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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Galvanic Displacement Reaction of Nickel to Form One-dimensional Trigonal Tellurium
Structures in Acidic Solutions

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

Master of Science

in

Chemical and Environmental Engineering

by

Dung Thi Hanh To

September 2020

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Up to this point of my journey, I could not have been where I am without the generous support from professors, colleagues, and family.

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Last but not least, I would like to appreciate my family for their endless love and support.

ABSTRACT OF THE THESIS

Galvanic Displacement Reaction of Nickel to Form One-dimensional Trigonal Tellurium Structures in Acidic Solutions

by

Dung Thi Hanh To

Master of Science, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, September 2020
Dr. Nosang V. Myung, Chairperson

Tellurium, a p-type semiconductor with a narrow bandgap of 0.35eV, has a preferential growth in one dimension owing to its instinctually anisotropic crystal structure. Tellurium, therefore, has been employed for various applications (*e.g.* chemiresistive gas sensors and piezoelectric generators). One-dimensional (1-D) tellurium structures have been used also as a template to synthesize different binary and ternary telluride compounds (*e.g.* CdTe, Ag₂Te, AgSeTe) for other applications. Various synthesis methods have been utilized to control the morphology and crystallinity to optimize the performance of devices based on 1-D tellurium structures. Among them, galvanic displacement reaction has drawn much attention due to not only the low-operating cost and moderate fabrication conditions but also its ability to study the growth mechanism via monitoring thermodynamic and kinetic aspects of the system.

In this work, tellurium morphology and crystallinity were tuned by controlling three variables: concentration of tellurium precursor (TeO₂) and acidic anion (SO₄²⁻) as well as

three types of anion (*i.e.* SO_4^{2-} , Cl^- , NO_3^-). The growth mechanism was systematically investigated using various electrochemical methods and materials characterization. Increasing HTeO_2^+ concentration led to transformation of trigonal micro-wires to tubes probably due to the comparable diffusion length scale of tellurium on the cylindrical seed surface to the radius of the seed. In contrast, the transition from trigonal microtubes to microwires with an increase in H_2SO_4 concentration might be attributed to reduction of deposition rate and limited mass transfer of HTeO_2^+ ions. Effect of different acidic anions on tellurium morphology was observed. Larger tellurium microtubes were formed in chloride bath due to the preferential adsorption of Cl^- , resulting in increases of both dissolution of nickel and the deposition of tellurium. As a strong oxidant, HNO_3 dissolved nickel faster than SO_4^{2-} and Cl^- , but showed slower tellurium deposition of tellurium nanowires which might be attributed to co-reduction of nitrate ions.

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CHAPTER 1

APPLICATIONS AND SYNTHESIS OF ONE-DIMENSIONAL TELLURIUM STRUCTURES

1.1 Tellurium structures and properties

Tellurium (Te), an element of group 16 of the periodic table, are commonly known as chalcogens. Te was discovered in 1798 by an Austruan mineralogist Franz-Joseph Muller von Reichenstein.

Tellurium has two allotropes, amorphous (a-Te) and crystalline trigonal (t-Te), in which the latter is the only stable form. Trigonal tellurium has a hexagonal crystal structure consisting of six spiral chains on the corner of the hexagon and one chain at the center. Each helical turn has three covalently bound tellurium atoms, while the spiral chains are held together via Van der Waals forces [1]. Strength of the covalent bonds within a chain results in a highly anisotropic crystalline structure of tellurium and a strong tendency to grow in [001] direction to form one-dimensional structures as shown in Figure 1.1.

The metallic character becomes more pronounced downward the group 16, including non-metallic sulfur and oxygen, semi-metallic selenium and tellurium, and metallic polonium. This sequence is reflected by the increase in electrical conductivity of the five elements. Tellurium, for instance, is the semiconductor with a narrow band gap of 0.35 eV which is smaller than that of 1.6 eV of selenium.

Tellurium is also an amphoteric element which can react in the form of cations and anions due to the multiple valence states from +VI to -II. Tellurium can react with many transitional metals to form metal tellurides which tune certain properties (*e.g.*, electric

conductivity, thermoelectricity and photoconductivity). Copper (I) telluride (Cu_2Te) [2], silver telluride (Ag_2Te) [3], and bismuth telluride (Bi_2Te_3) [4] have shown high electric conductivity of 40 KS/m, 20 KS/m, and 22 KS/m respectively, compared to 0.012 KS/m of tellurium [5] at 300°K. Moreover, cadmium telluride (CdTe) shows a wider energy band of 1.45eV and a larger photo-adsorption coefficient of more than $5 \times 10^5 \text{ cm}^{-1}$. [6] On the other hand, bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) narrows down the band gap to 0.15 eV and 0.21 eV respectively [7, 8].

1.2 Applications of tellurium and importance of one-dimensional structures

With such crystal structure and properties, tellurium has been considered as promising materials for different applications. Performance of certain applications has been enhanced by employing the one-dimensional (1-D) structures and/or alloying between tellurium and various transition metal.

1.2.1 Chemiresistive gas sensors

The narrow-band semi-conductivity of tellurium is useful for chemiresistive gas sensors. Upon exposure to target gases, the electrical properties of semiconductor are modified via electron transfer between the gas molecules and the sensing material. Electrical changes are transduced and correlated with concentration of the present gases. Therefore, the anisotropic crystal structure to form one-dimensional structure of tellurium brings a significant advantage to enhance sensitivity of sensors due to the high surface area to volume ratio as well as comparability between Debye length and radius of 1-D structures. The former enables more surface atoms of the sensing material to interact with

the gaseous molecules, consequently enlarging the electrical changes and amplifying sensors' sensitivities.

In addition, 1-D structures can magnify the receptivity level of sensor via larger portion of the sensing material being affected by gaseous molecules. Debye length is the measurement of how far electrostatic effect of charge carriers persisting in a material. The same scale of the Debye length and 1-D structures can considerably improve the sensor sensitivity. The virtue of two-dimension diffusion (*e.g.*, radial and longitudinal) also fasten the response time of 1-D structure-based gas sensors as shown in Figure 1.2.

Tubular tellurium structures with outer diameter of 100-500 nm were able to detect down to 1 ppm (part per million) chlorine gas and the response time of 30 seconds [9], 300-320 nm Te nanotube to 500 ppt NO₂ with response time less than 180s [10]. Sensitivity of tellurium nanotube of -5000% per ppm at the analyte concentration of 1ppb NO₂ [10] is much higher than that of tellurium thin film (-7.5% per ppm at 1.5 ppm NO₂) [11].

1.2.2 Piezoelectric devices

Piezoelectric effect is a phenomenon in which electric polarization is induced in materials as they are exposed to mechanical stresses. This effect has been employed for energy conversion using nanogenerator. An external load to collect electron is incorporated to balance the potential difference. For monatomic materials such as tellurium, the potential difference is generated by the strain-induced redistribution of electrons and the atom cores [12]. Due to the anisotropic crystal lattice, charge distribution of bulk tellurium can be polarized by positive longitudinal stress and torsional stress along the x- and c-axes respectively. The former stress leads to the piezoelectric polarization along the x-axis

owing to the displacement of tellurium atoms and electric charge. The latter stress causes the rearrangement of atom cores and spatial electron distribution, corresponding to an increased number of tellurium helical turn.

Tellurium-based piezoelectric generators for smart adaptive and wearable electronics were investigated using 1-D tellurium nanowires [13, 14] and nanobelts [15] with power current density up to 9 mW/cm^3 . As shown in the Figure 1.3 A, 1-D tellurium structures have the hexagonal cross-section under no strain. Horizontally stretched and vertically expanded hexagon are attributed to the tensile and compressive stresses along the radial direction as displayed in Figure 1.3 B-C. The shape of the cross-section is distorted upon applying the external stress, resulting in the crystallographic symmetry broken and the displacement of electronic distribution. On the other hand, the stress along the longitudinal direction does not cause an overall rearrangement of charges due to the offset of locally generated polarization [13].

