. All the drawings are based on scale.

**Figure 1.12** Research highlights on the development of thermoelectric nanostructures.

**Figure 1.13** Overview of thermoelectric performance ($zT$) of thermoelectric materials as function of temperature. (a) p-type materials and (b) n-type materials.

**Figure 1.14** TEM images of Si nanowire synthesized by (a) electroless etching process and (b) vapor-liquid-solid deposition. (c) Temperature dependent thermal conductivity of both types of nanowires with different diameters. (d) Temperature dependent power factor (red) and $ZT$ (blue) of electroless etching Si nanowires with a diameter of 52 nm.

**Figure 1.15** (a) High resolution TEM of ($\text{Pb}_{0.95}\text{Sn}_{0.05}\text{Te})_{0.84}(\text{PbS})_{0.16}$ nanocomposites with spinodal PbS (bright) and PbTe (dark) phase. (b) Structure of ($\text{PbTe})_{1-x}(\text{PbS})_x$ system with nanophase separation of PbS stripes and dots.

**Figure 1.16** Various applications of gas sensors.

**Figure 1.17** A generic diagram of a sensor and a typical sensing response.

**Figure 1.18** Gas sensors based on (a) 2D thin film and (b) 1D nanostructure.

**Figure 1.19** Scheme of a sensor that is based on a p-type nanowire bottom contacting with two electrodes. (a) Electrostatic gating effect with
electron withdrawing molecules (white particles) and electron donating molecules (yellow particles). (b) Schottky effect with dipole formation at transducer and electrode contact area.

Figure 1.20
(a) A graphic sheet consists of a hexagonal network of carbon atoms with $a_1$, $a_2$ as the unit vectors of the hexagonal planar lattice. The charity of the CNT is determined by $C = ma_1 + na_2$, where $m$ and $n$ are chirality indices. CNTs with indices $n = m$ are the armchair. Those with $n = 0$ are called zigzags and the rest are called chiral tubes. For example, a chiral CNT can be obtained by cutting the sheet along the direction $OT$ and $OA$ then rolled into a cylinder with $OA$ as the circumference with $\theta$ its chiral angle. (b) Examples of three different types of chirality of CNTs. (c) Scheme of a single-walled carbon nanotube (SWNT), a multiwalled carbon nanotube (MWNT), and a bundle of SWNTs.

Figure 2.1
Schematic illustration of galvanic displacement reaction of (a) Ni nanofibers to form (c, d) Pb$_x$Se$_y$ hollow nanofibers. Pb$_x$Se$_y$ particles are first deposited on the surface of Ni nanofibers (b), followed by the formation of continuous nanofibers (c, d). Morphology of the as-synthesized nanofibers, either (c) smooth or (b) rough, is dependent on the concentration of HSeO$_2$.$^+$

Figure 2.2
Deposited Pb content (a) and SEM images (b-d) of galvanic displaced
Pb$_x$Se$_y$ hollow nanofibers as a function of the HSeO$_2^+$ concentration (i.e. 0.01 (b), 0.05 (c), and 1 mM (d)). The concentration of Pb(NO$_3$)$_2$ and HNO$_3$ were fixed at 0.1 and 1.0 M, respectively. The galvanic displacement reaction was conducted for 24 hours at room temperature.

Figure 2.3 (a) TEM and (b) HR-TEM (inset: FFT) images of synthesized Pb$_{33}$Se$_{83}$Ni$_{14}$ hollow nanofibers. (c) Line-EDS and (d) EDS analysis confirmed the formation of Pb$_{33}$Se$_{83}$Ni$_{14}$ nanofibers after the galvanic displacement reaction. The electrolyte is consisted of 100 mM Pb$^{2+}$, 0.01 mM HSeO$_2^+$, 1 M HNO$_3$.

Figure 2.4 (a, b) TEM, (c) SAED pattern, (d) HR-TEM (inset: FFT) images, (e) line-EDS, and (f) EDS of synthesized Pb$_{28}$Se$_{53}$Ni$_{19}$ hollow nanofibers. The electrolyte is consisted of 100 mM Pb$^{2+}$, 0.05 mM HSeO$_2^+$, 1 M HNO$_3$ at room temperature. The peak of PbSe, Se and Ni$_3$Se$_2$ in SAED pattern was colored in yellow, blue and red, respectively.

Figure 2.5 (a, b) TEM, (c) SAED pattern, and (d) HR-TEM (inset: FFT) of synthesized Pb$_{42}$Se$_{42}$Ni$_{16}$ hollow nanofibers. The peak of PbSe and Ni$_3$Se$_2$ was colored in yellow and red, respectively. (e) Line-EDS and (f) EDS analysis confirmed the formation of Pb$_{42}$Se$_{42}$Ni$_{16}$ nanofibers after galvanic displacement reaction.

Figure 2.6 XRD pattern of synthesized PbSe hollow nanofibers. The Si peak is attributed to the substrate.
Figure 2.7 Average outer diameter (a) and wall-thickness (b) of as galvanic displaced Pb$_x$Se$_y$Ni$_z$ hollow nanofibers as a function of the Pb content. Theoretical data was shown in purple; this calculation is based on the assumption of 100% galvanic displacement reaction efficiency. 

Figure 2.8 (a) OCP transient, (b) Tafel plot and (c) corrosion current density of Ni films in electrolytes with 100 mM Pb$^{2+}$ and (i) 0, (ii) 0.01, (iii) 0.1, and (iv) 1 mM HSeO$_2^+$ in 1 M HNO$_3$. Electrolyte (v) contains no Pb$^{2+}$ but 1 mM HSeO$_2^+$ in 1 M HNO$_3$. 

Figure 2.9 (a, b) Full scale and (c) zoomed in cyclic voltammograms in the electrolytes with 100 mM Pb$^{2+}$ and (i) 0, (iii) 0.1, and (iv) 1 mM HSeO$_2^+$ in 1 M HNO$_3$. Electrolyte (v) contains no Pb$^{2+}$ but 1 mM HSeO$_2^+$ in 1 M HNO$_3$. Ni was anodized in the electrolyte containing 1 M HNO$_3$. (d) Tafol plots of Ni anodizing (anodic reaction), PbSe deposition (cathodic reaction) and galvanic displacement reaction. 

Figure 2.10 (a) Temperature dependent ΔV vs. ΔT characterization of Pb$_{37}$Se$_{59}$Ni$_4$ nanofiber mat. (b) Temperature dependent Seebeck coefficient of Pb$_{37}$Se$_{59}$Ni$_4$ (down triangle), Pb$_{39}$Se$_{51}$Ni$_{10}$ (star), and Pb$_{34}$Se$_{55}$Ni$_{11}$ (diamond) nanofiber mats. The dashed line indicates the maximum Seebeck coefficient of a bulk PbSe at certain temperature. (c) 3D plot of Seebeck coefficient of Pb$_x$Se$_y$Ni$_z$ nanofiber mat at 300 K as a function of Ni and Pb content.
Figure 2.S 1  SEM images of (a) electrospun PVP/Ni acetate nanofibers, (b) NiO nanofibers, (c) Ni nanofibers. ................................................................. 111

Figure 2.S 2  Temperature dependent (a) I-V characterization and (b) sheet resistance of Pb_{37}Se_{59}Ni_{4} NF mat. (c) 3D plot of Seebeck coefficient of Pb_{x}Se_{y}Ni_{z} nanofiber mat at 300 K as a function of Ni and Pb content. ............... 112

Figure 2.S 3  XRD pattern of (a) substrate, (b) Pb_{31}Se_{62}Ni_{7}, (c) Pb_{35}Se_{58}Ni_{7}, (d) Pb_{37}Se_{59}Ni_{4} hollow nanofiber mats. Substrate peaks are contributed from Si, Pt electrode and sample holder. ........................................ 113

Figure 2.S 4  3D plot of Pb_{x}Se_{y}Ni_{z} nanofiber mats’ (a) grain size as a function of Ni content and Pb/Se (b) Seebeck coefficient as a function of grain size and Pb/Se. ......................................................................................... 114

Figure 3. 1  SEM images of (a, b) electrospun CoAc_{2}/citric acid/PVP nanofibers and (c, d) Co nanofibers. 134

Figure 3. 2  SEM images of Pb_{x}Te_{y} hollow nanofibers. The concentration of Pb(NO_{3})_{2} are (1) 10 mM, (2) 50 mM, (3) 100 mM, (4) 200 mM, (5) 500 mM. The concentration of HTeO_{2}^{+} is (a) 0.1 mM, (b) 0.5 mM, (c) 1.0 mM. The concentration of HNO_{3} was fixed at 0.1 M. The galvanic displacement reactions were conducted for 30 min at room temperature. * The concentration of Pb(NO_{3})_{2} in c1 is 20 mM. The sale bars are 1 µm. ................................................................................................. 135
Figure 3.3  The Pb content of the galvanic displaced Pb\textsubscript{x}Te\textsubscript{y} hollow nanofibers as functions of the concentration of Pb\textsuperscript{2+} and HTeO\textsubscript{2}\textsuperscript{+}. ........................................... 136

Figure 3.4  The outer diameter of as galvanic displaced Pb\textsubscript{x}Te\textsubscript{y} hollow nanofibers as functions of (a) the concentration of Pb(NO\textsubscript{3})\textsubscript{2} and HTeO\textsubscript{2}\textsuperscript{+} as well as (b) the Pb content. Theoretical data was shown in dashed line; this calculation is based on the assumptions of 100 % GDR efficiency and smooth fiber formation. ................................................................. 137

Figure 3.5  XRD pattern of (a) Co nanofibers (b-e) synthesized Pb\textsubscript{x}Se\textsubscript{y} hollow nanofibers referring to Figure 2-c1, c2, c3, c5. The peaks with stars belong to the sample holder................................................................. 138

Figure 3.6  Temperature dependent (a) $\Delta V-\Delta T$ characterizations, (b) Seebeck coefficients of Pb\textsubscript{x}Te\textsubscript{y} nanofiber mats referring to Figure 2 c1-5. (c) Seebeck coefficients of the Pb\textsubscript{x}Te\textsubscript{y} nanofiber mat as functions of the Pb content and the grain size. ................................................................. 139

Figure 4.1  SEM images of Sb\textsubscript{x}Pb\textsubscript{y}Te\textsubscript{z} hollow nanofibers. The electrolytes consist of fixed concentrations of HTeO\textsubscript{2}\textsuperscript{+}, Pb(NO\textsubscript{3})\textsubscript{2} and HNO\textsubscript{3} at 0.1 mM, 50 mM and 0.1 M, respectively, while containing various concentrations of K\textsubscript{2}Sb\textsubscript{2}(C\textsubscript{4}H\textsubscript{2}O\textsubscript{6})\textsubscript{2}. The concentration of K\textsubscript{2}Sb\textsubscript{2}(C\textsubscript{4}H\textsubscript{2}O\textsubscript{6})\textsubscript{2} is (a) 0, (b) 0.50 $\mu$M, (c) 5.0 $\mu$M, (d) 12.5 $\mu$M, (e) 25 $\mu$M, (f) 50 $\mu$M, (g) 250 $\mu$M, (h) 500 $\mu$M. The galvanic displacement reactions were conducted for 12 h at room temperature. The scale bars are 500 nm.............................. 160
Figure 4.2  (a) The Pb (red circle), Sb (blue square) and Te (green triangle) content of as-deposited Pb$_x$Sb$_y$Te$_z$ hollow nanofibers as a function of the concentration of SbO$^+$. (b) The ratio of the Sb to Pb content in the Pb$_x$Sb$_y$Te$_z$ hollow nanofibers as a function of the ratio of [SbO$^+$] to [Pb$^{2+}$] in the electrolytes. The concentration of Pb(NO$_3$)$_2$ and HNO$_3$ were fixed at 50 mM and 0.1 M, respectively. The galvanic displacement reaction was conducted for 12 hours at room temperature. The dashed lines are guides to the eyes.

Figure 4.3  SEM images of Ag$_m$Pb$_x$Sb$_y$Te$_z$ nanofibers synthesized in the electrolytes containing various concentrations of AgNO$_3$ (i.e. (a) 0.01 µM, (b) 0.1 µM, (c) 1 µM, and (d) 10 µM). The concentrations of Pb(NO$_3$)$_2$, K$_2$Sb$_2$(C$_4$H$_2$O$_6$)$_2$, and HNO$_3$ were fixed at 50 mM, 12.5 µM, and 0.1 M, respectively. The galvanic displacement reactions were conducted for 12 h at room temperature. The scale bars are 1 µm.

Figure 4.4  (a) The Ag (orange diamond), Pb (red circle), Sb (blue square) and Te (green triangle) content of as-deposited Ag$_m$Pb$_x$Sb$_y$Te$_z$ nanofibers as a function of the concentration of Ag$^+$. The dashed lines are guides to the eyes.

Figure 4.5  XRD patterns of (a) Ag$_8$Pb$_{40}$Sb$_6$Te$_{46}$, (b) Ag$_{15}$Pb$_{33}$Sb$_3$Te$_{49}$, and (c) Ag$_{31}$Pb$_{21}$Sb$_4$Te$_{44}$ nanofiber mats. PbTe peaks are labeled with red circles and the peaks belong to the substrate are labeled with blue triangles.
**Figure 4.6** Temperature dependent I-V characterizations of (a) \( \text{Pb}_{45}\text{Te}_{55} \), (b) \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \) nanofiber mats. Temperature dependent of (c) Temperature dependent sheet resistance of \( \text{Pb}_{45}\text{Te}_{55} \) and \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \) nanofiber mats. Plot of \( \ln(\text{sheet resistance}) \) vs. \( 1000/T \) is inserted. .................. 165

**Figure 4.7** Temperature dependent \( \Delta V \) vs. \( \Delta T \) characterizations of (a) \( \text{Pb}_{45}\text{Te}_{55} \), (b) \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \) nanofiber mats. (c) Temperature dependent Seebeck coefficient of \( \text{Pb}_{45}\text{Te}_{55} \) and \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \) nanofiber mats. The dashed line indicates that the Seebeck coefficient is zero. .................. 166

**Figure 4.8** Temperature dependent \( \Delta V \) vs. \( \Delta T \) characterizations of (a) n-type \( \text{Ag}_1\text{Pb}_{43}\text{Sb}_5\text{Te}_{51} \) (b) p-type \( \text{Ag}_{11}\text{Pb}_{26}\text{Sb}_{11}\text{Te}_{51} \) nanofiber mats. (b) Temperature dependent Seebeck coefficient of \( \text{Ag}_1\text{Pb}_{43}\text{Sb}_5\text{Te}_{51} \) (red circle) and \( \text{Ag}_{11}\text{Pb}_{26}\text{Sb}_{11}\text{Te}_{51} \) (black circle) nanofiber mats. The dashed line indicates that the Seebeck coefficient is zero. .................. 167

**Figure 4.9** Seebeck coefficient of \( \text{Ag}_m\text{Pb}_x\text{Sb}_y\text{Te}_z \) nanofiber mats as functions of (a) Ag content, (b) Sb content, and (c) Pb content. The dashed lines indicate that the Seebeck coefficient is zero. .................. 168

**Figure 5.1** (a) Real-time sensing response, (b) calibration curve, (c) response time, and (d) recovery time of AC aligned SWNTs on Pd microelectrodes towards \( \text{H}_2 \) at different concentration. The sensing performance including sensitivity, response time and recovery time are characterized based on a sample number of 14. .................. 194

**Figure 5.2** (a-c) Real-time sensing response and (d) calibration curves of AC
aligned SWNTs on (a) Pt, (b) Cr and (c) Au electrodes towards H$_2$ at different concentrations.

**Figure 5.3** (a) Response time and (b) recovery time of AC aligned SWNTs on Pd, Pt, and Cr electrodes towards 2,000 ppm$_v$ H$_2$. No recovery time for Cr electrodes is included.

**Figure 5.4** (a) Current ($I_{DS}$)-voltage ($V_{DS}$) and (b) $I_{DS}^{-V_{DS}^{1/4}}$ characterization of AC aligned SWNTs on Pd electrodes in air (black) and 2,000 ppm$_v$ H$_2$ (red).

**Figure 5.5** (a) Schematic representation (b) band diagram and (c) equivalent circuit of SWNT devices in air (1) and H$_2$ (2).

**Figure 5.6** Current ($I_{SD}$) - back gated voltage ($V_G$) characterization of AC aligned SWNT on Pd electrodes in air (black triangle) and 2,000 ppm H$_2$ (red square).

**Figure 6.1** Optical images of sensor configuration: (a) Sensor arrays with 15 Pt paired microelectrodes as working electrodes (W.E.), integrated Pt reference electrode (REF) and counter electrode (C.E.): (b) Teflon cell with pin soic test clips for SWNT alignment and functionalization: (c) Teflon sensing cell with gas inlet and outlet.

**Figure 6.2** Linear Sweep Voltammetry (LSV) of Te deposition on SWNT. Electrolyte: 0.1, 1, 10 mM HTeO$_2^+$ in 1 M HNO$_3$. Total solution volume was fixed at 500 µL. LSVs were performed with a fixed scan rate: 10 mV/s.
Figure 6.3  Effect of concentration of $\text{HTeO}_2^+$ on the morphology of the Te-SWNT hybrid nanostructure at a fixed applied potential of -1 V and controlled charge density of 18.9 mC/cm$^2$: (a) 0.1 mM; (b) 1 mM; and (c) 10 mM.

Figure 6.4  Effect of applied potential on the morphology of the Te-SWNT hybrid nanostructure at a fixed $\text{HTeO}_2^+$ concentration of 10 mM and controlled charge density of 18.9 mC/cm$^2$: (a) -0.8 V; (b) -1 V; (c) -1.2 V; (d) -1.4 V.

Figure 6.5  Effect of charge density on the morphology of the Te-SWNT hybrid nanostructure at a fixed $\text{HTeO}_2^+$ concentration of 10 mM and controlled applied potential of -1 V. (a) 1.89 mC/cm$^2$; (b) 18.9 mC/cm$^2$; (c) 94.5 mC/cm$^2$; (d) 189 mC/cm$^2$. (e) Schematic illustration of Te nanostructure growth on SWNTs with increasing charge density.

Figure 6.6  Effect of (a) applied potential and (b) charge density on particle size and density of Te-SWNT hybrid nanostructure.

Figure 6.7  Current ($I_{SD}$) vs. back gated voltage ($V_G$) with a fixing the source-drain potential (VSD) at 1 V. (a) Electron transport properties of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively). (b) Mobility of AC aligned SWNT and Te-SWNT hybrid nanostructures.

Figure 6.8  (a, b) Real-time sensing response, (c) calibration curve, (d) response and
Figure 6.9  
(a) Real-time sensing performance and (b) calibration curve of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively) towards NO\(_2\) at different concentration.

Figure 6.10  
Sensitivity of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively) towards NH\(_3\), H\(_2\)S, H\(_2\)O, NO\(_2\) and H\(_2\).
TABLE LIST

Table 1.1  Thermoelectric properties overview of various nanowires, nanowire arrays or nanowire composites.................................................................69

Table 1.2  Thermoelectric properties overview of various nanocomposites. ........71

Table 4.1  Chemical composition, carrier type, and Seebeck coefficient of LAST nanofibers. ........................................................................................................169

Table 5.1  Characteristics of various Pd-CNT (graphene)-based room temperature H₂ sensors ............................................................................................................200

Table 6.1  Comparison of NO₂ sensing properties of different nanostructures counterpart at room temperature .................................................................233
CHAPTER 1
INTRODUCTION: NANOSTRUCTURED THERMOELECTRICS
AND GAS SENSORS

1.1 Nanostructured Thermoelectrics

1.1.1 An Overview of Thermoelectrics

The rising cost of compliance to laws and regulations (from the Clean Air Act to Geologic Sequestration) on operating non-renewable energy resources is the key driver to improve the efficiency of environmentally-friendly, renewable energy generation. Improving the efficiencies of renewable energy conversion technologies include research areas such as, solar cells [1], biomasses [2], fuel cells [3] and thermoelectrics [4]. Among these, thermoelectric materials offer simple, silent and reliable solid state energy conversion devices, due to their unique ability to directly convert heat to electricity and vice-versa [5] without moving parts or bulk fluids [6].

A brief glimpse of the possibilities of the applications of thermoelectric, from niche devices (e.g. remote power, “personal” micropower, etc.) to large scale waste heat recovery systems (e.g. vehicle waste heat, car cooling/heating, home cogeneration, etc.), is illustrated in Figure 1.1. For example, thermoelectric devices have been successfully utilized in space exploration missions (e.g. Apollo, Viking 2, and Voyager), due to their unique advantages of no moving parts and reliability. Although it has been 36 years (launching 1977) after Voyager’s landing, the radioisotope thermoelectric power generator (RTG) is still working. In addition, thermoelectric generators have been
successfully integrated into miniaturized autarkic sensor systems, wrist watches, and diagnostic medical equipment for self-powering.[7] More encouragingly, by installing thermoelectric energy converters on exhaust pipes, it may be possible to recover up to one-fifth of the exhaust heat and convert it into electricity to drive the car’s air conditioner and other electrical accessories. This would be equivalent to improving a typical car’s fuel economy by 7 miles per gallon. Scaling such fuel savings nationwide could save 2.5 million barrels of oil per day, equivalent to over 200 GW per year. This application of automotive waste heat scavenging is being pursued by research institutions such as the National Renewable Energy Lab and corporations such as General Motors.[8]

Three fundamental effects are associated with the thermoelectric phenomena, including the Seebeck effect, the Peltier effect and the Thomson effect. (1) The Seebeck effect is the conversion of temperature differences directly into electricity. When a temperature gradient exists at the ends of the material, charger carriers will diffuse from high temperature to low temperature therefore create a potential difference (Figure 1.2a). The generated voltage \( \Delta V \) is given by \( \Delta V = S \Delta T \), where \( S \) is the Seebeck coefficient or thermopower and \( \Delta T \) is the temperature difference. (2) Conversely, the Peltier effect is the generation of heat at an electrified junction of two different metals. When the material is supported by an external power supply, charge carriers that are initially uniform dispersed will drift to one end of the thermoelectric couple, resulting in a temperature difference between the two ends (Figure 1.2b). The heat flow is given as \( Q = \Pi I \), where \( Q \) is the heat absorbed or emitted, \( \Pi \) is the Peltier coefficient, and \( I \) is the applied current. The Seebeck effect and Peltier effect are interrelated through the Kelvin relations,
The working principles of a thermoelectric generator and a Peltier cooler are based on the Seebeck effect and the Peltier effect, respectively. The Thomson effect is the change of the heat content within a single conductor. When an electric current passes through the material, a temperature gradient will be generated along the material, leading to a redistribution of charge carriers thereafter creating a difference in material’s heat content. A thermoelectric device is normally based on the Seebeck or Peltier effect, with its unit made of n-type and p-type materials (Figure 1.2).

However, one p-n junction thermoelectric unit cell can only create a Seebeck voltage of several microvolt per Kelvin, which is far lower than the practical requirement. Therefore, practical devices normally consist of several unit legs connected electrically in series and thermally in parallel in order to increases the operating voltage of the module while reducing its electric current. Such an arrangement minimizes parasitic losses in the series electrical resistance of the wires and interconnects (Figure 1.3).

1.1.2 Efficiency of Thermoelectrics

The efficiency $\eta$ of a thermoelectric device is defined as the energy provided to the load ($W$) divided by the heat energy absorbed at the hot junction ($Q$). It is related to the temperature of the hot and the cold side ($T_H, T_C$) as well as the dimensionless figure-of-merit ($ZT$).

$$\eta = \frac{W}{Q} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$  

Equation 1.1

Thus, $\eta$ is proportional to the Carnot efficiency ($\eta_c$).
Equation 1.2

\[ \eta_c = \frac{T_H - T_C}{T_H} \]

which is the maximum efficiency of a heat engine operating between two temperatures.

In thermoelectric devices, ZT is defined by

\[ ZT = \frac{S^2 \sigma}{\kappa} T \]

Equation 1.3

where \( S \) (V/K), \( \sigma \) (S/m), \( \kappa \) (W/mK) and \( T \) (K) are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. \( S^2 \sigma \) is referred to as the power factor. ZT determines the electrothermal energy conversion efficiency as well as the maximum cooling temperature for Peltier device.

Figure 1.4 shows that various commercially available power generating technology display an average ZT > 4 over the entire temperature range shown. Compared to these mechanical systems, even the best thermoelectrics (ZT=3.5, for n-type only) achieved so far show less efficiency.[9] Thus, despite the advantages and various applications of thermoelectric devices, overcoming their low efficiency (ZT~1) is the single greatest hurdle keeping them from being widely deployed.

1.1.3 Interdependence of Thermoelectric Parameters

Seebeck coefficient \( S \), electrical conductivity \( \sigma \), and thermal conductivity \( \kappa \) are key thermoelectric parameters. However, the interdependence of these parameters pose a stumbling block when searching for high ZT materials. These materials must have a high Seebeck coefficient and electrical conductivity but a low thermal conductivity.

(1) \( S \) and \( \sigma \)
Typically, for metallic or highly degenerated semiconductors, the Seebeck coefficient \( S \) can be written as

\[
S = \frac{8n^2k_B^2}{3e\hbar^2} m^* T \left( \frac{\pi}{3n} \right)^2
\]

\text{Equation 1.4}

where \( k_B \) is Boltzmann’s constant, \( e \) is the carrier charge, \( \hbar \) is Plank’s constant, \( m^* \) is the effective mass of the charge carrier, and \( n \) is the carrier concentration.

Because charge carriers collide frequently with lattice atoms and with charged impurities within the lattice, they quickly develop a constant drift velocity \( v \) under an applied electric field \( E \). Under limiting constraints, the drift velocity is found proportional to \( E \), \( v = \mu E \), where \( \mu \) is called the mobility of the charge carrier. Thus, from a microscopic perspective, electrical conductivity can be viewed as being proportional to the product of how many (\( n \)) and how fast (\( v \)) charge carriers can drift through the lattice. For semiconductors which have both electron \( n_e \) and hole \( n_h \) charge carriers, and using the definition for current density \( j = \sigma E \), we have

\[
\sigma = e (n_e \mu_e + n_h \mu_h)
\]

\text{Equation 1.5}

where \( e \) is the unit charge, \( n_e \) and \( n_h \) are the concentrations of electrons and holes, respectively, along with their mobilities \( \mu_e \) and \( \mu_h \). For intrinsic semiconductors, \( n_e = n_h \).

Based on Equations 1.4 and 1.5, increasing the carrier concentration increases the electrical conductivity but decreases the thermopower—making the improvement in the power factor \( S^2 \sigma \) difficult.

\( \sigma \) and \( \kappa \)
The parameter interdependence is also represented in the relation between thermal conductivity and electrical conductivity. The thermal conductivity $\kappa$ is composed of both electron and phonon transport; given by

$$\kappa = \kappa_e + \kappa_l \quad \text{Equation 1.6}$$

where $\kappa_e$ is the electrical thermal conductivity and $\kappa_l$ is the lattice thermal conductivity.

The electrical thermal conductivity can be expressed by the Wiedemann-Franz law, which is

$$\kappa_e = \sigma LT \quad \text{Equation 1.7}$$

where $L$ is the Lorentz number, typically taken as $2.4 \times 10^{-8} \text{ J/}^{2}\text{K}^{2}\text{C}^{2}$ for a highly degenerate semiconductor. The equation shows that the electrical thermal conductivity is coupled with the electrical conductivity by the constant $L$.

The lattice thermal conductivity describes the ability of phonons to transport thermal energy from a hot side to a cold side and can be approximated by

$$\kappa_L = C_L v l \quad \text{Equation 1.8}$$

where $C_L$ is the heat capacity, $v$ is the phonon velocity and $l$ is the phonon mean free path. Semiconductors that have low sound velocity and a short phonon mean free path are expected to have a low thermal conductivity, therefore a greater $ZT$. Besides Equation 1.8, $\kappa_l$ can be expressed by Keyes’ empirical relationship,

$$\kappa_L T = B(T_m^3 \rho^2/A^{7/6}) \quad \text{Equation 1.9}$$

where $B$ is a constant, $T_m$ is the material’s melting point, $\rho$ is density, and $A$ is atomic weight. This equation indicates that soft materials (those of low density) with a high
atomic weight and low melting point possess a lower $\kappa_L$ (by Equation 1.3) and potentially a higher ZT. Therefore, materials such as chalcogenides (e.g. Bi$_2$Te$_3$, PbTe, etc.) that are composed of heavy elements should have good thermoelectric properties. From Equations 1.8 and 1.9, $\kappa_l$ seems to be the only parameter that is independent of the others (i.e. $S$, $\sigma$, $\kappa_e$). However, in real crystal lattices phonon transport is much more complicated, and the phonon thermal conductivity is found to be related to these other parameters.

The interdependency of the Seebeck coefficient, the electrical conductivity and the thermal conductivity is depicted in Figure 1.5. Metals have relatively low ZT for two reasons; (1) an inherently small $S$ and (2) a large electrical thermal conductivity $\kappa_e$ due to a large $\sigma$.

Since heat transport in metals is mainly through the movement of electrons, the lattice thermal conductivity can be neglected ($\kappa \approx \kappa_e$). Under this condition, $ZT \approx \frac{S^2}{L}$. In the case of an insulator or non-degenerate semiconductor, the heat transport is mostly achieved by means of lattice vibrations or the phonon transport ($\kappa \approx \kappa_l$). In this case, $ZT \approx \frac{S^2 \sigma}{\kappa_l} T$. Here, a low ZT is also expected due to a small $\sigma$. For a degenerate semiconductor, the thermal conductivity is primarily carried by lattice heat transport and some electron transport, therefore $ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} T$. The highest ZT is normally obtained in these types of materials (e.g. metal chalcogenides), which have high carrier
mobility to yield high electrical conductivity, but a low electronic thermal contribution to diminish thermal conductivity.

1.1.4 Thermoelectric Materials

The ZT of the state-of-art commercial thermoelectric materials as a function of temperature was shown in Figure 1.6. Optimal ZT were reached at different temperatures for different materials. Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are considered to be the most promising materials for thermoelectric applications at near room temperature, with a zT value close to one. PbTe and its alloys (e.g. AgGeSbTe or TAGS) show a great potential in the middle-high temperature range of 400 °C to 600 °C, with the highest ZT of ~ 0.8 and 1.2, respectively. The skutterudites and clathrates (e.g. CoSb$_3$) show a maximized ZT around one in the similar temperature range. SiGe systems were usually operated in a high temperature range (i.e. over 900 °C), with remarkable reliability and stability. Since a ZT of at least 3 are required for facilitating thermoelectric devices to be widely deployed, active search for the materials with higher ZT have been attempted (Section 1.1.6).

1.1.5 Fundamental Physics for Electrical Transport in Thermoelectric Materials

The thermoelectric figure-of-merit ZT is based on the electrical transport behavior in the material. The electron transport coefficient, including the three key parameters (S, σ, κ), can be derived from the solution of the Boltzmann transport equation[10], which describes the momentum and position of the particles in a system under a perturbation (temperature gradient in Seebeck effect).
At equilibrium, the electron distribution follows the Fermi-Dirac statistics through

$$ f_0(E) = \frac{1}{\exp((E-E_F)/k_B T)+1} \quad \text{Equation 1.10} $$

where $E$ is the energy of the electron, $E_F$ is the Fermi level, $k_B$ is the Boltzmann constant, and $T$ is the temperature. $f_0(E)$ as a function of electron energy (solid line) is plotted in Figure 1.7, with its first-order derivative (dotted line) sharply peaked symmetrically around the Fermi level. The figure indicates that only electrons with energy close to the Fermi level ($\Delta E \approx 10 k_B T$) contribute to electrical or thermal transport, which is critical to understanding the electrical transport behavior.

1.1.5.1 Density of state (DOS)

The density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied by electrons. Because it is usually sufficient to consider only the lowest sub-band (refer to Figure 1.7), DOS per unit volume in 3D, 2D, and 1D systems are described solely by the power law function, which is

$$ g(E) = \frac{N}{g_D a^{3-D}} \left(\frac{2m_d}{\hbar^2}\right)^{\frac{D}{2}} (E - E_0)^{\frac{D}{2}-1} $$

$$ g_D = \begin{cases} 2\pi^2, & D = 3 \\ D\pi, & D = 2, 1 \end{cases} $$

$$ m_d = \sqrt{\prod_{i=1}^{3-D} m_i} \quad \text{Equation 1.11} $$

where $N$ is the degeneracy factor; $E_0$ is the ground state energy level, $D = 3, 2, 1$ for 3-, 2-, 1D system, respectively; $a$ is the thickness of the quantum well or wire in nm; $m_d$ is the
geometric mean of the principal effective masses \((m_i)\); and \(h\) is the Planck’s constant. [5, 10]

For a single band system, the DOS for bulk material, a quantum well, and a quantum wire is shown in Figure 1.8. The staggered pattern in the 2D and 1D materials are due to the superposition of multiple sub-bands, each of which is shifted from the bulk ground state energy \(E_0\) (the energy at the lowest point of the conduction band or at the highest point of the valence band) by the quantum confinement energy (e.g. \(E_1, E_2\)).

