Facile large scale solution synthesis of nanostructured iron, nickel and cobalt telluride and possible applications

Sungbum Hong
Iowa State University

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Facile large scale solution synthesis of nanostructured iron, nickel and cobalt telluride and possible applications

by

Sungbum Hong

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
Yue Wu, Major Professor
Zengyi Shao
Xinwei Wang

The student author and the program of study committee are solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2017

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DEDICATION

In memory of

my Father Hong, Neung-pyo and Mother Kwon, Kyung-hee
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ABSTRACT

Transition metal chalcogenides existing in a wide variety of stoichiometries have shown captivating electrical performances. Among them, the earth-abundance and environmental friendliness of iron (Fe), cobalt (Co) and nickel (Ni) chalcogenides have dragged scientists’ attention. Moreover, as state-of-art nanotechnology has impacted on conventional bulk technology in regard to enhancement in performance and discovery of new characteristics, it has been found that nanostructured the Fe, Co and Ni chalcogenides can be exploited for many applications such as superconductor, battery, thermoelectric materials and magnetic material, yet synthesis of these materials has been only accomplished in several milligram scales and normally involved costly equipment and extreme reaction conditions.

This thesis proposes facile one-pot solution synthesis methods of nanostructured FeTe$_2$, CoTe and NiTe with over 80% yielding and ~7.0g of final product per batch. An ethylene glycol based system enables a mild reaction condition and short reaction time. The as-synthesized FeTe$_2$ show 1-D nanowires with 26 ± 6nm diameters and a usage of hydrazine for the reaction is appeared to be a key factor to acquire uniform morphology. CoTe and NiTe are synthesized by a one-step reaction. The CoTe 1-D nanorods with uniform thickness of 11 ± 2nm are synthesized only by 5 minutes of reaction and the NiTe 2-D nanoparticles and its conjugated structures with 12 ± 3nm diameters are obtained by 4 hours of reaction. The final solution is further washed, dried and pulverized.

The materials powder is spark plasma sintered (SPSed) into disks, and then seebeck coefficient and electrical conductivity are measured. For FeTe$_2$, although it behaves as an intrinsic semiconductor materials, an unusual p-n conduction switching behavior of FeTe$_2$ is
observed, which is possibly because of the unintentional tellurium n-type doping generated by thermally expanded cell can attribute to the behavior. As an application of this behavior, a preliminary experiment of thermally controllable p-n junction diode is managed to show a partial success. Meanwhile, the substantially lower seebeck coefficient and higher electrical conductivity in of NiTe and CoTe agree with the highly metallic behaviors, leaving a possible application as dopants for other semiconductor application.
CHAPTER I
INTRODUCTION

1.1 Transition Metal Chalcogenides

Chalcogenides materials indicate chemical compounds containing chalcogens which are generally selenium (Se), sulfur (S), and tellurium (Te). Transition metal chalcogenides which are made up of covalent bonding between transition metals and the chalcogens, and their interesting unique electronic properties and structural and morphological chemistry have been extensively discovered [1]. The unique properties are ascribed to a countless variety of both stoichiometric and non-stoichiometric phases of transition metal chalcogenides, combined with several different oxidation states of chalcogen atoms in the structure, for instance -2, +2, +4 and +6 are most common oxidation states for tellurium [2]. Especially the non-stoichiometric phases can be categorized into two phases, chalcogen-rich and metal-rich. As expected by the names, chalcogen rich phase such as FeS$_2$, MoS$_2$, features non-metallic covalent bonding and the metal-rich phase, whereas, often exhibits metallic characteristics by holding additional metallic bonds in compounds. For this reason, the controllable stoichiometry and its properties have been attractive for decades and especially molybdenum (Mo), copper (Cu), silver (Ag), iron (Fe), and cadmium (Cd) are most commonly discovered transition metals chosen for chalcogenides binary compounds.

Among transition metal chalcogenides, molybdenum (Mo) has intriguing monolayer structures which resembles graphene and the dimension of the materials can be adjusted to a single atomic layer [3]. In contrast to the graphene, an interesting semiconductor property of the MoS$_2$ with 1.29eV of a band gap widens its potentials as a transistor [4]. With the
noticeable property, recent researches have been focused on optoelectronic devices (emitters and detectors) [5-12], electrocatalyst [13, 14], and energy storage [15-17].

Unlike the MoS$_2$, copper chalcogenides and silver tellurides have shown a great variety of stoichiometric phases and nanostructures. Therefore, a lot researches on these materials have been focused on developing different stoichiometric chalcogenides and nanostructure fabrications. For example, copper chalcogenides can be controlled within a range of Cu$_x$E, (E = Te, Se, S), (1<x<2) such as Cu$_4$Te$_3$ and Cu$_7$Te$_4$ nanocrystal [18], CuTe nanosheet [19] and nanoribbon [20], nanoparticles, Cu$_{2-x}$Se, Cu$_3$Se$_2$ nanoparticles [21], polycrystalline [22], thin film [23]. Cu$_2$Se thin film [24] and Cu$_{2-x}$Se$_y$S$_{1-y}$, Cu$_{2-x}$Te$_y$S$_{1-y}$, nanoparticles [25]. Copper chalcogenides are considered as promising nominees for battery [21] and thermoelectric [26] applications. For the same reason, different phases and morphologies of silver chalcogenides have been noticeable as well. Current researches found several distinguishable nanostructured silver chalcogenides, including Ag$_5$Te$_3$ [27], Ag$_7$Te$_4$ single crystal thin film [28], Ag$_{30}$Te$_{21}$ and Ag$_{46}$Te$_{29}$ complex clusters [29], Ag$_2$Te nanotube [30] and thin nanowire [31-35], Ag$_2$Se single crystal [36-38] and these materials are highly anticipated to be utilized for thermoelectric dues to a low band gap [39, 40].

Furthermore, iron (Fe) which is one of the earth-abundant transition metals is widely used for chalcogenides compounds. For easily achievable variations of iron monochalcogenides such as FeTe, FeSe and their ternary compounds, FeTe$_x$Se$_y$, (0 ≤ x ≤ 1, 0 ≤ y ≤ 1), the stoichiometric effects on superconductivity were examined by many scientists [41-44]. Interestingly, metal-rich phase of iron chalcogenides such as Fe$_3$Se (y ≥ 0.01) was also synthesized by solid state reaction and their magnetic, superconducting properties are also discussed [45, 46]. iron dichalcogenides such as FeTe$_2$, FeSe$_2$ have synthesized in
nanoscales, for instance FeTe\textsubscript{2} nanorods\cite{47}, nanocrystals\cite{48} and FeSe\textsubscript{2} nanocrystals\cite{49}. Lastly, iron sulfides have the most variations in stoichiometry and structures among other iron chalcogenides. FeS nanotubes\cite{50}, FeS\textsubscript{2} nanocrystals\cite{51}, Fe\textsubscript{7}S\textsubscript{8} nanowires\cite{52, 53} and their controllable magnetic\cite{52, 54}, electronic properties\cite{55} have been motivating the researches.

Cadmium chalcogenides, mostly found in monochalcogenides (CdX, X = Chalcogen), have been also importantly studied in solar cell application. Even though its potential environmental disadvantage, its production cost and competitive efficiency have led successful commercialization\cite{56, 57}. Also, optoelectronic properties of quantum sized nanomaterials, particles with less than 10nm of diameter, are commonly studied to enhance the overall performance\cite{58, 59}.

1.2 Solution Synthesis Methods of Nanomaterial

According to Recommendation on the definition of a nanomaterial adopted by European Union, it is defined as nanomaterials when more than half of distribution is comprised of particles in the size range from 1nm to 100nm\cite{60}. The size variance comparing to bulk materials comes with distinctive physical, electrical and chemical properties in due to various effects from enormously larger surface area of nanomaterials\cite{61}. For example, the tunable optoelectrical property was significant in quantum dot nanoparticles (≤ 10nm diameter)\cite{59} and metal nanoparticles showed catalytic property that does not exist in bulk materials\cite{62}. Also, the nanotechnology has been extensively employed in semiconductor memory and drug delivery field.