1.2.3 Thermoelectric devices

Thermoelectric devices are the means for conversion between thermal and electrical energy based on Seebeck and Peltier effects. As a temperature difference occurs at material terminals, a potential difference is generated owing to charger carriers, traveling down the gradient from the hot to the cold sides. Opposite to Seebeck effect, Peltier effect induces a temperate difference from a potential gradient also by the diffusion of charge carriers. The conversion efficiency between heat and electricity is directly proportional to the thermoelectric figure of merit (ZT) as shown in equation (1.1).

$$ZT = \frac{S^2 \sigma}{k} T \quad (1.1)$$

where S (V/K), σ (S/m), k (W/mK), and T (K) are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature respectively. The value of ZT augments with an increase of Seebeck coefficient and electrical and a reduction of thermal conductivities at a certain temperature. Although Te has a high Seebeck coefficient of $400 \mu\text{V/K}$ at 300°K [16], it is not a good thermoelectric material due to the low electrical conductivity of 12S/m [17]. Therefore, various of binary and ternary tellurium alloys have been investigated to achieve a higher value of ZT by balancing between Seebeck coefficient and electrical conductivities. On the other hand, the thermal conductivity of tellurium derivatives has been controlled by tuning the morphology. 1-D structures have demonstrated the reduction of thermal conductivity due to increasing number of scattering sites compared to bulk material [18, 19]. Te nanowires as sacrificial templates was used to synthesize polycrystalline nanotubular Bi_2Te_3 and PbTe which showed their lowest thermal conductivity of approximately 0.5 W/mK , while their melted samples had that of 2.5 W/mK [8].

1.3 Synthesis of one-dimensional tellurium structures

Being such a promising material for many electronic devices, synthesis of tellurium, especially 1-D structures, has been investigated by various methods to control morphology and crystallinity to further enhance tellurium electrical, thermal, and mechanical properties. Synthesis methods are generally categorized into physical and chemical approaches.

1.3.1 Physical synthesis of tellurium

The former, which involves the crystallization of tellurium from the amorphous phase, includes typically physical evaporation.

Mohanty et al. reported the synthesis of single crystalline Te nanotubes, nanowires and nanorods via evaporation (350°C) and recrystallization of Te on Si substrate in an inert atmosphere. Morphology of 1-D Te nanostructures were strongly controlled by condensation temperature of Te, flow rate of argon gas, and surface orientation of the substrate. When the deposition temperature passed the point of 150 °C, the transition from nanowires to nanotubes. In addition, increases of the Ar flow rate and pressure from 25 sccm and 1 Torr to 500 sccm and 15 Torr respectively. Nanotubes and nanorods had triangular and hexagonal cross-sections. As the deposition temperature, pressure, and Ar flow rate were fixed at 350 °C, 1Torr, and 25 sccm, Te nanotubes and nanowires were synthesized on Si (100) and Si(111) [20].

Metraux et al. utilized the same technique to investigate the effect of not only substrate and temperature but also deposition environment (*e.g.*, argon gas and vacuum). Under Ar atmosphere, the amount of rounded particles and hexagonal hollow crystals were reduced and increased respectively as the temperature increased from 150 °C to 175 °C. As reaction time prolonged at 175 °C, the Te tubular structures were transformed into Te wires with a helicoidal geometry. Although the same Te structures were deposited on silicon (111) and polycrystalline aluminum substrates, Te elongated platelets and nanorods were formed on the silicon and aluminum substrates respectively under vacuum environment [21].

Se et al. varied both temperature of Te source and Te deposition to achieve different Te 1-D structures. Nanowires was only obtained as source and deposition temperatures were fixed at 430 °C. As the former temperature augmented to 550 °C and deposition temperature increased from 30 °C to 400 °C, Te nanotubes were changed to radial nanotubes and microrods respectively. Furthermore, Te morphology transition from particles to microrods occurred when source temperature was at the range of 600 to 900 °C and deposition temperature was varied from 30 to 400 °C [22].

1.3.2 Chemical synthesis of tellurium

Chemical approaches, in contrast, requires changes in oxidation state of tellurium commonly from positive four to zero in redox reactions. In comparison to the physical approach, a wide variety of solution parameters (*e.g.*, solvents, tellurium precursors, reducing agents, surfactant and pH) as well as synthesis techniques (*e.g.*, hydrothermal, solvothermal, reflux, microwave assisted and electrodeposition) have been utilized.

1.3.2.1 Hydrothermal and solvothermal methods

Synthesize Te 1-D structures was reported by many communications using hydrothermal method. Mo et al. observed the formation of single crystal tellurium 1-D nanostructures by the disproportionation reaction of sodium tellurite (Na_2TeO_3) in ammonium solution. A mixture of nanobelts (50-75%), nanotubes (10-15%), and nanorods were formed at 0.5 mM Te precursor and 180 °C. However, when the Te precursor concentration or the reaction temperature increased to 5 mM and 220 °C, only nanorods were synthesized [23].

Xi et al. utilized sodium tellurate (Na_2TeO_4) and formamide (HCONH_2) as tellurium precursor and reducing agents to synthesize tellurium via nucleation-dissolution-recrystallization process. Trigonal tellurium nanoparticles were formed after 5 hours and then groove-like nanorod grew on the nanoparticles with the expense of the latter after 12 hours. Groove-like nanotubes and complete nanotubes were observed at 16 and 20 hours [24].

The formation of different Te structures (*e.g.*, nanotube, nanorods, and feather-like nanostructures) was achieved by Zhu et al. via hydrothermal reduction of K_2TeO_3 by NaH_2PO_2 . The presence of NaOH, temperature, and polyvinyl pyrrolidone (PVP) as surfactant considerably affected the morphology of Te structures. Te nanotube was formed without NaOH, while the presence of NaOH induced formation of Te nanorods. In addition, the transition of nanotubes to microtubes was attributed to the increase in concentration of NaOH (0.1 to 1 M). As reaction temperature increased from 120 to 160 and 180 °C, the nanotubes were transformed to microrods and feather-like structures respectively. Similarly, increasing concentration of NaH_2PO_2 ten times (0.25 to 2.5M) resulted in the morphological change from nanotubes to feather-like nanostructures. Furthermore, the presence of PVP induced the growth of Te nanowires [25].

1.3.2.2 Aqueous based reflux method

Mayers et al. used aqueous based reflux method to show the significant effects of electrolyte composition (*e.g.*, solvents, Te precursor types and concentrations) and reaction temperature on the morphology of Te structures. Various combinations of solvents (*e.g.*, pure water, anhydrous ethylene glycol, and mixture of water and ethylene glycol) and Te

precursor types (orthotelluric acid and tellurium dioxide) were studied. Orthotelluric acid (H_6TeO_6) was reduced by hydrazine in water to form single crystalline Te wires. However, structures of nanowires slightly changed with the reduction of temperatures in which equilateral triangular cross-sectional nanowires with tapered end and spine-shaped nanowires were synthesized at 20 °C and 100 °C respectively. Also, H_6TeO_6 concentration of 10^{-2} mM was a critical value below which only spherical colloids of amorphous Te formed and above which trigonal Te nanowires were observed for the entire range temperature (20-100 °C). As pure ethylene glycol was used as the solvent, the reduction temperature of 100°C is a transition point of morphology from colloids of amorphous Te to whiskers. Furthermore, the length of nanowires augmented with the increase in temperature from 100-180 °C. At 196 °C, the presence of reducing agent (*i.e.*, hydrazine) strongly influenced the morphology of Te. Nanowires with hexagonal cross section were formed without hydrazine, while hydrazine induced the growth of filamentary nanowires off alternating corners of the hexagonal seeds. The transformation from nanowires with triangular cross section and tapered end to nanowires with hexagonal cross section and then tubular structures with tri-tipped whiskers was observed by varying the reduction temperature (174-200 °C) and the weight percent of water in ethylene glycol (1.7-3.0%). Ethylene glycol was served as a solvent and reducing agent for tellurium dioxide to form needle-like Te nanowires with hexagonal cross section [26].

In another communication, Mayer et al. reported the synthesis of Te nanotubes and nanowires from the reduction of orthotelluric acid by ethylene glycol. As the precursor concentration increased from 0.7mM to 40mM, the cylindrical seeds were formed with

larger outer diameter. Consequently, the nanorods evolved to nanotubes owing to the incomparability between Te atom diffusion scale and seed diameters. In other words, the depletion of Te atoms occurred at the center of seed surface, resulting in the hollow nanostructures [27].

1.3.2.3 Microwave-assisted method

Microwave irradiation was also employed by Liu et al. to assist the reaction between NaTeO_3 and hydrazine hydrate to form 1-D Te nanostructures. The effects of different parameters (*e.g.*, surfactant types and concentrations, reaction time, and pH) were also investigated. Ultralong nanowires were synthesized in the presence of PVP, while polyacrylic acid or cetyltrimethylammonium bromide induced the formation of only nanorods and aggregated rods. Furthermore, short nanorods and spherical particles were observed in the absence of PVP. As the amount of PVP increased from 0.5 to 1.5 g, the number of nanoparticles was reduced and the aspect ratio of nanowires was optimized at 1.0g of PVP. Microwave irradiation time also influenced the Te morphology. Short nanorods were obtained after 30 seconds of microwave heating, while a mixture of long nanowires and small amount of Te nanoparticles were formed after heating for 12 minutes. The aspect ratio of Te 1-D nanostructures was also controlled by pH. Within the pH range of 8 to 14, the aspect ratio was maximized at pH 10 and nanorods were formed at two ends of the pH range [28].