1.1.5.2 Electrical conductivity \(\sigma\)

The electrical conductivity is proportional to the product of the carrier concentration \(n\) and carrier mobility \(\mu\) \((Equation 1.5)\). For carrier concentration, all of the carriers above the bulk ground state energy \(E_0\) should be taken into consideration, which is

\[
n \equiv \int_{E_0}^{+\infty} g(E)f_0(E)dE \quad \text{Equation 1.12}
\]

Where \(g(E)\) is a material’s density of state, \(f_0(E)\) is the equilibrium distribution function, and \(E\) is the electron’s energy level. Assuming parabolic energy dispersion with power law relaxation time, the carrier concentration is written as

\[
n = \frac{N}{g_D a^{3-D}} \left( \frac{2k_B T m_d}{\hbar^2} \right)^{\frac{D}{2}} F_{D-1}(\eta)
\]

\[
F_j(\eta) = \int_0^{+\infty} \frac{x^j}{\exp(x-\eta)+1} dx \quad \text{Equation 1.13}
\]
Here $F_j(\eta)$ is the $j^{th}$ order Fermi integral. Due to the variation of the absolute number of Fermi levels in different materials, the Fermi level is normalized to be the reduced Fermi level $\eta$. This indicates the position of $E_F$ relative to the bulk ground state energy $E_0$, which is described as follows

$$\eta = \frac{E_F - E_0}{k_B T} \quad \text{Equation 1.14}$$

Equation 1.13 can be normalized with a normalization factor $\theta$

$$\theta = \frac{N}{a^{3-D}} \left( \frac{m_d}{m_0} \frac{T}{300 K} \right)^{D/2} \quad \text{Equation 1.15}$$

where $m_0$ is the element mass. Therefore, the normalized carrier concentration is written as

$$\bar{n} = \frac{n}{\theta} = M F_{D_{-1}}(\eta) \quad \text{Equation 1.16}$$

with

$$M = \frac{1}{\theta_D} \left( \frac{2k_B m_0}{\hbar^2} \right)^{D/2}$$

Therefore, the normalized carrier concentration is only a function of $\eta$ and can be used to determine $n$ at a given $E_F$ for any material and temperature. The normalized carrier concentration as a function of $\eta$ is shown in Figure 1.9.

From Figure 1.9, one can easily see that for $\eta > 0$, as is the case for metals or degenerate semiconductors, the carrier concentration is a weak function (shallow positive slope) of $\eta$. However, for $\eta < 0$, as is the case for insulators or non-degenerate semiconductor, the carrier concentration is a strong function (steep positive slope) of $\eta$. For a given Fermi level, decreasing the dimension of the material from 3D to 1D will
dramatically increase its carrier concentration due to the expansion in the magnitude of the DOS in lower dimensional materials. Conversely, with a fixed carrier concentration, lowering the dimension of the material will push the Fermi level in a more negative direction, therefore increasing the Seebeck coefficient (Section 1.1.5.3).

The mobility $\mu$ of the carriers is determined by the carrier scattering type. Various scattering mechanisms including neutral impurities scattering, the lattice deformation potential scattering by acoustic and optical phonons as well as the weakly or strongly screened ionized impurity scattering have been found in different material systems. For the simplest case, in which the carriers are scattered by a neutral impurity, the mobility remains constant with increasing $\eta$. Consequently, $\sigma$ is totally dependent on the carrier concentration and shows a similar trend to Figure 1.9. However, in most cases, $\mu$ may increase or decrease with increasing $\eta$ for other scattering types, thus contributing to variation in $\sigma$.

1.1.5.3 Seebeck coefficient $S$

The Seebeck coefficient can be deduced by the Boltzmann transport equation, which is

$$S = \frac{1}{eT} \int_{E_0}^{+\infty} g(E)\tau(E)E v^2(E) \frac{\partial f_0(E)}{\partial E} dE - E_F = \frac{1}{eT} \left( \frac{\langle \tau E \rangle}{\tau} - E_F \right)$$ \hspace{1cm} \text{Equation 1.17}$$

Here $\tau(E)$ is relaxation time and $v(E)$ is the carrier velocity. In the case of constant relaxation time, $\langle \tau E \rangle/\tau$ simplifies to the average energy of electrons $\langle E \rangle$. Therefore,

$$S = \frac{1}{eT} (\langle E \rangle - E_F)$$ \hspace{1cm} \text{Equation 1.18}
For a highly degenerate semiconductor, Mott’s relation can be applied and give a simplified formula of $S$ to be

$$S = \frac{\pi^2}{3} \frac{k_B T}{e} \left( \frac{\partial \ln \sigma(E)}{\partial E} \right)_{E=E_F}$$  \hspace{1cm} \textit{Equation 1.19} \hspace{1cm}

Specially, in a degenerate semiconductor with a single parabolic band and an acoustic phonon transport mode, $S$ can be further simplified reducing to Equation 1.4. Equation 1.18 describes the fundamental physics behind the Seebeck coefficient, indicating that the ability of heat to drive charge carriers ($S$) is directly proportional to the difference in the average energy of electrons in the conduction band and the Fermi level. Therefore, theoretically, the enhancement in the Seebeck coefficient can only be achieved in band gap engineering.[10, 11]

The Seebeck coefficient within 3D, 2D and 1D materials as a function of $\eta$ at temperature of 300 K is illustrated in Figure 1.10. Within the same dimension, an improvement in the Seebeck coefficient can be easily achieved by decreasing $\eta$. However, one must be cautious when using this plot. Although the figure shows that the magnitude of $S$ is greater in 3D than in 1D or 2D for any $\eta$, it is misleading. This is because as the material’s dimension is reduced from 3D to 2D to 1D, the position of the Fermi level as well as the average energy of the electron changes accordingly, which means that $\eta$ in the x-axis also changes. Therefore, getting the values of $S$ with different dimensions is not simply obtained by this plot by just substituting the same $\eta$ into the plot, but one needs to include more information about the changes of $\eta$. 
1.1.5.4 Power factor $S^2\sigma$

The interdependence of Seebeck coefficient and electrical conductivity (Figure 1.9 vs. Figure 1.10) indicates the existence of an optimal power factor at a certain $\eta$. And the quantum confinement suggests that this optimal number will increase as the dimension of the material is decreased.[12, 13] This concept is illustrated in the case of Si as shown in Figure 1.11.

Given a constant carrier concentration of $1.7 \times 10^{20}$ cm$^{-3}$, the Fermi level of bulk Si can be calculated to be 0.1 eV ($\eta=3.86$), with an average electron energy of 0.13 eV. They are marked in solid and broken lines in Figure 1.11a, respectively. A Seebeck coefficient of $-100$ $\mu$V/K was calculated according to Equation 1.18. Assuming the mobility $\mu$ remains constant within the region of interest, the power factor $S^2\sigma$ will be proportional to $S^2n$, which is $17\times10^{23}$ $\mu$V$^2$K$^{-2}$cm$^{-3}$.

When the dimension of the Si sample is reduced (Si nanowire with a diameter of 2 nm), both the Fermi level and average electron energy shift to the negative side to be -0.01 eV and 0.05 eV, respectively. The difference between $\langle E \rangle$ and $E_F$ now is 0.06 eV. As a result, the Seebeck coefficient increases to $-200$ $\mu$V/K, giving an improved power factor 4 times higher than that in bulk Si.

However, even though the enhancement of the power factor though quantum confinement has been widely suggested in theoretical studies, the enhancement has not been observed in individual nanowires or nanowire arrays in experiments so far.[14-39] This lack of results can be explained in most cases as either: (1) the diameter of the investigated nanowires are too large to observe quantum confinement effects, or (2) the
magnitude of the staggered DOS is not high enough to facilitate the enhancement of the thermoelectric properties, even with a quantum confinement being triggered.[7] Case (2) is explained as follows. Quantum confinement is expected in a 5 nm Si nanowire since the Bohr radius of this material is 5 nm. However, due to the low magnitude of the DOS, the Fermi level and the average energy of electrons increase significantly (Figure 1.11c). Consequently, the Seebeck coefficient and the power factor decrease almost by an order of magnitude compared to that of bulk Si.

Therefore, the enhancement in the power factor can only be achieved when the size of the materials are sufficiently small that the DOS becomes larger than that in the bulk material. A change in the shape of the DOS to a staggered pattern is not sufficient to improve the power factor. Pichanusakorn and Bandaru have calculated the maximal size for the enhancement in the power factor to occur in Bi$_2$Te$_3$, PbTe and SiGe, showing that the size of nanowires or quantum wells should be much smaller than the Bohr radius.[10] This results explain why the enhancement in the power factor could not be observed so far in most of the nanowires, even though their diameter is close to the Bohr radius.

1.1.5.5 Thermal conductivity $\kappa$

Thermal conductivity is the sum of electrical thermal conductivity $\kappa_e$ and lattice thermal conductivity $\kappa_l$, where heat is transported by electrons and phonons, respectively. Electrical thermal conductivity $\kappa_e$ is directly proportional to electrical conductivity $\sigma$ and temperature $T$ through the Wiedemann-Franz law (Equation 1.7 in Section 1.1.3). Lattice
thermal conductivity $\kappa_l$ can be expressed in a more general formula as follows, which is deduced from the Boltzmann transport equation[10].

$$\kappa_l = \int \tau v^2 \nabla T f_p E(k) g(E) dE \quad \text{Equation 1.20}$$

In this equation, $\tau$ is the relaxation time, $v$ is the velocity of sound, $f_p$ is the Planck distribution function, and $g(E)$ is the DOS. The lattice heat capacity $C_L$ is defined as the partial derivative of the internal energy $U$ with respect to temperature $T$ under constant volume, given by

$$C_L = \left(\frac{\partial U}{\partial T}\right)_V = d\left[\int f_p E(k) g(E) dE\right]/dT \quad \text{Equation 1.21}$$

Because the phonon mean free path $l$ is equal to $\tau \times v$, Equation 1.20 can be simplified to Equation 1.8.

When the size of the material is significantly larger than the phonon mean free path, phonon scattering is dominated by the phonon-phonon cross section. It includes the N-process (Normal) and the U-process (Umklapp), after the German for “flipping over”. While the N-process describes the redistribution of the phonon energy from one phonon to another yielding a net wavevector change of zero (infinite $\kappa_L$), the U-process indicates that the total wavevector change may not be zero, but may be a reciprocal lattice vector $G$; where there is a net phonon backscattering and energy consumption in the phonon and thermal transport (finite $\kappa_L$). In this case, there is a minimum value for $\kappa_L$, which can be achieved when the phonon mean free path is equal to the phonon wavelength. The exponential onset of the Umklapp process requires a minimum thermal energy of order $k_B\theta/2$ to be achieved, where $\theta$ is the Debye temperature.
However, when the dimension of the material becomes smaller than the phonon mean free path, phonon scattering is dominated by scattering factors such as boundary and interface scattering, rather than phonon-phonon scattering. Thus, in principle, the electrical conductivity and the thermal conductivity can be decoupled by engineering the nanostructured materials with a dimension that is smaller than the phonon mean free path but larger than the electron (or hole) mean free path.\cite{24, 25, 40} This will lead to the reduction of the thermal conductivity without diminishing the electrical conductivity - a double combination that will greatly increase the ZT.

1.1.6 Recent Development of Thermoelectric Materials with Improved ZTs

For the past several years, significant progress has been made to improve ZT within various materials. Figure 1.12 shows an overview of the thermoelectric performances of n-type and p-type materials. A majority of the work conducted to date enhances ZT by reducing the contribution of the thermal conductivity, especially the lattice thermal conductivity, while limited work has been reported on the improvement of the power factor. These attempts can be placed into three categories (Figure 1.13):

1. One-dimensional nanowires and nanotubes
2. Two-dimensional epitaxial multilayers and superlattices
3. Three-dimensional nanocomposites
1.1.6.1 One-dimensional nanowires and nanotubes

Increasing ZT in 1D nanowires or nanotubes can be achieved by enhancing the power factor through quantum confinement and by reducing the thermal conductivity through stronger phonon scattering. Even though the enhancement of the power factor in 1D nanostructures has been theoretically demonstrated in Si nanowires (Section 1.15), no experimental data about the enhancement has been reported. However, reductions in thermal conductivity in 1D Si nanowires were experimentally verified independently by two groups [24, 25].

Health et al. synthesized their Si nanowires by using the superlattice nanowire pattern transfer method.[24] The optimal Seebeck coefficient was obtained by carefully controlling the doping level and the wires’ diameter. When the diameters of the highly doped nanowires were reduced to 10 nm, their thermal conductivities decreased by almost orders of magnitude compared to the bulk values. As a result, the ZT values represent an approximately 100-fold improvement over the bulk Si, with \( ZT \approx 1 \) at 200 K. In the same year, Yang et al. prepared highly doped single crystal Si nanowires by electroless etching (EE) process.[25] By comparing the performance of the nanowire to a smooth vapor-liquid-solid (VLS)-grown wire, they claimed that the thermal conductivity of the EE-grown nanowire was significantly suppressed due to the rough surface. The ZT values of the Si nanowires were 0.6 at 300 K (Figure 1.14).

Significant effort has been made to investigate the thermoelectric properties of Bi\(_2\)Te\(_3\) based nanotubes or nanowires.[20-22, 26-39] Even though a dramatic increase in ZT due to quantum confinement is promised by theoretical studies, the figure-of-merit of
a single Bi$_2$Te$_3$ nanowire obtained from experiment is much lower than that of the bulk material. This may be due to (1) the relatively big diameter of the nanowire (> 40 nm) as well as (2) the difficulties in maintaining the nanowires’ structural and chemical composition during the lithographic contacting. One of the solutions to the problem of lithographic contacting is the utilization of highly-packed nanowire films or pellets, which are hot-pressed from a large number of nanowires. For example, Bi$_2$Te$_3$ nanowires, with an average diameter of 8 nm, were synthesized by a hydrothermal method and then hot pressed into a pellet. The highest ZT of 0.96 was obtained at 380 K in the pellet due to a significant reduction in thermal conductivity derived from phonon scattering at the nanoscale interfaces.[36] Although these Bi$_2$Te$_3$ nanowires are the finest diameters characterized so far for their thermoelectric properties, an enhancement in the power factor was not observed. Heterostructures of the PbTe-Bi$_2$Te$_3$ nanowire pellet showed a higher figure-of-merit of 1.2 at 620 K, which again is owing to a large reduction in thermal conductivity.[39]

For PbTe, a higher Seebeck coefficient has been obtained in PbTe nanowire arrays or films compared to the bulk material.[22, 27, 33, 38] However, these nanowires have a low power factor due to their low conductivity. No figure-of-merit of PbTe nanowire arrays has been reported, due to the lack of thermal conductivity data. The thermoelectric properties of various nanowires, nanowire arrays or nanowire composites are summarized in Table 1.1.
Two-dimensional multilayers and superlattices

Thermoelectric materials that are based on superlattices hold the best records of figure-of-merit so far.[15-19] Both the enhancement in the power factor and the reduction in the thermal conductivity are observed in superlattices.[15, 18, 19] These superlattices are usually synthesized by “Dry” deposition methods, including molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). Additional care should be paid during the device preparation because a good superlattice requires not only near perfect crystallinity, but accurate and homogeneous film thickness, precise chemical composition, and stoichiometry. P-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices showed the highest thermoelectric figure-of-merit of 2.4 at 300 K as shown in Figure 1.3d. These two superlattices were prepared by metal-organic CVD and deposited at 1 nm and 5 nm, respectively. The significant reduction in the materials’ thermal conductivity may be attributed to strong phonon scattering, which is expected at the interfaces of the alternating layers of Bi$_2$Te$_3$ and Sb$_2$Te$_3$.[16-18] However, the enhancement in the power factor was not sufficient in this superlattice system.

An improvement in the power factor was observed in an n-type PbTe/Pb$_{0.927}$Eu$_{0.073}$Te superlattice.[14] The two multilayers were fabricated via molecular beam epitaxy and deposited at 2 nm and 45 nm, respectively. The enhancement in the Seebeck coefficient is clearly shown to be a result of quantum confinement, rather than a simple variation in the carrier concentration or in the Fermi level. However, no figure-of-merit value of this sample is available due to the lack of thermal conductivity data.
A superior thermoelectric performance (best recorded) was obtained from a PbSeTe/PbTe quantum dot superlattice, with a thermoelectric figure-of-merit of 1.6 at 300 K and of 3.5 at 570 K (Figure 1.13c). This multilayer was synthesized by MBE, using layers of BaF$_2$ and PbTe as a substrate and a buffer layer, respectively. The remarkable enhancement of figure-of-merits in the system is attributed to an increase in both the thermoelectric power factor ($S^2\sigma$) and a decrease in the thermal conductivity ($\kappa$).[16, 18, 19]

1.1.6.3 Three dimensional nanocomposites

Significant effort has been put into the development of thermoelectric nanocomposites with an enhanced interface-to-volume ratio and a lower thermal conductivity.[23, 42, 44-77] The nanostructured composites have been proposed to increase ZT by increasing phonon scattering, leading to a decrease in the phonon mean free path. It has been proven that phonons can be scattered more than electrons by inducing nanoparticles properly into the system, from which the thermal conductivity can be suppressed while the electrical conductivity is still maintained.[70] The thermoelectric performance of various nanocomposites was summarized in Table 1.2.

Bi$_2$Te$_3$ based nanocomposites show great thermoelectric properties at near room temperature. Remarkable progress was made by Ren [42, 67], who fabricated a nanocrystalline (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ bulk alloy by ball-milling and hot-pressing from crystalline ingots under inert conditions. The as-obtained bulk alloy showed a peak ZT of
1.4 at 100°C and ZT value of 1.2 at room temperature (Figure 1.13f). After that, Fan [46] reported an even higher ZT in a Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nanocomposite, with the maximum value of 1.8 at 703 K and 1.5 at room temperature. These nanocomposites were synthesized by mixing the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nanoparticles which were obtained through melt spinning. Enhancement in ZT is mostly due to the reduction in the thermal conductivity.

A high thermoelectric figure-of-merit has been found in AgSbTe$_2$. [44] The anharmonicity of its chemical bonds drives a strong intrinsic phonon scattering, resulting in a behavior of “minimum thermal conductivity”. [59] Single-phase AgSbTe$_2$ has an extremely low lattice thermal conductivity $\kappa$ of around 0.63 W/mK and a large Seebeck coefficient of about 200 $\mu$V/ K at room temperature. The thermoelectric properties of bulk AgSbTe$_2$ strongly depend on the composition, since the single phase of AgSbTe$_2$ is unstable and normally found together with SbTe or Ag$_2$Te phase precipitation in different temperature windows. [57] Furthermore, experimental evidence for ZT improvement has been demonstrated in the AgSbTe$_2$ system with mixed phases of AgSbTe$_2$ and Ag$_2$Te. The highest ZT achieved so far is 1.65 at 673 K within AgSbTe$_2$ fabricated by melt-spinning (MS) and spark-plasma-sintering (SPS). [71]

Nanocomposites based on PbTe and its alloys have received great attention. [47, 51, 52, 55, 64, 69, 70] Remarkable ZT values ranging from 1.2 to 2.2 have been observed by alloying PbTe with other elements or binary and ternary components such as SrTe [70], SnTe [52], and AgSbTe [47]. The introduction of group three elements as dopants, such as Tl, is believed to set up a resonance level in the valence band of PbTe that has very little impact on the compound’s Fermi level. This explained why only enhancement in the
Seebeck coefficient was observed in the nanocomposites while the carrier concentration remains almost the same. Consequently, significant improvement in the power factor was observed.[55]

In addition, a surprisingly high figure of merit was reported in the alloy of AgSbTe$_2$ and PbTe, AgPb$_m$SbTe$_{m+2}$, or LAST-m materials (Figure 1.13e).[47] LAST-m is considered to have a cubic NaCl structure with Ag, Pb and Sb occupying Na sites, whereas the chalcogen atom is substituted at the Cl site. However, the compound doesn’t exhibit the classical behavior of a solid solution between AgSbTe$_2$ and PbTe, but displays nanoscopic inhomogeneity with an Ag-Sb-rich phase embedded in a PbTe matrix. The inhomogeneous structure results in the reduction of the thermal conductivity while maintaining the Seebeck coefficient at a relatively high value.[50] Depending on the m value, high ZT values of ~ 1.2 (LAST-10) to ~ 2.2 (LAST-18) at 800 K have been demonstrated.[47] Since the thermoelectric properties of LAST-m strongly depend on the composition and size of nanocomposites in the compound, it is intensely sensitive to the experimental conditions applied to prepare the LAST family of materials.[63]

The alloy of GeTe and AgSbTe$_2$ at some proper ratio has been suggested will serve as an ideal thermoelectric material in the temperature range of 200 °C to 500 °C. The thermoelectric performance of TAGS-x is strongly temperature-dependent since the crystal structure transformation occurs within different temperatures. Due to the composition-dependent phase change of the GeTe in the compound, the crystal structure of TAGS can be transformed from cubic to rhombohedral (preferred) at temperatures ranging from 430 °C to 400 °C. So far, (GeTe)$_{0.85}$(AgSbTe$_2$)$_{0.15}$ (TAGS-85) is considered...
to be the optimum composition that has potential commercial applications due to its relatively high figure of merit of 1.4 and a good mechanical stability. Similar to LAST-m, nanoscale inhomogeneities were observed in TAGS-x compounds, which lead to a higher ZT value with decreased thermal conductivity.[53, 65]

Introducing PbS content into Sn doped PbTe significantly reduced the lattice thermal conductivity. Instead of the precipitation of PbS nanoparticles or nanodots, PbS strips were observed in the PbTe lattice matrix (Figure 1.15). These strips are considered to be very effective scattering centers greatly enhancing phonon scattering. The decoupling of phonon and electron transport mechanisms is anticipated in the (PbTe)_{0.98}(SrTe)_{0.02} system due to the crystallographic alignment of SrTe and PbTe lattices. This allows the system to reach a ZT of 1.7 at around 800 K.[52]

A sister material of LAST, AgPbSbSe, (substituting the more economically available Se has a low thermal conductivity of 0.8 Wm^{-1}K^{-1} but a low electrical conductivity (almost 2 orders of magnitude lower than LAST). However, the carrier concentration and power factor can be effectively increased by doping the material with small amounts of Cl, which dramatically improved the figure-of-merit from 0.15 to 1.3 at 873 K.[77]

Another strategy for high ZT is the application of low density materials with complex crystal structures; ideally a phonon glass electron crystal (PGEC). These type of materials have high electrical conductivity due to their high crystallinity but low thermal conductivity resulting from the complex structural features of the crystal lattice. Two types of materials (i.e. skutterudite and clathrate) are considered to be PGEC.
Skutterudite (e.g. IrSb₃, CoSb₃ etc.) crystal structures have loosely bonded metal guest atoms with the host lattices, which rattlers perturbing phonon thermal energy transport “rattling effect”. A remarkable reduction in lattice thermal conductivity was observed in skutterudites when it goes from single- to double- or triple-filled skutterudites.[78] In addition, notable improvement in thermoelectric properties has been achieved in half-Heusler alloys, showing a ZT with 60% improvement to 0.8 in p-type Hf₀.₅Zr₀.₅CoSb₁ₓSnₓ and 25% enhancement to 1.0 in n-type Hf₀.₇₅Zr₀.₂₅NiSn₁₋ₓSb. [73, 76]

For the silicon-based nanocomposites, the thermoelectric figure-of-merit in the Si has been significantly improved by alloying with Ge. Small quantities of Ge can significantly reduce the thermal conductivity of Si since a stronger phonon scattering occurs not only from the grain boundaries, but also from the point defects in the Ge sites. However, the commercial application of SiGe alloys is restricted by the limited amount of Ge in the world supply as well as its high market prizes. Therefore, great effort has been put to reduce the Ge content while maintaining the low thermal conductivity of Si.[56, 60, 61, 68, 74]
1.2 Nanostructured Gas sensors

1.2.1 An Overview of Gas Sensors

The ability to detect gaseous molecules in the atmosphere by means of miniature and portable sensors is of great importance for environmental pollution analysis, homeland security, industrial emission control and monitoring, outer space exploration, medical diagnostics, and agriculture (Figure 1.16).[79, 80] A gas sensor is a device that interacts with gaseous chemical compounds and then changes its electrical, thermal or mechanical properties in term of resistance, current or capacity, to output signals that can be quantified directly or indirectly. A gas sensor consists of two important parts: a layer sensitive to chemical compounds and transducer materials. The sensitive material directly interacts with the gaseous compound and is recognizes the analyte gas while the transducer, interfaced with an electrical signal, will transfer the change in the state of the chemical compounds of the sensing element to a measurable signal (Figure 1.17). A good sensor should have high sensitivity, a quick response/recovery time, a high upper detection limit (UDL), a low lower detection limit (LDL), good selectivity and a large dynamic range.

Various complementary and competing gas sensor technologies including electrical, optical, calorimetric, gas chromatograph, as well as acoustic methods have been investigated. Gas sensing by optical methods is usually straightforward and can achieve higher sensitivities, a higher selectivity and better stability than non-optical methods with a longer lifetime of the sensor. However, their applications are restricted due to the difficulties in the miniaturization of the components and the relatively high cost.
associated with it. Calorimetric sensors (pellistors) are adequately sensitive enough to detect industrial level gas emissions. They are usually cost-effective and stable at ambient temperatures. However, drawbacks include the risk of catalyst poisoning and the bad selectivity of the gases to be analyzed. Gas chromatography is also a common method used for gas sensing, which provides excellent separation of compounds, a high sensitivity and good selectivity. However, it is typically used in a lab as an analytical technique because the equipment is expensive and particularly difficult to miniaturize for portable application. Sensors based on acoustic analysis have long life times and can avoid secondary pollution problems, but normally suffer from low sensitivities as well as bad selectivities. Electrical method-based sensors including conductometric, potentiometric and amperometric have been widely developed. Among them, conductometric sensors have dominated the field because of their robust nature and simple circuit design. Especially, chemiresistor/chem-field effect transport (FET) sensors, which enable detection of gases at a high sensitivity, a fast response, low power consumption, easy miniaturization, as well as low cost, have gathered significant attention within the realm of gas sensing.

Traditional chemiresistor/chemFET sensors apply metal oxides, predominantly SnO$_2$, as sensing elements in the form of thin or thick films as well as compressed powders. These sensors generally require a high operating temperature in order to obtain decent sensitivities and faster response/recovery times. This feature can significantly reduce overall selectivity, as many analytes interact with the oxide surface all at once, while also increasing power consumption and device complexity. In fact,
temperature control systems can overshadow both overall operating costs and design of the actual sensing element. These have been the focus of several nanostructured gas sensor platforms, which have demonstrated advanced thermal control architectures through a series of lithographical fabrication steps. Additionally, low sensitivity in the traditional sensors place another inherent limitation. When a charged analyte binds to the sensor surface, a zone of charge difference is created. This current can bypass the region of the charge zone, since the affected region is only a small fraction of the total area, which will lower the overall sensitivity of the sensor (Figure 1.18a). Consequently, traditional sensors have inherent limitations in terms of the sensitivity and components needed for analysis, which cause hurdles in this type of sensor being deployed widely. Sensors that can provide rapid, reversible and sensitive detection in the ambient environment are in great need in order to facilitate the sensors’ applications in either environmental monitoring or medical diagnosis.

One-dimensional (1D) nanomaterials are being suggested as promising candidates for impressively sensitive gas sensors. Substantially increasing surface-to-volume ratio in the 1D nanostructures enables more surface atoms that can interact with gases, which significantly improve sensors’ sensitivities. In addition, changes in current can be detected easier and at a lower receptivity level due to the larger fraction of the region being affected (Figure 18b). The Debye length, the measure of a charge carrier’s net electrostatic effect in a material and how far those electrostatic effects persist, is comparable or at the same scale as the 1D nanostructures, which can significantly enhance the sensitivity of the sensor. Moreover, the response time is expected to be
enhanced in 1D nanomaterials due to the virtue of two dimensional diffusion. The ultra-small size of the nanostructures also makes it possible to develop high density devices with duplicate to reduce false signals therefore a more accurate output.

1.2.2 Gas Sensing Mechanism

Modulation in semiconductors’ material or electrical process, attributed from either a reversible/irreversible chemical reaction or an electrostatic gating effect as well as variations in the Schottky barrier height on the contact between the metal and the semiconductor are the most widely-accepted gas sensing mechanisms.

The semiconductors can induce reactions by acting either as the reactant or the catalyst. For example, in a gas sensor based on metal oxides, exposure to the reducing analytes will lead to the discharge of adsorbed oxygen, which results in an increase in the majority carrier density and conductivity in the semiconductor. The electrostatic gating effect induces the electrical property changes of the semiconductor its’ exposure to the charged gaseous molecules. In a p-type sensor, electron donating gases, such as NH₃ and H₂S, cause the hole concentration to decrease, causing the sensor’s resistance to increase. On the contrary, a strong electron acceptor, such as NO₂, can receive electrons from the valence band of the semiconductor, resulting in the enhancement of the hole density, thus decreasing the resistance (Figure 19a). The net electrostatic effect of the charge carrier in 1D material can be quantified according to the Debye length:

$$\lambda_D = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{p e^2}\right)^\frac{1}{2}$$

Equation 1.22
In the Debye length, $\varepsilon_r$ is dielectric constant of 1-D NS, $\varepsilon_0$ is the permittivity of free space (F/m), $k_B$ is the Boltzmann constant (eV/K), $T$ is temperature (K), $p$ is the carrier concentration ($m^{-3}$), $e$ is the elementary charge (C). To achieve a high sensitivity, a gas sensor must possess a low carrier concentration as well as a dimension that is comparable to the Debye length.

Schottky contact-based gas sensors focus on the contact area between metal electrode and the semiconductor, where the modulation of contact barrier height is the key factor in determining the performance of a sensor (Figure 1.19b). A metal-semiconductor interface can possess rectifying or non-rectifying energy levels; namely, Schottky or ohmic contacts, respectively. In an ohmic contact, resistance is inversely proportional to the cross sectional area perpendicular to the current and the charge carriers can flow in either direction without rectification under an applied potential. In an ohmic contact-based sensor the interface resistivity is made as low and as stable as possible to place emphasize on the signal contribution coming from the semiconductor itself. For a rectifying SB contact-based sensor, the opposite effects are desired. Since a SBH acts as an exponential bottleneck to current flow in accordance with the law of thermionic emission [81], the aim of making the modulation of SBH, the key factor in sensor performance can be achieved by making the SBH a dynamic, sensitive and reversible function of the target analyte concentration. In accordance with the Schottky-Mott model there is a linear dependence between the SBH and the metal work function. Thus, modulation in the metal work function leads to a direct modulation in the SBH in the
metal-semiconductor junction causing an exponential change in the conductance of the sensor.

Compared to the gating effect based-gas sensors, the Schottky contact-based sensors have been found to show higher sensitivities to analyte gases due to the exponential dependence on a key factor, which naturally overrides a linear dependency yielding an enhanced sensitivity in the sensing response. However, due to the difficulties in the controlling of the interface state of the contact, the Schottky barrier based sensors suffer from the low reproducibility, low stability as well as the easily contaminate. In addition, also a vast improvement in sensitivity and low detection limits have been achieved within the Schottky contacted configurations, the SBH on most semiconductors are found to have a much weaker dependence on the metal work function than the Schottky-Mott model suggests. This phenomenon, known as Fermi level pinning, where interface states tend to pin the center of the band gap to the Fermi level, along with undesired compound formation [82], reduce the expected SBH thus diminishing the sensor performance.

1.2.3 Carbon Nanotubes

Carbon nanotubes (CNTs) are graphitic sheets seamlessly rolled into hollow cylinders with a diameter of several nanometers and a length of up to several centimeters.[80] They consist of a hexagonal network of carbon atoms with three $sp^2$ hybridized valence electrons that give rise to covalent in-plane $\sigma$-bonds while the remaining p-orbital gives rise to $\pi$-bonds.[83]
The electronic properties of CNT vary significantly depending on their chirality. In other words, how the original graphic sheet is rolled. It is anticipated that the CNTs with chirality indices that fulfill the requirement \( m - n = 3p \), where \( p \) is an integer, are metallic and those that don’t are semiconductors (Figure 1.20a, b). The metallic CNTs have zero band-gap energy while the semiconductors have band-gap energy that can vary. The band-gap energy of a semiconducting CNT can be expressed as \( E_g = (2a_{c-c} \gamma_0)/d \), where \( a_{c-c} = 1.42 \) Å is the nearest neighbor distance in the hexagonal lattice, \( \gamma_0 = 2.9 \) eV is the tight-binding overlap integral, and \( d \) is the diameter of the CNT. However, due to the large discrepancy in the calculated and measured constant of \( a_{c-c} \gamma_0 \), the value of the band-gap can vary between 0.71 eV to 1.1 eV. Additionally, the CNTs can also be single-walled CNT (SWNT), multi-walled CNTs (MWNT), and CNT bundles (Figure 1.20c), depending on the number of the layers as well as the dispersion. The SWNTs consist of only one sheet of graphic while the MWNTs are made out of several graphic sheets that share the same center axis with 2.7 nm in between each layer. The SWNTs are found to be both semiconducting and metallic depending on their chirality, while the MWNTs are all metallic. Many SWNTs exhibit a p-type behavior with dominant holes as transport carriers in the air, but can be changed to n-type when stored in vacuum. It is reported that this change in characteristics is due primarily to a change of the work function of the metal contact when exposed to oxygen. However, p-type semiconductor behavior has also been observed in SWNTs in air, which indicates the contacted metal may have less effect on the characteristics of SWNTs due to the material being doped by oxygen. The mechanism of this process is not been fully understood. It seems, though,
that CNTs have the simplest chemical composition and atomic bonding configuration but exhibit extreme diversity and richness among nanomaterials in structures and structure-property relations.