Solution synthesis is one of the bottom-up approaches in nanomaterial synthesis and has been widely employed to achieve uniform and tunable nanostructures\cite{63}. Various kind
of methods using liquid media as solvents have been chosen, for instance, solvothermal method (hydrothermal method) involving sealed reactors and high reaction temperature and pressure above the boiling point of the media [64] and hot injection method involve that requires normally extremely high reaction temperature, normally higher than 240°C [61,65,66]. Even though both relatively new technologies have widely adapted by many researches, their scalability for future commercialization remains doubtful.

On the contrary, solution synthesis method that requires relatively mild heat sources and inexpensive equipment has been advantageous over the other methods due to easiness of large-scale synthesis shorter synthesis time [40]. Choice of solvents such as deionized water [67], ethylene glycol [68,69], oleylamine [70], etc., are often made based on solubility of precursors and boiling temperature and it is crucial to find an optimal solvent because selection of solvents affect the materials’ structure [71] and property [72]. As it is often inevitable to obtain final products with surface ligands during the process, thorough washing the final products in solution phase is followed to get rid of them and it was shown that hydrazine (N₂H₄) can remove the most of ligands selectively [73].

1.3 Bulk Sample Fabrication

The solution phase synthesized nanomaterials sample must be washed and dried into powder and the powder is sintered into bulk materials by several techniques to be used in actual device architecture, for example a thermoelectric device consists of hundreds of millimeter scale thermoelectric material bars. The sintering technologies greatly reinforces mechanical strength by densifying and binding particles, which facilitate future application. However, a structural ripening of nanomaterials which is involved during sintering process is unavoidable, so that several different sintering techniques such as hot-press sintering,
pressureless sintering, and spark plasma sintering (SPS) have been developed in order to achieve best performance depending on research purposes.

Conventionally, hot-press method has been widely employed where the powders are consolidated by continuous pressure and heat for hours. The conventional hot-press method has strength in production cost [74]. However, when it comes to a sintering of nanostructured materials, the longtime of process involves more degree of ripening of the nanoscale materials than other methods, forming undesired structures in the bulk sample because it only uses joule heating [75].

Meanwhile, pressureless sintering technique has been emerged to overcome the disadvantage that the hot-press method has. It has an advantage that it can prevents some degree of ripening, so that it maintains porous structure in the materials as best as it can, especially functionally graded materials and ceramics [76,77]. However, it requires extreme temperature to compensate the pressureless condition and long process time, which are considered as a disadvantage of the technique.

Besides, spark plasma sintering (SPS) has been favored over the conventional sintering technology. Unlike the hot-pressing and pressureless sintering, the SPS provides thermal energy by not only using the joule heating, but also electrical current flowing through the sample as well as a continuous pressure. Thus, the combination of the three factors extremely shortens the duration of process, thus, this method limits the unwanted ripening the most compared to other two methods [78,79].
1.4 Seebeck Effect

In 1821, Thomas Seebeck, a German scientist, discovered when an electric circuit consists of two different metals and their joint at which the metals meet currently forms significant temperature difference, voltage difference is made [80].

Despite that the discovery was found between metals, semiconductors have shown more obvious seebeck effect due to energy gaps that charge carriers either electrons or holes should jump over make them difficult to diffuse, so that the seebeck effect in metals is commonly utilized for thermocouples where there does not require high voltage, and the effect in semiconductor is mostly harnessed for thermoelectric application where a direct conversion of heat to electrical energy [81].

Figure 1.1 depicts the seebeck effect in a single conductor. When a temperature gradient is applied, the charge carriers in the hot side (Top/Red) earn higher energy and
diffuse to the cool side (Bottom/Blue) to balance its energy state. In this case, a
quantitative value of the seebeck effect, seebeck coefficient \( S \) is defined as the voltage
difference per the temperature gradient made in the material.

\[
S = \frac{\Delta V}{\Delta T}
\]

(1)

Furthermore, a lot of efforts to reveal the transport phenomena that decides the
seebeck coefficient have been studied and the quantitative characterization for the
thermoelectric power has been firstly suggested by Mott’s formula [82],

\[
S = \frac{\pi^2}{3} \left( \frac{k_B^2 T}{e} \right) \left( \frac{d \ln \sigma(E)}{d E} \right)
\]

(2)

According to (2), it is a function of temperature and a logarithmic derivative of conductivity
when the fermi level is equal to \( E \). Applying the equation, extensive studies further simplified
the seebeck coefficient for metals and semiconductors with high carrier concentration to
explain a relationship between seebeck coefficient and carrier concentration which is closely
related to electrical conductivity [83]:

\[
S = \left[ \frac{2\pi^2 k_B^2 T m_d^*}{3^3 e \hbar} \right] \cdot \left( r + \frac{3}{2} \right)
\]

(3)

For low carrier concentration semiconductor, the equation can be written [83]:

\[
S = \frac{k_B}{e} \left\{ \left( r + \frac{5}{2} \right) + \ln \left[ \frac{2(2\pi m_d^* k_B T)^{3} \hbar}{e n h} \right] \right\}
\]

(4)

The efforts to explain the factors that affect the seebeck coefficient has shed light on
the inverse proportionality between the seebeck coefficient and electrical conductivity which
has been a major challenge in the thermoelectric field [84].
In addition, the seebeck coefficient provides information of the type of major carriers of semiconductor materials since different charge carriers generate voltage difference opposite directions. Therefore, by acquiring seebeck coefficient, a sign of the major and minor charge carriers can be readily observed.

1.5 Conduction Switching Behavior and Its Potential Applications

Since a feasibility of phase change memory device in 1960s has discussed [85, 86], phase change materials consisting of the devices have attracted a lot of attentions as those semiconductor materials reversibly switch their crystal structure to either amorphous or the other crystalline by being triggered by external sources, typically joule heating. Also, ideal candidates are chalcogenides due to electrical contrast, high crystallization temperature and rapid crystallization [87]. The two most developed phase change materials are Ge$_2$Sb$_2$Te$_5$ and GeTe/Sb$_2$Te$_3$ which have shown repeatedly applicable crystallization time [88].

Apart from the developed materials, silver and copper based chalcogenides materials also have considered as possible candidates because of their multiple and controllable phases [21, 33, 37, 89-92] While those materials experience Additionally, the phase change in some specific silver based chalcogenides compounds caused a fascinating p-n-p conduction switching behavior, which means that at different temperature ranges, the type of major carriers (either holes or electrons) and the direction of current flow can be adjustable.

Ag$_{16}$Te$_4$Br$_3$, the firstly found p-n-p conduction switching material, was reported to show the behavior at 380K due to 4 different polymorphs [93]. As the temperature increases, the significant transition in the atomic structure gives rise to the change in dimensional arrangement and causes structural disorder. AgBiSe$_2$, dimetal chalcogenides, also showed p-n-p switching behavior [94]. AgBiSe$_2$, originally p-type, was switched to n-type at 560K,
and returned to p-type at 610K. This behavior was due to its crystalline transition (hexagonal – rhombohedral – cubic) that occurs due to the rise in temperature. AgCuS, a ternary metal chalcogenide, also experiences phase transition from orthorhombic to hexagonal and to cubic [95]. It was revealed that a semi-metallic intermediate state can derive the phase transition, resulting in the conduction switching.