1.3.2.4 Electrochemical method

Although the above-mentioned techniques have ability to control the morphology and crystallinity well, they required harsh operating conditions (*e.g.*, high temperature and pressure) which thereby limit the scalability and manufacturability. Therefore, electrochemical methods might be promising alternatives due to the ambient operating conditions. Additionally, the good adhesion between deposit and substrate is a significant advantage for certain applications (*e.g.*, gas sensors) owing to the lack of binder. Electrochemical techniques, a subcategory of chemical methods, are classified into electrodeposition and electroless deposition.

1.3.2.4.1 Electrodeposition of tellurium

Electrodeposition employs external power to supply electrons for tellurium ion reduction. Tellurium structures have been deposited in both acidic and alkaline solutions. However, the solubility of tellurium precursor is pH dependent and increases in the order of neutral (1.6×10^{-4} g/L at pH 7), acidic (1.6 g/L at pH 0), and alkaline pH (87.8 g/L at pH 10.5) [29]. The deposition rate of tellurium is limited to about 20 $\mu\text{m/h}$ in acidic solutions.

1.3.2.4.1.1 Electrodeposition of tellurium in acidic baths

Electrodeposition of Te was studied in different acidic baths (*e.g.*, HNO_3 , H_2SO_4 , HClO_4), only tellurium thin films however were formed rather than 1-D Te structures.

Qui et. al reported the electrodeposition of Te thin films from the saturated TeO_2 aqueous solution with pH around 1. The morphology of Te films were influenced by the orientation of the Te substrate. Monocrystalline Te film and needle-like defects with large

cleavage steps were synthesized from the monocrystalline and (10 $\bar{1}$ 0) surface respectively. Polycrystalline films with 1 μ m blades with random orientation were formed at high current densities [30].

Different coverage of well-order atomic layers of Te were observed by Suggs et al. on the low-index planes of Au in sulfate bath. Ordered arrays of isolated Te atoms were first formed and then conversed to that of Te dimers by the compression of Te atoms at higher coverages. The conversion required 300mV. Also, the reduction potentials for formation of Te atomic layer were more affected by chemical change than substrate structure [31].

Sulfate bath was also used by Ikemiya et al. to investigate the atomic structure and the growth morphologies of Te thin film on Au substrate with large lattice misfit (*i.e.*, Au(110) and Au(111)). A Stranski-Krastanov growth of bulk Te film even at low deposition rate indicated that Te adatoms diffused slowly on the monolayer-Te coated Au surface even on both Au substrate. The film thickness also controlled the adlattice structure of Te film [32].

Jiang et al. used polyaniline coated microporous phenolic foam as a substrate to deposit Te thin film in the nitrate bath (10 mM HTeO₂⁺ and 1 M HNO₃). The dense columnar-structure thin film was formed uniformly with the preferential orientation in the c-axis direction. The cauliflower-like surface on top of columnar structures suggested that Te grew vertically layer by layer from two neighbor struts and eventually join together [33].

Nitrate bath was also employed by Abad et al. to investigate the effect of sodium lignosulfonate (SLS) as a surfactant on the formation of Te thin film. Without SLS, the highly anisotropic crystal structure of Te resulted in larger particle size and decreased microstructure order at more negative potential. In contrast, the surfactant acted as an anti-coagulation agent and disturbed the typical growth of Te to form smoother and more compact films with minimal difference at various potential. The presence of SLS also inhibited the particle growth [34].

1.3.2.4.1.2 Electrodeposition of tellurium in alkaline baths

Ha et al. studied the electrodeposition of Te in alkaline solution (*i.e.*, 10mM TeO_3^{2-} and 2.5M NaOH). The deposit showed a very porous nature with needle-like radial growth in the pores. The more negative cathodic potential led to more hydrogen evolution reaction, therefore, the optimum potential range was from -0.8 to -0.95V vs Hg/HgO [35].

Wu et al. investigated the effect of Te precursor concentration, pH and applied potential on synthesis of thick dense Te films. Applied potential at more positive than -1.0V mitigated the dissolution of deposited Te by further reduction to Te_2^{2-} , thereby deteriorate the film density and morphology. Te dissolution as increasing the potential from -0.9 V to -1.0V alternated the preferential orientation of Te thin film from (001) to (101). In addition, the dense Te film was achieved at pH range of 11.3 to 12.5 with sufficient agitation (2000 rpm) [36].

1.3.2.4.2 Galvanic displacement reaction

1.3.2.4.2.1 Galvanic displacement reaction in alkaline baths

In contrast to electrodeposition, galvanic displacement reaction is an electrochemical process driven by the difference in redox potential between a sacrificial material and noble metal ions in solution, which are reduced on top of the sacrificial materials. GDR is described by two half-reactions that occur simultaneously on the surface of sacrificial materials: the oxidative dissolution of the sacrificial materials and the reductive deposition of the noble metal ions. The choices of sacrificial material and metal ion are therefore essential to determine the complexity of electrochemical reactions in the system. As mentioned above, solubility of tellurium precursor is pH dependent and increases in the order of neutral (1.6×10^{-4} g/L at pH 7), acidic (1.6 g/L at pH 0), and alkaline pH (87.8 g/L at pH 10.5) [29]. Although tellurium readily dissolves in alkaline solution, sacrificial metals are limited to a few metals owing to their insoluble oxide formation. Wu et al. investigated the effects of different solution parameters (*e.g.*, concentration of tellurium precursor, pH, temperature) on formation of tellurium structures in alkaline solution where tellurium precursor presents as TeO_3^{2-} as shown in Figure 1.4 [37, 38].

Using aluminum as the sacrificial material, morphology transition from nanowires to three dimensional branched nanorods was observed as TeO_3^{2-} concentration increased from 2mM to 10mM at pH 13.1. While higher pH yielded nanowires, the lower range of pH (12.8 to 13.1) formed branched nanorods at 10mM TeO_3^{2-} . As reaction temperature augmented from 4 °C to 50 °C, the diameter of increased from 49nm to 200mn [38].

On the other hand, when zinc foil was utilized as a reducing agent, Te rice-like structures which evolved from branched nanostructure were observed. The pH of 11.9 was indicated as the phase transition point from amorphous to crystalline. As concentration of increased from 30 to 550 mM, the dimension of Te nanostructures increased monotonically from 121 nm to 573nm for diameter and 0.7 μ m to 8.3 μ m for length [37].

1.3.2.4.2.2 Galvanic displacement reaction in acidic baths

In contrast, various sacrificial metals (*e.g.* nickel, cobalt, iron, silicon and copper) were employed in acidic solution [39-42].

Boron-doped silicon wafer as a sacrificial material was utilized to form trigonal Te nanowire in acidic fluoride solution (1 M CdCl₂, 1 mM HTeO₂⁺, and 4.5 M HF). Uniform nanowires with average diameter and length of 87 nm and 2.3 μ m respectively were observed owing to the instantaneous nucleation and growth. Jeong et al. also reported that both diameter and length of Te nanowires increased with increase in temperature due to higher reduction rate of Te and larger size of nuclei [43].

Chang et al. employed electrodeposition to fabricate nickel, cobalt, and iron thin films which were then used as sacrificial materials for galvanic displacement reaction. Formation of Te thin film from acidic nitrate bath (10mM HTeO₂⁺ and 1M HNO₃) at room temperature showed the strong dependence of morphology and crystallinity on the types and thickness of sacrificial metals. This might be attributed to different chemical dissolution rates and mixed potential of systems with different sacrificial materials [41].

Electrodeposited Ni thin films from chloride baths were used to synthesize hexagonal one-dimensional Te nanostructures with well-developed facets in 1M HNO₃.

Elazem et al. showed that the morphology of Te structures was strongly influenced by the crystal orientation of Ni thin film. Furthermore, the density per area, diameter and length of Te nanostructures were dependent on Te precursor concentration. As concentration of HTeO_2^+ increased from 1 to 10mM, the diameter and length augmented from 68 ± 21 nm and 1 ± 0.114 μm to 587 ± 156 nm and 2.5 μm respectively. However, the aspect ratio decreased with increase in HTeO_2^+ concentration, indicating the longitudinal growth is dominant over the radial growth [44].