Since their discovery in 1990, there has been a growing interest in carbon nanotubes (CNTs) owing to their unique electrical, physical, mechanical and chemical properties to develop devices with simplicity, reliability, reproducibility, and low cost. Various electronic devices including supercapacitors, electrodes, field emission devices, and sensors have been synthesized based on single carbon nanotubes, carbon nanotube networks or carbon nanotube films. SWNT based chemiresistive/chemical field effect transistors (ChemFETs) have been widely used as gas sensors due to their sensitivity to charge transfers and chemical doping effect of various gaseous molecules. For example, Kong first applied CNT as sensor material to detect electron donating gas NH\textsubscript{3} and electron excepting gas NO\textsubscript{2} in 1990. Opposite responses were observed showing an increase in the sensor conductivity when exposed to NH\textsubscript{3} while the conductivity decreased when exposed to NO\textsubscript{2}. However, pristine SWNT based gas sensors have limitations such as low sensitivity to some analytes, lack of selectivity as well as long response and recovery times that hinder their use as stand-alone sensing elements. Therefore, significant effort has been devoted to surface functionalization of SWNT to modify the sensor properties. Recent reports have discussed the incorporation of typical metal or metal oxide catalysts such as Pd, Au, TiO\textsubscript{2} and SnO\textsubscript{2} for enhancement of both sensitivity and selectivity toward
analyte gases. Furthermore, many of these reports demonstrate improved performance at lower operating temperatures with respect to their thin film counterparts.
1.3 Research Objectives

The global objective of this work is to develop advanced one-dimensional nanostructures for thermoelectric and gas sensor applications. In order to fabricate a thermoelectric device with high thermopower, a novel and cost-effective method has been developed to synthesize ultra-long hollow binary, ternary, and quaternary chalcogenide nanofibers with controlled composition, dimensions, morphology, crystallinity and crystal structure. To conceive a sensor with high sensitivity and selectivity, an electrochemical route was developed to synthesize carbon nanotube hybrid structures with optimized structural and electrical properties. The specific aims of this work were the following:

1. Synthesize chalcogenide binary (i.e. Pb$_x$Se$_y$ and Pb$_x$Te$_y$), ternary (i.e. Sb$_x$Pb$_y$Te$_z$), and quaternary [i.e. Ag$_{m}$Pb$_x$Sb$_y$Te$_z$ (LAST)] hollow nanofibers by electrochemical synthesis methods (i.e. galvanic displacement reaction) and electrospinning techniques. Investigate the impact of the galvanic displacement reaction conditions (i.e. electrolyte concentration) on the material properties of the nanofibers. Understand the mechanism of the galvanic displacement reaction by electrochemical analysis tools.

2. Characterize the thermoelectric performances of these nanofibers in terms of sheet resistance and the Seebeck coefficient. Correlate the nanofibers’ thermoelectric performances with their material properties.

3. Establish a simple and scalable method to fabricate hybrid Te/CNT network device for room temperature NO$_2$ gas detection. Characterize the material
properties of the hybrids based on Te electrolyte concentration, deposition potential and charge density. Investigate the sensing performance as a function of the structure of the Te.

4. Fabricate a sensor based on the Schottky contact between Pd and SWNT for room temperature H₂ gas detection. Study the underlying fundamental sensing mechanisms based on an intensive sensor review.
1.4 Thesis Organization

The presentation of this thesis is as follows:

Chapter 2-4 will detail the development of the synthesis of chalcogenide Pb_xSe_y (Chapter 2), Pb_xTe_y (Chapter 3), Sb_xPb_yTe_z and Ag_mPb_xSb_yTe_z (LAST) (Chapter 4) hollow nanofibers by combing electrospinning and the galvanic displacement reaction. The electrical and thermoelectric properties of these nanofibers were characterized and elucidated in each chapter.

Chapter 5 will detail the development of an electrodeposition conditions to synthesize Te on the surface of SWNT with controlled morphology, particle size and density. The fabrication of a sensor array with SWNT bridged on several metal electrodes was demonstrated in Chapter 6.
1.5 References


49. Liu, W., X.F. Tang, and J. Sharp, Low-temperature solid state reaction synthesis and thermoelectric properties of high-performance and low-cost Sb-doped Mg2Si0.6Sn0.4. Journal of Physics D-Applied Physics, 2010. 43(8).


52. Androulakis, J., et al., Spinodal decomposition and nucleation and growth as a means to bulk nanostructured thermoelectrics: Enhanced performance in


65. Salvador, J.R., et al., *Transport and mechanical property evaluation of (AgSbTe)(1-x)(GeTe)(x) (x=0.80, 0.82, 0.85, 0.87, 0.90)*. Journal of Solid State Chemistry, 2009. 182(8): p. 2088-2095.


76. Joshi, G., et al., Enhancement of thermoelectric figure-of-merit at low temperatures by titanium substitution for hafnium in n-type half-Heuslers Hf0.75-xTixZr0.25NiSn0.99Sb0.01. Nano Energy, 2013. 2(1): p. 82-87.


**Figure 1.1** Various energy conversion applications of thermoelectric devices.
Figure 1.2  A generic diagram of a thermoelectric unit. Red denotes hotter temperature, and blue denotes colder temperatures.
Figure 1.3 Practical thermoelectric module that consists of several unit legs connected electrically in series and thermally in parallel.
Figure 1.4 Thermoelectric power generation efficiency (grey area) versus $T_H$. Efficiency for conventional mechanical engines as well as the Carnot limit are shown.[6]
Figure 1.5  Interdependence of the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). [5]
Figure 1.6  Thermoelectric performance ($zT$) of the state-of-art commercial (a) n-type and  (b) p-type thermoelectric materials as function of temperature[4]
Figure 1.7  The Fermi-Dirac distribution function $f_0(E)$ (solid line) and its first-order derivative $df_0/dE$ (dotted line). [10]
Figure 1. 8 Density of states of 3D, 2D, and 1D semiconductors.
Figure 1.9  Normalized carrier concentration as a function of $\eta$ at temperature of 300 K [10]
Figure 1. 10  Seebeck coefficient as a function of $\eta$ at temperature of 300 K for 1D, 2D, and 3D semiconductors. [11]
Figure 1.11  DOS (blue line) and electrons density distribution (yellow area) in the conduction band of (a) bulk Si, (b) 2 nm Si nanowire, and (c) 5 nm Si nanowire. All the drawings are based on scale.
Figure 1. Research highlights on the development of thermoelectric nanostructures.
Figure 1.13 Overview of thermoelectric performance ($zT$) of thermoelectric materials as function of temperature[4, 41]. (a) p-type materials[42-45] and (b) n-type materials[46-49]
Figure 1.14  TEM images of Si nanowire synthesized by (a) electroless etching process and (b) vapor-liquid-solid deposition. (c) Temperature dependent thermal conductivity of both types of nanowires with different diameters. (d) Temperature dependent power factor (red) and ZT (blue) of electroless etching Si nanowires with a diameter of 52 nm.
Figure 1.15  (a) High resolution TEM of \((\text{Pb}_{0.95}\text{Sn}_{0.05}\text{Te})_{0.84}\text{(PbS)}_{0.16}\) nanocomposites with spinodal PbS (bright) and PbTe (dark) phase. (b) Structure of \((\text{PbTe})_{1-x}\text{(PbS)}_x\) system with nanophase separation of PbS stripes and dots.
Figure 1. 16  Various applications of gas sensors.
**Figure 1.17** A generic diagram of a sensor and a typical sensing response.
Figure 1.18  Gas sensors based on (a) 2D thin film and (b) 1D nanostructure.
Figure 1.19  Scheme of a sensor that is based on a p-type nanowire bottom contacting with two electrodes. (a) Electrostatic gating effect with electron withdrawing molecules (white particles) and electron donating molecules (yellow particles). (b) Schottky effect with dipole formation at transducer and electrode contact area.
Figure 1. (a) A graphic sheet consists of a hexagonal network of carbon atoms with $\mathbf{a}_1$, $\mathbf{a}_2$ as the unit vectors of the hexagonal planar lattice. The chirality of the CNT is determined by $\mathbf{C} = m\mathbf{a}_1 + n\mathbf{a}_2$, where $m$ and $n$ are chirality indices. CNTs with indices $n = m$ are the armchair. Those with $n = 0$ are called zigzags and the rest are called chiral tubes. For example, a chiral CNT can be obtained by cutting the sheet along the direction $OT$ and $OA$ then rolled into a cylinder with $OA$ as the circumference with $\theta$ its chiral angle. (b) Examples of three different types of chirality of CNTs. (c) Scheme of a single-walled carbon nanotube (SWNT), a multiwalled carbon nanotube (MWNT), and a bundle of SWNTs. Adapted from ref [2] and ref [5].
Table 1.1  Thermoelectric properties overview of various nanowires, nanowire arrays or nanowire composites.

<table>
<thead>
<tr>
<th>Material system</th>
<th>Dia. (nm)</th>
<th>Carrier type</th>
<th>S (µV/K) @ 300 K</th>
<th>σ (S/cm) @ 300 K</th>
<th>κ (W/(Km)) @ 300 K</th>
<th>S²σ x 10⁻⁴ (W/K²m) @ 300 K</th>
<th>ZT</th>
<th>ZTmax @ Temp. (K)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₈.₅Te₅₁.₅</td>
<td>81</td>
<td>n</td>
<td>-30</td>
<td>700</td>
<td>1.05</td>
<td>0.66</td>
<td>0.019</td>
<td>--</td>
<td>ED</td>
<td>2005[21]</td>
</tr>
<tr>
<td>Bi₂Te₃</td>
<td>100</td>
<td>n</td>
<td>-130</td>
<td>1300</td>
<td>0.95</td>
<td>21.97</td>
<td>0.7</td>
<td>1.0</td>
<td>450</td>
<td>HT</td>
</tr>
<tr>
<td>Bi₂Te₃</td>
<td>40</td>
<td>p</td>
<td>12-33</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>ED</td>
<td>2008[26]</td>
</tr>
<tr>
<td>Bi₇₄Te₂₆</td>
<td>52</td>
<td>n</td>
<td>-52</td>
<td>2173.9</td>
<td>2.9</td>
<td>5.81</td>
<td>0.06</td>
<td>0.13</td>
<td>450</td>
<td>ED</td>
</tr>
<tr>
<td>Bi₃Te₆₉</td>
<td>100</td>
<td>n</td>
<td>180</td>
<td>34.6</td>
<td>--</td>
<td>1.1</td>
<td>--</td>
<td>--</td>
<td>LPNE</td>
<td>2010[30]</td>
</tr>
<tr>
<td>Bi₂Sb₅Te₃</td>
<td>110</td>
<td>n</td>
<td>-630</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>ED</td>
<td>2010[31]</td>
</tr>
<tr>
<td>Bi/Te</td>
<td>170</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.43</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>OFF-ON</td>
<td>2011[32]</td>
</tr>
<tr>
<td>Bi₂Te₃</td>
<td>8</td>
<td>n</td>
<td>205</td>
<td>507.5</td>
<td>1.42</td>
<td>21.4</td>
<td>0.45</td>
<td>0.96</td>
<td>380</td>
<td>HT</td>
</tr>
<tr>
<td>Te-Bi₂Te₃</td>
<td>37</td>
<td>p</td>
<td>609</td>
<td>3.0</td>
<td>0.36</td>
<td>1.75</td>
<td>0.09</td>
<td>0.24</td>
<td>400</td>
<td>HT</td>
</tr>
<tr>
<td>PbTe-Bi₂Te₃</td>
<td>32</td>
<td>n</td>
<td>-290</td>
<td>40</td>
<td>0.57</td>
<td>3.1</td>
<td>0.2</td>
<td>1.2</td>
<td>625</td>
<td>HT</td>
</tr>
<tr>
<td>Te-Bi₂Te₃</td>
<td>200</td>
<td>n</td>
<td>-163</td>
<td>714.2</td>
<td>0.96</td>
<td>19.2</td>
<td>0.6</td>
<td>0.72</td>
<td>340</td>
<td>ST</td>
</tr>
<tr>
<td>PbTe</td>
<td>180</td>
<td>p</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>0.067</td>
<td>--</td>
<td>--</td>
<td>CVD</td>
<td>2007[22]</td>
</tr>
<tr>
<td>Material</td>
<td>Width (nm)</td>
<td>Type</td>
<td>Length (um)</td>
<td>Thickness (um)</td>
<td>Conduction</td>
<td>Resistance (Ω·m)</td>
<td>Impedance (MΩ)</td>
<td>V (V)</td>
<td>Method</td>
<td>Year</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>------</td>
<td>-------------</td>
<td>----------------</td>
<td>------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>PbTe</td>
<td>30</td>
<td>n</td>
<td>628</td>
<td>--</td>
<td>0.53</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>HT</td>
<td>2008</td>
</tr>
<tr>
<td>PbTe</td>
<td>60</td>
<td>n</td>
<td>41</td>
<td>81</td>
<td>0.14</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>LPNE</td>
<td>2010</td>
</tr>
<tr>
<td>PbTe</td>
<td>60</td>
<td>n</td>
<td>445</td>
<td>0.63</td>
<td>0.13</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>LPNE</td>
<td>2010</td>
</tr>
<tr>
<td>PbTe</td>
<td>217</td>
<td>n</td>
<td>342.28</td>
<td>8.91</td>
<td>1.04</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>SI</td>
<td>2013</td>
</tr>
<tr>
<td>PbTe</td>
<td>75</td>
<td>n</td>
<td>54.76</td>
<td>15.26</td>
<td>0.046</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>SI</td>
<td>2013</td>
</tr>
<tr>
<td>PbSe</td>
<td>110</td>
<td>--</td>
<td>--</td>
<td>0.15</td>
<td>0.09</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CVD</td>
<td>2007</td>
</tr>
<tr>
<td>PbSe</td>
<td>100</td>
<td>p</td>
<td>380</td>
<td>25.0</td>
<td>3.5</td>
<td>0.8</td>
<td>0.12</td>
<td>--</td>
<td>Solution</td>
<td>2009</td>
</tr>
<tr>
<td>Si</td>
<td>20</td>
<td>p</td>
<td>200</td>
<td>500</td>
<td>5.83</td>
<td>0.7</td>
<td>0.25</td>
<td>1.2</td>
<td>200</td>
<td>SNAP</td>
</tr>
<tr>
<td>Si</td>
<td>48</td>
<td>p</td>
<td>240</td>
<td>571.4</td>
<td>1.2</td>
<td>33.0</td>
<td>0.6</td>
<td>0.6</td>
<td>300</td>
<td>EE</td>
</tr>
<tr>
<td>SiGe</td>
<td>26</td>
<td>n</td>
<td>-110</td>
<td>800</td>
<td>1.2</td>
<td>4.8</td>
<td>0.12</td>
<td>0.46</td>
<td>450</td>
<td>VLS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material system</th>
<th>Carrier type</th>
<th>@ 300 K</th>
<th>ZT max</th>
<th>@ Temp. (K)</th>
<th>Method</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S (µV/K)</td>
<td>σ (S/cm)</td>
<td>κ (W/(Km))</td>
<td>S²σ x 10⁴ (W/K²m)</td>
<td>ZT</td>
</tr>
<tr>
<td>Bi₂Te₃</td>
<td>p</td>
<td>211</td>
<td>1100</td>
<td>1.09</td>
<td>48.97</td>
<td>1.35</td>
</tr>
<tr>
<td>(Sb,Bi)₂Te₃</td>
<td>p</td>
<td>185</td>
<td>1250</td>
<td>1.11</td>
<td>44</td>
<td>1.2</td>
</tr>
<tr>
<td>Bi₀.₅₂Sb₁.₄₈Te₃</td>
<td>p</td>
<td>228</td>
<td>700</td>
<td>0.70</td>
<td>35</td>
<td>1.56</td>
</tr>
<tr>
<td>Bi₂Te₂.₇Se₀.₃</td>
<td>n</td>
<td>-180</td>
<td>750</td>
<td>1.07</td>
<td>25</td>
<td>0.7</td>
</tr>
<tr>
<td>Bi₂Te₂.₇Se₀.₃</td>
<td>n</td>
<td>-180</td>
<td>680</td>
<td>0.95</td>
<td>22</td>
<td>0.7</td>
</tr>
<tr>
<td>Bi₀.₄Sb₁.₆Te₃</td>
<td>p</td>
<td>193</td>
<td>950</td>
<td>0.92</td>
<td>35.4</td>
<td>1.15</td>
</tr>
<tr>
<td>GaSb₁₀Te₁₆</td>
<td>P</td>
<td>106</td>
<td>2000</td>
<td>0.21</td>
<td>22.5</td>
<td>0.6</td>
</tr>
<tr>
<td>AgSbTe₂</td>
<td>p</td>
<td>275</td>
<td>150</td>
<td>0.50</td>
<td>11.34</td>
<td>0.7</td>
</tr>
<tr>
<td>AgPb₁₈SbTe₂₀</td>
<td>n</td>
<td>-130</td>
<td>1850</td>
<td>2.10</td>
<td>31.5</td>
<td>0.45</td>
</tr>
<tr>
<td>Composition</td>
<td>Polarity</td>
<td>T (°C)</td>
<td>V (V/cm)</td>
<td>j (A/cm²)</td>
<td>d (μm)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>------------------------------</td>
<td>----------</td>
<td>--------</td>
<td>----------</td>
<td>-----------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Ag₀.₈⁻Pb₂⁻SbTe₂₀</td>
<td>n</td>
<td>-265</td>
<td>100</td>
<td>1.35</td>
<td>6.5</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>673</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pb₀.₉₅Sn₀.₀₅Te)₀.₉₂</td>
<td>n</td>
<td>-107</td>
<td>2090</td>
<td>2.00</td>
<td>0.24</td>
<td>0.36</td>
</tr>
<tr>
<td>(PbS)₀.₀₈</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>642</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbTe:TI (2%)</td>
<td>P</td>
<td>125</td>
<td>40</td>
<td>2.30</td>
<td>7.7</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>773</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbTe</td>
<td>p</td>
<td>268</td>
<td>89</td>
<td>1.15</td>
<td>6</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(AgSbTe)₀.₁₅(GeTe)₀.₈₅</td>
<td>p</td>
<td>100</td>
<td>2000</td>
<td>1.6</td>
<td>20</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbTe:TI (2%)</td>
<td>p</td>
<td>137</td>
<td>450</td>
<td>1.90</td>
<td>8.5</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>673</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PbTe)₀.₉₈(SrTe)₀.₀₂</td>
<td>p</td>
<td>60</td>
<td>2500</td>
<td>3.10</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>803</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgPb₁₈SbSe₁₉.₉₂₈Cl₁₀.₀₇₂</td>
<td>n</td>
<td>-103</td>
<td>379</td>
<td>1.42</td>
<td>4.05</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>873</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂CdSnSe₄</td>
<td>p</td>
<td>95</td>
<td>185</td>
<td>1.67</td>
<td>1.7</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>723</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂Se</td>
<td>p</td>
<td>80</td>
<td>1176</td>
<td>0.96</td>
<td>7.5</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>973</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₀.₈⁻Ni₀.₂⁻Sb₃.₀₅</td>
<td>n</td>
<td>-110</td>
<td>750</td>
<td>3.10</td>
<td>9.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>773</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb₀.₂⁻Co₁⁻Sb₁₂.₃</td>
<td>n</td>
<td>-142</td>
<td>1250</td>
<td>2.40</td>
<td>24</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>803</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb₀.₃₅⁻Co₁⁻Sb₁₂.₃</td>
<td>n</td>
<td>-130</td>
<td>2130</td>
<td>1.76</td>
<td>36.0</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>823</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg₀.₂⁻Si₀.₆⁻Sn₀.₄⁻Sb</td>
<td>n</td>
<td>-95</td>
<td>1729</td>
<td>2.95</td>
<td>15.8</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>860</td>
</tr>
<tr>
<td>Composition</td>
<td>Type</td>
<td>Volumetric</td>
<td>Density (g cm⁻³)</td>
<td>Thermal Conductivity (W cm⁻¹ K⁻¹)</td>
<td>Thermal Diffusivity (cm² s⁻¹)</td>
<td>Thermoelectric Power Factor (μV K⁻¹ cm⁻¹)</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------</td>
<td>------------</td>
<td>-----------------</td>
<td>-----------------------------------</td>
<td>-----------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Zr₀.₅Hf₀.₅CoSb₀.₈S</td>
<td>n</td>
<td>-142</td>
<td>900</td>
<td>3.40</td>
<td>18.2</td>
<td>0.16</td>
</tr>
<tr>
<td>Hf₀.₅Ti₀.₂₅Zr₀.₅NiSn₀.₉₉Sb₀.₀₁</td>
<td>n</td>
<td>-150</td>
<td>1490</td>
<td>3.₃₀</td>
<td>33.₅</td>
<td>0.₄</td>
</tr>
<tr>
<td>Si₈₀Ge₂₀</td>
<td>p</td>
<td>110</td>
<td>880</td>
<td>2.₃₀</td>
<td>10.₅</td>
<td>0.₆</td>
</tr>
<tr>
<td>Si₈₀Ge₂₀</td>
<td>n</td>
<td>-90</td>
<td>820</td>
<td>2.₃₀</td>
<td>10.₅</td>
<td>0.₁₅</td>
</tr>
<tr>
<td>Si₉₅Ge₅</td>
<td>n</td>
<td>-80</td>
<td>2000</td>
<td>6.₁₀</td>
<td>12.₈</td>
<td>0.₆₅</td>
</tr>
<tr>
<td>Si</td>
<td>n</td>
<td>-₇₀</td>
<td>1099</td>
<td>7.₀</td>
<td>₅.₃₈</td>
<td>0.₉₂</td>
</tr>
<tr>
<td>(Si₉₅Ge₅)₀.₆₅(Si₇₀Ge₅₀P₃)₀.₃₅</td>
<td>n</td>
<td>-₈₅</td>
<td>1₆₀₀₃</td>
<td>4.₄ₐ</td>
<td>₁₁₅₆₃</td>
<td>₀.₈₂</td>
</tr>
</tbody>
</table>

CHAPTER 2

THERMOELECTRIC PROPERTIES OF ULTRA-LONG LEAD SELENIDE HOLLOW NANOFIBERS

2.1 Abstract

A cost-effective process that combines electrospinning and a galvanic displacement reaction is utilized to synthesize ultra-long hollow Pb\textsubscript{x}Se\textsubscript{y}Ni\textsubscript{z} nanofibers with controlled dimensions, morphology, composition and crystal structure. Ni nanofibers are electrospun with an average diameter of 150 nm and are used as the sacrificial material for the gavanic displacement reaction. The composition and morphology of the nanofibers are controlled during the reaction by tuning the concentration of HSeO\textsubscript{2}\textsuperscript{+} in the electrolytes. Hollow Pb\textsubscript{x}Se\textsubscript{y}Ni\textsubscript{z} nanofibers with smooth surfaces are obtained from the low HSeO\textsubscript{2}\textsuperscript{+} concentration solution (i.e. 0.01 and 0.05 mM), but the hollow nanofibers synthesized from the high HSeO\textsubscript{2}\textsuperscript{+} concentration solution (i.e. 1 mM) have rough outer surfaces with nanocrystal protrusions. The Pb content of the nanofibers’ composition is varied from 3% to 42% by adjusting HSeO\textsubscript{2}\textsuperscript{+} concentrations. The thermoelectric properties of nanofiber mats are characterized, with the highest Seebeck coefficient of approx. 449 μV/K at 300 K in the Pb\textsubscript{37}Se\textsubscript{59}Ni\textsubscript{4} nanofiber mat.
2.2 Introduction

Recent research into low-dimensional nanoengineered thermoelectrics has invigorated the field by identifying classical and quantum mechanical size effects on electrons and phonons, which provide additional mechanisms to tune the thermoelectric figure of merit ($ZT$).[1] Several experiments on painstakingly grown two-dimensional (2D) nanostructures showed a $ZT$ of ~2–3,[2-4] shattering previous limits. Even more exciting are the theoretical predictions for one-dimensional (1D) nanostructures including nanowires and nanotubes, which are thought to have a $ZT$ exceeding 5.[5] In the design of 1D thermoelectric materials, nanotubes offer an extra degree of freedom compared to other 1D nanostructures, because wall-thickness can be another important parameter to tune the material properties, in addition to the variation in length and diameter. Changes in wall-thickness are expected to strongly alter the electrical and phonon transport properties and thereby enhance the overall thermoelectric properties.[6] Nevertheless, limited study has been reported on the thermoelectric properties of nanotubes, owing to the challenges in the synthesis processes.

Lead selenide (PbSe), a sister material of lead telluride (PbTe), has been less focused on for thermoelectric applications due to its smaller band gap energy and an expected higher thermal conductivity.[7] Recently an additional notion has been placed on this material, since a $ZT$ up to 1.2 at 850 K was experimentally achieved, which is approaching the theoretical value of 1.6 at that temperature.[8] Moreover, significant progress has been made to enhance the Seebeck coefficient while diminishing the thermal conductivity by lowering down the dimension of PbSe. However, even though a thermal
power 3 times greater than that of bulk has been reported in PbSe quantum dot superlattices, only a low power factor was extracted attributing to its high electrical resistivity.[9] 1D PbSe, on the other hand, showed a higher electrical conductivity with a significantly decreased thermal conductivity,[10] but the prevailing difficulty and high cost in a device fabrication hinders its application in a real TE apparatus. Therefore, new geometries of PbSe with superior thermoelectric performance are in highly demand, through a cost-effective fabrication process.

Various synthesis methods which include solution phase synthesis,[11] seeded solution approach,[12] oriented attachment of nanoparticles,[13] colloidal synthesis,[14] chemical vapor transport,[15] vapor-liquid-solid growth,[16] hard and soft template directed synthesis,[17,18] were utilized to synthesize 1D PbSe nanostructures. Even though most of the methods can provide materials with well-defined crystal structures, limitations in the length (normally tens of micrometers) of as-produced nanowires essentially require post processes (i.e. spark plasma sintering) to consolidate the structures to form devices. Among all the techniques that synthesize 1D nanostructures, electrospinning has emerged as the most versatile, scalable and cost-effective method to synthesize ultra-long nanofibers with controlled diameter and composition.[19] Although various nanofibers have been synthesized using this technique, limited work has been reported on synthesis of metal chalcogenide nanofibers due to the incompatibility of the precursors. Therefore, synthesis of PbSe was conducted with an addition process of a galvanic displacement reaction,[20,21] which is a spontaneous electrochemical process driven by the difference in materials’ redox potentials. In this approach, electrospinning
is exploited to fabricate ultra-long sacrificial nanofibers with controlled dimensions, morphology and crystal structures, providing a large materials’ data base to tune electrode potentials and thereby imparting control over the composition and shape of the nanostructures evolved during the galvanic displacement reaction. Synthesized samples are designed to be in a bulk scale for easy device fabrication and characterization, and reserve the superior properties of nanoscale materials. Previous work in our group has demonstrated the synthesis of ultra-long Te [22] and Bi₅Te₉ nanotubes [23] by combining electrospinning and galvanic displacement reaction, which further supports this method as a powerful route to synthesize semiconductors especially metal chalcogenide materials with potential high performances.

In this work, we demonstrated a cost-effective, high scalable nanofabrication technique to synthesize ultra-long hollow PbₓSeᵧNiₜ nanofibers by combining electrospinning and galvanic displacement reaction. Ultra-long Ni nanofibers, with controlled dimension and morphology, were fabricated by electropinning as a high volume sacrificial material source for galvanic displacement reaction. Subsequently, PbₓSeᵧNiₜ nanofibers with tunable composition, morphology, and dimension can be displaced by simply tailoring the electrolyte concentration. Electrochemical analysis including open circuit potential (OCP), linear potentiodynamic polarization (LP) as well as cyclic voltammetry (CV) were carried out in order to get a better understanding of the underlying fundamental reaction mechanism. Structure-related Thermopower of as-synthesized nanofiber mats were characterized.
2.3 Experimental

Electrospinning of Ni nanofibers. The procedure for Electrospinning of Ni nanofibers has been described in our recently published paper with some minor changes.[23] Sol-gel that contains both Ni source and a polymer was prepared by mixing 40 wt.% of nickel acetate tetrahydrate (Ni(CH$_3$COO)$_2$•4H$_2$O, Acros organics) in aqueous solution and 10 wt.% PVP (Polyvinylpyrrolidone, MW=360,000 g/mol, Sigma Aldrich, MO) in anhydrous ethanol (Fisher Scientific, PA) at a weight ratio of 1:3, followed by stirring at 300 RPM in a 60°C water bath for 1 h for complete dissolution. The obtained gel was then placed in a plastic capillary and delivered to a stainless steel needle (an inner diameter of 0.25 mm, NanoNC, Korea) by a peristaltic pump (Pump Systems Inc. NY) at a constant rate of 0.5 ml/h. The needle was connected to a high-voltage power supply (High voltage AC-DC Acopian, PA) and vertically faced to a grounded plane collector located 10 cm away. Two pieces of parallel brass sheets with a gap of 4 cm between each other were placed on the collector for the fiber alignment. Silicon substrates (3 × 3 cm in size) covered with a 300 nm layer of insulating thermal silicon oxide were pasted in the gap for fiber collection. 10 kV was applied to the system. The electrospinning time was controlled to 2 h to obtain Ni nanofiber mats. Experiments were carried out in an environmental chamber with a temperature and a relative humidity (RH) of 23 ± 1°C and 50 ± 3%. The obtained nanofibers were first dried overnight at 60°C for solvent evaporation, and then calcined at 500°C for 3 h in air to form the nickel oxide. Finally, the metal oxide nanofibers were annealed at 400°C for 3 h in forming gas (5% H$_2$ + 95 % N$_2$) to give metallic nanofibers. The heating rates were 5 and 3 °C/min, respectively.
Galvanic displacement reaction of dispersed Pb$_x$Se$_y$Ni$_z$ nanofibers and nanofiber mats. Galvanic displacement reaction of dispersed Pb$_x$Se$_y$Ni$_z$ nanofibers was carried out by mixing a Ni nanofiber suspension with a certain amount of an electrolyte that contains lead nitrate (Pb(NO$_3$)$_2$, Fisher Chemical), selenium oxide (SeO$_2$, 99.4%, Alfa Aesar) and nitric acid (HNO$_3$, Certified ACS Plus, Fisher Chemical) at room temperature for 24 h. The Ni nanofiber suspension was prepared by adding 0.4 mg of as-obtained nanofibers into 10 mL of nanopure water, followed by sonicating the contents for 15 minutes to obtain a uniform suspension. In order to minimize the effect of electrolyte concentration change on the mass transport profile of reactant ions, the amount of sacrificial material was controlled at 10% of the necessary quantity for a complete consumption of selenium oxide ions in the electrolyte. The effect of electrolyte concentration on the dimension and morphology of the hollow Pb$_x$Se$_y$Ni$_z$ nanofibers were investigated by fixing the concentration of Pb$^{2+}$ and HNO$_3$ to be 0.1 and 1 M, respectively, while varying the SeO$_2$ concentration from 0.01 to 1 mM. Once the reaction was completed, the nanofibers were cleaned by nanopure water three times and dispersed in isopropanol.

The galvanic displacement reaction for Pb$_x$Se$_y$Ni$_z$ nanofiber mats was carried out by the same procedure but using Ni nanofiber mats instead of a well-dispersed Ni nanofiber solution as the starting material.

Electrochemical analysis of galvanic displacement reaction. Electrochemical analysis including open circuit potential (OCP), linear potentiodynamic polarization (LP) as well as cyclic voltammetry (CV) were carried out to understand the mechanism of
galvanic displacement reaction. Characterizations of OCP, LP and Ni anodizing were carried out in a 100 ml 3-electrode cell; with Ni foil, Ag/AgCl, and Pt coated Ti strip as working, reference and counter electrode, respectively. The potential was swept from -0.1 V to 0.1 V for LP measurements and from -0.5 V to 0.5 V for the Ni anodizing. An E-beamed Pt film with a thickness of 100 nm on a Si substrate was used as the working electrode in the CV study of PbSe electrodeposition, with a potential sweep from OCP to -0.5 V, then back to OCP. Scan rate in all the potential profiles is 1 mV/s.

**Material characterization.** Morphologies, compositions, crystal structures and crystallinity of the obtained nanofibers were confirmed using emission-scanning electron microscopy (SEM, FEG-Philips XL30) with energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD, D8 Advance Diffractometer, Bruker) and transmission electron microscopy (TEM, JEOL JEM-2100F).