The p-n conduction switching phenomena of bulk phase synthesized iron chalcogenides, FeTe$_2$, FeSe$_2$ FeS$_2$, was firstly found by Harada in 1996 [96] and thereafter solvothermal synthesized FeSe$_2$ also showed a similar p-n conduction switching behavior [97]. Differentiated from that the silver chalcogenides family shows a sudden change in seebeck coefficient, the iron chalcogenides’ seebeck coefficient changes continuously and gradually, which means that their conduction switching region is wider than the other materials and it could benefit to the semiconductor diode and transistor application.
CHAPTER 2

SOLUTION SYNTHESIS OF IRON DITELLURIDE NANOWIRES AND ITS P-N CONDUCTION SWITCHING BEHAVIOR

2.1 Introduction

Iron is the forth abundant element in earth crust followed by oxygen, silicon and aluminum and this has held scientists’ attention to iron chalcogenides. Previously, their attentions have focused on the utilization of magnetic property [98-101], superconductivity [102-104], and photovoltaic (especially pyrite FeS₂) [105,106].

While the stoichiometric iron telluride, FeTe, has been attractive in the superconductor field, semiconductor non-stoichiometric marcasite (frohbergite) phase iron ditelluride (FeTe₂ and FeSe₂) was firstly suggested by Pischel [107] and Dudkin [108]. Theoretically, FeTe₂ FeSe₂ have two different phases, the marcasite and pyrite (like FeS₂). However, the pyrite phase has never been found naturally, but was once synthesized in an extremely high pressure (65kbar) and temperature (1200°C) [109]. Both marcasite and pyrite phase FeTe₂ are expected to have a relatively narrow band gap, 0.328eV and 0.432eV respectively compared to those of FeSe₂, 1.234eV and 0.694eV also respectively [110]. The narrow bandgap could mean a great potential for thermoelectric application since lead telluride which is believed as one of the most developed thermoelectric materials has a similar bandgap 0.32eV [111]. Currently, a bulk synthesized marcasite FeTe₂ was achieved by using pure Fe (≥ 99.999%)and Te (≥ 99.999%) powders at 700°C [112] and 650°C [96] and the thermoelectric performance was not significantly notable [112]. However, interestingly, an unusual behavior in seebeck coefficient of FeTe₂ was firstly found in
Harada’s research [96] as mentioned in the previous section and it left a possibility of direct semiconductor application of FeTe$_2$.

Nanostructured marcasite FeTe$_2$ have been synthesized by different research groups and the hydrothermal method was mostly chosen. One dimensional FeTe$_2$ nanorods complex was prepared in a range from 120°C to 170°C for 12 to 24 hours and EDTA aqueous solution was used to prevent the oxidation of iron ions [113]. Similarly, two dimensional nanocrystalline FeTe$_2$ was achieved at 140°C for 12 hours [114]. A nanosheet of FeTe and FeTe$_2$ was synthesized by differing the initial precursor ratio of tellurium and iron and the reaction was conducted at 290°C [115]. Hot injection method, which has been widely used for quantum dot synthesis [116], was firstly utilized recently by Ebin and coworkers [117]. The highest yield of FeTe$_2$ nanocrystal was given at 300°C. Besides, FeTe nanorod was formed at 60°C for 20 mins, assisted with hexadecyltrimethylammonium bromide (CTAB) as a {110} facet binder and a stabilizer [118]. However, thin and long nanowires of FeTe$_2$ has not been discussed yet. In addition to other intriguing properties, long nanowires can be a great advantage in building nano-sized device [119]. Also, the previous methods have proven some controllable nanostructures only in small-scale reaction and the most of synthesis have involved complex reactions, extreme synthesis temperature.

Herein, two dimensional FeTe$_2$ nanowire complex was synthesized in the mild-temperature solution based system and further successfully optimized for a large-scale synthesis which could be feasible for mass-production. The FeTe$_2$ nanowire synthesis was completed by two steps reaction: 1) ultrathin Te nanowires synthesis [120] and 2) FeTe$_2$ nanowire complex synthesis. Thereafter, the as-synthesized FeTe$_2$ nanowires sample was prepared by drop casting method and characterized by XRD and TEM. In addition to the
morphological analysis, the FeTe$_2$ solution was further fabricated to bulk disks by using spark plasma sintering. The sintered FeTe$_2$ sample showed p-n conduction switching behavior at around 220°C according to the seebeck coefficient measurement. In order to use this interesting behavior, a pilot study of a thermally controllable p-n junction diode was conducted and showed a limited diode performance.

2.2 Synthesis and Characterization Methods

2.2.1 Materials

Tellurium dioxide (TeO$_2$, ≥99%), Polyvinylpyrrolidone (PVP, Molecular Weight ~40,000), Potassium Hydroxide (KOH, 90%), hydrazine (N$_2$H$_4$, ~99%), hydrazine monohydrate (N$_2$H$_4$•H$_2$O,78%~82%), and Iron (III) chloride (FeCl$_3$, ≥97%) were purchased from Sigma Aldrich. Ethylene glycol (EG, ≥99%) and Reagent alcohol (EtOH, ≥99%) were purchased from VWR. All chemicals were used as received without any further purification.

2.2.2 Preparation of small-scale one-pot synthesis of FeTe$_2$ nanowire

Te nanowire is firstly synthesized in a small batch reaction by using 50ml three-neck flask. The flask is equipped with a condenser used for continuous nitrogen flow, a k-type thermocouple adaptor and a rubber stopper and then placed in a heating mantle. In the first step of the reaction, 0.344g (2.15mmol) of TeO$_2$ and 0.975g of KOH are dissolved in 30ml of EG until the solution becomes transparent. Then, the temperature is increased to 70°C and 1.075g of PVP is added into the solution. The solution is further refluxed with vigorous stirring until the PVP is dissolved completely, changing the color of solution from transparent to golden yellow. The temperature is further increased to 95°C and the batch is purged with N$_2$ gas for enough time, then the 1.5ml N$_2$H$_4$ is quickly injected to the solution,
which involves a dramatic color change to dark navy. At last, the final temperature is set to 100°C and the reaction undergoes a continuous stirring for 1 hour.

FeTe₂ nanowire complex synthesis is directly followed without a purification or separation of the completed Te reaction. 0.349 g (2.15 mmol) of FeCl₃ is dissolved in 5 ml of EG at 80°C until the solution becomes brown color. The addition 1.5 ml of N₂H₄ is added dropwise to the FeCl₃ solution and the solution becomes a white slurry solution. As soon as it turned to be white, it is injected quickly to the Te nanowire solution at 100°C. The temperature is increased to 120°C and reacted for 4 hours.

2.2.3 Preparation of large-scale synthesis of FeTe₂ nanowire

For the large-scale synthesis, 1L three neck reactor is used with same components as the small-scale reaction. The materials used for the previous synthesis are modified to the large scale: 5.154 g (32.25 mmol) of TeO₂, 5.240 g (32.25 mmol) of FeCl₃, 14.625 g of KOH, 9.0 g of PVP, 450 ml and 70 ml of EG for the Te and FeTe₂ nanowire growth respectively, and 5.5 ml and 30 ml of N₂H₄ for the Te and FeTe₂. The overall procedure is also similar, but the temperatures to inject the hydrazine and to conduct the Te nanowire growth are adjusted to 100°C and 110°C. When the reaction is done, the mixture cool down to near room temperature and the final product is stored in 1L glass container.