Electrodeposited sacrificial material was also utilized by Rheem et al. for synthesis of tellurium nanotubes. Cobalt nanowires with varied diameters (*i.e.*, 70-220 nm) was formed by a templated-directed electrodeposition using polycarbonate as scaffolds. The diameter and thickness of Te nanotubes was directly proportional to the diameter of Co nanowire. The Te nanotubes were nanocrystalline with average grain size of 10nm [39].

One-dimensional sacrificial material was also studied by Park et al. using electrospinning to fabricate Ni nanofiber. Ultra-long hollow Te nanofibers with smooth and branched surface were synthesized by controlling the concentration of Te precursor in 1M HNO_3 . At the low range of HTeO_2^+ concentration (*i.e.*, 0.5 and 1mM), the branched Te hollow nanofibers were formed, while 10mM HTeO_2^+ solution resulted in smooth Te hollow nanofibers. By controlling concentration of HTeO_2^+ (*i.e.*, 0.5 to 10mM), the branch diameters and wall thickness increased from 10 ± 2 and 17 ± 5 nm to 19 ± 3 nm and 27 ± 4 nm respectively [45].

Above-mentioned studies in synthesis of Te structures in acidic solution mostly investigated the effect of types, crystal orientations, and dimensions (*i.e.*, 1-D and 2-D) of

sacrificial materials, reaction temperature as well as concentration of Te precursor (*i.e.*, HTeO_2^+) on morphology and crystal structure. However, rate of GDR depends not only on the reduction of tellurium but also the dissolution rate of sacrificial materials. Dissolution of metals in acidic solution occurs due to complexation between metal and anions. Therefore, types and concentration of acidic anion also plays important roles in controlling morphology and crystal structure. Concentration of anions would determine the abundance of complexing agents for transfer metal from crystal lattice into solution. In addition to concentration, types of acidic anion can vary the dissolution rate significantly by modulating the activation energy of dissolution reaction.

1.4 References

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Figure 1.1. Crystal structure of tellurium, (a) side-view and (b) top-view [1]

Figure 1. 2. Schematic diagram of conduction channel in (a) one- and (b) two-dimensional structure sensing material for chemiresistive gas sensing

Figure 1.3. (a) Cross-section of tellurium one-dimensional structure, The induced dipole moment under tensile stress (b) and compressive stress (c) [13]

Figure 1.4. Pourbaix diagram of tellurium [46]

CHAPTER 2

GALVANIC DISPLACEMENT REACTION OF NICKEL TO FORM ONE-DIMENSIONAL TRIGONAL TELLURIUM STRUCTURES IN ACIDIC SOLUTIONS

2.1 Introduction

Single crystalline, one-dimensional (1-D) structures have gained considerable amount of interest due to their unique physical, material, and chemical properties that enable potential applications in various fields [1-3]. To optimize the performance of devices based on the 1-D structures, such properties could be fine-tuned by promptly controlled morphology, typically dictated by the structure formation mechanism during synthesis. Thus, understanding the complex mechanism of nucleation and growth is crucial in enhancement of 1-D structure-based applications. Tellurium (Te) presents a strong tendency to grow in one dimension due to its instinctually anisotropic crystal structure. It exhibits a hexagonal lattice, including seven long polymeric helical chains of covalently bonded atoms in trans conformation. Each spiral turn consists of three atoms which are connected to atoms from other chains by Van der Waals interaction. Additionally, Te exhibits as a p-type semiconductor with a narrow band-gap energy of 0.35eV at room temperature. It has been evaluated as a suitable material for high-efficient photoconductors, thermoelectric, and piezoelectric applications [4].

Various methods have been employed for the controlled synthesis of 1-D Te structures, such as: facile vaporization [4], microwaved-assisted [5, 6], self-seeding

solution process [7], polyol process [8], hydrothermal [9-11], and electrochemical method [12-17]. Among the approaches, galvanic displacement reaction (GDR) exhibits several advantages including low-operating cost and moderate fabrication conditions. GDR is an electrochemical process driven by the difference in redox potential between a sacrificial material and noble metal ions in solution, which are reduced on top of the sacrificial materials. GDR is described by two half-reactions that occur simultaneously on the surface of sacrificial materials: the oxidative dissolution of the sacrificial materials and the reductive deposition of the noble metal ions. The choices of sacrificial material and metal ion are therefore essential to determine the complexity of electrochemical reactions in the system.

Elemental tellurium can be reduced from tetravalent tellurium ions such as TeO_3^{2-} and HTeO_2^+ in alkaline and acidic solutions respectively. For alkaline conditions, the sacrificial materials are limited to a few materials (*e.g.*, zinc and aluminum) due to oxide formation of sacrificial metal [12, 13]. In contrast, many different sacrificial metals including nickel, cobalt, iron, and copper can be utilized in acidic conditions [14, 18-20].

The dissolution rate of nickel in acidic solutions varies considerably depending on the types of anions in the electrolyte. Nickel dissolution in acidic solution occurs due to complex formation between nickel atom and anions, which reduces the activation energy of the dissolution reaction. Hydroxide ions have been reported as a carrier to transfer nickel atoms from crystal lattice into solution [21]. Also, the anion counterparts of acids have a significant effect on the dissolution of nickel. Among common inorganic acids, nitric acid is the most oxidizing agent that accelerates the dissolution of nickel, since the nitrate ions

can be reduced to different compounds and ions (*i.e.*, nitrous, nitrogen dioxide, and ammonia) [22, 23]. Chloride has a preferential adsorption over hydroxide, due to its high electronegativity and small size. Kronenberg *et al.* showed that adsorption of chloride ions resulted in an increase in the rate of dissolution, owing to the potential reduction of the Helmholtz inner plane [24]. Sulfate is the most weakly adsorbed anion in comparison to chloride and nitrate ions; therefore, nickel dissolution rate in sulfuric acid will be slower which may result in low rate of deposition [25].

In this work, the morphology, crystallinity, dimensions of 1-D Te structures were systematically studied as functions of reaction time and electrolyte composition. The thermodynamic and kinetic aspect of the GDR were scrutinized via electroanalytical methods, including the measurement of open-circuit potential (OCP) and linear polarization (LP). A feasible deposition mechanism behind the formation of 1-D Te structure was also suggested.

2.2 Experimental section

2.2.1 Sample preparation and galvanic displacement reaction.

The tellurium-based electrolyte was first prepared by dissolving tellurium dioxide (TeO_2 , 99%, Acros Organics) in acidic solution with various amounts. Commercially pure Nickel foil (Ni, 0.03mm thick, 99.9%, MTI, corp.) was cut into a circular shape with a diameter of 1.27 cm and it was used as the sacrificial material. Before reaction, the foils were cleaned with 1 M H_2SO_4 for one minute to remove the surface oxide, rinsed with deionized water, and then blow dried with air. All GDRs were carried out in a Teflon cell

with a fitted O-ring around an open area of 0.2 cm². A clean piece of Ni foil was sandwiched between two Teflon pieces, which were held together with an O-ring and two screws to prevent leakage as shown in Figure 2.1. The GDRs were initiated by adding 0.9 mL of the electrolyte solution containing Te precursor onto the Ni foil through the opening of the top Teflon piece. The Teflon cell was then placed in a small box covered by aluminum foil to prevent photoexcitation of tellurium. The reactions were stopped by simply removing the solution. The sample was then carefully removed from the Teflon cell and rinsed three times with distilled water. In order to determine the amount of nickel consumed and tellurium deposited during the GDR, the Ni foils were weighed at three different times: after surface oxide removal, reaction, and tellurium removal by sonication.

2.2.2 Material and electrochemical characterization

The morphology of the Te structures were observed by scanning electron microscope (SEM, TESCAN VEGA3). The dimensions of forty tellurium structures synthesized at each condition were characterized by measuring length and diameter of 40 individual structures visible in cross-sectional SEM images. Diameters of nonuniform cylindrical structures were measured at their half-length. The crystal structure of the structures was examined by powder X-ray diffraction (XRD, PAN analytical Empyrean) with copper ($\lambda=1.5405$ Å) as anticathode and 0.026-degree increments from 20 to 80°.

The electrochemical reaction kinetics were investigated via open-circuit potential (OCP) measurement and linear polarization (LP) using a potentiostat (Princeton Research Application, VMP2). Typical three-electrode system was used with the Teflon cell setup, which consisted of Ni foil, an Ag/AgCl and a Pt mesh-folded strip as the working,

reference, and counter electrodes, respectively. OCP was measured from when the electrolyte was added to the cell for 24 hours. LP curves were obtained by scanning the potential from -0.1 V to +0.1 V vs. OCP at a scan rate of 1 mV/s. In order to study the effect of dissolved oxygen on the GDR, the electrolyte was deaerated by ultra-high purity (UHP) nitrogen for one hour and LP curve was obtained at the same scanning conditions with an UHP nitrogen blanket.