**Electrical and thermoelectric properties characterization.** Electrical contact to the nanofiber mats was obtained by sputtering four Pt electrodes with a gap size of 1 mm, using a home-made mask. Temperature dependent sheet resistances of the nanofiber mats were measured by a four probe measurement system in the temperature range from 300 K to 360 K in vacuum. Seebeck coefficients of the mats were measured by a customer-made system in the same temperature range as the resistance measurements. The system was calibrated with a standard single crystal Bi$_2$Te$_3$ bulk before taking measurements of the nanofiber samples.
2.4 Results and Discussion

Synthesis and material characterization of \( \text{Pb}_x\text{Se}_y\text{Ni}_z \) hollow nanofibers.

Sacrificial materials that have a suitable corrosive rate and can provide an appropriate driving force to the galvanic displacement reaction are one of the key parameters for the displacement of metal chalcogenides. Ni was chosen as the sacrificial material to be galvanically displaced by \( \text{Pb}^{2+} \) and \( \text{HSeO}_2^+ \), owing to the more negative cathodic standard reduction potential of \( \text{Ni}^{2+}/\text{Ni} \) pair (-0.257 V vs. standard hydrogen electrode, SHE) than that of \( \text{Pb}^{2+}/\text{Pb} \) (-0.13 V vs. SHE) and \( \text{HSeO}_2^+/\text{Se} \) (0.778 V vs. SHE). The synthesized Ni nanofibers (Figure 2. S1c) were continuous and smooth, with an average diameter of 150 ± 14 nm. Mixing of the nanofiber suspension and the acidic electrolyte led to the oxidation of Ni to \( \text{Ni}^{2+} \) (Equation 2.1), which then provided electrons as well as templates for the formation of target material. Meanwhile, deposition of \( \text{PbSe} \) had started with the overpotential deposition (OPD) of Se (Equation 2.2), followed by an underpotential deposition (UPD) of Pb on Se to form \( \text{PbSe} \). The later reaction occurred spontaneously, due to the negative Gibbs free energy of \( \text{PbSe} \) formation (Equation 2.3).[24] The whole reaction of galvanically displaced \( \text{PbSe} \) from Ni can be described in Equation 2.4:

\[
\text{Ni}^0(s) - 2e^- \rightarrow \text{Ni}^{2+}(aq), \quad E^0 = -0.257V \text{ vs. SHE}
\]

Equation 2.1

\[
\text{HSeO}_2^+(aq) + 4e^- + 3\text{H}^+(aq) \rightarrow \text{Se}^0(s) + 2\text{H}_2\text{O} (aq),
\]

\[ E^0 = 0.778V \text{ vs. SHE}, \quad \text{Equation 2.2} \]

\[
\text{Pb}^{2+}(aq) + \text{Se}^0(s) + 2e^- \rightarrow \text{PbSe}(s), \quad \text{Equation 2.3}
\]

\[
\text{Pb}^{2+}(aq) + \text{HSeO}_2^+(aq) + 3\text{Ni}^0(s) + 3\text{H}^+(aq) \rightarrow \text{PbSe}(s) + 3\text{Ni}^{2+}(aq) + 2\text{H}_2\text{O} (aq)
\]
\[ \Delta G_f^0 = -101.7 \text{ kJ/mol}, \quad \text{Equation 2.4} \]

**Figure 2.1** schematically illustrates the reaction mechanism, starting from the formation of PbSe nuclei, followed by the growth of either smooth (**Figure 2.1c**) or nanocrystallized hollow Pb\(_x\)Se\(_y\) nanofibers (**Figure 2.1d**). Synthesis of the metallic Pb nanofibers did not succeed, even though galvanically displaced Pb from Ni is thermodynamically possible.

Control over the morphology, composition and crystal structure of hollow Pb\(_x\)Se\(_y\) nanofibers (**Figure 2.2**) was achieved by varying the concentration of HSeO\(_2^+\) in the electrolyte from 0.01 to 1 mM. Uniform hollow nanofibers (**Figure 2.2b, c**) were obtained at low concentrations of HSeO\(_2^+\), below 0.05 mM, while nanofibers with nanocrystals (**Figure 2.2d**) were observed with the utilization of an electrolyte of higher HSeO\(_2^+\) content ~ 1 mM. The formation of PbSe nanocrystals, most likely taking place at the nanofiber defect sites, were actually polyhedrons rather than spheres due to the anisotropic growth of nanocrystals under non-equilibrium kinetic growth conditions.\[25\]

Also, the difference in particle size, ranging from 60 to 220 nm, suggests a limit in mass transport during the nodules’ growth. The disparity in particle size as well as the irregularity in particle location gave various gap sizes within the adjacent nodules, which is believed to contribute to the modulation of electrical conducting paths along the nanofibers.

The composition of the nanofibers depending on the concentration of HSeO\(_2^+\) was shown in **Figure 2.2a**. The Pb content increased almost linearly with the concentration of HSeO\(_2^+\) from 0.01 to 0.1 mM and plateaued thereafter (0.1 mM < [HSeO\(_2^+\)] <1 mM).
However, the Pb content was fairly constant except for an uncharacteristic dip at 0.5 mM HSeO$_2^+$, which likely reflects an error. In contrast to the galvanic displacement reaction of Bi$_x$Te$_y$ hollow nanofibers reported previously, where the Bi content initially increased with increased [Bi$^{3+}$]/[HTeO$_2^+$] ratio,[23] the displaced PbSe possessed an opposite trend. Further study of the reason and the mechanism in galvanic displacement reaction of PbSe was characterized by electrochemical analysis, which will be described in the later section of this paper.

More detailed material properties were characterized by transmission electron microscopy (TEM). Figure 2.3 shows the TEM analysis of nanofibers synthesized by the electrolyte containing 100 mM Pb$^{2+}$ and 0.01 mM HSeO$_2^+$ in 1 M HNO$_3$. The as-formed nanofiber (Figure 2.3a) shows a tubular feature with a cotton-like, waved surface. High resolution TEM (HR-TEM) images with fast Fourier transform (FFT)-converted selected area electron diffraction (SAED) patterns (Figure 2.3b) indicated the distances between lattice planes are 0.30 and 0.378 nm, which confirmed the formation of hexagonal phase Se with crystal orientation of (1 0 1) and (1 0 0) direction. The EDS spectrum (Figure 2.3d) identified the main elemental components as O, Cu, Pb, Se and Ni, where the former elements were attributed to the copper grid. Stronger Se intensity at the edge of the nanofiber from the line-EDS (Figure 2.3c) provides additional evidence for the hollow nature of the nanofibers.

Nanofibers with clearer tube structure (Figure 2.4) were observed with the utilization of an electrolyte containing a higher HSeO$_2^+$ concentration of 0.05 mM. The diffraction peaks in the SAED pattern (Figure 2.4c) could be indexed as (2 0 0), (2 2 2),
(4 2 0), (4 2 2) and (4 4 0) planes of cube phase polycrystalline PbSe, with corresponding d-spacings of 0.306, 0.177, 0.153, 0.137 and 0.108 nm, respectively. In addition, (1 0 1), (1 1 0), (1 0 2), (1 1 1) and (2 1 0) planes of Se and (1 1 1) plane of Ni$_3$Se$_2$ were detected, suggesting the presence of excess Se and Ni in the component. These results agree with EDS analysis (Figure 2.4e, f), in which the composition of the nanofibers was found to be Pb$_{28}$Se$_{53}$Ni$_{19}$, once again proving that the nanofibers are PbSe with additional Se and Ni. The existence of elemental Se was anticipated based on the phase diagram, and resulted from the precipitation of excess Se from Se-rich PbSe. The remaining sacrificial materials in the target hollow nanostructures after the galvanic displacement reaction had been reported previously, either in the element [26] or metal alloy [22] form, which may be attributed to the Kirkendall effect.

The highest HSeO$_2^+$ concentration produced hollow nanofibers with dense nanocrystals along their surfaces. Individual or coalescent grains with a size distributed of 60 to 150 nm are shown in Figure 2.5a and b, consistent with the SEM image (Figure 2.2d). The SAED pattern (Figure 2.5c) reveals the formation of polycrystalline fiber with the presence of cubic PbSe and Ni$_3$Se$_2$, but no Se. A representative HR-TEM image of a single nanofiber is shown in Figure 2.5d, confirming the existing of crystallized PbSe. The composition of the nanofiber (Figure 2.5e, f) was confirmed as Pb$_{42}$Se$_{42}$Ni$_{16}$. The composition and crystal structure of nanofibers were further characterized by XRD, where all the reflections in the pattern (Figure 2.6) could be clearly assigned to a pure phase of PbSe (JCPDS #06-0354). Calculation of the text coefficient indicates that there is no preferred orientation of the crystal structure, showing a polycrystallinity nature of
the sample. No XRD peaks arising from Ni$_3$Se$_2$ could be observed. This may be attributed to the mostly amorphous state of Ni$_3$Se$_2$ as well as the high signal-to-noise level resulted from the low intensity of XRD signal, bringing extra difficulties in weak peaks’ recognition. Average grain size of 50 ± 23 nm was calculated based on the Scherrer equation, confirming the TEM analysis. Additional XRD characterizations of Pb$_x$Se$_y$Ni$_z$ nanofiber mats with various x values were shown in Figure 2.S3. All the peaks in the patterns belong to PbSe, except for the ones from the substrate (Figure 2.S3a). These substrate peaks are from Pt (39.7°, 46.2°, 67.4°), Si (69.1°) and the sample holder (33.0°, 61.7°). Since these XRD characterizations were done in the nanofiber mats with four Pt electrodes sputtered on the top (for the measurement of electrical and thermoelectric properties), peaks from Pt and sample holder were observed. Similar to the Pb$_{42}$Se$_{42}$Ni$_{16}$ sample shown in Figure 2.6, all of the samples are polycrystallinity in nature. No Ni$_3$Se$_2$ or Se peak was observed in these Se-rich nanofiber mats. This again may be due to the mainly amorphous state of these two compounds as well as the high signal-to-noise level in these XRD measurements.

There is slight variation in the text coefficients of these samples, which is likely attributed to the dissimilarity of the nanofibers’ orientation. Grain size based on the main peak of PbSe (2 0 0) as a function of Pb and Ni content was plotted in Figure 2.S4a, where a smaller grain size was obtained in a sample rich in Pb.

Quantitative assessment of the Pb content on the average outer diameter and wall-thickness is shown in Figure 2.7. As expected, both the outer diameter and wall-thickness of the nanofibers increased as the Pb content increased. When the Pb
content increased from 3 to 40%, the average outer diameter increased from 144±00 to 210±53 nm, and the wall-thickness changed from 21±8 to 62±21 nm. The expansion in the dimensions of the nanofibers is due to the Pb’s heavier atomic weight, as well as the presence of nanocrystals on the nanofibers. Theoretical fiber dimensions including average outer diameter and wall-thickness were calculated based on an assumption of 100% reaction efficiency, shown as purple lines in the Figures. Besides the efficiency assumption, the inner diameter of the hollow nanofibers was assumed to be the same as the outer diameter of the sacrificial material, which is 150 nm. These two assumptions may not be true in a real galvanic displacement reaction, but can help simplify the complexity of the reaction and better predict the experimental results. The experimental data were smaller for the whole range of Pb content, especially for the nanofibers with low Pb content (i.e. 3% and 10%), when compared to the calculated outer diameter. The nanofibers’ outer diameters were even smaller than that of the Ni nanofibers. This could be attributed to the lower reaction efficiency in a real galvanic displacement reaction due to hydrogen evolution reaction (HER), as well as the shrinkage in the fibers’ inner diameters during the reaction. As the Pb content reached over 30%, the deviation between the experimental and theoretical data became smaller, owing to the formation of nanocrystals on the fibers’ surface. In addition, bigger error bars in the fiber diameters were observed in this range, which would be a result of the large disparity in the size of the nodules. For the wall-thickness, the experimental data was smaller than the theoretical data for the nanofibers that contained the lowest content of Pb (i.e. 3 %), but larger than the calculated value in the nanofibers with a higher Pb content (i.e. 28 % and 42 %).
The larger value of the experimental wall-thickness is again due to the formation of nanocrystals, in contrast to the smooth nanofiber formation on which the calculations were based. Overall, the results of Figure 2.2 through 2.7 show that the morphology, composition and crystallinity of the hollow Pb$_x$Se$_y$Ni$_z$ nanofibers could be precisely controlled by varying the concentration of electrolytes.

**Electrochemical behavior of galvanic displacement reaction.** A mechanistic study of the galvanic displacement reaction between the metal ions (Pb$^{2+}$ and HSeO$_2^{+}$) in the electrolytes and the sacrificial metal Ni was performed using electrochemical methods, including open circuit potential (OCP), linear potentiodynamic polarization (LP) and cyclic voltammetry (CV) analysis (Figure 2.8 and 2.9). Electrolytes composed of 100 mM Pb$^{2+}$ + 0 mM HSeO$_2^{+}$, 100 mM Pb$^{2+}$ + 0.1 mM HSeO$_2^{+}$, 100 mM Pb$^{2+}$ + 0.5 mM HSeO$_2^{+}$, 100 mM Pb$^{2+}$ + 1 mM HSeO$_2^{+}$, and 0 mM Pb$^{2+}$ + 1 mM HSeO$_2$ in 1 M HNO$_3$ were utilized in the analysis and were named as electrolyte $i$, $ii$, $iii$, $iv$, $v$, respectively, for easy description.

Transient OCP measurements were carried out in each of the five electrolytes for 30 min. Identified as a mixed potential, OCP is directly linked to both the redox potential and the anodic/cathodic exchange current densities from thermodynamic and kinetic aspects [27]:

$$E_{(OCP)} = \frac{1}{2} E_{sacrificial \ material}^{0} + \frac{kT}{e} \ln \left( \frac{j_{oc}}{j_{oa}} \right) \quad Equation \ 2.5$$

where $E_{sacrificial \ material}^{0}$ is the standard redox potential of the sacrificial material, $k$ is the Boltzmann’s constant, $T$ is the temperature, $e$ is the elementary charge, $j_{oc}$ and $j_{oa}$ are the cathodic and anodic exchange current densities, which represent the charge transfer
rate of cathodic and anodic processes. An electrochemical process with steady reactivity of cathodic and anodic sites will result in a stable OCP value. As shown in Figure 2.8a, after an initial sharp drop which may be related to the discharge of the double layer,[28] the potentials remained in an almost constant over time. Stabilized OCPs in bi-metal ion systems (electrolyte ii, iii, iv) are similar to each other with a potential around 0 V vs. Ag/AgCl, suggesting a negligible difference in the ratio of cathodic to anodic reaction rates in those systems. The highest steady-state OCP was found in the electrolyte i, which contained only Pb$^{2+}$, indicating the presence of a greater cathodic exchange current density due to the dominated HER instead of metal deposition. Most negative OCPs have been seen within electrolyte v that includes only HSeO$_2^+$, which could be attributed to the formation of reddish amorphous Se with a relatively low cathodic site rate.

Linear potentiodynamic polarization (Figure 2.8b) of the nickel surface in the electrolytes was characterized by the same method used for the OCP measurements. The corrosion potential and current density were obtained from the intersections of Tafel slope lines, which were determined form the anodic and cathodic curves respectively. As shown in the figure, the negativity of $E_{corr}$ decreased with different electrolytes in an order of HSeO$_2^+$ only, bi-metal ions and Pb$^{2+}$ only, with a ~50 mV deviation apart from each other. An overlapping was observed in the Tafel plots from the three bi-metal ion electrolytes ii, iii, iv, consistent with the OCP data. Although the augment in the corrosion current densities (Figure 2.8c) is inconsistent with the steady-state of the reaction activity reflected from the OCP data, this can be explained by the non-quantified increase in the actual reaction area that resulted from the construction of
hetero-nanostructures. As expected, once the Pb\(^{2+}\) was set into the electrolyte, the reaction rate was boosted up to give a larger \(I_{\text{corr}}\), which went along with the OCP results.

Cyclic voltammetry (CV) of Pb, Se and PbSe deposition (Figure 2.9a) as well as Ni anodizing (Figure 2.9b) were characterized to study the cathodic and anodic side of galvanic displacement reaction separately. Electrolyte composition for Pb, Se and PbSe were 100 mM Pb\(^{2+}\) + 1 M HNO\(_3\) (electrolyte \(i\)), 1 mM HSeO\(_2^+\) + 1 M HNO\(_3\) (electrolyte \(v\)) and 100 mM Pb\(^{2+}\) + 0.1 (electrolyte \(iii\)) or 1 mM HSeO\(_2^+\) (electrolyte \(iv\)) + 1 M HNO\(_3\), respectively. The reduction peak \(C_1\) and anodizing peak \(A_1\) in the full scale Pb and PbSe cyclic voltammograms can be attributed to the Pb deposition and oxidization thereafter. Deposition of Se, labeled as \(C_2\), was observed in the cathodic scan which could be represented by Equation 2.2. Ni was anodized in 1 M HNO\(_3\), showing a clear anodizing peak \(A_3\) in Figure 2.9b. Zoomed in Pb, Se and PbSe deposition curves with a return potential scan (-0.5 V \(\rightarrow\) OCP) was displayed in Figure 2.9c, with clear reduction waves \(C_3\) in the electrolyte \(iii\) and \(iv\) owing to the UPD process of Pb on Se (Equation 2.3). No obvious peak, except for a slight current dip at -0.3 V that belongs to the formation of H\(_2\)Se, was observed in Se (\(v\)) element deposition; this may be due to the amorphous nature of as-deposited Se. A flat zone in wave \(C_3\) indicates a limiting current region in the PbSe electrodeposition, where the electrodeposition rate was primarily controlled by the diffusion of chalcogen ions when the Pb\(^{2+}\) concentration was sufficiently high.[29] Therefore, the limiting current density of PbSe deposition in this potential window is proportional to the concentration of HSeO\(_2^+\), as calculated from Equation 2.6:

\[
\dot{i}_{l,PbSe} = \frac{nFD[HSeO_2^+]}{\delta} \quad \text{Equation 2.6}
\]
where \( n \) is the number of reaction electrons involved, \( F \) is the Faraday constant, \( D \) is the diffusion coefficient of \( \text{HSeO}_2^+ \) ions, \( \delta \) is the thickness of the diffusion layer and \([\text{HSeO}_2^+]\) is the concentration of \( \text{HSeO}_2^+ \).[29] As expected, the limiting current density was boosted by an order of magnitude when the concentration of \( \text{HSeO}_2^+ \) increased from 0.1 to 1 mM, suggesting an order of magnitude higher reaction rate in the later electrolyte. The intersections of the Ni anodizing curve and PbSe deposition curves indicate that the galvanic displacement reactions happened in the limiting current region of the PbSe deposition, with a much higher reaction rate in the electrolyte that contains a higher concentration of \( \text{HSeO}_2^+ \). The faster reaction rate is likely to result in the growth of hetero-structures, which would contribute to the nanocrystals formation in the galvanic displacement reaction of PbSe nanofibers. In addition, the intersection potential is around 0 V vs. Ag/AgCl, which correlates with the OCP data. As shown in Figure 2.9d, the electrochemical behavior of galvanic displacement reaction is believed to be more similar to the anodic site of Ni oxidation rather than the cathodic site of PbSe deposition, with an actual OCP of 20 mV more negative than the predicted value from the intersection.

**Electrical property of nanofiber mats.** The sheet resistance of the nanofiber mats was characterized in the temperature range from 300 K to 360 K by a 4-probe measurement in vacuum. As shown in Figure 2.S2a, current measured against voltage demonstrates a linear characteristic throughout the temperature range. The sample shows a typical semiconductor behavior, since the sheet resistance decreased linearly as the temperature increased (Figure 2.S2b), suggesting the presence of an activation
barrier at the grain boundaries. The thermal activation energy \( E_a \) was calculated using the Arrhenius equation, which can be expressed as follows:

\[
R = R_0 \exp\left(-\frac{E_a}{kT}\right)
\]

Equation 2.7

where \( R \) is the resistance at a given temperature, \( R_0 \) is the resistance at \( T \rightarrow \infty \), \( E_a \) is the thermal activation energy, \( k \) is Boltzmann’s constant, and \( T \) is temperature. The activation energy \( E_a \) was determined to be 159.1 meV, from which the band gap energy \( E_g \) can be calculated as 0.318 eV \([E_g = 2E_a (@ 300 K)]\), which is qualitatively consistent with the literature data of 0.30 eV [7].

Higher sheet resistance was observed in the nanofiber mats that contain more Pb but less Ni (Figure 2.52c). It is believed that excess Se in semiconducting PbSe nanofibers acts as a p-type dopant as well as a defect for charge carrier scattering. This may increase carrier concentration and therefore decrease the sheet resistance. However, the Ni remainder is likely related to the diminishment of sheet resistance as well, since \( \text{Ni}_3\text{Se}_2 \) is a semi-metal with a high electrical conductivity. In addition, the increase in the sheet resistance in the higher Pb contented nanofibers may also be attributed to the construction of isotype hetero-junctions as a consequence of the presence of nanocrystals in those fibers.

**Thermoelectric property of nanofiber mats.** The thermoelectric properties of nanofiber mats were characterized by measuring their Seebeck coefficient in vacuum in the temperature ranged of 300 K to 360 K. A temperature difference of -4 ~ 2.5 K was maintained across the length of the samples and the as-generated open circuit voltage was recorded (Figure 2.10a). The linear relationship between the voltage and the applied
temperature difference was observed over the entire temperature range, resulting in the Seebeck coefficient by fitting the slope.

**Figure 2.10b** shows the typical temperature dependent Seebeck coefficients of samples with various composition \( i.e. \) \( \text{Pb}_{37}\text{Se}_{59}\text{Ni}_4 \) (triangle), \( \text{Pb}_{39}\text{Se}_{51}\text{Ni}_{10} \) (star), and \( \text{Pb}_{34}\text{Se}_{55}\text{Ni}_{11} \) (diamond). The Seebeck coefficients were positive in all the samples, indicating that those nanofibers were \( p \)-type with holes responsible for the charge transport. This is consistent with the \( p \)-type nature of a self-doped Se-rich PbSe sample. It is known that for an intrinsic semiconductor that has an equal number of electrons and holes, the Seebeck coefficient drops with increasing temperature due to the higher mobility of electrons than holes.\[30\] While for a degraded semiconductor (heavily \( p \)-doped semiconductor in this case), the Seebeck coefficient increases with temperature maximizing at the onset temperature above which it drops thereafter. The improvement in the Seebeck coefficient with temperature is attributed to the movement of the Fermi level away from the edge of the band, and the decrease of the Seebeck coefficient beyond the onset temperature is due to the bipolar effect.\[31\] In the latter case, minority carriers (\( i.e. \) electrons) can be excited across the band gap, resulting in a reduction in the absolute value of the Seebeck coefficient. Normally, the rate of increase in the Seebeck coefficient with increasing temperature before reaching the onset temperature is less than the fall rate after onset. This is due to the high mobility of electrons. As shown in the figure, the Seebeck coefficient decreased with an increasing temperature in \( \text{Pb}_{37}\text{Se}_{59}\text{Ni}_4 \) and \( \text{Pb}_{39}\text{Se}_{51}\text{Ni}_{10} \) nanofibers, showing a behavior similar to intrinsic semiconductors with relatively low carrier concentration. However, in the sample containing the lowest Pb
content \( (i.e. \text{Pb}_{34}\text{Se}_{55}\text{Ni}_{11}) \), the Seebeck coefficient plateaued or increased slightly at the low temperature range (from R.T. to 335 K), then dropped sharply when the temperature was increased up to 335 K or higher. This is more like the expected behavior of a degraded semiconductor that possess sufficient carriers.

For the single crystal PbSe, the Seebeck coefficient decreases with temperature in the more intrinsic sample (carrier concentration \( = 5 \times 10^{17} \text{ cm}^{-3} \)), while maximum values are reached at high temperature in the lightly doped samples.\(^{[30]}\) Pb\(_{37}\text{Se}_{59}\text{Ni}_4\) nanofibers showed a similar trend to the intrinsic single crystal PbSe bulk, indicating an intrinsic semiconducting properties of the nanofibers. The highest Seebeck coefficient of 449 \( \mu \text{V/K} \) was obtained in the same sample at a temperature of 300 K, greater than the bulk sample \(^{[30]}\) and nanowires.\(^{[10]}\) This value is also approaching the theoretical maximum value that a bulk PbSe sample can have. For a bulk sample, the maximum Seebeck coefficient \( S_{\text{max}} \) at a certain temperature can be predicted using \( S_{\text{max}} = \frac{E_g}{2eT_{\text{max}}} \), where \( E_g \) and \( T_{\text{max}} \) represents the effective band gap and the temperature at which \( S_{\text{max}} \) is achieved.\(^{[32]}\) Since the band gap of PbSe bulk at 0 K has been reported as 0.16 ± 0.02 eV and increases with temperature at a rate of \( 4 \times 10^{-4} \text{ eV K}^{-1} \), the equation can be written as \( S_{\text{max}} = \frac{(0.0004 T+0.16)}{2eT_{\text{max}}} \), as shown by the dashed line in Figure 2.10b. One possibility yielding the superior Seebeck coefficient in the PbSe nanofibers may be quantum confinement in the wall area. Even though the average outer diameter of the nanofibers (210 nm) was almost 5 times bigger than the exciton Bohr radius of PbSe (46 nm \(^{[33]}\)), the average wall-thickness is in the same range of the radius, at which quantum
confinement may happen. Further enhancement of the Seebeck number can be achieved by decreasing the outer diameter as well as the wall-thickness of Pb$_x$Se$_y$Ni$_z$ nanofibers.

The Seebeck coefficients as a function of both Pb and Ni content in the nanofibers are plotted in Figure 2.10c. Higher Seebeck coefficient was obtained in the nanofiber mats that contain more Pb but less Ni. These samples are believed to have a lower carrier concentration than the heavily doped nanofibers since excess Se in semiconducting PbSe acts as a p-type dopant as well as a defect for charge carrier scattering, which may increase carrier concentration. Unfortunately, the effect of Ni$_3$Se$_2$ on the thermoelectric properties of nanofibers is not clear yet. One of the explanations may be that the existence of Ni$_3$Se$_2$ acts as a charge-carrier energy filter to filter out the low energy carriers, therefore augmenting the Seebeck coefficient. On the other hand, since Ni$_3$Se$_2$ is known as a semi-metal with a high carrier concentration, excess Ni is likely to diminish the Seebeck coefficient as well.

In addition, the effect of grain size on the Seebeck coefficient was invastigated. Since the variation in the grain size goes along with their composition change, a 3D plot of Seebeck coefficient as a function of both the grain size and the Pb to Se ratio was shown (Figure 2.S4b). The effect of Ni remainder was excluded by plotting the data only from the samples with the same amount of Ni around 7 at.%. A greater Seebeck coefficient was obtained in the nanofibers with a richer Pb content and a smaller grain size. The increase obtained in the Seebeck coefficient with decreased grain size is possibly caused by potential barrier scattering at grain boundaries. [34]
2.5 Conclusions

Ultra-long $\text{Pb}_x\text{Se}_y\text{Ni}_z$ hollow nanofibers were synthesized by combining electropinning and galvanic displacement reaction. Shape, morphology, composition and crystal structure of the nanofibers were controlled by adjusting the electrolyte composition, especially the concentration of chalcogen ions. Smooth, hollow nanofibers were synthesized by utilizing an electrolyte containing low concentrations of HSeO$_2^+$ (i.e. 0.01 and 0.05 mM), but nanofibers with rough surfaces dotted with nanocrystals were obtained in a high [HSeO$_2^+$] solution (i.e. 1 mM). The formation of the nanocrystals appears to be a consequence of a faster cathodic reaction rate in a high [HSeO$_2^+$] solution, leading to the growth of hetero-structures. The Pb content in the nanofibers increased with the increase in HSeO$_2^+$ concentration, with a maximum number up to 42%. The nanofibers with high Pb contained (i.e. $\text{Pb}_{42}\text{Se}_{42}\text{Ni}_{16}$) are polycrystalline in nature, while the nanofibers with less Pb (i.e. $\text{Pb}_{28}\text{Se}_{53}\text{Ni}_{19}$) contain additional crystallized element Se, suggesting a phase segregation of excess Se. The average outer diameter and wall-thickness of the nanofibers increased from 144 nm to 210±53 nm and 21±8 nm to 62±21 nm, respectively, as the Pb content increased from 3 to 42%. The deviation between the experimental and calculated data is likely due to a lower galvanic displacement reaction efficiency as well as the formation of nanocrystals which conflicts the assumptions on which the calculation are based.

The bandgap energy of $\text{Pb}_{37}\text{Se}_{59}\text{Ni}_{4}$ nanofiber mat is found to be 0.318 eV at 300 K, which is consistent with other literature reports. Sheet resistance of nanofibers with various compositions were measured, which found that a lower sheet resistance was
obtained in the sample that has a higher amount of Se and Ni. The existence of the excess Se in the nanofibers is likely acting as a p-type dopant as well as a defect for charge carrier scattering, therefore decreasing sample’s resistance. In addition, the presence of Ni$_3$Se$_2$ may further decrease the nanofibers’ resistance, due to the semi-metal nature of Ni$_3$Se$_2$.

The temperature-dependent Seebeck coefficient of Pb$_x$Se$_y$Ni$_z$ nanofibers with various compositions was characterized. Positive values were obtained in all of the samples, showing the p-type nature of these Se-rich Pb$_x$Se$_y$Ni$_z$ nanofibers. A higher Seebeck coefficient was obtained in the samples with higher Pb but lower Ni content. This is possibly caused by the nanofibers’ lower carrier concentration compared to those heavily doped nanofibers, as well as their smaller grain size. The highest thermopower of 449 $\mu$V/K was obtained in the sample Pb$_{37}$Se$_{59}$Ni$_4$ at 300 K, which is greater than that of the bulk sample and nanowires.
2.6 References


Figure 2.1  Schematic illustration of galvanic displacement reaction of (a) Ni nanofibers to form (c, d) PbₓSeᵧ hollow nanofibers. PbₓSeᵧ particles are first deposited on the surface of Ni nanofibers (b), followed by the formation of continuous nanofibers (c, d). Morphology of the as-synthesized nanofibers, either (c) smooth or (b) rough, is dependent on the concentration of HSeO₂⁺.
Figure 2.2  Deposited Pb content (a) and SEM images (b-d) of galvanic displaced Pb$_3$Se$_y$ hollow nanofibers as a function of the HSeO$_2^+$ concentration (i.e. 0.01 (b), 0.05 (c), and 1 mM (d)). The concentration of Pb(NO$_3$)$_2$ and HNO$_3$ were fixed at 0.1 and 1.0 M, respectively. The galvanic displacement reaction was conducted for 24 hours at room temperature.
Figure 2.3  (a) TEM and (b) HR-TEM (inset: FFT) images of synthesized Pb$_3$Se$_{83}$Ni$_{14}$ hollow nanofibers. (c) Line-EDS and (d) EDS analysis confirmed the formation of Pb$_3$Se$_{83}$Ni$_{14}$ nanofibers after the galvanic displacement reaction. The electrolyte is consisted of 100 mM Pb$^{2+}$, 0.01 mM HSeO$_2^+$, 1 M HNO$_3$. 
Figure 2. 4  (a, b) TEM, (c) SAED pattern, (d) HR-TEM (inset: FFT) images, (e) line-EDS, and (f) EDS of synthesized Pb_{28}Se_{53}Ni_{19} hollow nanofibers. The electrolyte is consisted of 100 mM Pb^{2+}, 0.05 mM HSeO_{2}^+, 1 M HNO_{3} at room temperature. The peak of PbSe, Se and Ni_{3}Se_{2} in SAED pattern was colored in yellow, blue and red, respectively.
Figure 2.5 (a, b) TEM, (c) SAED pattern, and (d) HR-TEM (inset: FFT) of synthesized Pb\textsubscript{42}Se\textsubscript{42}Ni\textsubscript{16} hollow nanofibers. The peak of PbSe and Ni\textsubscript{3}Se\textsubscript{2} was colored in yellow and red, respectively. (e) Line-EDS and (f) EDS analysis confirmed the formation of Pb\textsubscript{42}Se\textsubscript{42}Ni\textsubscript{16} nanofibers after galvanic displacement reaction.
Figure 2.6  XRD pattern of synthesized PbSe hollow nanofibers. The Si peak is attributed to the substrate.
Figure 2.7  Average outer diameter (a) and wall-thickness (b) of as galvanic displaced Pb$_x$Se$_y$Ni$_z$ hollow nanofibers as a function of the Pb content. Theoretical data was shown in purple; this calculation is based on the assumption of 100 % galvanic displacement reaction efficiency.
Figure 2.8  (a) OCP transient, (b) Tafel plot and (c) corrosion current density of Ni films in electrolytes with 100 mM Pb$^{2+}$ and (i) 0, (ii) 0.01, (iii) 0.1, and (iv) 1 mM HSeO$_2^+$ in 1 M HNO$_3$. Electrolyte (v) contains no Pb$^{2+}$ but 1 mM HSeO$_2^+$ in 1 M HNO$_3$. 