2.2.4 FeTe₂ nanowire disk preparation

The as-synthesized solution removes surface-ligands and other impurities by washing for three days with DI water, reagent alcohol and hydrazine hydrate. In the first day, 25 ml of the mixture is moved to a 50 ml centrifuge bottle and 12 of the bottles are prepared. Each bottle is filled up with DI water to 45 ml (Addition of 20 ml DI water) and shaken for 3 minutes with a fixed speed vortex shaker to ensure homogeneous mixing between the DI
water and the solvent, ethylene glycol. The total 12 bottles are centrifuged for 2 hours and clear colored supernatant is removed after the round. The sediments in each bottle is evenly dispersed in the 40ml of DI water one more time and centrifuged for 2 hours again. For the final run, the sediment is dispersed in 40ml of reagent alcohol with mild sonication for uniform dispersion. After another 2 hours of centrifugation, the washed sediments are collected in 600ml glass beaker and reagent alcohol fills up the beaker to 300ml. For effective ligand removal, 50ml of N$_2$H$_4$·H$_2$O is added. The ratio of the reagent alcohol to the hydrazine monohydrate is maintained between 5:1 and 10:1. The final mixture is processed for overnight. For the next day, the washed sediment is collected in the centrifuged bottles and repeated 3 times of centrifugation for 2 hours in each round. Again, the final sediment is washed over night in the reagent alcohol and hydrazine with same ratio and this procedure is repeated for one more overnight to achieve a higher purity of the final product.

The sediments are dried in vacuum chamber for, at least, 24 hours at room temperature. The completely dried sediments are later transferred to a nitrogen filled glove box to prevent further oxidation of iron. Then, the grinding of the sediments are conducted with a mortar and pestle and stored in a 20ml glass vial.

The spark plasma sintering is used to consolidate the collected FeTe$_2$ powder. Based on purposes, 10mm and 15mm internal diameter graphite dies and punches (all the parts have 30mm height). In the glove box, ~1.2g and ~2.5g of powders, for 10mm and 15mm diameter disks, respectively, are pressed by hands and further pressurized by hydraulic press to minimize exposure of the pressed powder. The sintering is completed at 600°C for 3 mins and 40MPa of continuous pressure. Cracking on the disks are often caused by internally generated gas from evaporation of impurity, thus, is limited as releasing all uniaxial pressure
immediately after the sintering process until it cools down to near room temperature. The thickness of sintered disks varies from 1.0mm to 1.5mm. The disk is cut to bar-shape to make disk into I-V curve measurement device, then soldered with two copper or silver electric wires on the two ends of disk.

2.2.5 Characterization methods

The X-ray diffraction (XRD) study is performed by using Rigaku Ultima IV and operated at 44kV and 40mA using Cu-Kα radiation. The sample for XRD is fabricated by drop casting method. The As-synthesized solution of each step is washed with DI water and reagent alcohol to minimize the interruption from the amorphous materials and the small amount of materials is dispersed uniformly in 5ml of reagent alcohol. Then, the mixture is drop-casted on a 25mm x 75mm slide glass. Temperature controlled XRD used to examine the SPSed sample and is done by Panalytical X'Pert Pro equipped with Anton Paar HTK1200N furnace and Co-Kα radiation is used.

Transmission Electron Microscopy (TEM) imaging was performed by JEOL 2100 TEM, using an acceleration voltage of 200kV. Similar to the XRD sample preparation, the aliquots taken from each step are also washed and dispersed in a 5ml of reagent alcohol. The dilute solution is dropped on TEM grid and dried completely.

After the SPS process, the sintered disk is characterized with LSR-3 system for seebeck coefficient measurement. The operation chamber is filled with helium gas, was controlled by off-axis 4-points geometry. The temperature deviation between the top and the bottom is maintained at 50°C and the data point is obtained at every 25°C.
2.3 Result and Discussion

2.3.1 Morphological analysis and reaction mechanism

Figure 2.1 XRD patterns of as-synthesized products. (a) Ultrathin Te nanowire. (b) The solid blue lines are reference peaks of Te (JCPDS PDF no. 36-1452) and the solid red lines are reference peaks of FeTe\textsubscript{2} (JCPDS PDF no. 14-0419)

Figure 2.2 FeTe\textsubscript{2} nanowire diameter distribution

According to the XRD data of the signals of both Te and FeTe\textsubscript{2} nanowire highly correspond to the reference peaks (Te, JCPDS no. 36-1452 and FeTe\textsubscript{2} JCPDS no. 14-0419)
Calculated lattice parameters of FeTe$_2$ nanowire are $a \sim 5.29\text{Å}$, $b \sim 6.27\text{Å}$ and $c \sim 3.86\text{Å}$ which are highly identical to the reference cell parameters. Although various nanostructures of FeTe$_2$ are found depending on synthesis conditions the XRD resulted in same.

Figure 2.3 the as-synthesized TEM images. a) Te nanowires, b) high magnification image of a single ultrathin Te nanowire, c) FeTe$_2$ nanowire complex, and d) high magnification image of single FeTe$_2$ nanowire.

TEM images suggest the uniformly grown Te and FeTe$_2$ nanowire. In the figure 2.3 (a), the Te nanowire has longer than the length of 1μm and have the diameter of 6 ± 2 nm. The Te nanowire grows one-dimensionally by the following reaction mechanism.

$$\text{TeO}_2 + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{TeO}_3^{2-}$$ (5)
\[ \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \]  
(6)

\[ 4\text{e}^- + 3\text{H}_2\text{O} + 3\text{TeO}_2^{2-} \rightarrow 6\text{OH}^- + \text{Te} \]  
(7)

The FeTe\textsubscript{2} nanowire forms a complex with a relatively larger distribution of diameters. Both the average diameter and distribution FeTe\textsubscript{2} nanowire is relatively larger than Te nanowire, 26 ± 6 nm, as shown in figure 2.2. Unlike Te nuclei stacks in one direction [121], FeTe\textsubscript{2} seeds tend to form a small nanoflake then the flakes are conjugated into wires later. The reaction scheme for the FeTe\textsubscript{2} nanowire growth is depicted in the figure 2.3.

![Figure 2.4 FeTe\textsubscript{2} nanowire synthesis reaction scheme.](image-url)

One important factor to achieve FeTe\textsubscript{2} nanowires is the additional amount of hydrazine injected to the iron (III) ion dissolved in ethylene glycol to form hydrazine – iron complex.
(II) ion complex. The transition metal – hydrazine complex has been suggested previously and it was reported that the metal ion complex is reduced easily under base condition [122, 123].

As described in the figure 2.4, the iron chloride solution in ethylene glycol appears as brown color, which means the formation of iron (III) ions dissolved in ethylene glycol by the following reaction.

$$2\text{Fe}^{3+} + 3\text{C}_2\text{H}_6\text{O}_2 \rightarrow 2\text{Fe}[\text{C}_2\text{H}_6\text{O}_2]_{3}^{3+}$$ \hspace{1cm} (8)

Then, as soon as the hydrazine is injected to the iron chloride solution, it is seen that the color of solution rapidly changes to pale green color, which indicates the reduction of Fe$^{3+}$ complex ions to Fe$^{2+}$ complex ion by the following reactions.

$$2\text{Fe}[\text{C}_2\text{H}_6\text{O}_2]_{3}^{3+} + \text{N}_2\text{H}_4 \rightarrow 2\text{Fe}[\text{C}_2\text{H}_6\text{O}_2]_{3}^{2+} + 2\text{H}^+ + 2\text{N}_2\text{H}_2$$ \hspace{1cm} (9)

$$2\text{Fe}[\text{C}_2\text{H}_6\text{O}_2]_{3}^{3+} + \text{N}_2\text{H}_2 \rightarrow 2\text{Fe}[\text{C}_2\text{H}_6\text{O}_2]_{3}^{2+} + 2\text{H}^+ + 2\text{N}_2(g)$$ \hspace{1cm} (10)

In an extremely short time later, even before the injection of hydrazine is done, the hydrazine turns the solution into a slurry white solution, which means that the Fe$^{2+}$-hydrazine complex is formed as described below.

$$\text{Fe}[\text{C}_2\text{H}_6\text{O}_2]_{3}^{2+} + 6\text{N}_2\text{H}_4 \rightarrow 2\text{Fe}[\text{N}_2\text{H}_4]_{6}^{2+} + 3\text{C}_2\text{H}_6\text{O}_2$$ \hspace{1cm} (11)

After this step, the injection of the Fe$^{2+}$ - N$_2$H$_4$ complex is reacted with the Te nanowire solution. It has been known that the presence of hydroxides ions (OH$^-$) accelerates the formation of metal ions [124,125]. Therefore, here, the Te nanowire solution that contains surplus number of hydroxides ions at the end of reaction is used without any purification steps. The mixture undergoes the following reaction mechanism, resulting in the FeTe$_2$ nanowire complex.
2.3.2 Reaction optimization

There are many factors that determine the nanostructures in solution synthesis such as temperature, solvents, reactants, surfactants. Besides, it was continuously observed that the morphology of FeTe₂ is especially sensitive to the usage of hydrazine, the reducing agent. Therefore, in the given system, the optimization of hydrazine effect has been considered as a key to achieve nanowire structure.