2.3 Results and discussion

2.3.1 Synthesis and material characterization of tellurium structures

Figure 2.2 A-C shows the SEM images of synthesized Te structures by varying the HTeO_2^+ concentration, while fixing the H_2SO_4 concentration and the reaction temperature and time at 2 M, 23 °C, 24 hours, respectively. The SEM micrographs showed that Te wires were formed using both 0.1 and 1 mM HTeO_2^+ , while the length of the wires significantly increased from 1.15 μm to 14.2 μm , as shown in Figure 1A and B. Microtubes with the average length of 35.6 μm were observed at the HTeO_2^+ of 10 mM (Figure 1C). Figure 1E shows that the length variation is larger at higher concentration of HTeO_2^+ indicating by the length of the boxes and the whiskers. The diameter of microtubes was 4.4 times larger and had more variation than that of microwires obtained at 1 mM HTeO_2^+ (3.54 μm and 0.8 μm respectively) as shown in Figure. 1 D. Although the diameter range of these two conditions overlap, they are statistically considered different due to the separation of the interquartile or the boxes. Elazem *et al.* also observed the same increase in length during the evolution of tellurium microwire to microrod with increasing HTeO_2^+ concentration in

nitric acid, describing an enhanced reaction rate [26]. Park *et al.* studied the effect of $[\text{HTeO}_2^+]$ in nitric acid on the Te morphology by using electrospun Ni nanofibers as a sacrificial substrate [27]. In this work, the surface of resulting Te nanofibers changed from branched to smooth with increasing Te precursor concentration, to which they attributed higher amount of mass transfer of HTeO_2^+ to Ni surface, resulting in higher reaction rate and therefore a decrease in preferential growth in [001] direction.

Another factor that affected the growth of Te structures was the concentration of H_2SO_4 , or proton (H^+). Figure 2.3 A-B shows SEM images of Te structures synthesized at a fixed HTeO_2^+ concentration of 10 mM at 23 °C for 24 hours. The concentration of H_2SO_4 was varied from 1, 2, to 5 M. Micro-tubular structures were generated at low $[\text{H}_2\text{SO}_4]$ (*i.e.*, 1 and 2 M), while microwires were obtained at higher $[\text{H}_2\text{SO}_4]$ (*i.e.*, 5M). The average length and diameter of Te structures augmented with the increase of H_2SO_4 as shown in Figure 2.3 C-D. However, the length and diameter of Te structures at 2 and 5M H_2SO_4 had no statistical difference due to the overlap extent of the boxes and medians. This behavior is confirmed by the similar range of consuming nickel amount and the mol fraction of generated electrons which was consumed by telluryl ion reduction as displayed in Figure 2.4.

The change in the morphology of tellurium deposits could be explained by the nucleation and growth process. Precursor tellurium ions were first reduced to form elemental tellurium atoms, which accumulated in the electrolyte as dissolved atoms. Until the tellurium atom concentration reached supersaturation (*i.e.* above its solubility), the nucleation started to generate seeds, which then grew to form crystals [28]. The cross-

sectional SEM micrographs of tellurium structures in Figures 2.2 and 2.3 show that the electrochemical reaction of nickel (*i.e.*, dissolution) and tellurium (*i.e.*, reduction) resulted in the progressive nucleation and growth mechanism, in which the distribution of diameter and length were wide. At high degree of supersaturation, diffusion rate in axial and lateral direction were equivalent, leading to the formation of rod or wire structures, as shown in Figures 2.2 A-B and 2.3 C. Similarly, high supersaturation of free tellurium atoms was reported to form large number of nuclei and reduce the mobility of tellurium atoms [4]. Solid nanorods and nanowires were synthesized with high supersaturation of tellurium achieved by different methods from thermal evaporation to hydrothermal route [4, 29].

As the amount of available Te atoms in solution decreased, the electrolyte reached “light” supersaturation, in which the free tellurium atoms tended to diffuse towards the edge of the microrod and microwire, where the free surface energy was higher than the center [30, 31]. This led to the higher axial growth rate than the lateral, leading to the formation of tubular structure. As the concentration of free Te atoms reached undersaturation (*i.e.*, below solubility), insufficient feed of tellurium atoms resulted in the continued growth of the microtubular wall, while the central portion remained hollow [8, 11]. Mohanty *et al.* reported the formation of Te nanotubes when slight supersaturation of tellurium was observed at higher temperature [4]. Vasileiadis *et al.* showed that at low supersaturation, the free tellurium atoms had high mobility to diffuse to the edge of the seed [32]. The undersaturation of tellurium could happen right after the nucleation stage or later during the structure growth process. Zhu *et al.* reported that evolution of nanorod to nanotube was observed in time-dependent experiments at 10 mM HTeO_2^+ and 2 M H_2SO_4

[29]. It is important to note that depending on the reduction rate and the solubility of tellurium in the electrolytes, seed diameter and growth rate might vary, leading to different crystal structures. For example, at lower $[\text{HTeO}_2^+]$ (*i.e.*, 0.1 and 1 mM), the amount of Te atoms produced by the reduction of HTeO_2^+ was low, and thus formed smaller seeds than when 10 mM HTeO_2^+ was used. At such a low seed diameter, the diffusion length scale of tellurium was comparable and, as a result, formation of solid nanowire occurred due to the overlap of the diffusion zones from two sides across the seed [8]. On the other hand, hollow nanotubes were observed at higher $[\text{HTeO}_2^+]$ (*i.e.*, 10 mM), because of the dominance of nuclei size over the diffusion length, and thus preferential growth along the axis was exhibited, as tellurium atoms preferred to deposit at the circumferential edge, where the free surface energy was higher. This further explained the morphological transition from microwires to microtubes as the HTeO_2^+ concentration increased from 0.1 to 10 mM at fixed H_2SO_4 concentration of 2 M. The opposing transition from microtubes to microwires with increase in H_2SO_4 concentration from 1 to 5 M might be attributed to higher concentration of tellurium atoms at higher H_2SO_4 . The high tellurium atom concentration also led to a more progressive nucleation and growth process in which the large dimension variation caused no statistic difference between 2 M and 5 M H_2SO_4 conditions.

In order to monitor the nucleation and growth process of Te structures, time-dependent experiments were conducted at fixed HTeO_2^+ concentration of 10 mM and varied H_2SO_4 concentration of 2 and 5 M (Figures 2.5 and 2.6). While the time intervals of 6, 12, and 24 hours were fixed for both conditions, earlier time intervals were chosen differently to better visualize the growth process. For a lower H_2SO_4 concentration of 2 M,

the growth began as a thin film of columnar structure with hexagonal cross-section after 3 hours, as shown in Figure 2.5 A. The thin film then evolved to micro-rods after 6 hours, microtubes after 12 hours, which continued to grow in length up to 24 hours. The average diameter and length increased 10 and 9 times, respectively, from 3 to 24 hours. Meanwhile, by utilizing 5 M H_2SO_4 , needle-like wires with triangular cross-section were observed after 1 hour. The microwires grew in both radial and longitudinal directions throughout the 24-hour period. The average diameter and length increased 18 and 12 times from 6 to 24 hours respectively (*i.e.* 0.21 μm and 4.10 μm to 5.41 μm and 35.5 μm). Figures 2.5 D and 2.6 D indicate that the diameter variation was small in the first six hours and became larger as reaction time was longer. This suggests that at the later stage of the reaction, the abundance of tellurium atoms in the bulk was not enough to diffuse towards the substrate and grow the smaller structures. Zhu *et al.* indicated that the formation of tellurium tubular structures was associated with high pH when studying the effect of acidic and alkaline electrolyte on the reduction reaction of K_2TeO_3 and NaH_2PO_2 [29].

At earlier stages of GDR (Figures 2.5 A and 2.6 A), microtubes and microwires were formed by layer-by-layer growth and island growth (Volmer-Weber mode), respectively. During the layer-by-layer growth, atoms would bind to the surface more strongly and prefer having a complete layer before starting another layer on top. In contrast, atoms in island mode would bind more strongly to each other than to the substrate, leading to the formation of clusters or islands.

Figure 2.6 C shows that the tellurium microwires formed with either needle-like tips or spine-like tips with triangular cross-sections. Higher concentration of sulfuric acid

led to higher mass transfer rate of proton to the substrate surface and higher reaction rate. The high supersaturation of reduced tellurium atoms caused the low mobility of tellurium adatoms and thus high probability of defect formation. Jeong *et al.* indicated that the divergence of hexagonal to triangular tellurium structure might be attributed to the trapped defect and slow mobility adatoms [33]. The formation of both structures might be attributed to the high supersaturation of Te atoms which led to the trapped defects (axial dislocation) and adatoms with slow mobility.