108
Figure 2.9  (a, b) Full scale and (c) zoomed in cyclic voltammograms in the electrolytes with 100 mM Pb$^{2+}$ and (i) 0, (iii) 0.1, and (iv) 1 mM HSeO$_2^+$ in 1 M HNO$_3$. Electrolyte (v) contains no Pb$^{2+}$ but 1 mM HSeO$_2^+$ in 1 M HNO$_3$. Ni was anodized in the electrolyte containing 1 M HNO$_3$. (d) Tafol plots of Ni anodizing (anodic reaction), PbSe deposition (cathodic reaction) and galvanic displacement reaction.
Figure 2.10  (a) Temperature dependent $\Delta V$ vs. $\Delta T$ characterization of $\text{Pb}_{37}\text{Se}_{59}\text{Ni}_4$ nanofiber mat. (b) Temperature dependent Seebeck coefficient of $\text{Pb}_{37}\text{Se}_{59}\text{Ni}_4$ (down triangle), $\text{Pb}_{39}\text{Se}_{51}\text{Ni}_{10}$ (star), and $\text{Pb}_{34}\text{Se}_{55}\text{Ni}_{11}$ (diamond) nanofiber mats. The dashed line indicates the maxium Seebeck coefficient of a bulk PbSe at certain temperature. (c) 3D plot of Seebeck coefficient of $\text{Pb}_x\text{Se}_y\text{Ni}_z$ nanofiber mat at 300 K as a function of Ni and Pb content.
Figure 2.S 1  SEM images of (a) electrospun PVP/Ni acetate nanofibers, (b) NiO nanofibers, (c) Ni nanofibers.
Figure 2.S2  Temperature dependent (a) I-V characterization and (b) sheet resistance of Pb$_{37}$Se$_{59}$Ni$_4$ NF mat. (c) 3D plot of Seebeck coefficient of Pb$_x$Se$_y$Ni$_z$ nanofiber mat at 300 K as a function of Ni and Pb content.
Figure 2.S 3  XRD pattern of (a) substrate, (b) Pb_{31}Se_{62}Ni_{7}, (c) Pb_{35}Se_{58}Ni_{7}, (d) Pb_{37}Se_{59}Ni_{4} hollow nanofiber mats. Substrate peaks are contributed from Si, Pt electrode and sample holder.
Figure 2.S 4  3D plot of Pb$_x$Se$_y$Ni$_z$ nanofiber mats’ (a) grain size as a function of Ni content and Pb/Se (b) Seebeck coefficient as a function of grain size and Pb/Se.
CHAPTER 3

THERMOELECTRIC PROPERTIES OF ULTRA-LONG LEAD TELLURIDE HOLLOW NANOFIBERS

3.1 Abstract

Electrospinning and galvanic displacement reaction were combined to synthesize ultra-long \( \text{Pb}_x\text{Te}_y \) hollow nanofibers. Smooth, continuous Co nanofibers with an average diameter of 124 nm were electrospun and serve as sacrificial materials for the subsequent galvanic displacement of \( \text{Pb}_x\text{Te}_y \). The morphology and composition of the \( \text{Pb}_x\text{Te}_y \) nanofibers were tuned by varying the concentrations of \( \text{Pb}^{2+} \) and \( \text{HTeO}_2^+ \) in the electrolytes. Smooth, hollow \( \text{Pb}_x\text{Te}_y \) nanofibers were synthesized by utilizing electrolytes with low concentrations of \( \text{Pb}^{2+} \) (i.e. 10 mM) and \( \text{HTeO}_2^+ \) (i.e. 0.1 mM), while rough nanotubes were obtained with high metal and chalcogen ion concentrations (i.e. \( [\text{Pb}^{2+}] = 500 \text{ mM}, [\text{HTeO}_2^+] = 1.0 \text{ mM} \)). The highest Pb content achieved was 46 at. %. The average outer diameter of the \( \text{Pb}_x\text{Te}_y \) nanofibers increased from 147 nm to 337 nm as the Pb content increased from 36 at.% to 46 at.%.. The temperature-dependent Seebeck coefficients of as-prepared nanofiber mats were systematically measured and showed the highest value of 356 \( \mu \text{V/K} \) at 308 K in the sample of \( \text{Pb}_{45}\text{Te}_{55} \).
3.2 Introduction

The restriction of non-renewable resources along with the threat of environmental and ecological degradation is a key driver for improving the energy generation and efficiency. Active searches for efficient renewable energy conversion technologies have been attempted in various research areas such as solar cells [1], biomasses [2], fuel cells [3] and thermoelectrics [4]. Among these, thermoelectric materials offer simple, silent and reliable solid state energy conversion devices due to their unique ability to directly convert heat into electricity and vice-versa without moving parts or bulk fluids [6]. The efficiency of a thermoelectric device can be determined by the thermoelectric figure-of-merit (ZT), given by \( ZT = S^2 \sigma T/\kappa \). Here \( S \) (V/K), \( \sigma \) (S/m), \( \kappa \) (W/mK), \( T \) (K), and \( S^2 \sigma \) (W/mK) are Seebeck coefficient, electrical conductivity, thermal conductivity, absolute temperature and power factor, respectively. In order to maximize ZT, a material must have a high Seebeck coefficient as well as a high electrical conductivity but a low thermal conductivity. However, the interdependence of these parameters poses a stumbling block to the ZT improvement.[5]

Facilitation of ZT can be achieved in one-dimensional (1D) nanostructures due to the enhancement of the power factor through quantum confinement and the reduction of thermal conductivity through stronger phonon scattering. The Seebeck coefficient describes the ability of heat to drive charge carriers between two different temperatures, so it is a function of the energy difference between the conduction band and the Fermi level. As a result of quantum confinement in 1D nanostructure, the Fermi level will shift away from the conduction band. This will lead to a greater energy difference between the
Fermi level and the conduction band thus an improvement in materials’ Seebeck coefficient.[6] For electrical conductivity, since only small changes in carrier concentration and mobility are expected in the degenerated semiconductors when the Fermi level decreases, the electrical conductivity remains almost the same compared to the three-dimensional (3D) bulk materials.[6] As a result, an improvement in the power factor is expected in 1D nanomaterials. Additionally, due to the larger surface-to-volume ratio in 1D nanomaterials, stronger phonon scattering at the grain boundaries and interfaces of the nanostructures is anticipated, which can significantly decreases the thermal conductivity.[7, 8] Therefore, the ZT can be improved in 1D nanostructures originating from an improvement in the power factor and a reduction in the thermal conductivity. Among the different geometries of 1D nanostructures (e.g. nanowires and nanoribbons), nanotubes offer an extra degree of freedom in the design of 1D thermoelectric materials. This is because the diameter and length as well as the wall-thickness of the materials can be varied. The wall-thickness can strongly alter the electrical and phonon transport properties and thereby affect the overall thermoelectric properties.[9]

Lead telluride (PbTe) is a semiconductor with a narrow band-gap energy of 0.31 eV at 300 K and a rocksalt crystal structure. PbTe can be n- or p-type as a result of departures from stoichiometry (Pb-rich PbTe is n-type, while Te-rich PbTe is p-type).[10] The state-of-the-art commercially available PbTe-based thermoelectric devices have the highest ZT of ~ 0.8 at ~ 600 K, which makes the materials a good candidate for thermoelectric application in the middle-high temperature range. The enhancement of the
thermoelectric properties of PbTe has been already realized by band-gap engineering. Dramatic enhancement in the thermoelectric efficiency of PbTe was achieved by doping the material with thallium (Tl), which caused a local distortion of the band rather than a shift of the Fermi level. This distortion augmented the Seebeck coefficient but diminished the contributions from electrical thermal conductivity, thus facilitating the ZT. [11] In addition, improvement of ZT was achieved by nanoengineering of the Se alloyed PbTe quantum dot superlattice, with a ZT of 1.6 at 300 K and of 3.5 at 570 K. The remarkable enhancement of ZT in this system is attributed to an increase in the thermoelectric power factor and a decrease in the lattice thermal conductivity. [12-14] Furthermore, single crystal PbTe nanowires with a diameter of 30 nm showed a Seebeck coefficient of 628 μV/K, which is about 137% over that of the state-of-the-art bulk PbTe. [15]

Various methods including hydrothermal synthesis [15], stress-induced method[16], lithographically patterned nanowire electrodeposition (LPNE) [17], and chemical vapor deposition (CVD) [18] were utilized to synthesize 1D PbTe nanostructures. Because single wire-based thermoelectric devices have difficulties in maintaining the nanowires’ structural and chemical composition during the lithographic contacting, nanowire arrays or highly-packed nanowire films (pellets) were normally utilized for the thermoelectric property characterizations. [15-17] For example, p-type PbTe nanowires with a diameter of 30 nm were synthesized by the hydrothermal method. The nanowires were then hot pressed into a pellet for measuring thermoelectric properties, showing the highest Seebeck coefficient of 628 μV/K.[15] N-type PbTe nanoribbon arrays with a diameter of 60 nm were synthesized by LPNE, which showed a Seebeck coefficient and an electrical
conductivity of -445 µV/K and 0.63 S/cm, respectively. [17] However, no ZT values of PbTe nanowires were reported due to the lack of thermal conductivity data.

Electrospinning technology is based on the uniaxial stretching of a viscoelastic jet derived from a polymer solution or a melt by electrical force.[19] Compared to other conventional methods, electrospinning is able to fabricate ultra-long polymer, [20] metal, [21] and metal oxide [22] nanofibers with controllable diameters, compositions and structures in a simple and versatile way. Although various nanofibers have been synthesized using this technique, limited work has been reported on the synthesis of chalcogenide nanofibers due to the incompatibility of the precursor solutions. Therefore, to address this issue, galvanic displacement reaction was applied post-electrospinning, converting the electrospun materials to the desired hollow chalcogenide nanofibers. This method has been successfully exploited to synthesize Te[23] and PbₓSeᵧ hollow nanofibers by our group.

In this paper, ultra-long hollow PbₓTeᵧ nanofibers with controlled diameters and compositions were synthesized by combing electrospinning and galvanic displacement reaction. Electrospinning was exploited to fabricate ultra-long Co nanofibers, providing sacrificial materials with controlled dimensions, morphologies and crystallinity for the subsequent galvanic displacement reaction. Various morphologies and compositions of the PbₓTeᵧ hollow nanofibers were synthesized by tuning the electrolyte concentrations in the galvanic displacement reactions. Temperature- and composition-dependent thermoelectric properties of the PbₓTeᵧ nanofiber mats were also characterized.
3.3 Experimental

**Electrospinning of Co NFs.** The procedure of electrospinning of Co nanofibers is similar to that of Ni nanofibers, which has been described in our recently published paper with minor changes.[23] An aqueous solution that contains 1.6 M of citric acid (C₆H₈O₇, anhydrous, enzyme grade, Fisher Chemical) and 1.6 M of cobalt acetate (C₄H₆CoO₄·4H₂O, 98%, Sigma-Aldrich) in 3.34 g of water was mixed with a polymer solution containing 5.2 wt. % of PVP (Polyvinylpyrrolidone, MW= 1,300,000 g/mol) in 6.3 g of anhydrous ethanol (Fisher Scientific, PA). After complete dissolution, the solution was fed through a metallic needle with an inner diameter of 0.25 mm. A peristaltic pump was used to give a constant feed-rate of 0.5 ml/h. As a high voltage (i.e. 8 kV) was applied to the tip of the needle, fibers were stretched from the solution and collected on a 3 cm by 3 cm Si/SiO₂ chip. This chip was attached to a grounded collector 10 cm away from the needle tip. The electrospinning time was 15 min for the collection of nanofiber mats with consistent thicknesses. The temperature and relative humidity were 40 ± 2°C and 8 ± 1 %, respectively. The collected nanofibers were first aged at 60 °C overnight and then calcined at 500 °C in pure H₂ for 5 h to obtain Co nanofibers.

**Galvanic displacement of PbₓTeᵧ nanofiber mats.** The galvanic displacement reaction of PbₓTeᵧ nanofiber mat was conducted by dipping a free-standing Co nanofiber mat of the desired amount into an electrolyte containing lead nitrate (Pb(NO₃)₂, Fisher Chemical), tellurium oxide (TeO₂, 99+%, Acros Organic) and nitric acid (HNO₃, Certified ACS Plus, Fisher Chemical) at room temperature for 30 min. A 1 cm by 1 cm Si/SiO₂ chip was used as a substrate and placed underneath the nanofiber mat in the
solution. In order to minimize the effect of electrolyte concentration change on the mass transport profile of reactant ions, the amount of sacrificial material was controlled at 10% of the necessary quantity for a complete consumption of chalcogen ions in the electrolyte. No interruption was introduced to the reactions. The effects of electrolyte concentrations on the dimensions and morphologies of the hollow Pb$_x$Te$_y$ nanofiber mats were investigated by varying the concentrations of Pb$^{2+}$ and HTeO$_2^+$ from 10 mM to 500 mM and 0.1 mM to 1 mM, respectively. Once the reactions were complete, the nanofiber mats were carefully cleaned by nanopure water five times and air dried.

**Material characterization.** Morphologies, compositions, crystal structures and crystallinity of the obtained nanofiber mats were characterized using emission-scanning electron microscopy (SEM, FEG-Philips XL30) with energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD, D8 Advance Diffractometer, Bruker).

**Electrical and thermoelectric property characterizations.** Electrical contacts were obtained by sputtering four Pt electrodes with both the gap width and the electrode size of 1 mm onto the nanofiber mats, using a homemade shadow mask. Seebeck coefficients of the mats were measured by a homemade system at a temperature range from 300 K to 360 K. This system was calibrated by a standard single crystal Bi$_2$Te$_3$ bulk before use.

### 3.4 Results and Discussion

**Electrospinning of Co nanofibers as sacrificial materials.** The viscosity and conductivity of the electrospinning solution were 130.3 cP and 1.05 mS/cm, respectively.
Smooth, cylindrical CoAc₂/citric acid/PVP nanofibers with diameters of 519 ± 168 nm were electrospun as shown in Figure 3.1a, b. The significant standard deviation of 168 nm is likely due to the inhomogeneous electrical bending instability of the fibers as well as the formation of the branched fibers. The latter originates from the nonuniform charge density distribution on the surface of the jet. [24] Annealing of the hybrid fibers at 500 °C for 5 h in H₂ gas led to a complete decomposition of the polymer and acid as well as the formation of smooth and continuous Co nanofibers. The diameter of the Co nanofibers is 124 ± 13 nm (Figure 3.1c, d).

**Synthesis and material characterization of PbₓTeᵧ hollow NFs.** Co was chosen as the sacrificial material for galvanic displacement reaction of PbₓTeᵧ due to its suitable corrosive rate and its ability to provide an appropriate driving force for the chalcogenide displacement. Owing to the more cathodic standard reduction potential of Co²⁺/Co pair (-0.28 V vs. standard hydrogen electrode, SHE) than of the Pb²⁺/Pb (-0.13 V vs. SHE) and HTeO₂⁺/Te (0.551 V vs. SHE) pairs, the displacement reaction of PbₓTeᵧ from Co is spontaneous. In the reaction, Co nanofibers serve both as the electron sources and the templates for the PbₓTeᵧ deposition. Dipping the Co nanofiber mats into the acidic electrolytes containing Pb²⁺ and HTeO₂⁺ will led to the oxidation of Co to Co²⁺ as well as the formation of PbₓTeᵧ. The deposition of PbₓTeᵧ begins with the formation of Te nuclei on the surface of the Co nanofibers (due to a more negative standard reduction potential of Te than that of Pb), followed by an underpotential deposition of Pb on Te to form PbTe. This is a spontaneous reaction because of the negative Gibbs free energy of PbTe.
formation (Equation 3.3).[25] Galvanically displacing Pb\textsubscript{x}Te\textsubscript{y} from Co can be described in the Equation 3.1- 4:

\[ Co^0(s) - 2e^- \rightarrow Co^{2+}(aq) \quad \text{Equation 3.1} \]

\[ HTeO_2^+(aq) + 4e^- + 3H^+(aq) \rightarrow Te^0(s) + 2H_2O(aq) \quad \text{Equation 3.2} \]

\[ Pb^{2+}(aq) + Te^0(s) + 2e^- \rightarrow PbTe(s) \quad \text{Equation 3.3} \]

\[ Pb^{2+}(aq) + HTeO_2^+(aq) + 3Co^0(s) + 3H^+(aq) \rightarrow PbTe(s) + 3Co^{2+}(aq) + 2H_2O(aq) \]

\[ \Delta G_f^0 = -69.5 \text{ kJ/mol} \quad \text{Equation 3.4} \]

In addition, a suitable dissolution rate of the sacrificial materials is one of the key parameters for a successful displacement. Sacrificial materials with a dissolution rate comparable with the deposition rate of the target materials are required in order to achieve high deposition efficiency and a low sacrificial material residual.

Control over the morphologies and compositions of the Pb\textsubscript{x}Te\textsubscript{y} nanofibers was achieved by varying the concentrations of Pb\textsuperscript{2+} and HTeO\textsubscript{2+} in the electrolytes. Solutions with a fixed HNO\textsubscript{3} concentration of 0.1M and various concentrations of Pb\textsuperscript{2+} (10 mM ~ 500 mM) and HTeO\textsubscript{2+} (0.1 mM to 1.0 mM) were utilized. Compared to the galvanic displacement reaction of PbSe, the concentration of HNO\textsubscript{3} in the PbTe’s electrolytes was 10 times lower and the reaction time was 48 times shorter. The choice of the lower acid concentration as well as the shorter reaction time in the PbTe case was due to the faster dissolution rate of Co in an acidic solution compared to that of Ni.[26]

The morphologies of Pb\textsubscript{x}Te\textsubscript{y} nanofibers are shown in Figure 3.2. In the electrolytes that contain 0.1 mM and 1.0 mM of HTeO\textsubscript{2+}, hollow nanofibers with smooth surfaces (Figure 3.2a1-a3, c1-c3) were obtained at low concentrations of Pb\textsuperscript{2+} (e.g. 10 mM),
while rough nanofibers with nanocrystals (Figure 3.2a4-a5) were obtained when the concentration of Pb$^{2+}$ was over 200 mM. The formation of the nanocrystals (e.g. Figure 3.2a5, c5) may be due to a higher reaction rate in the electrolytes that contain a higher concentration of Pb$^{2+}$, resulting in the growth of hetero-structures. Opened nanotubes were observed in the low concentration of HTeO$_2^+$ (i.e. 0.1 mM) as shown in Figure 3.2a3, a4, which may be attributed to the incomplete coverage of the deposits on the templates or the dissolution process of the as-deposited materials. No clear chain was found in the nanofibers from the electrolytes that contain 0.5 mM of HTeO$_2^+$ (Figure 3.2b1-b5), which is likely an error.

The composition of Pb$_x$Te$_y$ as functions of the concentration of Pb$^{2+}$ and HTeO$_2^+$ is shown in Figure 3.3. Variations in the ion concentrations have minor effects on the fibers’ composition because only a 10 at. % (from 36 at.% to 46 at.%) change in the Pb content was observed corresponding to almost a 2 orders of magnitude change in the electrolyte concentration. In the electrolyte of 1.0 mM HTeO$_2^+$, the Pb content increased from 38 at.% to 45 at.% abruptly as the concentration of Pb$^{2+}$ increased from 20 mM to 50 mM. Then the Pb content plateaued at a higher level of Pb$^{2+}$ concentration. However, in the electrolytes of 0.1 mM and 0.5 mM HTeO$_2^+$, a slight decrease in the Pb content at the low Pb$^{2+}$ concentration region (10 mM $\leq$ [Pb$^{2+}$] $\leq$ 50 mM) was first observed, followed by a gradual increase in the Pb content when the concentration of Pb$^{2+}$ is higher than 50 mM. Here, the slight decrease at the low Pb$^{2+}$ concentration region was considered an insignificant event since the variations are within the error bars. This insignificant effect of a high Pb$^{2+}$ concentration ([Pb$^{2+}$] $\geq$ 50 mM) on the composition of PbTe has been
suggested in our previously published paper.[25] Additionally, the Pb content increased with an increase in the concentration of HTeO$_2^+$ at any fixed Pb$^{2+}$ concentration over 50 mM, which may be again attributed to the faster reaction rate in the electrolytes containing concentrated chalcogen ions. The same phenomenon has been observed in the galvanic displacement reaction of PbSe nanofibers from Ni.

A quantitative assessment of the Pb$^{2+}$ concentrations and the Pb content on the average outer diameter of the Pb$_x$Te$_y$ nanofibers is shown in Figure 3.4. A greater outer diameter was found in the nanofibers displaced in the electrolytes with a higher Pb$^{2+}$ and HTeO$_2^+$ concentration. When the concentration of Pb$^{2+}$ increased from 20 mM to 500 mM, the outer diameters increased from 129 nm, 149 nm and 183 nm to 177 nm, 229 nm and 337 nm in the electrolytes containing 0.1 mM, 0.5 mM, and 1.0 mM HTeO$_2^+$, respectively. For a fixed Pb$^{2+}$ concentration of 500 mM, the outer diameter increased from 177 nm to 337 nm as the concentration of HTeO$_2^+$ increased from 0.1 mM to 1.0 mM. Greater outer diameters are expected in the electrolytes containing higher concentrations of Pb$^{2+}$ and HTeO$_2^+$, owing to the formation of nanocrystals on the surfaces of the fibers which resulted from a faster deposition rate. Theoretical fiber outer diameters were calculated based on assumptions of 100% GDR efficiency and smooth fiber formation, shown as dashed line in Figure 3.4a. The experimental data were smaller than the calculated data for the nanofibers with low Pb content, ranging from 36 at.% to 44 at.%. This could be attributed to the lower efficiency of the galvanic displacement reaction in the real experiments due to hydrogen gas evolution reactions, as well as the dissolution of the PbTe nanofibers in the acid bath during the reaction. In addition,
continuous dissolution of the Co templates could shrink the inner diameters of the PbTe nanofibers, thus reducing their outer diameters. As the Pb content is equal to or over 45 at.%, the outer diameters are found to be greater than the theoretical values. These diameters are due to the formation of nanocrystals on the surfaces, in contrast to the smooth nanofiber formation on which the calculations were based. In addition, larger error bars in the fiber diameters were observed in this range, which could be a result of the large disparity in the size of the nodules.

X-ray diffraction patterns of the Co nanofibers and the Pb$_x$Te$_y$ nanofibers with tailored compositions were analyzed and shown in Figure 3.5. As-electrospun Co nanofibers have a diffraction pattern of a hexagonal crystal structure. All the reflections in the PbTe (Figure 3.5b-e) could be clearly assigned to a pure phase of PbTe (JCPDS 38-1435) except for the peaks that belong to the sample holder, which were marked with stars. The asymmetric peaks at 39.5 °C are contributed from both the $\langle 2 2 0 \rangle$ orientation of PbTe as well as the $\langle 1 1 1 \rangle$ plane of the sputtered Pt electrodes. Calculation of the text coefficient indicates that there is no preferred orientation of the PbTe crystal structure, showing a polycrystallinity nature of the sample. The average grain size was calculated to be 61 nm, 62 nm, 56 nm, and 61 nm for the sample c1, c2, c3, c5 in the Figure 3.2, respectively. No peak from element Te was observed, which may be due to the amorphous nature of the deposited Te.

The Seebeck coefficients of the Pb$_x$Te$_y$ nanofiber mats were measured in the temperature range of 300 K to 360 K as shown in Figure 3.6a. A temperature difference of -6 ~ 4 K was maintained across the length of the samples and the as-generated open
circuit voltage was recorded. The linear relationship between the voltage and the applied
temperature gradient was observed over the entire temperature range, resulting in the
Seebeck coefficient by fitting the slope. The temperature-dependent Seebeck coefficients
of sample c1-c5 were plotted in Figure 3.6b. Positive Seebeck coefficients indicate the
p-type nature of the materials. This is consistent with the p-type nature of a self-doped
Te-rich PbTe sample. In all of the samples, the Seebeck coefficient decreased with an
increasing temperature, showing a behavior similar to intrinsic semiconductors with
relatively low carrier concentrations. The highest Seebeck coefficient of 356 $\mu$V/K was
obtained in the sample Pb$_{45}$Te$_{55}$ at a temperature of 308 K, which is greater than that of
the single crystal bulk sample [27]. The Seebeck coefficients as functions of the Pb
content and the grain size were shown in Figure 3.6c. Higher Seebeck coefficients
were obtained in the nanofiber mats that have a higher Pb content and a smaller grain size.
Samples that is close to the stoichiometric composition are believed to have a lower
carrier concentration than that of the heavily-doped nanofibers since excess Te acts as a
p-type dopant as well as a defect for charge carrier scattering. The Seebeck coefficient
describes the ability of the carriers transport from the Fermi level to the conduction band
corresponding to a temperature difference. Therefore, a lower Seebeck coefficient is
expected in a heavily-doped semiconductor since its Fermi level has been pushed into the
conduction band. In addition, energy filtering effect is anticipated in a sample with a
small grain size, which enables only the contributions from carriers with high energy to
the carrier transport thus an enhanced Seebeck coefficient. Future enhancement of the
Seebeck coefficient of PbTe could be achieved by controlling the materials’ crystal
orientation to be in \( \langle 1 1 1 \rangle \) direction, since the effective mass component of PbTe along the \( \langle 1 1 1 \rangle \) axis of the constant energy ellipsoid is about 10 times larger than the perpendicular component. [28]

### 3.5 Conclusions

\( \text{Pb}_x\text{Te}_y \) nanofiber mats with controlled dimensions, morphologies and compositions were synthesized by galvanically displacing electrospun Co nanofibers. Hollow nanofibers with smooth surfaces were synthesized by utilizing electrolytes containing low concentrations of Pb and \( \text{HTeO}_2^+ \), while nanofibers with rough surfaces dotted with nanocrystals were fabricated in high \( \text{Pb}^{2+} \) and \( \text{HTeO}_2^+ \) contained solutions. The formation of the nanocrystals in the latter case may be due to a faster reaction rate resulting from higher ion concentration. Both the metal and chalcogen ions have insignificant effects on the fibers’ composition in the currently studied range. The highest Pb content achieved is 46 at.%. No residue of Co was observed in the fibers, which indicates a complete reaction. As the Pb content increased from 36 at.% to 46 at.%, the average outer diameter of the nanofibers increased from 147 nm to 377 nm. All the samples are polycrystalline in nature with an average grain size of 60 nm.

The temperature-dependent Seebeck coefficients of the prepared nanofiber mats were systematically measured in the temperature range from 300 K to 360 K, using a custom-made apparatus. Positive Seebeck coefficients indicate the samples are p-type with holes as charge carriers. The Seebeck coefficient decreased with increased temperature, showing an intrinsic semiconductor behavior in the sample. A greater
Seebeck coefficient was observed in the sample with a higher Pb content and a smaller gain sizes. The highest Seebeck coefficient of 356 µV/K was obtained in the Pb_{45}Te_{55} sample at 308 K.
### 3.6 References


Figure 3.1  SEM images of (a, b) electrospun CoAc$_2$/citric acid/PVP nanofibers and (c, d) Co nanofibers.
**Figure 3.2** SEM images of Pb$_x$Te$_y$ hollow nanofibers. The concentration of Pb(NO$_3$)$_2$ are (1) 10 mM, (2) 50 mM, (3) 100 mM, (4) 200 mM, (5) 500 mM. The concentration of HTeO$_2^+$ is (a) 0.1 mM, (b) 0.5 mM, (c) 1.0 mM. The concentration of HNO$_3$ was fixed at 0.1 M. The galvanic displacement reactions were conducted for 30 min at room temperature. *The concentration of Pb(NO$_3$)$_2$ in c1 is 20 mM. The sale bars are 1 µm.
Figure 3.3  The Pb content of the galvanic displaced Pb$_x$Te$_y$ hollow nanofibers as functions of the concentration of Pb$^{2+}$ and HTeO$_2^+$. 
Figure 3.4 The outer diameter of as galvanic displaced Pb$_x$Te$_y$ hollow nanofibers as functions of (a) the concentration of Pb(NO$_3$)$_2$ and HTeO$_2^+$ as well as (b) the Pb content. Theoretical data was shown in dashed line; this calculation is based on the assumptions of 100 % GDR efficiency and smooth fiber formation.
Figure 3.5  XRD pattern of (a) Co nanofibers (b-e) synthesized Pb$_x$Te$_y$ hollow nanofibers referring to Figure 2-c1, c2, c3, c5. The peaks with stars belong to the sample holder.
Figure 3.6 Temperature dependent (a) $\Delta V - \Delta T$ characterizations, (b) Seebeck coefficients of Pb$_x$Te$_y$ nanofiber mats referring to Figure 2 c1-5. (c) Seebeck coefficients of the Pb$_x$Te$_y$ nanofiber mat as functions of the Pb content and the grain size.
CHAPTER 4

THERMOELECTRIC PROPERTIES OF ULTRA-LONG SILVER ANTIMONY LEAD TELLURIDE HOLLOW NANOFIBERS

4.1 Abstract

Ag_xPb_ySb_zTe_b (LAST) nanofiber mats with controlled dimensions, morphologies and compositions were synthesized by galvanically displacing electrospun Co nanofibers. Control over the compositions of the nanofibers was obtained by tuning the concentrations of the cations (i.e. SbO^+ and Ag^+) in the electrolytes. The temperature-dependent Seebeck coefficients of these LAST nanofibers were characterized, showing either n- or p-type semiconductor behaviors depending on their compositions.

4.2 Introduction

The rising cost of compliance to laws and regulations (from the Clean Air Act to Geologic Sequestration) for consuming non-renewable energy resources is the key driver to improve the efficiency of environmentally-friendly, renewable energy generation.[1] Thermoelectric energy converters are solid-state devices that can generate electricity by harvesting waste thermal energy, thereby improving the efficiency of a system.[2] The many advantages of thermoelectric devices include solid-state operation, zero-emissions, vast scalability, no maintenance and a long operating lifetime. Nonetheless, due to their
limited energy conversion efficiencies, and therefore high cost, thermoelectrics currently have a rather limited set of applications.[1] Recent research in low-dimensional thermoelectric nanostructures has invigorated the field by identifying classical and quantum mechanical size effects on electrons and phonons, which provide additional mechanisms to enhance energy conversion efficiencies. Theoretical predictions of the figure-of-merit (ZT) values have exceeded 5, particularly for one-dimensional (1-D) nanostructures.[3] Among 1-D thermoelectric materials, nanotubes benefit from their unique wall thickness, which provides an extra degree of freedom for tuning thermoelectric properties. Changes in the wall thickness are expected to strongly alter the electrical and phonon transport properties and thereby enhance the overall thermoelectric properties.[4] Nevertheless, limited research has been performed on the thermoelectric properties of nanotubes, owing to the challenges in synthesis processes as well as device fabrication.

Recently, silver and antimony containing lead chalcogenides, AgPb$_m$SbTe$_{m+2}$ or LAST-m materials (LAST for lead, antimony, silver, and telluride), have shown great ZTs ranging from 1.2-1.7 at 700 K.[5-9] The coherent nanoscale inclusions (Ag-Sb nanodots) discovered in the PbTe matrix, were proposed to correlate with their high ZTs.[8, 10] A strain field around the coherent precipitations created by these nanodots was anticipated to cause a pronounced decrease in the lattice thermal conductivity while maintaining the electrical conductivity.[11] These nanodots are similar to the pyramidal-shaped PbSe nanodots found in molecular beam epitaxy-grown PbSe$_{0.98}$Te$_{0.02}$/PbTe thin films, which also exhibited a high ZT of 2.5 at 500 K.[12-14]
However, the reproducibility of the reported data is a challenge due to the extreme sensitivity of these microstructures and the thermoelectric properties to the processing routes.

Most commonly used methods to synthesize LAST are based on vacuum annealing. In this process, appropriate stoichiometric ratio of the elements are mixed and annealed under the vacuum for several hours. Both the temperatures as well as the ramping rates for heating and cooling steps are important and can significantly affect the material properties. Mechanical alloying followed by spark plasma sintering is widely reported for the synthesis of thermoelectric materials including LAST, which requires a lower temperature compared to the vacuum annealing process.[1, 7] The LAST-18 nanocomposite that possesses the greatest thermoelectric properties in the LAST family was synthesized by this method.[8] To date, a majority of research has been conducted on the LAST bulk materials or nanocomposites, whereas little work has been completed on the low-dimensional LAST nanostructures. Recently, LAST nanocrystals have been synthesized by reverse micellar approach[15] and hydrothermal method [16]. However, materials synthesized from these methods normally suffer from poor dispersion and low electrical conductivity due to the presence of an organic coating on the surface. Nanorods and nanocubes were synthesized by a solvothermal method and then hot-pressed into the bulk LAST-18 to determine their thermoelectric property characterizations.[17] However, this is not a direct measurement of the thermoelectric properties in a low-dimensional LAST, but a composite-like microstructure. Synthesis and the thermoelectric property characterizations of the low-dimensional LAST nanostructures haven’t been reported yet,
owing to the prevailing difficulty and high cost in the material synthesis as well as the device fabrication.