Figure 2.5 describes how the additional hydrazine used to affects the morphology. As mentioned in the reaction mechanism, the additionally added hydrazine into the iron

\[
2\text{Fe}[\text{N}_2\text{H}_4]_6^{2+} + 2\text{OH}^- \rightarrow \text{Fe} + 5\text{N}_2\text{H}_4 + \text{N}_2(\text{g}) + \text{H}_2(\text{g}) \quad (12)
\]

\[
\text{Fe} + 2\text{Te} \rightarrow \text{FeTe}_2 \quad (13)
\]

Figure 2.5 (a) is FeTe₂ with no additional hydrazine and (b) is FeTe₂ nanowire with additional hydrazine.
precursor prohibits the randomly-oriented ripening of FeTe₂, providing faster growth at the same time.

Secondly, the effect of formation of Fe₂⁺-N₂H₄ complex to the overall structure was examined by adding the additional hydrazine separately, not making the complex first. In the figure 2.6 (b), the separate injection causes rapid ripening of FeTe₂ nanoflake instead of nanowire. It supports that the Fe²⁺-N₂H₄ complex aligns the FeTe₂ seeds in one direction. In addition, it also could be understood by the fact that, in figure 2.6 (b), the Fe²⁺ ions which are firstly introduced readily react with the OH⁻ ions existing in the Te solution to form iron hydroxide, Fe(OH)₂. Referring to the standard potential of of Fe(OH)₂ (Fe(OH)₂(s) + 2 e⁻ → Fe(s) + 2 OH⁻(aq), -0.877V), it is more difficult to be reduced than that of Fe²⁺ (Fe²⁺(aq) + 2 e⁻ → Fe(s), -0.49V). Therefore, the one-dimensional ripening is rather diminished when Fe(OH)₂ is existing first.
Thirdly, it is also shed light on that the amount of hydrazine should be very carefully chosen as described in the figure 2.7. A hypothesis based on the previous observations is that there can be two different forces to the FeTe\(_2\) growth, the first is to make FeTe\(_2\) seeds conjugated into flakes, and the second is to bind the seeds then grow them into 1-D structure. Therefore, the structure could be adjusted by the amount of hydrazine used to form the Fe\(^{2+}\)-N\(_2\)H\(_4\) complex since it affects the conjugation rate of seeds when only 1/5 of the original amount of hydrazine, (a), the rate of formation of FeTe\(_2\) nuclei becomes hugely slow, which fails to initiate the uniaxial arraying. On the other hand, how the excessive amount of hydrazine affects is shown in (c). Too much of hydrazine accelerates ripening to all directions, resulting in irregular shapes and the thickness is at least doubled (~55nm).
Lastly and interestingly, figure 2.8 shows that how the time for formation of Fe$^{2+}$-N$_2$H$_4$ gives an influence to the structure. Even though the color change from brown to white happens in a few seconds and stay white until it is added, the longer is the reaction, the thinner and straighter wires are formed. It could be affected by the oxidation by the air, producing Fe(OH)$_2$ in the solution slowly. As addressed before, the presence of Fe(OH)$_2$ can interrupt the uniaxial growth of FeTe$_2$. Thus, the flakes shapes seem to connect to nanowires but the borders between flakes are more obvious, meaning that the 1-D growth is disrupted, whereas, ripening of FeTe$_2$ seed is more favored.

Moreover, the reaction condition is more adjusted at different reaction temperature. Reaction temperature is a primary factor that decides how fast the reaction is ended and which direction the reaction proceeds to. The reaction was remarkably successful only at 120°C and other reaction temperatures such as 110°C, 130°C, 140°C were examined and the morphology at difference temperature is summed in figure 2.9.
When the FeTe$_2$ synthesis is conducted at 110°C, it seems that the Fe$^{2+}$-N$_2$H$_4$ complex binds the conjugated FeTe$_2$ seeds, but insufficient temperature causes the incompleation of the growth of seeds, which produces irregularly oriented nanowires as well as the non-uniform thickness of each wire. On the contrary, the result from the synthesis conducted at 130°C and 140°C shows the unnecessarily high temperature could trigger rapid ripening of FeTe$_2$ seeds into randomly-shaped flakes and later they rather stack in more than one direction.

Figure 2.9 FeTe$_2$ synthesis conducted at (a) 110°C, (b) 120°C, (c) 130°C and (d) 140°C
In conclusion, it was suggested that there are two competitive reaction tendencies in FeTe$_2$ nanowire growth, conjugation of seeds into nanoflakes and stacking of growing flakes into nanowires, and they can be controlled by the usage of hydrazine (Fe$^{2+}$-N$_2$H$_4$ complex) and the reaction temperature. Therefore, as the reaction scheme of FeTe$_2$ nanowire can be summarized as described in figure 2.10, the Te nanowires grown in the first step meets the Fe$^{2+}$-N$_2$H$_4$ complex then form FeTe$_2$ seeds. In the optimized condition, the seeds are driven to grow into nanowires rather than 2-D nanoflakes.

2.3.3 p-n conduction switching behavior of FeTe$_2$

Semiconductor properties (Seebeck coefficient and electrical conductivity) of FeTe$_2$ sintered disk are evaluated by Linseis LSR-3 system simultaneously. As shown in the figure 2.11, the seebeck coefficient starts from a positive value at 45μV/k at room temperature then gradually decreases to -45μV/K at 360°C. The p-type region ends at around 200°C and enters the electrons-dominating region reversibly. The measured seebeck coefficient behaves
similar as the previously reported data of bulk-synthesized FeTe$_2$ [96], but three discrepancies in the p-n conduction switching temperature (97°C), the magnitude of seebeck coefficient (150uV/K ~ -80uV/K) and electrical conductivity (~ 100000S/m at 300°C). The electrical conductivity of FeTe$_2$ nanowires exponentially increases until the value is 4 times larger at 360°C then at the room temperature. Meanwhile, it is significantly lower than the conductivity in bulk synthesized material [96]. This comes from the decrease in mean free path of charge carriers in nanomaterials than bulk materials and the movement of scattered carriers are fairly limited at grain boundaries that greatly exist in nanoscale structure [126]. Combining the two factors, the surge in electron contribution to the system may drive the conduction switching behavior. Even though the reason for the p-n conduction switching behavior has been unclear, a similar phenomenon was observed with iron selenide (FeSe$_2$) and it was suggested that unavoidable selenium vacancies during its synthesis procedure

Figure 2.11 Seebeck coefficient and Electrical conductivity of a sintered FeTe$_2$ nanowire disk
were doped [97]. The doped vacancies reconstruct band structures, switching the materials to be more n-type. In addition to the vacancy doping, thermally decomposed tellurium, an n-type dopant originally consisting of FeTe$_2$ might change its electronic structure to be more favorable condition that electrons can be more excited by thermal energy. According to figure 2.12 (a), the tellurium peaks in XRD which are not present in as-synthesized XRD sample are found in the bulk sintered sample and they even become larger along the increase of temperature, whereas, the size FeTe$_2$ peaks remains same. The general trend in the shifted reflections (figure 2.12 (b) and (c)) to the lower degree is ascribed to two reasons, a

![Figure 2.12 FeTe$_2$ XRD analysis at different temperature](image)

Figure 2.12 FeTe$_2$ XRD analysis at different temperature (a) XRD data of unintentionally Te-doped FeTe$_2$ from 20° to 80°, a specific reflection plot of (a), (1 0 1) plane of Te and (b), (1 1 1) plane of FeTe$_2$ as a function of temperature
stoichiometric change in compounds [127] and thermal expansion of crystalline [128]. It is difficult to differentiate which factor determines the trend, but both effects can influence the transition behavior.