Jianfei *et al.* reported that synthesized tellurium structures chemically dissolved back to electrolyte due to a long exposure in acidic medium [18]. Tellurium nanowire diameter was found decreasing with time. Dissolution of tellurium structures was reported to be promoted in alkaline solution [12, 13, 29]. Zhu *et al.* observed corroded tellurium nanorod as an intermediate structure of the morphological transition between nanorod and nanotube [29]. In this work, the dimension of tellurium structures increased over the period of reaction time, and the corroded surface was not observed in any of the time-dependent experiments.

X-ray diffraction patterns of the synthesized Te structures at varied concentration of HTeO_2^+ and H_2SO_4 are shown in Figures 2.7 and 2.8. The equations for calculating grain size and texture coefficient are provided below.

Scherrer's formula was used to estimate the grain size from the full width at half-maximum (FWHM) of each peak

$$D_{hkl} = \frac{K\lambda}{B_{hkl}\cos\theta} \quad (2.1)$$

where D_{hkl} is the grain size, K is the crystallite shape factor (which is 0.9 in this work), B_{hkl} is the FWHM, and θ is the Bragg angle.

The texture coefficient was estimated by comparing the measured peak intensity with reference data as follows

$$T_{hkl} = \frac{I_{hkl}}{I_{o,hkl}} \left[\frac{1}{n} \sum_1^n \frac{I_{hkl}}{I_{o,hkl}} \right]^{-1} \quad (2.2)$$

where I_{hkl} and $I_{o,hkl}$ are the measured peak intensity and the reference intensity respectively, n is the number of diffraction planes.

The spectra indicated that all of the synthesized Te structures were hexagonal crystals. The preferential growth of the structures was along the c-axis (001), which was expected due to the anisotropic structure of Te crystals. As the HTeO_2^+ concentration increased, the intensities of peaks corresponding to the (101) and (003) plane increased, which supported the increase in the Te. Furthermore, (113) peak was observed for Te microtubes and Te microwires synthesized using 10 mM HTeO_2^+ , 2 and 5 M H_2SO_4 respectively. This implies all four peaks might exist for both microtubes and micro-wires but the intensity is not strong enough to be detectable for the small Te structures. Also, the peak intensity also depends on the orientation of Te structure with respect to the substrate. XRD spectrum in Figure 2.7 showed that the peak intensities augmented with an increase of H_2SO_4 concentration from 1 to 2 M.

The acidic anion types also crucially impact the growth of Te structures through the dissolution of nickel. Since nickel oxidation rate in sulfate bath is the slowest among three common inorganic acidic baths, acid concentrations of 2 and 5M at the fixed HTeO_2^+

concentration of 10mM were first chosen to investigate the effect of acidic anions. Solution containing 5M HNO_3 and 10mM HTeO_2^+ dissolved the nickel foil completely in less than 1 hour; therefore, acidic anion dependent experiments were investigated at HTeO_2^+ concentration of 10mM and acid concentration of 2M. As shown in Figure 2.9 A-C, hexagonal columnar structures, microtubes with sloping cross section, nanowires were observed in the sulfate, chloride, and nitrate baths respectively. Te structures which were obtained from chloride bath had the largest diameter and length of 0.758 and 16.8 μm respectively.

Xu [34] and Tena-Zaera [35] indicated that chloride ions preferentially adsorbed on the (001) ZnO surface to hinder the crystal growth along the c axis using the electrodeposition method. However, this mechanism might not apply to this work since the length-to-diameter ratio was about 22 for Te structures in the acidic chloride bath. The Te microtubes with sloping cross section might have the same mechanism as the microtubes obtained at 10mM HTeO_2^+ and 2M H_2SO_4 , in which the degree of Te supersaturation reduced over time. Te structures in the chloride bath however had the longitudinal growth rate much faster than the lateral growth rate, thus the wall of the tube was not completed. A part of the wall dominantly grew to form the microtube with sloping cross section as shown in Figure 2.9 B.

GDR in nitrate bath resulted in the smallest dimension of Te structures in which the diameter and length were 0.0969 and 0.451 μm , respectively. The growth mechanism of Te microwires might be the same as that of the microwires at 10mM HTeO_2^+ and 5M H_2SO_4 in which the high degree of Te supersaturation led to defect formation. The small

dimension of Te wires from nitrate bath, a strong oxidant, will be explained in the next section.

2.3.2 Electrochemistry of Tellurium during GDR

During the GDR, the anodic reaction (oxidative dissolution of nickel) and cathodic reactions (reduction of dissolved oxygen, telluryl ions, and hydronium ions) occurred simultaneously at various locations across the surface of nickel. The possible electrochemical reactions and standard reduction potentials of tellurium and nickel in aqueous solution are listed below:

In nitrate bath, an additional cathodic reaction occurs as follow.

This reduction reaction comprises of the two following reactions [36].

The oxidation of nickel in acidic electrolyte, as shown in equation (2.6), could consist of the constitute reactions (2.10-2.12) for sulfate and nitrate baths in which X stands for OH^- and NO_3^- [21, 37, 38], and reactions (2.14-2.16) for chloride baths [37]

With a wide standard reduction potential gap of 0.808 V, Ni/Ni^{2+} and Te/HTeO_2^+ were appropriate reactants for a successful GDR. The electron generation from the oxidation of Ni would be consumed by the reduction reactions, as shown in reactions 2.3-2.5. Therefore, the rate of electrons released and consumed would determine the abundance of bulk Te atoms, which would then affect the diffusion rate of Te atoms as well as the morphology of Te structure. In order to monitor the electron transfer rate correlating with the reduction and oxidation reaction rates, open-circuit potential (OCP) measurements and linear polarization (LP) were conducted.

As shown in Figure 2.10 A, the transient OCPs were obtained at varied HTeO_2^+ concentration from 0.1 to 10 mM with a fixed 2 M H_2SO_4 at 23 °C for 24 hr. All three transient OCP curves exhibited similar shape, including two perturbations of the potential. The first deviation might be attributed to formation of nickel oxide as shown in equation (2.13). The formation of NiO formed a passivation layer on nickel surface, which led to the sudden potential change to a more positive value. The higher mass transfer at higher concentration of telluryl ions (*i.e.*, 10 mM HTeO_2^+) resulted in higher reduction reaction rate, depicted by the shortest time to reach the first potential deviation and the fastest rate

of potential going to cathodic direction. The second potential perturbation might come from almost full coverage of nickel surface.

The polarization curves, which characterize the kinetic aspect of the electrochemical reaction, were obtained using the same setup for the OCP measurements. The Tafel curve was split into anodic and cathodic sides, which associated with oxidation and reduction reactions, respectively. The mixed potential and mixed current density were extrapolated from the intersection of two linear fitted lines of anodic and cathodic sides. The mixed potential and mixed current density at different telluryl ion concentration were monitored as a function of time, as shown in Figures 2.10 C-D. More positive mixed potentials were observed at higher HTeO_2^+ concentrations in Figure 2.10 C, which was consistent with the OCP. This implied that the driving force for GDR reaction was lower at higher HTeO_2^+ concentration. An increment of HTeO_2^+ concentration will increase its reduction potential and correspond to a more positive mixed potential and OCP according to the mixed-potential theory. As shown in Figure 2.10 A, OCP value at 0.1 mM HTeO_2^+ had the most positive value owing to the slow reaction and unsteady state potential after 24 hours.

The higher mixed current density indicated the higher reaction rate and explained the larger dimension of tellurium structures at higher HTeO_2^+ concentration. This is consistent with the higher mass of depositing tellurium at higher concentration of HTeO_2^+ as shown in Figure 2.11 A. The higher concentration of HTeO_2^+ also led to higher mass transfer and corresponding higher fraction of electrons generated by nickel used for telluryl ion reduction as shown in Figure 2.11 B. Park *et al.* also reported that concentration of

HTeO_2^+ affected not only the driving force through the redox potential but also the deposition rate of Te elements [27]. While the mixed potentials seemed to approach the equilibrium after 8 hours, the current densities generally increased throughout 24 hours of reaction. Also, electrolyte containing 10 mM HTeO_2^+ had a considerable reduction in the first 4 hours, corresponding to the increasing current density. The drastic increase in current density might indicate the activation of more and larger seeds than the conditions of lower $[\text{HTeO}_2^+]$ (*i.e.*, 0.1 and 1 mM HTeO_2^+). The formation of enormous nucleation seeds dropped the degree of $[\text{HTeO}_2^+]$ supersaturation in the electrolyte, resulting in the formation of the tubular structures.