While several techniques exist for creating 1-D heterostructures, electrospinning has emerged as the most versatile, scalable, and cost-effective method to synthesize ultra-long nanofibers with controlled diameters (a few nanometers to several micrometers) and compositions.[18] In addition, different morphologies (e.g., nano-webs, beaded or smooth cylindrical fibers, and nanoribbons) and structures (e.g., core-shell, hollow, branched, helical and porous structures) can be readily obtained by controlling the electrospinning parameters. Although various nanofibers including polymers, carbon, ceramics and metals have been synthesized using direct electrospinning or through post-spinning processes, limited works have been reported on the electrospinning of semiconductor compounds because of incompatibility of precursors.[19-21] Therefore, synthesis of semiconductor compounds (i.e. LAST) by electrospinning was conducted with an addition process, called the galvanic displacement reaction. A galvanic displacement reaction is a spontaneous electrochemical process driven by the difference in redox potentials between the solid substrates and the ions of the source materials, leading to deposition of the more noble material and dissolution of the less noble material.[22] Due to the ease of fabrication, galvanic displacement reaction has become an intriguing method to create various nanostructures including hollow or even multilayer nanoconstructions with controllable morphology and compositions.[22] This approach exploits electrospinning to synthesize ultra-long nanofibers as the sacrificial materials for the galvanic displacement reaction, by which the sacrificial materials can be converted to
ultra-long hollow nanofibers with controlled dimensions, morphologies, and compositions. This approach that combines electrospinning and the galvanic displacement reaction has been demonstrated by our group previously to synthesize ultra-long Te[23] and Bi_xTe_y nanotubes[24].

In this work, the synthesis of LAST hollow nanofibers was first demonstrated by combining electrospinning with galvanic displacement. Co nanofibers with controlled dimensions and morphology were synthesized by electrospinning to provide a large quantity of sacrificial materials for the subsequent galvanic displacement step, which then converted the sacrificial nanofibers to LAST. Nanofibers with tunable compositions were synthesized by simply tailoring the electrolyte concentrations in the displacement reaction. The structure-related thermopower of these nanofiber mats was then characterized using a homebuilt system discussed below.

4.3 Experimental

Electrospinning of Co nanofibers. 3.579 g of citric acid (C_6H_8O_7, anhydrous, enzyme grade, Fisher Chemical) was dissolved in 3.34 g of water followed by the dissolution of 2.511 g of cobalt acetate (C_4H_6CoO_4 \cdot 4H_2O, 98%, Sigma-Aldrich). The aqueous solution was then added into a polymer solution containing 5.2 wt. % of PVP (Polyvinylpyrrolidone, MW= 1,300,000 g/mol) in 6.3 g of anhydrous ethanol (Fisher Scientific, PA) and stirred at 300 RPM for 1 h for a complete dissolution. The obtained clear solution was fed though a metallic needle with an inner diameter of 0.25 mm by a peristaltic pump at a constant feed-rate of 0.5 ml/h. 8 kV was applied to the system by a
high voltage power supply connected to the needle tip. The nanofibers were electrospun to a 3 cm by 3 cm Si/SiO₂ chip, attached to a grounded collector 10 cm away from the needle tip for 15 min. The temperature and relative humidity were 40 ± 2°C and 8 ± 1 %, respectively. The collected nanofiber mats were first aged at 60 °C overnight and then calcined at 500 °C in pure H₂ for 5 h to obtain Co nanofiber mats. The metal nanofiber mat was then cut into a rectangular shape with 1 cm in length and 0.2 cm in width for the consequent galvanic displacement reaction.

**GDR of LAST nanofiber mats.** The galvanic displacement reaction of LAST was carried out by submerging a sacrificial Co nanofiber mat into the electrolyte containing lead nitrate (Pb(NO₃)₂, Fisher Chemical), tellurium oxide (TeO₂, 99+%, Acros Organic), potassium antimony tartaric trihydrate [K₂Sb₂(C₄H₂O₆)₂·3H₂O,Fisher Chemical], silver nitrate (AgNO₃, Certified ACS Plus, Fisher Chemical), and nitric acid (HNO₃, Certified ACS Plus, Fisher Chemical) at room temperature. A 1 cm by 1 cm Si/SiO₂ chip was used as a substrate and placed underneath the nanofiber mat in the solution. In order to minimize the effect of electrolyte concentration change on the mass transfer profile of the ions during the reaction, the amount of sacrificial materials was controlled at 10% of the necessary quantity for a complete consumption of chalcogen ions present in the electrolytes. The compositions of the nanofibers were tuned by varying the Ag⁺ concentration from 0.01 µM to 10 µM in the electrolytes. After 12 h, the nanofiber mats were washed by nanopure water five times and air dried.

**Material characterization.** Morphology, composition, crystal structure and crystallinity of the obtained nanofibers was confirmed using emission-scanning electron
microscopy (SEM, FEG-Philips XL30) with energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD, D8 Advance Diffractometer, Bruker).

**Thermoelectric property characterization.** Four Pt electrodes were sputtered on top of the nanofiber mat perpendicular to its length by using a home-made shadow mask. Both the gap size and electrode width were 1 cm. Seebeck coefficients of the mats were measured by a custom-made system with a temperature range of 300 to 360 K. The system was calibrated by using a standard single crystal Bi$_2$Te$_3$ bulk material before taking measurements of the nanofiber samples.

4.4 Results and Discussion

**Synthesis and material characterizations of LAST hollow nanofibers.** The sacrificial material with a suitable redox potential and a proper dissolution rate are the key parameters for driving the galvanic displacement reaction. Co was chosen as the sacrificial material to form LAST nanofibers due to the more negative cathodic standard reduction potential of Co$^{2+}$/Co pair (-0.28 V vs. standard hydrogen electrode, SHE) than that of the Pb$^{2+}$/Pb (-0.13 V vs. SHE), SbO$^+$/Sb (0.212 V vs. SHE), Ag$^+$/Ag (0.799 vs. SHE), and HTeO$_2^+$/Te (0.551 V vs. SHE) pairs. The electrospun Co nanofibers are shown in **Figure 4.1**, with diameters of 124 ± 13 nm.

The galvanic displacement reaction conditions for the quaternary system LAST was investigated step by step, beginning with displacement of the binary chalcogenide Pb$_x$Te$_y$ followed by the ternary compound Sb$_x$Pb$_y$Te$_z$, then the LAST. Galvanic displacement of Pb$_x$Te$_y$ nanofibers from Co was demonstrated in the previous chapter. Synthesis of the
ternary system $\text{Sb}_x\text{Pb}_y\text{Te}_z$ is thermodynamically possible due to the negative Gibbs formation energy of PbTe and $\text{Sb}_2\text{Te}_3$.\cite{25, 26}

$$\text{Co}^0(s) - 2e^- \rightarrow \text{Co}^{2+}(aq) \quad \text{Equation 4.1}$$

$$\text{HTeO}_2^+(aq) + 4e^- + 3\text{H}^+(aq) \rightarrow \text{Te}^0(s) + 2\text{H}_2\text{O} \quad \text{(aq)} \quad \text{Equation 4.2}$$

$$\text{Pb}^{2+}(aq) + \text{Te}^0(s) + 2e^- \rightarrow \text{PbTe}(s) \quad \text{Equation 4.3}$$

$$2\text{SbO}^+ + 3\text{Te} + 4\text{H}^+ + 6e^- \rightarrow \text{Sb}_2\text{Te}_3 + 2\text{H}_2\text{O} \quad \text{Equation 4.4}$$

$$\text{SbO}^+ + 2\text{H}^+ + 3e^- \rightarrow \text{Sb} + 2\text{H}_2\text{O} \quad \text{Equation 4.5}$$

$$\text{Pb}^{2+}(aq) + \text{HTeO}_2^+(aq) + 3\text{Co}^0(s) + 3\text{H}^+(aq) \rightarrow \text{PbTe}(s) + 3\text{Co}^{2+}(aq) + 2\text{H}_2\text{O} \quad \text{(aq)},$$

$$\Delta G_f^0 = -69.5 \text{ kJ/mol} \quad \text{Equation 4.6}$$

$$2\text{SbO}^+(aq) + 3\text{HTeO}_2^+(aq) + 9\text{Co}^0(s) + 13\text{H}^+(aq) \rightarrow \text{Sb}_2\text{Te}_3(s) + 9\text{Co}^{2+}(aq) + 8\text{H}_2\text{O} \quad \text{(aq)}$$

$$\Delta G_f^0 = -57.5 \text{ kJ/mol} \quad \text{Equation 4.7}$$

Mixing of the Co nanofiber mat and the acidic electrolyte that contains Pb$^{2+}$, SbO$^+$, and HTeO$_2^+$ led to the oxidation of Co to Co$^{2+}$ (Equation 4.1) as well as the deposition of PbTe, Sb$_2$Te$_3$, or Sb$_x$Pb$_y$Te$_z$. The deposition began with the overpotential deposition (OPD) of Te (Equation 4.2), followed by an underpotential deposition (UPD) of Sb or Pb on Te to form Sb$_2$Te$_3$ or PbTe, respectively (Equation 4.3, 4).\cite{26} These UPD reactions occurred spontaneously, due to their negative Gibbs free energies. OPD of the element Sb is also thermodynamically feasible (Equation 4.5).\cite{25} The overall reactions for the deposition of PbTe and Sb$_2$Te$_3$ are shown in Equation 4.6 and 4.7. Because of the relative close Gibbs free energy of PbTe and Sb$_2$Te$_3$, codeposition of Sb$_x$Pb$_y$Te$_z$ is feasible.

Control over the morphologies and compositions of the Sb$_x$Pb$_y$Se$_z$ nanofibers was achieved by varying the concentration of SbO$^+$ in the electrolytes from 0 to 500 µM.
Nanofibers with tubular structures were obtained at low concentrations of SbO\(^+\), below 25 µM, while solid nanofibers were observed with the utilization of electrolytes with a higher SbO\(^+\) content over 25 µM. The diameters of the nanofibers increased with increased concentrations of SbO\(^+\).

The composition of the nanofibers as a function of the concentrations of SbO\(^+\) is shown in Figure 4.2. The Sb content (blue rectangular) increased almost exponentially from 0 to 24 at.% when the concentration of SbO\(^+\) increased from 1.0 to 100 µM and plateaued at 60 at.% thereafter ([SbO\(^+\)] ≥ 1 mM). Significant error bars were observed when the concentrations of SbO\(^+\) were 0.01 mM and 0.25 mM, this could be attributed to the high signal-to-noise level from the low intensity Sb peaks in the EDS spectrum. OPD of the Sb element is anticipated when the concentration of SbO\(^+\) is higher than 0.1 mM, since the Sb content is richer than the stoichiometric content (i.e. 40 at.%). Conversely, the Pb content (red circle) decreased almost exponentially from 43 at.% to 19 at.% when the concentration of SbO\(^+\) increased from 1.0 to 100 µM, then stabilized at around 6 at.% when [SbO\(^+\)] was over 1 mM. With the same sacrificial material, it is expected that the deposition of PbTe and Sb\(_2\)Te\(_3\) compete with each other since they share the same electron sources. A higher SbO\(^+\) concentration in the electrolyte resulted in a more negative overpotential of the deposition of Sb\(_2\)Te\(_3\), which increased the content of Sb\(_2\)Te\(_3\) while diminishing the content of PbTe in the nanofibers. The Te content (green triangle) was fairly constant at around 56 at.% when the concentration of SbO\(^+\) increased from 1.0 to 100 µM, then abruptly dropped to 32 at.% at [SbO\(^+\)] ≥ 1 mM. This may more proof that the OPD of Sb was triggered at [SbO\(^+\)] > 0.1 mM, before which the depositions of
PbTe and Sb$_2$Te$_3$ at [SbO$^+$] $\leq$ 0.1 mM are likely to be UPD processes. **Figure 4.2b** shows the ratio of deposited Sb to Pb content in the nanofibers as a function of the ratio of [SbO$^+$] to [Pb$^{2+}$] in the electrolytes. Among the current reported data, LAST-18 [(AgSbTe$_2$)(PbTe)$_{18}$ or Ag$_{2.5}$Pb$_{45}$Sb$_{2.5}$Te$_{50}$] with the ratio of Sb to Pb of 0.056 showed the best thermoelectric performance. Therefore, the concentration of SbO$^+$ was chosen to be 25 µM in the following displacement of the quaternary chalcogenides, in order to synthesize the “stoichiometric” LAST material.

The galvanic displacement reactions of LAST were conducted in the electrolytes containing various concentrations of AgNO$_3$ (i.e. 0.01, 0.1, 1, and 10 µM) and fixed concentrations of Pb(NO$_3$)$_2$, K$_2$Sb$_2$(C$_4$H$_8$O$_6$)$_2$, and HNO$_3$ at 50 mM, 12.5 µM, and 1.0 M, respectively. As shown in the **Figure 4.3**, nanofibers with smooth surfaces were obtained in all the concentrations of Ag$^+$ ranging from 0.01 to 10 µM. The composition change as a function of the concentration of Ag$^+$ is shown in **Figure 4.4**. No Ag was observed in the nanofibers at the lowest concentration of Ag$^+$. When the concentration of Ag$^+$ increased from 0.01 to 10 µM, the Ag content (orange diamond) increased gradually from 0 to 28 at.%, while the Pb content (red circle) decreased from 45 at.% to 24 at.%. The Sb content (blue rectangular) slightly decreased in the same range of [Ag$^+$]. The Te content (green triangle) was fairly constant at around 50 at.%, except for a slight dip at 10 µM Ag$^+$. Because the Ag$^+/Ag$ pair has a more positive redox potential than the SbO$^+/Sb$ and Pb$^{2+}/Pb$ pairs, deposition of Ag is preferred than the latter two. Increasing the concentration of Ag$^+$ will dramatically increase the Ag content but at the cost of losing other elements. In addition, significant competition between the Ag and Pb deposition
rather than between the Ag and Sb deposition is observed, indicating that deposition of Sb is thermodynamically preferred than that of Pb. LAST-18 can be obtained within the electrolyte containing 0.1 µM AgNO$_3$, 50 mM Pb(NO$_3$)$_2$, 12.5 µM K$_2$Sb$_2$(C$_4$H$_2$O$_6$)$_2$, and 1.0 M HNO$_3$.

XRD patterns of the ternary and quaternary nanofibers suggest that as-prepared nanofibers were polycrystalline PbTe compounds with characteristic cubic NaCl structures (Figure 4.8 a, b, c). The average grain size of the nanofibers was 60.0 nm. No impurity peaks indicative of AgSbTe$_2$, Ag$_2$Te, Sb$_2$Te$_3$, element Ag, Sb, or Te were observed.

**Thermoelectric property of nanofiber mats.** Temperature-dependent I-V characterizations of Pb$_{45}$Te$_{55}$ and Sb$_3$Pb$_{45}$Te$_{50}$ nanofibers were conducted in a temperature range of 300 K to 360 K (Figure 4.6a and b). Linear I-V curves are observed for both samples in all the temperature range. The temperature-dependent sheet resistance of these two samples are showed in Figure 4.6c, with the plot of ln(sheet resistance) as a function of 1000/T inserted. Both of them show typical semiconductor behaviors since the sheet resistance decreased linearly as the temperature increased, suggesting the presence of an activation barrier at the grain boundaries. The thermal activation energy $E_a$ was calculated using Arrhenius equation [27], which can be expressed as follows:

$$ R = R_0 \exp \left( - \frac{E_a}{kT} \right) $$  \hspace{1cm} Equation 4.8

where R is the resistance at a given temperature, $R_0$ is the resistance at $T \rightarrow \infty$, $E_a$ is the thermal activation energy, k is Boltzmann’s constant and T is temperature. The activation energy of Pb$_{45}$Te$_{55}$ and Sb$_3$Pb$_{45}$Te$_{50}$ were calculated to be 213 meV and 198 meV,
respectively. The band gap energy \( E_g = 2E_a (\text{@ } 300 \text{ K}) \) are determined as 0.426 eV and 0.396 eV, respectively, higher than the literature data of 0.31 eV.

The Seebeck coefficients of the nanofiber mats with various compositions were measured in a homemade system in vacuum in a temperature range of 300 K to 360 K. A temperature difference of \(-1 \sim 6\,\text{K}\) was maintained across the length of the samples and the as-generated open circuit voltage was recorded. The linear relationship between the voltage and the applied temperature gradient was observed over the entire temperature range, resulting in the Seebeck coefficient by fitting the slope. Figure 4.7a and b show \( \Delta V \text{ vs. } \Delta T \) characterizations of the \( \text{Pb}_{45}\text{Te}_{55} \) and \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \) nanofibers, with positive slopes in the sample \( \text{Pb}_{45}\text{Te}_{55} \) and negative slopes in the sample \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \). The temperature-dependent Seebeck coefficients of \( \text{Pb}_{45}\text{Te}_{55} \) and \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \) nanofibers are showed in Figure 4.7c. The Seebeck coefficients were positive in the \( \text{Pb}_{45}\text{Te}_{55} \) nanofibers, indicating that this sample was p-type with holes responsible for the charge transport. This is consistent with the p-type nature of a self-doped Te-rich PbTe sample. Negative Seebeck coefficients were obtained in the sample \( \text{Sb}_5\text{Pb}_{45}\text{Te}_{50} \), signifying that the major carriers in this Sb-doped PbTe were electrons. It is known that substitution of \( \text{Pb}^{2+} \) by \( \text{Sb}^{3+} \) in PbTe matrix can produce an electron, resulting in n-type doping.[28] Therefore, the nanofibers that contain trace amounts of Sb should show an n-type semiconducting behavior, which consistent with the previous report.

Figure 4.8a and b show two \( \Delta V \text{ vs. } \Delta T \) characterizations of the LAST nanofibers, with negative slopes in the sample \( \text{Ag}_7\text{Pb}_{43}\text{Sb}_5\text{Te}_{51} \) and positive slopes in the sample \( \text{Ag}_{24}\text{Pb}_{27}\text{Sb}_5\text{Te}_{41} \). The temperature-dependent Seebeck coefficients of these two samples
Figure 4.8c. The $\text{Ag}_{24}\text{Pb}_{27}\text{Sb}_{3}\text{Te}_{41}$ nanofiber mat was p-type and behaved as a degraded semiconductor with the Seebeck coefficient increasing gradually with temperature and maximizing at the onset temperature (i.e. 52 °C).[5] The highest Seebeck coefficient of 148 $\mu$V/K was achieved at this temperature, above which it dropped thereafter. In the n-type $\text{Ag}_{1}\text{Pb}_{43}\text{Sb}_{5}\text{Te}_{51}$ nanofibers, the Seebeck coefficient dropped with increasing temperature, which is more likely a behavior belonging to an intrinsic semiconductor with relatively low carrier concentrations.

The Chemical composition, carrier type, and Seebeck coefficient of LAST nanofibers were summarized in Table 4.1. Addition of Ag and/or Sb significantly altered the electron transport properties of PbTe and thus the thermoelectric properties. The Seebeck coefficients of LAST nanofiber mats as a function of Ag content are shown in Figure 4.9a. N-type semiconductor behavior was observed in the LAST with a small amount of Ag addition (less than 10 at.%) while p-type behavior was found in the nanofiber with a high Ag content (over 10 at.%). It is known that substitution of Pb$^{2+}$ by Ag$^+$ in a PbTe matrix will lead to a formation of a hole.[28] Therefore, Ag doped PbTe is a p-type semiconductor with holes carrying charge. In addition, excess Ag in the PbTe will precipitate into $\text{Ag}_5\text{Te}_3$ or $\text{Ag}_2\text{Te}$, both of which are p-type semiconductors.[28] Thus, both p-type element of matrix (Ag doping) and the second phase ($\text{Ag}_5\text{Te}_3$ or $\text{Ag}_2\text{Te}$) should result in p-type transport for the Ag-PbTe. However, in the nanofibers with deficient Ag, n-type characteristics were observed. This may be attributed to the existence of Sb in the PbTe matrix additional to Ag. As mentioned before, Sb-doped
PbTe is an n-type semiconductor due to the generation of electrons induced by the Sb$^{3+}$. The effect of Sb doping may overshadow the p-type characteristics of Ag-doping and the second phase (Ag$_5$Te$_3$ or Ag$_2$Te), especially in the samples containing small amount of Ag but sufficient Sb (i.e. Ag$_0$Pb$_{45}$Sb$_5$Te$_{50}$, Ag$_1$Pb$_{43}$Sb$_5$Te$_{50}$, and Ag$_8$Pb$_{40}$Sb$_6$Te$_{46}$).

The Seebeck coefficients of LAST nanofiber mats as a function of Sb content are shown in Figure 4.9b. The nanofibers converted from n- to p-type when the Sb reached 6 at. %. The p-type characteristics of the fibers may attribute to the formation of p-type Sb$_2$Te$_3$, which is induced by the excess Sb in the PbTe. This indicates that the carrier type of Sb-doped PbTe is dependent on the amount of Sb in the compound, proving to be n-type with deficient Sb and p-type with excess Sb. The Seebeck coefficients of LAST nanofiber mats as a function of Pb content are shown in Figure 4.9c. Nanofibers with a high Pb content (> 40 at.%) were n-type semiconductors while the ones with a low Pb content (< 34 at.%) were p-type. It was elucidated that the p-type characteristics can be a result of Ag-doping as well as the formation of silver or antimony chalcogenides. In addition, the p-type transport properties may also be a result of substituting Pb with Te, generating a hole. P-n transition in LAST has also been observed by Wang et al., suggesting that the Seebeck coefficient can be tuned from positive to negative depending on the amount of Pb present in the alloy. [7]

An interaction between Ag and Sb is anticipated in the LAST nanofibers. This is because Ag$^+$ and Sb$^{3+}$ ions are inclined to form Ag$^+$-Sb$^{3+}$ pairs to keep local charge balance for electroneutrality reasons as well as the formation of a strain field around the pairs [8]. The formation of the AgSb nanoprecipitate has been clearly observed in several
experiments for LAST-18 and known for reducing the thermal conductivity.[6] In addition, the presence of these nanodots has been reported to significantly alter the electronic states near the band extrema that determine the transport properties. Alloying of Ag into the Sb-PbTe system pushes the Sb-induced bands to higher levels relative to the Fermi level, modifying the band gap characteristics.[29, 30] However, the effect of the nanodots on the Seebeck coefficient is still not clear due to the lack of experimental data.

4.5 Conclusions

Ultra-long LAST nanofibers were synthesized by combining electrospinning and the galvanic displacement reaction. Control over the composition of the nanofiber was achieved by adjusting the SbO$^+$ and Ag$^+$ concentration in the electrolytes. The effect of the electrolyte concentrations on the composition of the ternary system Sb$_x$Pb$_y$Te$_z$ was studied by varying the concentration of SbO$^+$ from 0 to 0.5 mM, whereas the concentrations of HTeO$_2^+$, Pb$^{2+}$ and HNO$_3$ were fixed at 0.1 mM, 50 mM and 100 mM, respectively. The Sb content increased exponentially with the concentration of SbO$^+$, while the Pb content decreased accordingly. Control over the composition of the LAST nanofibers was realized by tuning the Ag$^+$ concentration from 0.01 to 10 µM and maintaining fixed concentrations of 0.025 mM SbO$^+$, 50 mM Pb$^{2+}$, 0.1 mM HTeO$_2^+$, and 100 mM HNO$_3$. Smooth nanofibers were obtained in the entire range of Ag$^+$ concentrations. The Ag content in the nanofibers increased gradually with [Ag$^+$] while the Pb content decreased from 45 at.% to 24 at.% accordingly. LAST-18 was obtained
within the electrolyte containing 0.1 µM AgNO₃, 50 mM Pb(NO₃)₂, 12.5 µM K₂Sb₂(C₄H₂O₆)₂, 0.1 mM TeO₂, and 1.0 M HNO₃. The crystal structure of the LAST nanofibers with various compositions was confirmed by XRD, showing a polycrystalline PbTe with an average grain size of 60 nm.

The Seebeck coefficients of the LAST nanofibers with various compositions were characterized. Nanofibers with a low Ag content possessed n-type transport properties, while the ones with a high Ag content expressed p-type semiconductor behaviors. The n-type characteristics can be attributed to the n-type nature of the Sb-doped PbTe, while silver and antimony chalcogenides may contribute to the p-type transport behavior. In addition, an interaction between Ag and Sb doping is anticipated in the LAST nanofiber, which can significantly alter their thermoelectric performance.
4.6 References


Figure 4.1  SEM images of SbₓPbᵧTeₜ hollow nanofibers. The electrolytes consist of fixed concentrations of HTeO₂⁺, Pb(NO₃)₂ and HNO₃ at 0.1 mM, 50 mM and 0.1 M, respectively, while containing various concentrations of K₂Sb₂(C₄H₂O₆)₂. The concentration of K₂Sb₂(C₄H₂O₆)₂ is (a) 0, (b) 0.50 µM, (c) 5.0 µM, (d) 12.5 µM, (e) 25 µM, (f) 50 µM, (g) 250 µM, (h) 500 µM. The galvanic displacement reactions were conducted for 12 h at room temperature. The scale bars are 500 nm.
Figure 4.2  (a) The Pb (red circle), Sb (blue square) and Te (green triangle) content of as-deposited Sb$_x$Pb$_y$Te$_z$ hollow nanofibers as a function of the concentration of SbO$^+$.
(b) The ratio of the Sb to Pb content in the Sb$_x$Pb$_y$Te$_z$ hollow nanofibers as a function of the ratio of [SbO$^+$] to [Pb$^{2+}$] in the electrolytes. The concentration of Pb(NO$_3$)$_2$ and HNO$_3$ were fixed at 50 mM and 0.1 M, respectively. The galvanic displacement reaction was conducted for 12 hours at room temperature. The dashed lines are guides to the eyes.
Figure 4.3 SEM images of $\text{Ag}_m\text{Pb}_x\text{Sb}_y\text{Te}_z$ nanofibers synthesized in the electrolytes containing various concentrations of AgNO$_3$ (i.e. (a) 0.01 µM, (b) 0.1 µM, (c) 1 µM, and (d) 10 µM). The concentrations of Pb(NO$_3$)$_2$, K$_2$Sb$_2$(C$_4$H$_2$O$_6$)$_2$, and HNO$_3$ were fixed at 50 mM, 12.5 µM, and 0.1 M, respectively. The galvanic displacement reactions were conducted for 12 h at room temperature. The scale bars are 1 µm.
Figure 4. 4 (a) The Ag (orange diamond), Pb (red circle), Sb (blue square) and Te (green triangle) content of as-deposited Ag$_m$Pb$_x$Sb$_y$Te$_z$ nanofibers as a function of the concentration of Ag$^+$. The dashed lines are guides to the eyes.
Figure 4.5 XRD patterns of (a) Ag$_8$Pb$_{40}$Sb$_6$Te$_{46}$, (b) Ag$_{15}$Pb$_{33}$Sb$_3$Te$_{49}$, and (c) Ag$_{31}$Pb$_{21}$Sb$_4$Te$_{44}$ nanofiber mats. PbTe peaks are labeled with red circles and the peaks belong to the substrate are labeled with blue triangles.
Figure 4.6 Temperature dependent I-V characterizations of (a) Pb$_{45}$Te$_{55}$, (b) Sb$_3$Pb$_{45}$Te$_{50}$ nanofiber mats. Temperature dependent of (c) Temperature dependent sheet resistance of Pb$_{45}$Te$_{55}$ and Sb$_3$Pb$_{45}$Te$_{50}$ nanofiber mats. Plot of ln(sheet resistance) vs. 1000/T is inserted.
Figure 4.7  Temperature dependent $\Delta V$ vs. $\Delta T$ characterizations of (a) Pb$_{45}$Te$_{55}$, (b) Sb$_3$Pb$_{45}$Te$_{50}$ nanofiber mats. (c) Temperature dependent Seebeck coefficient of Pb$_{45}$Te$_{55}$ and Sb$_3$Pb$_{45}$Te$_{50}$ nanofiber mats. The dashed line indicates that the Seebeck coefficient is zero.
Figure 4.8  Temperature dependent $\Delta V$ vs. $\Delta T$ characterizations of (a) n-type Ag$_4$Pb$_{43}$Sb$_5$Te$_{51}$ (b) p-type Ag$_{11}$Pb$_{26}$Sb$_{11}$Te$_{51}$ nanofiber mats. (b) Temperature dependent Seebeck coefficient of Ag$_4$Pb$_{43}$Sb$_5$Te$_{51}$ (red circle) and Ag$_{11}$Pb$_{26}$Sb$_{11}$Te$_{51}$ (black circle) nanofiber mats. The dashed line indicates that the Seebeck coefficient is zero.
Figure 4.9  Seebeck coefficient of $\text{Ag}_m\text{Pb}_x\text{Sb}_y\text{Te}_z$ nanofiber mats as functions of (a) Ag content, (b) Sb content, and (c) Pb content. The dashed lines indicate that the Seebeck coefficient is zero.
Table 4.1  Chemical composition, carrier type, and Seebeck coefficient of LAST nanofibers.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Ag (at. %)</th>
<th>Sb (at. %)</th>
<th>Pb (at. %)</th>
<th>Te (at. %)</th>
<th>Carrier type</th>
<th>Seebeck coefficient (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5</td>
<td>45</td>
<td>50</td>
<td>n</td>
<td>-67.6</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>5</td>
<td>43</td>
<td>51</td>
<td>n</td>
<td>-165.0</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>6</td>
<td>40</td>
<td>46</td>
<td>n</td>
<td>-39.8</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>11</td>
<td>26</td>
<td>49</td>
<td>p</td>
<td>110.2</td>
</tr>
</tbody>
</table>
CHAPTER 5
A HYDROGEN GAS SENSOR BASED ON
PALLADIUM/SINGLE-WALLED CARBON NANOTUBE
BACK-TO-BACK SCHOTTKY CONTACT

5.1 Abstract

A Schottky contact-based hydrogen (H\textsubscript{2}) gas sensor operable at room temperature was constructed by assembling single-walled carbon nanotubes (SWNTs) on a substrate bridged by Pd microelectrodes in a chemiresistive/chemical field effect transistor (chemFET) configuration. The Schottky barrier (SB) is formed by exposing the Pd-SWNT interfacial contacts to H\textsubscript{2} gas, the analyte it was designed to detect. Since a Schottky barrier height (SBH) acts as an exponential bottleneck to current flow, the electrical response of the sensor can be particularly sensitive to small changes in SBH, yielding an enhanced response to H\textsubscript{2} gas. The sensing mechanism was analyzed by \textit{I-V} and FET properties before and during H\textsubscript{2} exposure. \textit{I-V\textsubscript{sd}} characteristics clearly displayed an equivalent back-to-back Schottky diode configuration and demonstrated the formation of a SB during H\textsubscript{2} exposure. The \textit{I-V\textsubscript{g}} characteristics revealed a decrease in the carrier mobility without a change in carrier concentration; thus, it corroborates that modulation of a SB via H\textsubscript{2} adsorption at the Pd-SWNT interface is the main sensing mechanism.
5.2 Introduction

Hydrogen (H$_2$) is a potentially emission-free alternative fuel that is considered to be an ideal energy carrier in the foreseeable future. Rapid and accurate H$_2$ sensors with a low detection limit have been of significant interest and in high demand for safety concerns due to hydrogen’s low spark ignition energy (0.017 mJ) and wide flammable range (4~75%)[1]. Several types of H$_2$ sensors[2] have been developed based on metal oxides such as In$_2$O$_3$[3], SnO$_2$[4], ZnO[5], NiO[6] and TiO$_2$[7]. However, each selective gas response requires a well-controlled specific high temperature (a few hundred °C) to achieve optimal sensitivity. While elevating the temperature of the sensor accelerates the transport of gases thus improving both response and recovery times, it can also increase power consumption and device complexity.

Palladium (Pd) has been found to be an excellent sensing material for H$_2$ due to its catalytic properties and high solubility towards H$_2$ under ambient conditions. It has been reported that the reversible formation of palladium hydride (PdH$_x$) is the determining factor for Pd-based sensors, where any number of effects could be exploited, including modulating its lattice constant[8], conductivity[9], work function[10], or optical properties[11]. Pd sensors that take advantage of H$_2$-induced modulation in resistance show good sensitivity, but suffer from delayed response and recovery times due to slow gas transport processes. Pd nanocluster-based H$_2$ sensors exploiting a H$_2$-induced lattice expansion show improved sensor response times but albeit at the expense of low sensitivity.[8]
Schottky contact-based H₂ sensors focus on the contact area between the Pd electrode and the semiconductor, where the modulation of contact barrier height is the key factor in determining the performance of a sensor. A metal-semiconductor interface can possess rectifying or non-rectifying energy levels, namely, Schottky or ohmic contacts, respectively. In an ohmic contact, resistance is inversely proportional to the cross sectional area perpendicular to the current and the charge carriers can flow in either direction without rectification under an applied potential. In an ohmic contact-based sensor the interface resistivity is made as low and as stable as possible to place emphasis on the signal contribution coming from the semiconductor itself. For a rectifying SB contact-based sensor, the opposite effects are required. Since a SBH acts as an exponential limit to current flow in accordance with the law of thermionic emission[12], the aim of making the modulation of SBH, the key factor in performance, can be achieved by making the SBH a dynamic, sensitive and reversible function of the target analyte concentration. An exponential dependence on a key factor naturally overrides a linear dependency, yielding an enhanced sensitivity sensor. This corroborates the fact that Schottky contact-base sensors have been found to show higher sensitivities to analyte gases than ohmic contact-based sensors. In accordance with the Schottky-Mott model, there is a linear dependence between the SBH and the metal work function. Thus, modulation in the metal work function leads to a direct modulation in the SBH in the metal-semiconductor junction, causing an exponential change in the conductance of the sensor.
Over the past few decades, Schottky contact-based H₂ sensors have been fabricated by the utilization of Pd with various semiconductors, such as Si[13], TiO₂[14], and SnO₂[15]. Although a vast improvement in sensitivity and low detection limits have been achieved within these configurations, the SBH on most semiconductors are found to have a much weaker dependence on the metal work function than the Schottky-Mott model suggests. This phenomenon, known as Fermi level pinning, where interface states tend to pin the center of the band gap to the Fermi level, along with undesired compound formation[13], reduces the expected SBH and thus diminishing the sensor performance.