The original band structure can be expected as an intrinsic semiconductor from the seebeck and electrical conductivity behavior. Therefore, a sensitive change in band structure by the unexpected Te doping might cause a shift of fermi level closer to conduction band, which generate a larger number of electrons that can be easily excited by thermal energy.

Figure 2.13 illustrates the increase in lattice parameters in all directions, which leads the overall cell volume expansion and that in a-axis is more noticeable. In addition, it is found that the slope becomes larger as temperature increases especially around the conduction switching point (Table 2.1) and the expansion behavior somewhat resembles the behavior of electrical conductivity. The cell expansion of nanocrystal materials is induced by
defects in the grain boundaries from releasing stress between atoms [129]. Thus, the thermally freed electrons which were originally present in FeTe$_2$ are generated as the equation (10) continues upon temperature increase. Therefore, despite insufficient capability of XRD in quantitative analysis, the growth of tellurium peaks in both size and the shift of FeTe$_2$ could explain that the applied thermal energy instantly leads a separation of Te from FeTe$_2$, following the equation below.

FeTe$_2$↔FeTe$_{2-x}$ +xTe  \hspace{1cm} (14)

Table 2.1 Change in lattice parameters per temperature at four different temperature ranges.

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>a (10$^{-2}$ Å/°C)</th>
<th>b (10$^{-2}$ Å/°C)</th>
<th>c (10$^{-2}$ Å/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21°C – 150°C</td>
<td>0.85</td>
<td>0.70</td>
<td>0.37</td>
</tr>
<tr>
<td>150°C – 200°C</td>
<td>1.16</td>
<td>0.84</td>
<td>0.47</td>
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<td>1.08</td>
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</tr>
<tr>
<td>250°C – 300°C</td>
<td>2.44</td>
<td>1.40</td>
<td>0.73</td>
</tr>
</tbody>
</table>

2.3.4 Application of p-n conduction switching behavior of FeTe$_2$

Doping is a common technique that has been widely used to alter intrinsic semiconductors’ electrical property and it is often completed by introducing impurities in the material directly, where a reconstruction in charge carriers’ energy level is involved. For the reasons, the type of semiconductors is determined by the major charge carriers that are dominantly present in the material, which is normally regarded unchangable.
P-n junction Semiconductor diode, one of the widely commercialized semiconductor applications, is comprised of contacts of different types of heavily doped semiconductor, where a flow of electric current can be controlled upon a voltage applied to the system. In opposed to the need of two different conduction types, the p-n conduction switching materials can be anticipated to possess the current regulating performance, which is theoretically achievable by applying a significant temperature gradient at two ends of a bulk sample. As shown in figure 2.14 (a) – (d), the sintered disk which has a diameter of 15mm and a thickness of ~1.7mm is precisely cut into a bar shape by using a slow chain saw and two silver electric wires are welded on the two ends of sample with a high temperature endurable silver paste. Then, the sample was placed with a physical contact of a water cooler
at the top and a hot plate at the bottom to adjust thermal energy flowing in. The scope of application is depicted in figure 2.14 (e). As heat is gradually applied by the hotplate, the sample stays in p-type. However, once the hot side of sample reaches to a temperature where the material shows n-type and remains the other side cool enough (p-type), a p-n junction appears in the middle of sample. Thereafter, when the entire region is heated over the transition temperature, the conduction type enters electron dominating region. The significance of idea is that the diode behavior can be reversibly controlled by thermal energy.

Figure 2.15 I-V curve measurement at various temperature. The sample had 190°C as a conduction switching temperature. “HOT” and “COLD” indicate the temperature readings of hot and cold side respectively when the voltage was swept

Figure 2.15 shows a preliminary result of I-V curve measurement. As hypothesized, When the entire sample is maintained below and above the conduction switching temperature(red, orange, yellow, green, sky blue and purple color), ohmic behaviors are observed. The resistance of FeTe₂ resulted in being inversely proportional to temperature,
which matches the increasing electrical conductivity upon temperature. When the
temperature of sample is kept at the switching region (Navy), a limited diode behavior is
observed. A reverse bias region is stretched until -0.55V, then a breakdown of diode occurs,
whereas, no remarkable threshold voltage is observed in the forward bias region. The main
reason that a p-n junction can limit an electrical current is a depletion region where no
significant amount of charge carriers are present due to ionised impurities that make difficult
for carriers to diffuse to the other side. However, it seems that the performance of
homogeneous FeTe$_2$ diode is not exactly prominent as an ideal diode. It is probably because
of a very small depletion region is created because the gradual conduction switching
produces a vague border between p-type and n-type. In order to optimize this measurement,
FeTe$_2$ itself can be further fabricated to have a larger depletion region which probably require
more abrupt conduction switching or more dramatic temperature difference applied on the
sample. Also a single nanowire of FeTe$_2$ can be made into a nano-device by lithography to
minimize unwanted influences such as oxidation of materials and unexpected impurities.

Figure 2.16 (a) XRD pattern of FeTe$_2$ when initial ratio of FeCl$_3$ to TeO$_2$ is 1:1 (Red) and 1:2
(Blue). (b) Seebeck coefficient when that is 1:1 (Red) and 1:2 (Blue)
Moreover, a tunable conduction switching temperature would be beneficial for FeTe₂ to be applicable in this field. One simple approach to achieve this was conducted by varying initial ratio of FeCl₃, the iron precursor to TeO₂, the tellurium precursor. Other than the iron-rich ratio (1:1 ratio), another precursor ratio based on the stoichiometry of FeTe₂ (1:2 ratio) shows pure FeTe₂ phase as shown in figure 2.16 (a). However, a difference in seebeck coefficient is observed as illustrated in figure 2.16 (b), where the switching temperature of the ratio 1:1 is ~190°C and the 1:2 ratio is ~220°C and it means that the overall behavior of 1:2 ratio is shifted to p-type. It could be attributed to that the 1:1 ratio synthesis produces iron-rich phase due to the excessive iron precursor amount, then make the system more electron-rich state hence the 1:2 ratio holds a relatively electron-deficient state. This unintentional doping can be expected to utilize to tune the conduction switching temperature which would benefit for future application.

In conclusion, FeTe₂ 1-D nanowires complex is achieved by a facile solution synthesis. It was discovered that the hydrazine plays an significantly important role in binding nanoflakes into nanowires and the usage of hydrazine is optimized by many factors that determine the nanostructure. Moreover, the synthesis method is successfully scaled-up in a large size reactor which will benefit to future researches.