Transient OCPs at different H_2SO_4 concentrations were also characterized and shown in Figure 2.12 A. All OCPs showed the potential perturbation at the early stage owing to the formation of nickel ion passivation. The potential then went to more cathodic values, where the rate of potential change reduced with the decrease in H_2SO_4 concentration. Only did the OCP at lower H_2SO_4 (*i.e.* 1 and 2 M) exhibit the second potential perturbation, which might have resulted from the nearly full coverage of nickel surface. The different trend of OCP at low H_2SO_4 concentration (1 and 2 M) and the high concentration (5 M) might be correlated to the formation of microtubes and microwires, respectively. Dissolution of nickel was shifted to more negative potential at higher acid concentration, which caused lower OCP, as observed in Figure 2.12 A. The reaction at 1 M H_2SO_4 was not at steady state after 24 hours, shown by the potential continuing to decrease at 24 hours.

LP characterization at different H_2SO_4 concentration were also conducted and shown in Figure 2.12 B. The mixed potential was more positive with lower H_2SO_4 concentration, indicating that the reaction at higher H_2SO_4 concentration had more driving force. The reaction rate theoretically increased with H_2SO_4 concentration, which agreed with the mixed current density at 1 M H_2SO_4 , as shown in Figure 2.12 D. The overall higher mixed current density at 2 M H_2SO_4 than 5M H_2SO_4 was not explained in this work, and further studies are required to understand this finding.

The effect of dissolved oxygen on the GDR was studied using three different electrolytes at fixed 2M H_2SO_4 : naturally aerated electrolyte with and without 10mM HTeO_2^+ and deaerated 10mM HTeO_2^+ solution. The concentration of dissolved oxygen with and without deaeration by UHP nitrogen were 0.022 and 0.17 mM respectively which are much smaller than concentration of hydronium ions. As shown in Figure 2.13, the mixed potential of naturally aerated solution with telluryl ions is slightly more positive than the deaerated solution, but their anodic and cathodic branches have the similar shape. The difference in mixed potential might be attributed to the dissolved oxygen whose reduction potential is more positive than that of telluryl ions as indicated in equations (2.3-2.4). The more negative mixed potential of naturally aerated solution without telluryl ions further explain the negligible effect of dissolved oxygen on the GDR.

Although the dissolution of nickel via adsorbed intermediate species is similar for three anions as shown in equations (2.10-2.16), the effect of anions on the formation of tellurium structures is considerable. Reduction potential of nickel is slightly more negative than that of hydronium ion as shown in equations (2.6) and (2.5) respectively; therefore,

the dissolution of nickel is kinetically easier and faster in the presence of strong oxidants, such as HNO_3 [22]. Nitric acid is also known for the autocatalytic mechanism in nickel dissolution. As the concentration of nitric acid is lower than 6M, the mechanism of HNO_3 reduction is shown in equations (2.7-2.9) in which nitrous acid (HNO_2) plays the role as an electroactive species [36]. HNO_2 , which always exists in a small amount in nitric acid, is first reduced into nitrogen monoxide (NO). The gas adsorbs on nickel surface and undergoes a heterogeneous chemical reaction with HNO_3 to regenerate HNO_2 as shown in equations (2.8-2.9). Acidic nitrate bath has additional reduction reactions of nitrate anion besides three reduction reactions happening in both chloride and sulfate baths. This might be attributed to the Te nanowires because the electrons, which were generated from fast Ni dissolution in the nitrate bath, were consumed by mostly nitrate reduction reaction rather than telluryl reduction reaction. As a result, the concentration of dissolved Te atoms was only enough to form small seeds and nanowires, which was similar to the formation of Te structures at 0.1mM HTeO_2^+ and 2M H_2SO_4 . Figure 2.9 C also displays dark color clumps with dissimilar height which might be the nickel surface from vigorous dissolution.

Different from nitric acid, hydrochloric acid is not a strong oxidant; however, negativity of chlorine is only less than fluorine and with the small anionic diameter, chloride ions diffuse fast and have a preferential adsorption over hydroxyl ions. The adsorption of chloride ions at the inner Helmholtz plane of the double layer reduces the potential required to transfer nickel atoms from the crystal lattice into solution [24]. As a result, the larger dissolution rate of nickel leads to larger reduction rate of telluryl ions.

As displayed in Figure 2.14A, transient OCPs at different acidic baths have the same potential perturbation relating to almost full coverage of nickel surface. However, the potential deviation due to the surface passivation of nickel oxide occurs only a short period of time in the nitrate bath and does not exist in the chloride bath. The nickel oxide formation in both sulfate and nitrate baths is owing to the adsorption of OH^- ions as shown in equation (2.13). Nitrate bath only required 90 min to get to the steady state, indicated by the plateau of potential. The shift of positive potential as shown in the inset of Figure 2.14A might be due to the dissolution of deposited Te back to solution. After 2 hours of reaction, bubble formation was observed, suggesting complete dissolution of Te and the beginning of Ni dissolution. The most positive steady OCP of nitrate bath might be because the majority of reduction was nitrate reduction reaction whose reduction potential is more positive than the reduction potential of telluryl ions.

From the linear polarization, the mixed potential and the mixed current density at different acidic baths as functions of the reaction time were obtained and shown in Figure 2.14 C-D. With the potential shift to more negative value in the sequence of nitrate, sulfate, and chloride baths, the mixed potential exhibits consistency with the OCP data. The largest mixed current density at nitrate bath (Figure 2.14D) confirms the proposed mechanism that the formation Te nanowires is owing to the dominant reduction of nitrate rather than the slow dissolution of nickel. As expected, the mixed current density at the chloride bath is greater than that at the sulfate bath due to the preferential adsorption of chloride anion.

2.4 Conclusions

In this work, one-dimensional tellurium structures were synthesized by galvanic displacement reactions of nickel in acidic media. The transition of t-tellurium microwires to microtubes was observed as the HTeO_2^+ concentrations increased, and the opposite transition was obtained by increasing the H_2SO_4 concentration. However, the diameter and length of microstructures augmented with increase in HTeO_2^+ concentrations. Both phenomena might be attributed to the effect of tellurium reduction rate and mass transfer of tellurium atoms. For the tellurium precursor effect, the formation of tellurium microwire was preferred at low HTeO_2^+ concentration (*i.e.* 0.1 and 1mM), owing to the similarity of seed size and diffusion length scale. Tellurium microwires were also synthesized at high H_2SO_4 concentration because high mass transfer resulted in no preferential growth of tellurium. The dissolution of nickel mainly depends on the acidic anions which also influence the deposition of Te if the anion is a strong oxidizing agent (*e.g.*, NO_3^-). Te nanowires were synthesized in the nitrate bath, while microtubes with sloping cross section were obtained in the chloride bath due to the strong adsorption of Cl^- . Hydronium ions were responsible for dissolving nickel in the sulfate bath, resulting in Te microtubes.

2.5 References

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Figure 2.1. Schematic set up of the Teflon cell for galvanic displacement reactions

Figure 2.2. SEM images of Te structures synthesized from (A) 0.1 mM, (B) 1 mM, (C) 10 mM HTeO_2^+ in 2 M H_2SO_4 at 23 °C for 24 hours. Insets are cross-sectional SEM images. Scale bar 10 μm . Average diameter (D) and length (E) as a function of HTeO_2^+ concentration.

Figure 2.3. SEM images of Te structures synthesized from (A) 1 M and (B) 5 M H_2SO_4 with 10 mM HTeO_2^+ at 23°C for 24 hours. Insets: cross-sectional SEM images. Scale bar 10 μm . Average diameter (C) and length (D) as a function of H_2SO_4 concentration.

Figure 2.4. Mass of consuming nickel and depositing tellurium (A) and mol fraction of consuming nickel converted to tellurium (B) at varied concentrations of H_2SO_4

Figure 2.5. SEM images of the Te structures synthesized at (A) 3 h, (B) 6 h, and (C) 12 h with 10 mM HTeO_2^+ and 2 M H_2SO_4 at 23°C, and without illumination. Insets: cross-sectional SEM images. Scale bar without specification is 10 μm . Average diameter (D) and length (E) as a function of reaction time.

Figure 2.6. SEM images of the Te structures synthesized at (A) 1 h, (B) 6 h, and (C) 12 h with 10 mM HTeO_2^+ and 5 M H_2SO_4 at 23°C, and without illumination. Insets: cross-sectional SEM images. Scale bar without specification is 10 μm. Average diameter (D) and length (E) as a function of reaction time.