Carbon nanotubes (CNTs) have been of significant interest owing to their unique electrical, physical, mechanical and chemical properties, leading to a wide array of applications, including supercapacitors, electrodes, field emission devices, as well as sensors and other nanoelectronic devices.[16] By taking advantage of its quasi-one dimensional (1-D) transport properties, CNTs have been widely used as chemiresistive/chemical field effect transistors (ChemFETs) gas sensors, offering the potential to outperform the established two dimensional (2-D) thick- and thin-film sensors.[10] In particular, weak Fermi level pinning is anticipated in a metal-CNT contact because the pinning charge has to compete with the large charge density at the van Hove singularities in the density of states of CNTs.[17] In other words, the SBH should be completely controlled by the metal work function in a metal-CNT contact (i.e. display Schottky-Mott model behavior). This is in strong contrast to most bulk metal-semiconductor junctions where Fermi level pinning often dominates the SBH.[17]
In this work, we study the effects of p-type SWNTs in contact with Pd electrodes and show that the development of SBs at the contacts under H\textsubscript{2} exposure enhances their sensing performances. The sensing mechanism was confirmed by \textit{I-V} and FET properties characterization before and during H\textsubscript{2} exposure. Even though the modulation of the SBH by H\textsubscript{2} has already been reported for a Pd-CNT contact\cite{10}, a H\textsubscript{2} sensor based on this configuration with high sensitivity and fast response/recovery time has not been demonstrated. The Pd-SWNTs sensor showed an enhanced sensing performance when contrasted with other aligned SWNTs made with Pt, Cr and Au microelectrodes.

5.3 Experimental

Detailed information on these sensor configurations has been described in our recently published paper\cite{18}. Briefly, various metal microelectrodes including Pd, Pt, Cr, and Au patterned on oxidized Si substrates (with SiO\textsubscript{2} thickness of 300 nm) were fabricated via lift-off photolithography process. Prior to use, pre-fabricated microelectrode chips were sonicated in nanopure water, followed by an acetone rinse to remove residues. The CNT suspension was prepared by adding 0.2 mg commercially available carboxylated SWNTs (Carbon Solution, Inc. Riverside, CA) in 20 mL of N,N-dimethylformamide (DMF, Sigma Aldrich, MO) and sonicking the mixture solution for 90 minutes until a well-dispersed solution was obtained. The supernatant of the suspended SWNTs solution was collected after centrifuging at 15,000 RPM for 90 minutes.
To accurately align SWNTs across a pre-fabricated microelectrode, a customized Teflon cell was employed to hold the microelectrode chip and confine the suspended SWNTs solution for the AC dielectrophoretic alignment. The electrical connection between the external electronic equipment and the microelectrode chip was obtained by clipping the chip with two 32 pin SOIC test clips purchased from Pomona Electronics. Afterward, 200 µL of the supernatant was placed into the Teflon cell with the chip held for SWNT alignment. To obtain optimized SWNT alignment, a 2 peak to peak voltage ($V_{pp}$) at 4 MHz frequency was applied to the electrodes for an average of 10 seconds. A Labview program was designed to command the Keithley 3390 AC generator (aligner) and custom-made DAQ switcher for sequential SWNT alignment. The synthesized sensors were rinsed with nanopure water, and dried with ultra-pure N$_2$ gas, and then annealed at 300 °C for 2 hours in forming gas.

Back-gated FET properties ($I-V_g$ characteristics) were measured by sweeping the gate voltage from -20 V to 20 V with a fixed source-drain voltage of 1 V during exposures of ambient air and 2,000 ppm$_v$ H$_2$ gas in dry air, respectively. Furthermore, the sensing performance was investigated by assembling the sensing chip in a sealed Teflon sensing cell with gas inlet and outlet ports for gas flow and then clipping the chip to a Keithley 236 source measurement to obtain the electrical connection. An applied potential of 1 V was given to each sensor and the resistance was continuously monitored every 0.2 seconds for the fifteen sensors by a custom-made LabView program. H$_2$ gas was first diluted in dry air to various concentrations, and then introduced into the Teflon cell at a total gas flow of 200 sccm for gas sensing measurements.
5.4 Results and Discussion

The sensing performance to H₂ adsorption on the aligned SWNTs bridged across the Pd microelectrodes configured as chemiresistors was investigated at room temperature. These sensors were sequentially tested with varied concentrations of H₂ gas ranging from 50 to 2,000 ppm, with H₂ exposure duration of 15 minutes and period with dried air of 20 minutes, respectively. The transient response was plotted as the normalized change in electrical resistance \[ \frac{\Delta R}{R_0} \times 100 = \frac{R_f - R_0}{R_0} \times 100 \] % of sensors as shown in Figure 5.1a, where \( R_f \) is the peak resistance and \( R_0 \) is the initial baseline resistance prior to analyte exposure. The \( \Delta R/R_0 \) increased to a steady-state during H₂ exposure and returned to its initial baseline when switching H₂ back to dried air. Figure 5.1b presents the plot of \( \Delta R/R_0 \) as a function of H₂ concentration showing a logarithmic function relationship. The inset in Figure 5.1b depicts the plot of \( \Delta R/R_0 \) as a function of H₂ concentration on a semi-log scale, yielding a rather straight line given by \( \Delta R/R_0 (\%) = 3.440 \times \ln ([H_2]) - 8.584 \) with a correlation coefficient \( R^2 = 0.9987 \). This relationship projects \( \Delta R/R_0 (\%) \approx 2.5\% \) at 25 ppm, exposure.

Additionally, the response and recovery times are important key factors when evaluating the overall sensing performance. In general, the response time \( \tau_{90} \) and the recovery time \( \tau_{90} \) are calculated, which are defined as the time for the sensor to reach 90% of its steady-state value and the time required for the sensor to return to 10% of its maximum response. However, the recovery time \( \tau_{50} \) which indicates the time needed for the sensor response to restore 50% of its maximum response is chosen for sensor performance evaluation owing to slow recovery rates against rapid cycling of H₂.
concentration. Figure 5.1c and d illustrated the sensor response time \( \tau_{90} \) and recovery time \( \tau_{50} \) at room temperature as a function of \( \text{H}_2 \) concentration. The average response time for the Pd-SWNTs sensor was determined to be 10 minutes at \( \text{H}_2 \) concentration of 50 ppm\(_v\). The response time decreased rapidly to 1.13 minutes at \( \text{H}_2 \) concentration of 2,000 ppm\(_v\). A trend line of average response time \( \tau_{90} \) as a logarithmic function of \( \text{H}_2 \) concentration for the Pd-sensor gives \( \tau_{90} = -2.43 \times \ln ([\text{H}_2]) + 19.47 \) with a \( R^2 = 0.9989 \). Extrapolating to 25 ppm\(_v\) of \( \text{H}_2 \) gas gives an average response time \( \tau_{90} = 11.8 \) minutes. The average recovery time \( \tau_{50} \) was also reduced from 12.28 minutes at 50 ppm\(_v\) to 0.37 minutes at 2,000 ppm\(_v\) of \( \text{H}_2 \). Complete recovery was observed after the final \( \text{H}_2 \) exposure with recovery time \( \tau_{100} \) of 30 minutes at 2,000 ppm\(_v\).

The sensing performance (\( \Delta R/R_0 \times 100 \)% of Pd-SWNTs aligned sensor to \( \text{H}_2 \) gas exposure is contrasted with other aligned SWNTs made with Pt, Cr and Au microelectrodes in Figure 5.2a to c, respectively. The response of the Pt-SWNTs aligned sensor shown in Figure 5.2a is mainly attributed to the catalytic properties of Pt towards \( \text{H}_2 \) adsorption. The adsorbed hydrogen atoms exothermically react with oxygen molecules or weakly adsorbed oxygen atoms on the Pt surface, leading to hydroxyl radicals and/or water formation. The local heating from this catalytic reaction is considered to be a major contributor to the sensing response. However, this exothermic reaction was not activated until \( \text{H}_2 \) concentration exceeded 250 ppm\(_v\), and a very pronounced response (\( i.e., \Delta R/R_0 = 8.98\% \)) was obtained at 2,000 ppm\(_v\) of \( \text{H}_2 \) gas. The drawback to the Pt-SWNT aligned sensor is its slow response and recovery time due to the slow gas adsorption processes at room temperature. Even though the Cr-SWNT
aligned sensor gave about the same response ($\Delta R/R_o \approx 2.5\%$) at 250 ppm$_v$ of H$_2$ gas as the Pt-SWNT aligned sensor, the Cr-sensor’s signal was more distinct (less noisy). The Cr-sensor also gave a larger response than the Pt-sensor at 2000 ppm$_v$ of H$_2$ gas, with $\Delta R/R_o = 14.54\%$ vs 9%, respectively. The sensor response of this device is expected to be controlled by the trade-off between the resistance decrease induced by the reduction of the native oxide layer and the resistance increase from the CrH$_x$ formation. Once the sensor is exposed under H$_2$ gas, reduction of the native oxide layer on the surface of the Cr-electrode will release the oxygen bonded electrons, increasing the electron concentration and decreasing the resistance. On the other hand, H$_2$ is anticipated to cause an increase in the Fermi energy of Cr therefore decreasing its work function.[19] This leads to an augment in the SBH at the Cr-SWNT interface, resulting in the resistance to increase. In our work, Schottky becoming “Schottkier” is considered to be the key factor to generate a distinct positive sensor response, since the native oxide layer on the surface of Cr-electrode are normally too thin to produce any well-defined negative response. Note, however, that the Cr-sensor exhibited no recovery after exposed to 250 ppm$_v$ of H$_2$ gas and showed two distinguishable recovery rates in the higher H$_2$ concentration region. The plateaued $\Delta R/R_0$ region indicates that an irreversible process happened on the surface of the Cr-electrode such as a hydrogenation. Due to the much lower solubility of hydrogen in Cr than Pd, poorer performance was observed in Cr-SWNT aligned device than Pd-SWNT. The Au-SWNT aligned sensor showed an insignificant response at all tested H$_2$ concentrations.
**Figure 5.2d** shows the \((\Delta R/R_0 \times 100)\)% response calibration curve of the four (Pd, Pt, Cr, Au)-SWNT aligned chemiresistive H\(_2\) sensors, and the corresponding response/recovery times plotted as histograms referenced at 2000 ppm\(_v\) of H\(_2\) gas are shown in **Figure 5.3**. The response time of the Pd-sensor was 8 times faster than the Pt-sensor and about 11 times faster than the Cr-sensor, while the recovery time of the Pd-sensor was 46 times faster than the Pt-sensor and the Cr-sensor never did recover. This substantiated that aligned SWNTs bridged Pd microelectrodes had high affinity towards H\(_2\) gas and outperformed other fabricated sensors in this study.

In order to confirm that the superior sensing performance from the Pd-SWNT was primarily from the SB modulation at the metal-semiconductor interface, electrical characterizations of the sensors were performed. Room temperature \(I-V_{sd}\) characteristics show a linear response for SWNTs in air and a non-linear, S-shaped \(I-V\) curve when the sensor was exposed to 2,000 ppm\(_v\) of H\(_2\) gas (**Figure 5.4a**). An ohmic contact was anticipated at the Pd interface and SWNT due to the larger work function of Pd (5.22 eV[20]) than that of SWNT (5.05 eV[21]). This assumption was corroborated by the experimentally obtained linear \(I-V\) characteristic in air. During H\(_2\) adsorption, atomic hydrogen is believed to dissolve into the Pd. Formation of Pd-H rapidly lowers the electronic work function, \((i.e. \sim 0.4\) eV\) and creates a SB at the interfacial Pd-SWNT contact[22]. **Figure 5.5** shows the schematic diagrams of the sensor device and the band diagrams of Pd-SWNT-Pd contacts, demonstrating an equivalent back-to-back Schottky circuit.
Among those back-to-back Schottky configurations where the thermionic emission rule applies, three models were frequently observed with regard to the number of MS interfaces considered as well as the direction of the current flow. Some papers (Model 1) treated back-to-back Schottky as a Schottky diode where only one forward current is counted to calculate the total current while other papers (Model 2) considered the total current is a sum of two forward biased currents. In this paper[12] (Model 3), the total current is considered to be limited only by the reverse biased junction since this is the true bottleneck of the current. The reverse current can be explained by the following equations:

\[ I_r = I_s = A A^* T^2 \exp\left(\frac{-q \phi_b}{kT}\right) \quad \text{Equation 5.1} \]

with

\[ \phi_b = \phi_0 - \sqrt{\frac{qE}{4 \pi \varepsilon \varepsilon_0}} \quad \text{Equation 5.2} \]

and

\[ E = \sqrt{\frac{2 qN_D}{\varepsilon \varepsilon_0} (V_0 + V_{bi} - \frac{kT}{q})} \quad \text{Equation 5.3} \]

where \( I_r \) is the total current equal to the saturation current, \( A^* = 4 \pi m^* k^2 / h^3 \) is the effective Richardson constant, \( A \) is the cross section of the effective area perpendicular to the current, \( \phi_b \) is the effective barrier height, \( \phi_0 \) is the ideal barrier height, \( V_0 \) is the bias voltage, and \( V_{bi} = \phi_b - \xi \) is the built-in potential, with \( \xi \) being the energy of the Fermi level of the semiconductor measured from the bottom of the conduction band.
From these equations, the logarithm of the reverse thermionic current must be linear to the 4\textsuperscript{th} root of bias voltage, as shown in the Figure 5.4b. Hence, the reverse thermionic emission current gives a satisfactory explanation of the experimental results. However, the SBH is not able to be extracted from a single $I$-$V$ measurement since neither the effective Richardson’s constant nor the electrically active area of SWNT is known.[17]

FET characterization was carried out to confirm the SB based sensing mechanism in the Pd-SWNT system. Typical FET $I_{ds}$-$V_g$ curves in ambient air and H\textsubscript{2} gas are shown in Figure 5.6. Notably, a decrease in source-drain current after exposure to H\textsubscript{2} gas was observed irrespective of the gate voltages. This is consistent with the anticipated decrease in p-channel conductance due to the SB formation at Pd-SWNTs interface upon exposure to H\textsubscript{2}. If the charge transfer and chemical doping of the transducer is modulated by the gas molecules, an ion gating effect is anticipated as a sensing mechanism, resulting in a change in device carrier concentration with no change in its mobility.[23] In contrast, if an electrostatic gating effect becomes the dominating sensing mechanism, the charge transfer between a sensitive element and gas analyte or chemical doping caused by gas molecules would alter the sensor’s carrier concentration. Therefore, a redistribution of the charge carriers therefore reflects a shift in $V_{th}$, while transconductance (\textit{i.e.} carrier mobility) remains unchanged.

The carrier mobility was calculated using the following equations[24]:

$$\mu = \frac{L_{SD}W_{SD} \left( \frac{dI}{dV_G} \right)}{C_G V_{SD}}$$  

\textit{Equation 5.4}
with

$$C_G = \frac{\varepsilon \delta (L_{SD})(W_{SD})}{t_{DL}}$$

\textit{Equation 5.5}

where $\mu$ is the carrier mobility (cm$^2$/Vs), $L_{SD}$ is the length of the SWNT or the electrodes’
gap size (3 $\mu$m), $W_{SD}$ is the width of the CNT film (10 $\mu$m), $dI/dV_G$ is the
transconductance (A/V), $C_G$ is the capacitance ($F$), $V_{SD}$ is the applied source-drain voltage
(V), $\varepsilon$ is the permittivity constant ($8.85 \times 10^{-12} F/m$), $\delta$ is the dielectric constant of SiO$_2$
($\delta=3.9$ [25]), and $t_{DL}$ is the thickness of the dielectric layer (300 nm). A mobility change
of 23.2% was calculated. This result is consistent with the sensing data.

\textbf{Table 5.1} compares this work with the literature reported Pd-CNT
(graphene)-based room temperature H$_2$ sensors, including the sensors’ configurations and
sensing performance [i.e. dynamic range, sensitivity, response/recovery time, and lowest
detection limit (LDL)]. These sensors were grouped into two categories, depending on
whether the transducer (i.e. CNT, graphene) was decorated with Pd (Category 2) or
without (Category 1). Category (1) includes sensors that are based on either a single
Schottky diode[26, 27] or a back-to-back Schottky contact[10]. Their gas sensing
response is mainly attributed to the modulation of metal-semiconductor (MS) contacts in
the interface of electrode and transducer. For Category (2), Pd nanoparticles (NPs) or
clusters are functionalized to a single CNT or CNT films. Modulation in the
conductance of the transducer rather than the MS contact was dominated during the gas
detection, due to the local SBH change induced by the Pd on the transducer upon the H$_2$
gas exposure.
Sensors obtained in this work show the best sensitivity among the Pd-CNT based H₂ gas sensors in Category (1); our sensitivity is slightly higher than that of the Pd-single SWNT-based device[10], but 1 or 2 orders higher than that from SWNT films[28] and graphene[27]. In a single SWNT, sensitivity of 0.02 % ppm⁻¹ was achieved upon exposure to 0.5% of H₂ gas, with the presence of -5 V gate voltages. Sensitivity without the gate voltage cannot be quantified here due to the resolution of the figures provided, but should definitely be higher than 0.02 % ppm⁻¹ owing to the diminished tunneling effect. SWNTs used in this study are carboxylated SWNTs, which contain carboxylated defects and stone-wall defects.[29] Higher sensitivity obtained in our work may be due to the presence of defects in the SWNTs at the Pd/SWNT contact region, forming a defect-Pd-H₂ system therefore augment the sensing performance.[30] More detailed explanation will be given in a following paragraph of this paper.

In a SWNT film or network, the presence of a mixture of metallic (m-SWNTs) and semiconducting SWNT (s-SWNT) is expected. Hence, the carriers are more likely to flow though the m-SWNT where no SB is constructed[31], and bypass the barrier within the metal-s-SWNT contact, in accordance with the parallel resistor law. This leads to attenuation in the signal and lower the sensitivity of the sensor. In addition, the interactions of adjacent aligned CNTs may lead to carrier screening effects, hopping or even Schottky junctions as semiconducting and metallic tubes cross each other[32], therefore altering the carrier transport behavior and the sensing performances. A stronger “bypass” effect and interaction are anticipated in a CNT film, rather than the
aligned SWNTs in this work (a mixture of m-SWNTs and s-SWNTs with a ratio of 1:2), which leads to a diminished sensitivity in the film sample.

Compared to the sensors in Category 1, the Pd decorated SWNTs (Category 2) show an improved sensing performance. The highest sensitivity, almost one order higher than that of this work, was obtained in a Pd and DNA co-functionalized SWNT based device.[33] The Pd NPs are not only considered as the catalyst to oxidize the H₂ to H₂O, but also function as nanogate electrodes to scatter the carriers in the SWNTs. Therefore, the electrical resistance of the sensor can be altered significantly and its magnitude increases with the number of Pd NPs.[33] SWNT films that are electrochemically functionalized by Pd NPs also have a high sensitivity towards H₂ gas.[22] This could be attributed to the alteration of the electronic work function of the Pd upon the gas exposure, which leads to the modulation of the local SBs in the interface of Pd NPs and SWNTs, thereby resulting in the sensors’ electrical resistance change.

Presence of defects at the Pd/SWNT interfaces can also enhance the sensitivity. It is known that defects can alter the electronic properties of SWNTs since they can significantly limit the mean free path of the carriers, thereafter creating a potential drop along the SWNTs.[34] When exposed to gases, even though the adsorption of gas molecules (i.e. NH₃) on defective SWNTs are known to be easier than on defect-free SWNTs[35], both of the defective and defect-free SWNTs are reported to show no difference when exposed to H₂ gas[30]. However, Pd coverage on the defect has extraordinary consequences on the improvement of the sensitivity towards H₂ gas, showing a thousand-fold increase in resistance change. The author attributed this
augmentation to a specific interdependence between defect sites’ electronic transmission and the chemistry of the defect-Pd-H$_2$ system.[30] The effect of defects was also observed in the electrochemically functionalized SWNT films, where a superior sensitivity, over those are synthesized by vacuum evaporation and sputtering, was observed.[22]

In addition, existence of SBs within a CNT, except for between the metal contact and the CNT, may increase the sensitivity. When contacted with Pd, the local density of state of the SWNTs exhibits substantial hybridization between the SWNT and metal surfaces.[36] In this case, no potential barrier exists between the SWNTs and the Pd surface. This implies that the SWNTs are no longer acting as semiconductors once they are contacted with Pd. Therefore, any SB present would be between a metallic-like and a semiconducting segment in the same CNT.[37, 38] Those barriers are hosted along the CNT and can be altered upon the gas exposure, thereby modulating the electrical resistance of the sensor assembly.

Even though the sensitivity of SWNTs increases significantly by the Pd decoration, their sensing performances are still poorer than those are based on other semiconductors, such as these Si[13], ZnO[39], and AlGaN[40]. Those sensors are either based on a single Schottky diode[39, 40] or a back-to-back Schottky contact[13]. It is expected that superior sensing performances will be obtained from a CNT-based sensor, since the SBH should be fully controlled by the metal work function in a CNT-metal contact as opposed to most bulk metal-semiconductor junctions. However, in a side-contacted CNT where the depletion region extends perpendicular to the main axis of CNT, there is
only a short available distance on which the band can realign to equilibrate the Fermi levels.[32] Therefore, only partial band realignment is possible, which will introduce pinning to the surface of the CNT, causing the work function control over SBH to fail. In addition, an even stronger pinning effect is expected when a CNT is chemically functionalized with foreign groups. Since the chemical groups (i.e. carboxylic groups in this work) are mainly localized at the edges of the CNT, the interface states in the metal-CNT contact area are anticipated to increase. This will drive the junction’s performance away from the Schottky-Mott limit and result in Fermi level pinning. Therefore, pinning should still be taken into consideration in this work and be regarded as one of the main factors that weaken the control over SBH from the metal’s work function, consequently resulting in reduced sensing response.

Furthermore, electron tunneling may be another factor that alters the sensing performance of CNTs. In 2-D films or 1-D structures with large diameters, doping or a high gate voltage is necessary to narrow the SB width then activate the carrier tunneling. However, doping or a high gate voltage are not essential in CNTs due to its exceptionally small diameter (~1.4 nm) since the SB width can be narrowed by the internal electric field which is focused across the barrier. In other words, the effective SBH that an electron can “see” is lowered in the CNT because the electrons can tunnel though the SB instead of “jump” over the barrier. In our work, the tunneling effect is expected from the $I-V^{0.25}$ plot shown in Figure 5.4b, where the correlation coefficient ($< 1$) shows a deviation of the device’s behavior from the pure thermionic transport. In addition, extra
carriers which are induced by either the intrinsic defects in our CNTs or the chemical functionalization processes will further increase the possibility of tunneling effect[12].

Finally, the crystallographic structure of the metal surface is essential in determining a SBH.[41] Since the Pd electrodes in this work are synthesized by e-beam evaporation, they are polycrystalline with an average grain size of about 15 to 20 nm. In this case, non-uniform Fermi level is likely to position at the Pd/SWNT interface, leading to the construction of non-uniform SBHs. Variations in the modulation of these non-uniform SBHs, which deviate the sensing performances from sample to sample, explain the non-negligible error bars in the Figure 5.1b.

5.5 Conclusions

Chemiresistive H$_2$ gas sensors were fabricated using SWNTs as transducers bridged across various metal (e.g. Pd, Pt, Au and Cr) microelectrodes. The chemiresistive sensor with Pd-SWNTs combination in this study demonstrated a significantly higher sensitivity with notably faster response and recovery times as compared to other Pd-CNT sensors fabricated. $I$-$V$ characteristic of the sensors was fitted with a back-to-back SB configuration, where the reverse thermionic emission current gives a satisfactory explanation of the experimental results. The formation of Pd-H at the Pd-SWNT contacts lowers the work function of Pd, thus modulating the SBH after electronic band rearrangement. The sensors configured as FETs corroborates that modulation of the SBH at the interfacial Pd-SWNT dominates the sensing mechanism toward H$_2$ adsorption with a distinct signature; i.e. a decrease in carrier mobility without a change in carrier concentration.
5.6 References


Figure 5.1  (a) Real-time sensing response, (b) calibration curve, (c) response time, and (d) recovery time of AC aligned SWNTs on Pd microelectrodes towards H$_2$ at different concentration. The sensing performance including sensitivity, response time and recovery time are characterized based on a sample number of 14.
Figure 5.2  (a-c) Real-time sensing response and (d) calibration curves of AC aligned SWNTs on (a) Pt, (b) Cr and (c) Au electrodes towards H$_2$ at different concentration.
Figure 5.3  (a) Response time and (b) recovery time of AC aligned SWNTs on Pd, Pt, and Cr electrodes towards 2,000 ppm, H₂. No recovery time for Cr electrodes is included.
Figure 5.4  (a) Current ($I_{DS}$)-voltage ($V_{DS}$) and (b) $I_{DS}$-$V_{DS}^{1/4}$ characterization of AC aligned SWNTs on Pd electrodes in air (black) and 2,000 ppm$_v$ H$_2$ (red).
Figure 5.5  (a) Schematic representation (b) band diagram and (c) equivalent circuit of SWNT devices in air (1) and H$_2$ (2).
Figure 5.6  Current ($I_{SD}$) - back gated voltage ($V_G$) characterization of AC aligned SWNT on Pd electrodes in air (black triangle) and 2,000 ppm H$_2$ (red square).
Table 5.1  Characteristics of various Pd-CNT (graphene)-based room temperature H₂ sensors

<table>
<thead>
<tr>
<th>Category</th>
<th>Sensor configuration</th>
<th>Transducer</th>
<th>Pd Decoration</th>
<th>Dynamic range (ppm)</th>
<th>Sensitivity (%ppm⁻¹)</th>
<th>τ₉₀ (min)</th>
<th>τ₅₀ (min)</th>
<th>@ H₂ conc. (%)</th>
<th>LDL # (ppm)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S* Pd</td>
<td>Aligned SWNTs</td>
<td>N/A</td>
<td>25-2E3</td>
<td>0.074</td>
<td>1.1</td>
<td>0.37</td>
<td>0.2</td>
<td>25</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>S Pd</td>
<td>Single SWNT</td>
<td>N/A</td>
<td>5E3-5E5</td>
<td>0.020</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2003[10]</td>
</tr>
<tr>
<td></td>
<td>Si Pd</td>
<td>CNT film</td>
<td>N/A</td>
<td>--</td>
<td>1.1E-4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2003[26]</td>
</tr>
<tr>
<td></td>
<td>S Au</td>
<td>Graphene</td>
<td>N/A</td>
<td>50-1E4</td>
<td>6.8E-3</td>
<td>0.94</td>
<td>0.40</td>
<td>0.2</td>
<td>50</td>
<td>2013[27]</td>
</tr>
<tr>
<td>2</td>
<td>S Au/Ti</td>
<td>Single SWNT</td>
<td>NPs</td>
<td>--</td>
<td>0.12</td>
<td>0.1</td>
<td>3.3</td>
<td>0.04</td>
<td>&lt;40</td>
<td>2001[42]</td>
</tr>
<tr>
<td></td>
<td>S Au/Ti</td>
<td>SWNT film</td>
<td>NPs</td>
<td>--</td>
<td>0.060</td>
<td>0.3</td>
<td>3.3</td>
<td>0.04</td>
<td>&lt;40</td>
<td>2001[42]</td>
</tr>
<tr>
<td></td>
<td>S Pd</td>
<td>SWNT film</td>
<td>NPs</td>
<td>10-500</td>
<td>0.29</td>
<td>14</td>
<td>--</td>
<td>0.05</td>
<td>10</td>
<td>2005[28]</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃ Au</td>
<td>SWNT film</td>
<td>NPs</td>
<td>5E3-4E4</td>
<td>2.0E-3</td>
<td>6.0</td>
<td>12.1</td>
<td>0.5</td>
<td>&lt;5000</td>
<td>2005[15]</td>
</tr>
<tr>
<td></td>
<td>Glass Cr</td>
<td>SWNTs</td>
<td>NPs</td>
<td>100-1E4</td>
<td>1.0E-4</td>
<td>5.3</td>
<td>2.9</td>
<td>0.1</td>
<td>&lt;100</td>
<td>2007[43]</td>
</tr>
<tr>
<td>Material</td>
<td>Composition</td>
<td>Support</td>
<td>Clusters / NPs</td>
<td>LDL (ppm)</td>
<td>Response Time (s)</td>
<td>Recovery Time (s)</td>
<td>LDL (ppm)</td>
<td>Response Time (s)</td>
<td>Recovery Time (s)</td>
<td>Year</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>-----------</td>
<td>----------------</td>
<td>-----------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>-----------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>------</td>
</tr>
<tr>
<td>PET</td>
<td>Pd/Ti</td>
<td>SWNTs</td>
<td>CLs*</td>
<td>30 - 1E4</td>
<td>0.10</td>
<td>0.48</td>
<td>0.17</td>
<td>0.1</td>
<td>30</td>
<td>2007</td>
</tr>
<tr>
<td>S</td>
<td>Au/Ti</td>
<td>SWNT film</td>
<td>NPs</td>
<td>100 - 3E3</td>
<td>0.42</td>
<td>11.2</td>
<td>57</td>
<td>0.2</td>
<td>100</td>
<td>2007</td>
</tr>
<tr>
<td>PET</td>
<td>Pd/Ti</td>
<td>SWNTs</td>
<td>CLs</td>
<td>100 - ~1E4</td>
<td>0.26</td>
<td>1.11</td>
<td>--</td>
<td>0.1</td>
<td>100</td>
<td>2008</td>
</tr>
<tr>
<td>S</td>
<td>Pd/Ti</td>
<td>Single SWNT</td>
<td>NPs</td>
<td>--</td>
<td>0.06</td>
<td>0.095</td>
<td>0.62</td>
<td>100</td>
<td>--</td>
<td>2010</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Pt</td>
<td>SWNT film</td>
<td>SiO₂ NPs</td>
<td>1 - 100</td>
<td>0.21</td>
<td>0.17</td>
<td>--</td>
<td>0.01</td>
<td>1</td>
<td>2011</td>
</tr>
<tr>
<td>--</td>
<td>Fl*</td>
<td>MWNT yarns</td>
<td>CLs</td>
<td>20 - 4E4</td>
<td>6.0E-3</td>
<td>2.3</td>
<td>0.68</td>
<td>0.1</td>
<td>20</td>
<td>2012</td>
</tr>
<tr>
<td>S</td>
<td>Au</td>
<td>DWNTs</td>
<td>NPs</td>
<td>500 - 3E4</td>
<td>0.018</td>
<td>0.75</td>
<td>0.45</td>
<td>0.1</td>
<td>&lt;500</td>
<td>2012</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>CNT paper</td>
<td>NPs</td>
<td>--</td>
<td>-7.7E-5</td>
<td>1.9</td>
<td>0.54</td>
<td>5</td>
<td>360</td>
<td>2012</td>
</tr>
<tr>
<td>Glass</td>
<td>Pt</td>
<td>CNT/Ni film</td>
<td>NPs</td>
<td>200 - 1.6E4</td>
<td>1.4E-3</td>
<td>1.9E-3</td>
<td>0.038</td>
<td>0.2</td>
<td>200</td>
<td>2012</td>
</tr>
<tr>
<td>S</td>
<td>Au/Ti</td>
<td>SWNTs/DNA</td>
<td>NPs</td>
<td>100 - 2E3</td>
<td>0.5</td>
<td>10.6</td>
<td>1.6</td>
<td>0.1</td>
<td>100</td>
<td>2013</td>
</tr>
<tr>
<td>S</td>
<td>Au</td>
<td>MWNT array</td>
<td>NPs</td>
<td>500 - 1E4</td>
<td>2.8E-4</td>
<td>1.9</td>
<td>0.54</td>
<td>0.1</td>
<td>&lt;500</td>
<td>2013</td>
</tr>
<tr>
<td>S</td>
<td>Au</td>
<td>Graphene</td>
<td>NPs</td>
<td>1 - 1E3</td>
<td>0.027</td>
<td>0.90</td>
<td>4.62</td>
<td>0.1</td>
<td>1</td>
<td>2013</td>
</tr>
<tr>
<td>S</td>
<td>Au</td>
<td>SWNT film</td>
<td>NPs</td>
<td>250 - 2.5E4</td>
<td>5.8E-4</td>
<td>2.5</td>
<td>--</td>
<td>0.25</td>
<td>250</td>
<td>2013</td>
</tr>
</tbody>
</table>

\*S: Si/SiO₂ substrate, # LDL: lowest detection limit, CLs\*: clusters, Fl\*: filament, @ H₂ conc. (%) means at which H₂ concentration the response/recovery time was determined.
CHAPTER 6

A NITROGEN DIOXIDE GAS SENSOR BASED ON
TELLURIUM/SINGLE-WALLED CARBON NANOTUBE HYBRID
NANOSTRUCTURES

6.1 Abstract

One-dimensional nanostructure based chemiresistive sensors have received great attention because of their compact design and excellent sensing performance including high sensitivity, low detection limits, low power consumption, and ability to integrate multi-sensor arrays. However, these sensors generally suffer from slow response and recovery times when it operated at ambient conditions because of slow catalytic or absorption/desorption processes. The sensors overcome this obstacle by operating at high temperature, which increase device complexity with higher power consumption rate. In this work, we demonstrated the construction of an ultra-fast NO$_2$ sensor at ambient conditions by utilizing feather-like tellurium (Te) nanostructures functionalized on single-walled carbon nanotube (SWNTs) networks. By tailoring the morphology and density of Te nanostructures, hybrid nanostructures show an excellent response and recovery time of approx. 63 sec and 7 min to 100 ppb$_V$ NO$_2$ gas at room temperature.
6.2 Introduction

Over the past few decades, the detection of NO\textsubscript{2} in combustion exhaust or in the environment has been of significant interest because the presence of NO\textsubscript{2} has been correlated to the formation of acid rain, photochemical smog and some respiratory diseases including emphysema and bronchitis. Several types of NO\textsubscript{2} sensors have been developed including conductometric [1], potentiometric [2], and amperometric [3], based on metal oxides (e.g., WO\textsubscript{3} [4], SnO\textsubscript{2} [5], ZnO [6], NiO [7] and ZrO\textsubscript{2} [8]). Within the realm of gas sensing, conductometric metal oxide sensors have dominated the field because of their robust nature and simple circuit design. However, metal oxide based sensors generally require high operating temperature in order to obtain decent sensitivities and faster response/recovery times. This feature can significantly reduce selectivity as many analytes interact with oxide surface, while also increasing power consumption and device complexity. In fact, temperature control systems can overshadow both operating costs and design of the actual sensing element and have been the focus of several nanostructured gas sensor platforms, which have demonstrated advanced thermal control architectures through a series of lithographical fabrication steps. Consequently, facile approaches to rapid, reversible and selective chemical detection at room temperature can provide substantial gains in terms of cost and manufacturability to facilitate massive deployment or smart sensor arrays essential for environmental monitoring and medical diagnosis.