The solution phase sample is further processed to powders and SPS is used to dense the powders, keeping nanostructures at best. The seebeck coefficient and electrical conductivity of SPSed sample exhibit the p-n conduction switching behavior at around 200°C and it is suggested that the unexpected a generation of Te vacancies and Te separations from structure could involve a reconconstruction of band structure and also the cell expansion upon the increase in temperature can give rise to a substantial amount of electrons.
Finally, the initial study of a diode application of FeTe$_2$ is proposed. Theoretically, an internally made p-n junction in FeTe$_2$ can be controlled by heat and a trial to prove the behavior is done by I-V curve measurement. A small current flow is contrained in forward bias region at a p-n switching temperature range, but still an argument is left in the reverse bias region.
CHAPTER 3

SOLUTION SYNTHESIS OF NICKEL TELLURIDE NANOPARTICLE AND COBALT TELLURIDE NANOROD

3.1 Introduction

The two earth-abundant metals, nickel (Ni) and cobalt (Co) that are found in earth’s crust as much as copper have been used in various industries such as paint, magnet, coins, etc. Semiconductor materials, nickel and cobalt chalcogenides have also been intriguing scientists’ attention due to their magnetics property and high electrical performance [130-134]. In thermoelectric studies, the earth-abundant metals doping has been widely used to modify electrical performance to achieve higher thermoelectric performance [135-139] and it has been importantly studied that doping condition and dopant selection would significantly affect to the overall performance [140]. Also since an energy filtering effect which is an energy barrier that optimizes seebeck effect of thermoelectric materials was addressed [141], a use of NiTe nanoinclusions for the filtering effect was adapted to acquire a higher electrical conductivity without a loss of seebeck coefficient by Sumithra et al [142]. In addition, pseudo binary system between PbTe and CoSe$_2$ was examined by varying the CoSe$_2$ amount and found that a proper amount of CoSe$_2$ can enhance the conventional thermoelectric system [143]. Furthermore, the magnetic property of the semiconductors also potentially benefits the current thermoelectric technology. Recently, it was reported that the ferromagnetic BaFe$_{12}$O$_{19}$ nanocomposite doped thermoelectric materials can confine carriers’ movement by the electron-magnon interaction, resulting in enhanced thermoelectric performance [144].
Synthesis of nickel and cobalt telluride have been accomplished mainly by solvothermal method. By using hydrothermal methods, the hexagonal phase NiTe$_2$ nanorod was synthesized at 160ºC for 10 hours and 180ºC for 15 hours in one step [145] and 2-D NiTe$_2$ nanoplate is also made at 210ºC for 48 hours [146]. The other common stoichiometric nickel telluride, NiTe (also hexagonal phase), was synthesized. NiTe as well as CoTe were grown in 2-D nanocluster wires by using coreduction method with hydrazine hydrate (N$_2$H$_4$-H$_2$O). The hydrothermal method was used and the reaction condition was 140ºC for 5 hours [147]. Also, controllable stoichiometric NiTe$_x$ ($x = 1.00, 1.15, 1.33, 1.60, 1.80, 2$) synthesized for 20 hours and 180ºC was found by simply differing precursors and also paramagnetism of those compounds were investigated [130].

Moreover, a hexagonal phase CoTe has been also shown different morphologies in solvothermal synthesis, especially hydrothermal system. 2-D nanowires and nanotubes were achieved with various surfactant choices at 200ºC for 24hours [148]. CoTe and CoTe$_2$ (orthorhombic phase) were acquired by different stoichiometric ratio of initial precursors at 140ºC for 24hours [149]. A saw-like and nanorod CoTe$_2$ nanostructure were obtained by examining the role of PVP in the synthesis condition and the reaction was conducted at 200ºC for 12 hours. Except for the DI water based system, ethylenediamine was once used for solvothermal synthesis of CoTe$_2$ nanorod and the reaction condition was optimized at 160ºC for 10 hours. As reviewed so far, most of the cobalt and nickel telluride have been produced in solvothermal method with an autoclave, not only yielding small amount of materials, but also requiring a great amount of time of reactions.

Herein, zero-dimensional NiTe nanoparticle and one-dimensional CoTe nanorod were synthesized by using the ethylene glycol based solution method. Both reactions were
conducted in a large reactor system (1L) and CoTe synthesis, especially, was completed in extremely short reaction time (~5mins). The crystal structures were examined by XRD and TEM, then spark plasma sintered bulk disk was further used for electrical conductivity and seebeck coefficient measurement, which helped to discover semi-metallic behavior of NiTe and CoTe.

3.2 Synthesis and Characterization Methods

3.2.1 Materials

Sodium Tellurite (Na₂TeO₃, ≥99%), Polyvinylpyrrolidone (PVP, Molecular Weight ~40,000), hydrazine (N₂H₄, ~98%), hydrazine monohydrate (N₂H₄•H₂O, 78%~82%), Nickel (II) chloride (NiCl₂, ≥ 98%) and Cobalt chloride (CoCl₂ ≥ 98%) were purchased from Sigma Aldrich. Ethylene glycol (EG, ≥99%) and Reagent alcohol (EtOH, ≥99%) were purchased from VWR. All chemicals were used as received without any further purification.

3.2.2 Preparation of nickel telluride (NiTe) nanoparticle

NiTe nanoparticle synthesis is done in one step and conducted in a 1L large reactor scale. First, 3.89g of NiCl₂ (30mmol) is dissolved in 450ml of EG and the temperature of solution is increased to 70°C. The color of solution becomes light green. After the temperature reaches, 9.0g of PVP is added and completely dissolved. Then, 3.89g of NaTeO₃ (30mmol) is added. The solution color stays in green and the solution is heated to 100°C. The solution is stirred for one hour to mix precursors uniformly and 30ml of N₂H₄ is quickly injected to the solution by using a syringe. The color immediately changes to black, forming NiTe nanoparticles, and bubbles continuously come out on the surface for a few minutes. Lastly, the temperature is set to 150°C and the reaction goes for 5hours.
3.2.3 Preparation of cobalt telluride (CoTe) nanorods

CoTe nanorods synthesis is also done in one step and the same 1L large batch reactor is used. 3.895g of CoCl$_2$ (30mmol), 9.0g of PVP, 6.66g of NaTeO$_3$ (30mmol) is dissolved completely as same as the NiTe synthesis procedure. When CoCl$_2$ is dissolved the color of solution shows purple and the addition of NaTeO$_3$ changes it to deep dark purple. Then, N$_2$H$_4$ is, this time, injected dropwise and very slowly and the reaction generates gas violently. The reaction is done in just 5 minutes. After the all washing and drying procedure, the yield of both final product (CoTe and NiTe) after grinding is achieved up to 83%. A major source of loss occurs in washing procedure since there is always residual material onto the washing containers such as centrifuge tubes and glass beakers.

Later both of NiTe nanoparticle and CoTe nanorod are treated by same procedure (washing, powder making, disk fabrication and characterization) as described for FeTe$_2$

3.3 Result and Discussion

3.3.1 Morphological analysis and reaction mechanism

![Figure 3.1 XRD pattern of as-synthesized hexagonal (a) CoTe and (b) NiTe. The blue and red bars indicate reference peaks of CoTe (PDF#34-0420) and NiTe (PDF#38-1393) respectively](image)

Figure 3.1 XRD pattern of as-synthesized hexagonal (a) CoTe and (b) NiTe. The blue and red bars indicate reference peaks of CoTe (PDF#34-0420) and NiTe (PDF#38-1393) respectively.
XRD patterns of as-synthesized CoTe and NiTe nanostructures are given in the figure 3.1. Both materials have hexagonal structures with similar lattice parameters, thus the resemblance is observed. A relationship among interplanar spacing (d), miller indices and lattice parameters for the hexagonal structure can be described as the equation below [150].

\[
d_{(hkl)} = \frac{1}{\sqrt{\frac{4}{3} \left( \frac{h^2 + k^2 + hl}{a^2} + \frac{l^2}{c^2} \right)}}
\]

(15)

Table 3.1 compares the calculated and reference cell parameters. The calculated lattice parameter for CoTe indicates the structure of synthesized CoTe is slightly packed in a- and b- axis than the reference value. On the other hand, the calculated data closely fits well to the reference data.

Table 3.1 Lattice parameters of as-synthesized CoTe and NiTe

<table>
<thead>
<tr>
<th></th>
<th>CoTe</th>
<th>NiTe</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Reference</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.86</td>
<td>3.89</td>
</tr>
<tr>
<td>b (Å)</td>
<td>3.86</td>
<td>3.89</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.37</td>
<td>5.37</td>
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The CoTe peaks are relatively broader than NiTe, implying that particle size of CoTe is much smaller than NiTe and low intensity would be due to the interruption of amorphous surfactant trapped with a cluster of CoTe nanorods. These observations can be explained in the following sections.
Unlike the two-step reaction, for example the FeTe$_2$ nanorod synthesis in the previous section, one-pot synthesis greatly simplifies the entire reaction process. Briefly, well-refluxed transition metal ions and tellurium ions are reduced simultaneously reduced by hydrazine by following the react-ion.

$$2\text{CoCl}_2(\text{NiCl}_2) + 2\text{NaTeO}_3 + 3\text{N}_2\text{H}_4 \rightarrow 2\text{Co(Ni)} + 2\text{Te} + 3\text{N}_2 + 4\text{NaCl} + 6\text{H}_2\text{O} \quad (16)$$

$$\text{Co(Ni)} + \text{Te} \rightarrow \text{CoTe (NiTe)} \quad (17)$$

Upon the hydrazine injection into the ionic solution, a color change to black occurs immediately. However, observation of the two different reactions is slightly different and it can describe what happens during the reaction. The reacting batch of CoTe stays calm for the first few minutes. For this short period, Te ions are reduced to Te seeds and Co ions form a Co$^{3+}$-N$_2$H$_4$ complex as the iron ions experiences in FeTe$_2$ synthesis. Once this process ends,
Figure 3.3 TEM images of (a) NiTe nanoparticles and conjugated particles and (b) HRTEM image of NiTe nanoparticles

Figure 3.4 Size distribution of NiTe nanoparticles. Conjugated particles are not counted
the highly reactive complex and Te seeds start reacting extremely fast, generating a huge amount of nitrogen gas out of the reactor. Finally, CoTe is initially formed in very small nanoparticles and later conjugated into 1-D nanorods. The reaction batch of NiTe synthesis experiences same reaction mechanism, whereas the reaction rate is moderate, providing a relatively longer time for a nanoparticle to grow bigger.

TEM images of NiTe nanoparticles in low and high magnification are given in figure 3.3. After 4 hours of reaction, it can be suggested from the images that nano-sized nanoparticles are synthesized and conjugated as the reaction continues.

Size of the nanoparticles are counted and sorted in figure 3.4 but the counting did not include particles that are in the middle of conjugating to nanorods. A broad range of size distribution is acquired mainly from 9nm to 15nm. Particles that have diameters of smaller than 9nm or larger than 15nm are rarely found. As the observation, the NiTe synthesis is

Figure 3.5 TEM images of CoTe nanorods. (a) low magnification image and (b) HRTEM image of a single nanorod. Red box indicates arbitrarily oriented CoTe seeds consisting of the nanorod
significantly less violent than the CoTe synthesis, which promote radial growth than axial growth and ends up producing nanoparticles.

![Figure 3.6 Thickness distribution of CoTe nanorods](image)

TEM images of CoTe nanorods are given in figure 3.5 and the as-synthesized CoTe still has amorphos surfactant in the CoTe complex after the normal washing procedure. The low magnification image, (a), suggests that the length of nanorods has a wide range from ~100nm to ~800nm. Compared to the growth in length, the thickness is well limited within 11 ± 2nm (figure 3.6). The observation of a single nanorod can elucidate a growth mechanism of CoTe nanorods. In fact, it has been known that a Te nuclei formed by the reduction of TeO$_3^{2-}$ by hydrazine prefers to grow in axial growth under a presence of PVP [Intro Iron telluride ref. 24]. Therefore, during the co-reduction, the Co nuclei grows onto the axial-growing the Te nuclei, forming CoTe nuclei. However, the extremly fast reaction rate does not guarantee
enough time for the CoTe seeds to be oriented in one direction, which ends up producing randomly oriented CoTe nuclei on the nanorods as seen in the figure 3.5 (b)

3.3.2 Semimetallic properties of NiTe and CoTe

The electrical conductivity and seebeck coefficient of sintered disks of CoTe and NiTe are measured simultaneously by 4-terminals measurement. As shown in Fig. No. Electrical conductivity of NiTe starts from 850000 S/m at 60°C and gradually decreases to 700000 S/m at the at 460°C. At the temperature range, there is about 20% of conductivity drop. Besides, the value for CoTe starts from 370000 S/m also at 60°C which is less than the half of NiTe, but only drops to 340000 S/m at 420°C. Both values are much higher than conventional thermoelectric materials such as Bi$_2$Te$_3$ with ~120000 S/m at 27°C [151], Ag$_2$Te with ~37000 S/m [152] and PbTe with ~11000 S/m [153]. Contrarily, the absolute value of seebeck coefficients are ~-10 uV/k for NiTe and ~-8 to -22 uV/K for CoTe. These values are lower by one order of magnitude than the compared materials which usually range from 100 – 200 uV/K at a various temperature range. The trade-off relationship between the electrical conductivity and seebeck as depicted in the figure 3.8, can explain that CoTe and NiTe are closer to metallic materials with much higher electron concentration. In order to confirm the carrier

![Figure 3.7 Electrical conductivity (left) and seebeck coefficient (right) as a function of temperature.](image-url)
concentration of CoTe iron hydroxide and NiTe, hall measurement can be conducted in the future.

In conclusion, 0-D NiTe and 1-D CoTe nanostructures are synthesized in one-pot synthesis. The reaction process is notably simple and is easily adapted in a large scale reaction and the reaction only takes 5 minutes for CoTe synthesis to be done with a result of nanorods. The final product from a single pot is capable of producing multiple sintered disk, which is able to accelerate future research. The electrical conductivity and seebeck coefficients of SPSed disks of CoTe and NiTe reveal that both have more metallic properties. Even though it can hardly be expected that CoTe and NiTe are ideal candidates for high-performance thermoelectric materials themselves, but they can be considered as good dopants by providing prominent electrical performance as provided in this study, and also magnetic properties proven in previous studies by several scientists [84].

Figure 3.8 Trade-off between electrical conductivity and seebeck coefficient [84]. Copyright © 2011 by Annual Reviews. All rights reserved
CHAPTER 4
FUTURE WORK

As described in Chapter 2, the pilot experiment of thermally controllable FeTe$_2$ p-n junction diode has been conducted, but showed a limited performance as a diode. Therefore, a future research on this material can aim to improve the limited diode performance in synthesis steps, sample measurement setup.

It is believed that the conduction switching temperature is determined by the synthesis condition. As discussed in the previous sections, tellurium and tellurium vacancy dopings greatly influence the band structure of FeTe$_2$, thus various dopants can be added in the synthesis step to provide intentional impurities in the system, hence the various conduction switching behavior with different doping effects would shed light on the rationales of the behavior.

In addition, the previous method to apply heat on the FeTe$_2$ bulk device to see the diode behavior was achieved by hot plate, where temperature can be easily reached at high temperature, but only offer an aerial heating from bottom. However, a laser heating can be used for this experiment instead. It is advantageous over the hot plate due to the selective area heating. The precisely selected heating area would be able to form a sharp temperature gradient that probably makes more obvious p-n junction, improving the diode performance.

As described in Chapter 3, NiTe and CoTe nanostructures were synthesized in large scale and their electrical and seebeck coefficients revealed their semi-metallic property. These material can be further doped in thermoelectric materials such as Bi$_2$Te$_3$ and PbTe by providing additional electron contribution to the system.
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