One-dimensional (1-D) nanostructures such as nanowires and nanotubes have received great attention for fabrication of gas sensors due to their unique size-dependent
properties.[9] In particular, there has been growing interest in carbon nanotubes (CNTs) owing to their unique electrical, physical, mechanical and chemical properties to develop devices with simplicity, reliability, reproducibility, and low cost.[10] Various electronic devices including supercapacitors, electrodes, field emission devices, and sensors have been synthesized based on single carbon nanotubes, carbon nanotube networks or carbon nanotube films.[11-13] SWNT based chemiresistive/chemical field effect transistors (ChemFETs) have been widely used as gas sensors due to their sensitivity to charge transfer and chemical doping effect by various gaseous molecules.[11, 14] However, pristine SWNT based gas sensors have limitations such as low sensitivity to some analytes, lack of selectivity as well as long response and recovery times that hinder their use as stand-alone sensing elements. Therefore, significant effort has been devoted to surface functionalization of SWNT to modify the sensor properties. Recent reports have discussed the incorporation of typical metal or metal oxide catalysts such as Pd [15], Au [16], TiO₂[17] and SnO₂[18] for enhancement of both sensitivity and selectivity toward analyte gases. Furthermore, many of these reports demonstrate improved performance at lower operating temperatures with respect to their thin film counterparts.

Tellurium is a p-type semiconductor with band gap energy of 0.35 eV at room temperature. Single crystal Te is usually called t-Te due to its hexagonal crystal structure that contains six spiral chains in the corner and one in the center.[19] Based on its unique lattice structure, Te shows some interesting properties such as photoconductivity, thermoelectric effect, and catalytic activity and has been used in various devices such as thin film transistors, infrared detectors, and gas sensors.[1, 20, 21] Previous work has
demonstrated polycrystalline Te thin films fabricated by vacuum thermal evaporation can be used as promising NO\textsubscript{2} sensors at room temperature.[1] Moreover, Te nanotubes and nanorods made from vacuum or atmospheric thermal evaporation has been reported to detect Cl\textsubscript{2}, NO and other gases.[22] These Te based sensors exhibited ppm range sensitivity to various gases with response times of around several minutes at room temperature.

In this work, Te nanostructure decorated SWNT devices were synthesized by electrodeposition of Te on aligned SWNTs. Linear sweep voltammetry (LSV) was utilized to understand the electrodeposition of Te. The ability to tune Te morphologies, including porous beaded structures, needle or blade like geometries, rice shaped particles and extended feather growths, were demonstrated through control over the electrolyte concentration, applied potential and charge density. Decorated SWNT devices were exposure to NO\textsubscript{2} gas and the sensing performance was correlated to the morphology of Te nanostructure. Highly faceted Te feather structures yielded the highest sensitivity with a room temperature ppb\textsubscript{V} detection limit with fast rapid response/recovery times. Selectivity of the nanosensors was also tested by measuring its response towards various gases such as NH\textsubscript{3}, H\textsubscript{2}S, H\textsubscript{2} and H\textsubscript{2}O.

### 6.3 Experimental

Pt microelectrodes for 15 sensor arrays were fabricated via a photolithography process. Si wafer with 300 nm of oxidation layer was applied as the substrate (Figure 6.1a). Within the sensor arrays, integrated Pt counter and reference electrodes were
surrounded by sensor electrodes, which avoided the need to introduce external reference and counter electrodes during the electrodeposition of Te on SWNTs. Pre-fabricated chips were then cleaned with nanopure water and acetone for future use. A customized Teflon cell was used to hold the chip and locate the solution for the SWNT AC dielectrophoretic alignment and functionalization. The electrical connection between the external electronic equipment and the chip was obtained by clipping the chip with two 32 pin SOIC test clips purchased from Pomona Electronics (Figure 6.1b).

The carbon nanotube suspension was prepared by adding 0.2 mg of commercially available carboxylated single-walled carbon nanotubes (SWNTs, Carbon Solution, Inc. Riverside, CA) in 20 mL of N, N-dimethylformamide (DMF, Sigma Aldrich, MO), followed by sonicating the contents for 90 minutes until a uniform suspension was obtained. Then the suspension was centrifuged at 15,000 RPM for 90 min and the supernatant was subsequently collected. Afterwards, 200 µL of the supernatant was placed into the Teflon cell with chip held for SWNT alignment (Figure 6.1b). To obtain optimized SWNT alignment, a 2 V_{pp} and 4 MHz frequency was applied to the electrodes for 4 seconds. A Labview program was designed to command the Keithley 3390 AC generator (aligner) and custom-made DAQ switcher for sequential SWNT alignment. The synthesized sensors were rinsed with nanopure water, dried with ultra-pure N₂ gas and then annealed at 300 °C for 2 hours in forming gas.

SWNT functionalization was carried out by the electrodeposition of Te from an acidic nitric bath containing HTeO₂⁺. The effects of tellurium precursor concentration, applied potential as well as charge density on the morphology and the electrical
properties of the Te-SWNT hybrid nanostructures were investigated. The concentration effect was examined by applying 500 µL solutions of 0.1, 1 and 10 mM HTeO$_2$\(^+\) (99+%, Acros Organics) in 1 M nitric acid (Certified ACS Plus, Fisher Chemical) to the system. The deposition potential and charge density were maintained at -1 V vs. Pt and 18.9 mC/cm$^2$, respectively. The effect of deposition potential was investigated by varying the potential from -0.8 to -1.4 V with the same charge density applied. Finally, the charge density was varied from 1.89 to 189 mC/cm$^2$ at -1 V vs. Pt to study the influence of charge density on the morphology of deposited Te. After deposition, the sensors were rinsed with nanopure water and dried with nitrogen gas.

Morphologies and compositions of the obtained hybrid Te decorated SWNTs were investigated using field emission-scanning electron microscopy (FE-SEM, Leo model # 1550, Peabody, MA) and energy-dispersive X-ray spectroscopy (EDX). For electrical characterization, back-gated FET properties were measured by sweeping the gate voltage from -20 V to 20 V while fixing the source-drain potential at 1 V. Furthermore, the sensing performance of the Te-SWNT hybrid structure was studied by installing the sensing chip in a sealed Teflon sensing cell with gas inlet and outlet ports for gas flow and then clipping the chip to a Keithley 236 source measurement to obtain electrical connection (Figure 6.1c). A power supply of 1 V was provided to each sensor and the resistance was continuously recorded every 15 seconds for the fifteen sensors by a LabView program. NO$_2$, NH$_3$, H$_2$S and water vapor were first diluted in dry air, and then introduced into the Teflon cell at a total gas flow of 200 sccm for gas sensing measurements.
6.4 Results and Discussion

The effect of HTeO$_2^+$ concentration, applied potential and charge density on the Te growth was investigated with both LSV and scanning electron microscopy of Te nanostructure deposits. Figure 6.2 shows typical LSV of Te deposition on SWNTs using electrolytes with different concentrations of HTeO$_2^+$. The deposition potential was swept from 0 to -1.4 V vs. a pseudo Pt reference electrode at a rate of 10 mV/s. Three reduction waves ($a_1$, $a_2$, and $a_3$) were observed at -0.75 V, -1.1 V and -1.28 V from an electrolyte containing 10 mM HTeO$_2^+$ where $a_1$ may attributed to reduction of HTeO$_2^+$ to Te (Equation 6.1) and $a_2$ may attributed to a two-step reduction which involves the electrochemical reduction of HTeO$_2^+$ to H$_2$Te (Equation 6.2) followed by the chemical deposition of Te from HTeO$_2^+$ and H$_2$Te (Equation 6.3).[23] $a_3$ is attributed to hydrogen evolution.

\[ HTeO_2^+ + 4e^- + 3H^+ \rightarrow Te^0 + 2H_2O, \quad E^0 = +0.551 \, V \, vs. \, NHE \]  \hspace{0.5cm} \textit{Equation 6.1}  \\
\[ HTeO_2^+ + 6e^- + 5H^+ \rightarrow H_2Te \, (aq) + 2H_2O, \quad E^0 = +0.121 \, V \, vs. \, NHE \]  \hspace{0.5cm} \textit{Equation 6.2}  \\
\[ 2H_2Te + HTeO_2^+ \rightarrow 2Te \, (S) + 2H_2O + H^+, \quad G_f^0 = -498.118 \, kJ \, mol^{-1} \]  \hspace{0.5cm} \textit{Equation 6.3}

The effect of HTeO$_2^+$ concentration on Te electrodeposition was examined by conducting LSV with various of HTeO$_2^+$ concentration from 0.1 to 10 mM (Figure 6.2). As shown in the Figure 6.2 inset, the Te electrodeposition potential shifts more cathodic with decreasing HTeO$_2^+$ concentration. No obvious reduction peak was observed for 0.1 mM HTeO$_2^+$. Finally, as the HTeO$_2^+$ concentration increases the onset of hydrogen
evolution was shifted to more cathodic potentials as expected due to the larger HER overpotential on Te as opposed to the Pt microelectrodes, which is observed with greater Te deposition in the case of 10 mM HTeO$_2^+$. The effect of electrolyte concentration on the morphology of Te grown potentiostatically at -1V vs. Pt is shown in Figure 6.3 with a fixed deposition charge density of 18.9 mC/cm$^2$. The lowest concentration of Te (i.e., 0.1 mM) produced porous and somewhat jagged Te nanoparticles that likely result from the competition between diffusion limited HTeO$_2^+$ reduction and the dominating hydrogen evolution reaction (HER). These dendritic particles result from diffusion limited deposition, consistent with a negligible reduction peak in the LSV, where the growth was quickly dominated by hydrogen reduction, presumable from the Pt microelectrodes. Needle or blade-like Te nanostructures were obtained from a low Te deposition rate when an electrolyte of 1 mM HTeO$_2^+$ concentration was used, owing again to the limitations of mass transfer and mitigated hydrogen evolution with respect to 0.1mM HTeO$_2^+$ as observed in the inset of Figure 6.2. The highly faceted structures and incomplete SWNT coverage suggest the dendrite growth occurs first by instantaneous nucleation followed by diffusion limited growth, permitting extended structure growth by the smaller HER current, equivalent to that of the Te partial current. More compact Te particles that grow radially along the SWNTs were observed with the utilization of an electrolyte of higher concentration where HER was insignificant due to rapid Te deposition. The rice like appearance is attributed to instantaneous nucleation followed by three dimensional growths that is limited laterally by coalescence with neighboring Te grains creating a shell of oblate or
scalene ellipsoids due to the underlying substrate. The EDX spectrum (Figure 6.3d) identifies the main elemental components as O, Si, Pt and Te, where the former elements are from the silicon substrate and Pt electrodes.

Morphologies of Te nanoparticles obtained at different deposition potentials but with a fixed charge density (18.9 mC/cm²) and HTeO₂⁺ concentration (10 mM) are shown in Figure 6.4. The SWNTs used in this study are carboxylated SWNTs, meaning they contain carboxylated defects and stone-wall defects. At low applied overpotential, Te preferentially nucleated on these sites. However, as the applied potential becomes more negative, Te nucleated on entire surface of SWNTs because of the high driving force. Small and dispersed Te nanoparticles were nucleated on SWNTs at an intermediate potential (-0.8 V vs. pseudo Pt), indicating that nucleation was mostly taking place at the SWNT defect sites.

Furthermore, the disparity in particle size suggests a progressive nucleation mechanism, which would be consistent with defect site mediated nucleation and growth at intermediate overpotentials.[24] At slightly more negative deposition potential, -1 V, SWNTs covered with coalesced rice-like Te nodules described above. At more cathodic potentials, -1.2 V, both the size and coverage of the deposits decreased, which would be attributable to HER and the formation H₂Te according to the Equation 6.2. The slightly more spherical shape of these particles is also thought to be a consequence these parasitic reactions and the resulting decreased Te nucleation and growth. HER was expected to be quite significant when the applied potential reached -1.4 V, leading to the drastically decreased deposition efficiency and size diminution of Te particles.
Control over the size, shape and density of the deposits can also be achieved by varying the applied charge density. Small particles (~20 nm) first nucleated along the SWNTs (Figure 6.5a) and grew radially to the point of coalescence, thereafter proceeding as ellipsoids to ~100 nm along the major axis when the charge density was increased to 18.9 mC/cm$^2$. The formation of Te rice-like structures, as observed in Figure 6.5b and similarly Figure 6.3c, are actually oblate or scalene ellipsoids primarily due to the high nucleation density and particle coalescence described above. As higher charge (94.5~189 mC/cm$^2$) passed through SWNTs, gaps in the nodules appeared as the size of the particles decreased and feather-like structure immersed from these openings (Figure 6.5c, d). In contrast to the incomplete coverage observed at more cathodic potentials due to increased HER (Figure 6.4c, d), the decreased size with increasing charge density is progressive meaning the particles reach a maximum size and begin to shrink as more time or charge is passed. This type of growth is reconciled by chemical etching of particles after establishment of the boundary layer. Diffusion limited growth of Te has been shown to produce dendritic deposits, consistent with the feather structures observed in Figure 6.5c. Once these dendrites begin to grow, deposition of rice-like structures is disrupted and etching attacks the grain boundaries opening up regions of the SWNT. As more time passes (Figure 6.5d) the particles continue to decrease in size as diffusion limited Te is only deposited on the extended feather dendrites and the highly concentrated acid continues to etch away at the Te beads. Figure 6.5e clearly demonstrated the schematic growth of Te nanostructures with increasing charge density.
Quantitative assessment of the applied potential and charge density on particle size and number of particles per SWNT is provided in Figure 6.6. As expected, the potential dependent particles size reaches a maximum at -1V due to kinetically limited growth at more positive potentials and competition with HER at more negative potentials. The density of the particles is greater with more cathodic potentials, below -1.4 V, which is consistent with an instantaneous nucleation mechanism and HER limited growth. The effect of charge density on the deposited particle size and number of particles per SWNT is displayed in Figure 6.6b. The particle size is augmented by charge density up to 94.5 mC/cm$^2$ and decreases thereafter. On the other hand, the particle density is fairly constant except for an uncharacteristic dip at 94.5 mC/cm$^2$, which likely reflects an error due to undistinguishable coalescence of particles. Overall, the results of Figures 6.3 through 6 shows that the morphology and density of as-decorated metal structures can be controlled by varying the concentration of electrolyte, applied potential as well as charge density.

The room temperature back-gated FET measurements, shown in Figure 6.7, were carried out in order to confirm the electrical transfer characteristics of SWNT and the Te-SWNT hybrid nanostructures shown in Figures 6.5a, b and c. The source-drain current ($I_{SD}$) versus gate voltage ($V_G$) at fixed voltage ($V_{SD}$) curves were shown in Figure 6.7a. All the sensors exhibited p-type semiconducting behavior while deteriorated transport properties were observed after SWNT functionalization, showing neither on nor off values. The conductivity, however, did increase with increased deposition charge and greater Te coverage, doubling that of the SWNT for small Te charge densities and quadrupling for a charge density of 94.5 mC/cm$^2$. This is believed to be due to the isotype
heterojunction formed between the two p-type semiconductors. The similar small band gaps, 0.57 eV and 0.35 eV, and work functions, ~5.0 eV, for SWNT and Te, respectively, are believed to create small barriers for hole transport between the two materials resulting in parallel current flow through the Te particles, correlating well with the increased conductivity for greater Te coverage and particle diameter.[25, 26] The weakened gate dependence is an expected result of the increased diameter of these hybrid structures as the gate field does not penetrate their cross section as strongly but more importantly the small grain sizes of the Te particles disrupt highly conductive channel formation.[27] Figure 6.6b displays the diminished mobility of Te-SWNT hybrid structures, which reflects the dominant flow along Te particles and its interruption from limited Te grain size. [28] This is consistent with increased particle size and coverage observed in Figure 6.5 with the increases mobility in Figure 6.7b. Moreover, the low hole mobility and high conductivities of these hybrid structures are also in agreement with the Te dominated conduction mechanism as the high carrier concentration of Te with respect to SWNT permits the observed conductivities. Significant mobility enhancement of Te feather-SWNT sensors likely result from the charge flow through the Te-SWNT networks by feather bridging and the improved crystallinity associates with these dendritic Te nanostructures.[29]

Sensing responses of the bare SWNT network and three topographically different (Figure 6.5a, b and c) Te-SWNT nanosensors towards NO₂ at room temperature were investigated with custom sensing system described previously.[15, 16] These sensors were challenged with concentrations of NO₂ ranging from 5 ppb_V to 10 ppm_V with 15
minute expose and 20 minutes recovery times and the transient are shown in Figure 6.8a,b. The sensor response was determined by the resistance change and defined as $(R_f-R_0)/R_0 \times 100\%$ and is shown in Figure 6.8c as a function of analyte concentration; $R_f$ is the final resistance and $R_0$ is initial baseline resistance prior to analyte exposure. The response time is defined as the time for the sensor to reach 90% of its steady-state value. The recovery time is identified as the time required for the sensor after the exposure to return to 50% of its maximum response. The 50% recovery time instead of 90% was selected because of the slow recovery rates, which never reached 90% of the maximum response due to rapid cycling of analyte concentrations. The response and recovery times are depicted as a histogram in Figure 6.8d where the response time was ranging from 1.05 to 10.84 minutes and recovery time was ranging 7.0 to 19.7 minutes for 100 ppbV NO$_2$. In nearly all cases Te functionalization improved response/recovery time with respect to the SWNT network. In terms of sensitivity, the smaller Te charge densities displayed near negligible change in performance compared to SWNTs. Feather-like Te-SWNT structures showed the excellent sensing performance for all metrics with dramatically higher sensitivity and faster response/recovery times, clearly superior to the other devices. Upon exposure to 100 ppb$_V$ NO$_2$, a 40% change in electrical resistance was achieved with response and recovery times of 1.05 and 7 min, respectively. The minimum detection limit of NO$_2$ was found to be around 50 ppb$_V$, which is the lowest value for Te based NO$_2$ sensor to date (Insert in Figure 6.8c).

Importantly, these sensors were also challenged with background analytes to identify potential interferences and demonstrate sensor viability in real life conditions.
The selectivity of the gas sensors was determined by analyzing their response to various gases such as NH$_3$, H$_2$S, H$_2$ (not shown) and H$_2$O vapor (Figure 6.9). Morphology dependent sensing performance was observed with improved behavior in the Te feather-like structure. For the case of ammonia, all Te decorated devices displayed similar behavior doubling in sensitivity over that of the SWNT control with greater Te charge density giving the best performance. However the most dramatic improvement for these set of analytes was for H$_2$S in which a response of up to 130% was achieved at the PEL level (20 ppm) with the feather Te nanostructures, almost 10 times higher than the other structures. The response to water was mixed with lower Te loadings providing negligible difference from the SWNT control and the highest Te loading producing mixed responses, from negative to positive resistance changes, depending on concentration suggesting competitive sensing mechanism. While the positive change in resistance to NH$_3$ and H$_2$S gives little concern for sensor function, the large decrease in resistance at smaller H$_2$O concentration suggests this device would require a desiccant to dry the air prior to introduction with the sensor.

The sensitivities for each sensor to each analyte, as well as H$_2$, were calculated by taking the slope of the linear part of the sensing calibration curve and compiled in Figure 6.10. The combined responses give a unique picture or signature for each analyte by which the system can distinguish an individual gas and assist in quantitative assessment of concentration. Specifically, the direction change in response to NO$_2$ with respect to the other gases provides ease in analyte identification and establishes a means to bypass sample dehumidification. The magnitude of the these sensitivities displays fairly typical
or modest values with one notable exception, the Te-SWNT nanostructures showed the highest sensitivity of 230 % ppm$^{-1}$ towards NO$_2$, which is the highest room temperature sensitivity reported to date (Table 6.1).

Nevertheless, we acknowledge that the sensor may have difficult time to identify NO$_2$ in gas mixture due to the response averaging from different analytes. A sensor array, instead of single sensor element, generally comprised of different sensory materials (e.g., metals, metal oxides, conducting polymers, SWNTs and their hybrid structures), may be utilized when only a single transduction measurement is used. Currently, a high density sensor array with different sensory materials is integrated on single chip to identify and quantify the analytes.

The sensing mechanism of the Te and SWNT can be explained by the alteration of the transport properties owing to the interaction of adsorbed species to the SWNT and Te surfaces.[32, 33] It has been reported that the sensing response of Te thin films to NH$_3$ and H$_2$S could derive from the reduction of oxygen ion that absorbed on the surface and the inter-grain regions of Te film. When a stable state was obtained in the sensor exposed to air, oxygen molecules were adsorbed on the Te surface by capturing the free electrons. Upon exposure to reducing analytes such as NH$_3$ and H$_2$S, leads to the discharge of adsorbed oxygen, which results in the decrease of the majority carrier density in the Te along with its conductivity. Higher sensing response of Te feather structure obtained from H$_2$S than NH$_3$ may be attributed to the stronger reducibility of the former. Moreover, NH$_3$ and H$_2$S also act as electron donors that cause the hole concentration to decrease, leading to the sensor resistance to increase. On the contrary, as a strong electron acceptor
such as NO₂ can receive electrons from the valence band of Te resulting in the enhancement of the hole density in both Te and SWNTs, thus decreasing the resistance. The superior sensing performance by the Te feather-like structure is believed to be due to its larger surface-to-volume ratio and increased crystallinity which provides for its higher conductivity and field effect carrier mobility. For this sensor analyte is believed to directly interact with the Te feathers, the carrier super highways of the device, to strongly impact carrier transport. Similar behavior in both transient profile and sensitivity values between SWNT networks and hybrid devices with smaller Te loadings is a likely consequence of a SWNT nanotubes dominated resistance. The breaks in Te coverage are believed to be higher resistance sections and hence sensitivity is believed to be derived from exposed SWNT permitting similar results as the SWNT control.

6.5 Conclusions

A Te-SWNT hybrid nanostructure based NO₂ sensor was synthesized by means of AC dielectrophoretic alignment of SWNTs followed by Te electrodeposition. Shape, morphology and size of the Te particles were controlled by adjusting the electrodeposition conditions and electrolyte composition. Te rice-like and feather-like structures were synthesized by varying the applied charge density (i.e. 18.9 mC/cm² and 94.5 mC/cm²) at a fixed applied potential of -1V, using an electrolyte containing 10 mM of TeO₂. Te deposition appears to follow instantaneous nucleation of small particles along SWNTs followed by the growth of the nucleus to form rice-like structures and finally highly crystalline feather-like structures once mass transfer limitations set in. The
gating dependent effects of SWNTs were diminished upon Te decoration owing to transport though the Te particles and their small grains, but enhanced from transport through Te feather suggesting improved crystallinity in Te feathers.

Sensing results indicated the enhancement of the sensitivity by Te functionalization of SWNTs, especially by the feather-like Te-SWNT hybrid nanostructures. A NO$_2$ nanosensor was developed based on Te feather-SWNT structures with a superior selectivity, high sensitivity of -230.0 %/ppm$_V$, and quick response and recovery times of 63 sec and 7 min to 100 ppb NO$_2$ at room temperature. The sensing mechanism can be explained by the interaction between gas molecules and adsorbed oxygen as well as the change in carrier transport properties induced from the adsorption of analytes. The outstanding sensing performance of the Te feather-like SWNT structures is due to its large surface-to-volume ratio and higher field carrier mobility. The sensors were tested against background analytes to demonstrate viability in the field.
6.6 References


Figure 6.1 Optical images of sensor configuration: (a) Sensor arrays with 15 Pt paired microelectrodes as working electrodes (W.E.), integrated Pt reference electrode (REF) and counter electrode (C.E.); (b) Teflon cell with pin soic test clips for SWNT alignment and functionalization; (c) Teflon sensing cell with gas inlet and outlet.
Figure 6.2  Linear Sweep Voltammetry (LSV) of Te deposition on SWNT. Electrolyte: 0.1, 1, 10 mM HTeO$_2^+$ in 1 M HNO$_3$. Total solution volume was fixed at 500 µL. LSVs were performed with a fixed scan rate: 10 mV/s.
**Figure 6.3** Effect of concentration of HTeO$_2^+$ on the morphology of the Te-SWNT hybrid nanostructure at a fixed applied potential of -1 V and controlled charge density of 18.9 mC/cm$^2$: (a) 0.1 mM; (b) 1 mM; and (c) 10 mM.
Figure 6.4 Effect of applied potential on the morphology of the Te-SWNT hybrid nanostructure at a fixed HTeO₂⁺ concentration of 10 mM and controlled charge density of 18.9 mC/cm²: (a) -0.8 V; (b) -1 V; (c) -1.2 V; (d) -1.4 V.
Figure 6.5   Effect of charge density on the morphology of the Te-SWNT hybrid nanostructure at a fixed HTeO$_2^-$ concentration of 10 mM and controlled applied potential of -1 V. (a) 1.89 mC/cm$^2$; (b) 18.9 mC/cm$^2$; (c) 94.5 mC/cm$^2$; (d) 189 mC/cm$^2$. (e) Schematic illustration of Te nanostructure growth on SWNTs with increasing charge density.
Figure 6.6 Effect of (a) applied potential and (b) charge density on particle size and density of Te-SWNT hybrid nanostructure.
Figure 6.7  Current ($I_{SD}$) vs. back gated voltage ($V_G$) with a fixing the source-drain potential (VSD) at 1 V. (a) Electron transport properties of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively). (b) Mobility of AC aligned SWNT and Te-SWNT hybrid nanostructures.
Figure 6.8  (a, b) Real-time sensing response, (c) calibration curve, (d) response and recovery time of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively) towards NO$_2$ at different concentration.
(a) Real-time sensing performance and (b) calibration curve of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively) towards (1) NH$_3$, (2) H$_2$S and (3) H$_2$O. (Sensing performance towards H$_2$ was not shown here)
Figure 6.10  Sensitivity of AC aligned SWNT (black) and Te-SWNT hybrid nanostructures (blue, green, and red represent the responses acquired from hybrid structures shown in Figures 5a, b, and c, respectively) towards NH$_3$, H$_2$S, H$_2$O, NO$_2$ and H$_2$. 
Table 6.1  Comparison of NO$_2$ sensing properties of different nanostructures counterpart at room temperature

<table>
<thead>
<tr>
<th>Structures</th>
<th>Lowest Detection Limit (ppm)</th>
<th>Sensitivity (% ppm$^{-1}$)</th>
<th>Response time $t_{90}$ at 100 ppb (min)</th>
<th>Recovery time $\tau_{50}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te thin film[1]</td>
<td>0.1</td>
<td>-20</td>
<td>--</td>
<td>2.5</td>
</tr>
<tr>
<td>Te microtubes[30]</td>
<td>10</td>
<td>-0.25</td>
<td>--</td>
<td>5</td>
</tr>
<tr>
<td>PAni nanofibers[31]</td>
<td>0.125</td>
<td>-0.29</td>
<td>0.5</td>
<td>3.0</td>
</tr>
<tr>
<td>In$_2$O$_3$ nanowires[9]</td>
<td>0.005</td>
<td>-1973</td>
<td>7.07</td>
<td>1.67</td>
</tr>
<tr>
<td>SWNTs (this work)</td>
<td>&lt; 0.1</td>
<td>-6.4</td>
<td>10.84</td>
<td>84</td>
</tr>
<tr>
<td>This work</td>
<td>0.05</td>
<td>-230.0</td>
<td>1.05</td>
<td>7</td>
</tr>
</tbody>
</table>
CHAPTER 7

CONCLUSIONS

This work demonstrated the synthesis and characterization of one-dimensional nanostructures for the applications of gas sensors and thermoelectrics.

Chapter 2 demonstrated the synthesis of ultra-long Pb\textsubscript{x}Se\textsubscript{y}Ni\textsubscript{z} hollow nanofibers by combining electropinning and galvanic displacement reaction. Control over the shape, morphology, composition and crystal structure of the nanofibers were achieved by adjusting the concentrations of HSeO\textsubscript{2}\textsuperscript{+} in the electrolytes. Temperature dependent Seebeck coefficient of as-prepared Pb\textsubscript{x}Se\textsubscript{y}Ni\textsubscript{z} nanofibers with various compositions were characterized, showing the p-type nature of these Se-rich PbSeNi nanofibers. Samples that contain more Pb but less Ni show a higher Seebeck coefficient. The highest thermopower of 449 $\mu$V/K was obtained in the sample Pb\textsubscript{37}Se\textsubscript{59}Ni\textsubscript{4} at 300 K, greater than the one in the bulk sample and nanowires.

Chapter 3 detailed the fabrication of Pb\textsubscript{x}Te\textsubscript{y} nanofiber mats with controlled dimensions, morphologies and compositions by galvanically displacing electrospun Co nanofibers. Co, instead of Ni, was chosen as sacrificial materials because it can be completely dissolved during the reaction, leaving no residue in the target materials. The temperature-dependent Seebeck coefficients of the prepared nanofiber mats were measured in the same temperature range as Pb\textsubscript{x}Se\textsubscript{y}Ni\textsubscript{z}. The results indicate that the samples are p-type with holes as charge carriers. A greater Seebeck coefficient was
observed in the sample with a higher Pb content and a smaller gain sizes. The highest Seebeck coefficient of 356 µV/K was obtained in the Pb₄₅Te₅₅ sample at 308 K.

Chapter 4 elucidates the synthesis of AgₓPb₅Sb₇Te₃ (LAST) nanofiber mats with controlled dimensions, morphologies and compositions by galvanically displacing electrospun Co nanofibers. Control over the compositions of the nanofibers was obtained by tuning the concentrations of the cations (i.e. SbO⁺ and Ag⁺) in the electrolytes. The temperature-dependent Seebeck coefficients of these LAST nanofibers were characterized. Nanofibers with a low Ag content possessed n-type transport properties, while the ones with a high Ag content expressed p-type semiconductor behaviors. The n-type characteristics can be attributed to the n-type nature of the Sb-doped PbTe, while silver and antimony chalcogenides may contribute to the p-type transport behavior.

Chapter 5 detailed the fabrication of chemiresistive H₂ gas sensors using SWNTs as transducers bridged across various metal (e.g. Pd, Pt, Au and Cr) microelectrodes. The chemiresistive sensor with Pd-SWNTs combination demonstrated a significantly higher sensitivity with notably faster response and recovery times as compared to other Pd-CNT sensors reported. Modulation in the Schottky barrier height at the Pd-SWNT contact by the exposure to H₂ is considered to be the main reason for the great sensing response.

Chapter 6 described the synthesis of a Te-SWNT hybrid nanostructure based NO₂ sensor by means of AC dielectrophoretic alignment of SWNTs followed by Te electrodeposition. Effect of electrolyte concentration, deposition potential, and charge density on the morphology of the Te nanostructures was investigated. Sensing results indicated the enhancement of the sensitivity by Te functionalization of SWNTs,
especially by the feather-like Te-SWNT hybrid nanostructures. A NO$_2$ nanosensor was developed based on Te feather-SWNT structures with a superior selectivity, high sensitivity of -230.0 %/ppm$_V$, and quick response and recovery times of 63 sec and 7 min to 100 ppb NO$_2$ at room temperature.