B H ₂ TeO ₂ ⁺ (M)	(101)		(003)		(113)		(104)	
	Ave. Grain size (nm)	Text. Coef.	Ave. Grain size (nm)	Text. Coef.	Ave. Grain size (nm)	Text. Coef.	Ave. Grain size (nm)	Text. Coef.
0.1	160	0.246	97.0	1.75	No peak		No peak	
1	36.2	0.128	52.0	2.61	No peak		24.4	0.267
10	64.4	0.0157	105	2.98	73.3	0.0130	87.0	0.0029

Figure 2.7. (A) XRD patterns of tellurium structures at fixed H₂SO₄ concentration of 2M and H₂TeO₂⁺ concentration of 0.1mM (black), 1mM (red), and 10mM (blue) at 24 hours and (B) calculated grain size and texture coefficients.

B [H ₂ SO ₄] (M)	(101)		(003)		(113)		(104)	
	Ave. Grain size (nm)	Text. Coef.	Ave. Grain size (nm)	Text. Coef.	Ave. Grain size (nm)	Text. Coef.	Ave. Grain size (nm)	Text. Coef.
1	51.1	0.00487	77.8	2.90	No peak		79.1	0.097
2	64.4	0.0157	105	2.98	73.3	0.013	87.0	0.0029
5	34.1	0.091	41.3	2.74	44.8	0.296	40.3	0.870

Figure 2.8. (A) XRD patterns of tellurium structures at fixed HTeO_2^+ concentration of 10mM and H_2SO_4 concentration of 1M (black), 2M (blue), and 5M (red) at 24 hours and (B) calculated grain size and texture coefficients.

Figure 2.9. SEM images of the Te structures synthesized with 10 mM HTeO_2^+ and (A) H_2SO_4 , (B) HCl and (C) HNO_3 at concentration of 2M at 23°C for 1 hour, and without illumination. Insets: cross-sectional SEM images. Scale bar without specification is $2\ \mu\text{m}$. Average diameter (D) and length (E) as a function of acidic baths.

Figure 2.10. (A) Transient open-circuit potentials (OCP), (B) linear polarization curves, (C) calculated mixed potential, and (D) mixed current with HTeO_2^+ concentration of 0.1 mM (black), 1 mM (red), 10 mM (blue) and a fixed 2 M H_2SO_4 at 23 °C and no illumination for 24 hours.

Figure 2.11. Mass of consuming nickel and depositing tellurium (A) and mol fraction of consuming nickel converted to tellurium (B) at varied concentrations of HTeO_2^+

Figure 2.12. (A) Transient open-circuit potentials (OCP), (B) linear polarization curves, (C) calculated mixed potential, and (D) mixed current with H_2SO_4 concentration of 1 (black), 2 (blue), 5M (red) and a fixed 10 mM HTeO_2^+ at 24 hours.

Figure 2.13. Linear polarization curves at naturally aerated 0 mM HTeO_2^+ (black) and 10 mM HTeO_2^+ (red) and deaerated 10mM HTeO_2^+ (blue) and at a fixed 2 M H_2SO_4 at 1 hour.

Figure 2.14. (A) Transient open-circuit potentials (OCP), (B) linear polarization curves, (C) calculated mixed potential, and (D) mixed current density with H_2SO_4 (black), HCl (red) and HNO_3 (blue) at concentration of 2M and a fixed HTeO_2^+ concentration of 10 mM and no illumination for 1.5 hours

CHAPTER 3. (APPENDIX)

GALVANIC DISPLACEMENT OF NICKEL TO FORM SELENIUM

NANOWIRES AND GLOBULAR STRUCTURES IN ACIDIC SULFATE BATH

3.1 Introduction

Selenium (Se) is another element in the chalcogen group together with tellurium. Se and Te thereby have similar crystal structures and properties. Selenium has three allotropies: amorphous (a-Se), monoclinic (m-Se), and crystalline trigonal (t-Se). Non-crystalline Se has two stable forms at different temperature (*i.e.* red Se under 31°C and black Se at 31-230°C), while crystalline t-Se is the most stable phase at ambient conditions [1, 2]. Crystalline Se consists of seven spiral chains (six corners and one center) which were bound by Van der Waals force. Three Se atoms per turn of the helical chain were covalently bound together. Similar to tellurium, Se also has been widely used for different applications.

Selenium, possessing a relatively narrow band gap of 1.6 eV, has been employed as the sensing material for chemiresistive gas sensor at room temperature for many primary alcohols [3] and volatile organic compounds [4, 5]. With a high photoconductivity ($\sim 8 \times 10^4 \text{ S cm}^{-1}$), Se is a good photoconductor to almost the entire visible spectra [6, 7]. In addition, Se is a promising material for rectifiers, solar cells, and xerography [8]. With multiple valence states (+VI to -II), Se can react with many transitional metals to form metal selenides, resulting in modified properties for various applications. For instance, Sb_2Se_3 with orthorhombic crystal structure has good photovoltaic properties and high

thermoelectric power [9]. Iron-group transitional metal selenides showed promising storage capacities for sodium-ion and lithium-ion batteries [10].

Since the discovery of carbon nanotubes in 1990s, it is widely accepted that one-dimensional materials provide significant enhancement in material properties (e.g., electrical, chemical and thermal properties). Synthesis of one-dimensional Se structures thereby have been intensively investigated by various techniques, such as physical evaporation [11], hydrothermal [12-14], solvothermal [6, 15], reflux [16, 17], sonochemical [18-21], and electrochemical methods [22]. However, galvanic displacement reaction (GDR) exhibits several advantages over the other approaches, including cost-efficiency and moderate operation conditions. The difference in redox potential between a sacrificial material and noble metal ions results in the deposition of interested metal on the sacrificial material.

Elemental selenium is commonly reduced from Se (+IV) precursor which is present as SeO_3^{2-} in alkaline solution and H_2SeO_3 in acidic solution. As the number of metals that can serve as the sacrificial materials is much more in acidic solution than in alkaline solution, H_2SO_4 was chosen to control the acidity of the electrolyte. As nickel was also employed as the sacrificial metal, the GDR was driven by the standard reduction potential gap of 1.02 V between Ni/Ni^{2+} and $\text{Se}/\text{H}_2\text{SeO}_3$.

3.2 Experimental section

3.2.1 Sample preparation and galvanic displacement reaction

The selenium-based electrolyte was first prepared by dissolving selenium dioxide (SeO_2 , 99%, Acros Organics) in sulfuric acid solution with various amounts. Commercially pure Nickel foam (Ni, 0.03mm thick, 99.9%, MTI, corp.) was cut into a circular shape with a diameter of 1.27 cm and was used as the sacrificial material. Before reaction, the foams were cleaned with 1 M H_2SO_4 for one minute to remove the surface oxide, rinsed with deionized water, and then blow dried with air. All GDRs for Ni foam were carried out in 15 ml polypropylene tubes with screw cap which were initially filled with 12 ml of prepared electrolyte solution. The GDRs were initiated by placing the Ni foams into the tubes. The tubes were then attached to the holder of Cole-Parmer tube rotator at the rotating speed of 5. The reactions were stopped by carefully removing the Ni foams from the tubes and rinsed three times with distilled water.

3.2.2 Material characterization

The morphology of the Se structures were observed by optical microscope (Hirox KH-7700) and scanning electron microscope (SEM, TESCAN VEGA3). The identity of deposited elements on Ni foams was analyzed by electron-dispersive spectroscopy (EDS, Ametek EDAX)

3.3 Results and discussion

Figures 3.1 A-C shows the optical images of Ni foams after GDRs with varied concentration of H_2SeO_3 , while fixing H_2SO_4 concentration and reaction temperature and time at 5 M, 23 °C, 24 hours respectively. The reddish color of the optical micrographs implies the amorphous crystal structure of Se deposit. Furthermore, the shade of the color indicated that more Se amorphous structures were formed at higher concentration of H_2SeO_3 . The SEM images of synthesized Se structures, as shown in Figures 3.2 A-C, showed the transition of Se morphology from amorphous to aggregation and globular structures as the concentration of H_2SeO_3 increased. The EDS spectra in Figures 3.2 D-E confirmed that the deposited structures were selenium. Moreover, increasing concentration of H_2SeO_3 from 0.1 to 1 mM led to the ratio of Ni and Se peaks reversely switched. This was consistent with the density of Se structures shown in Figures 3.1 and 3.2 A-B.

Similar change in the shade of red color was exhibited in Figure 3.3 A-C as concentration of H_2SO_4 was varied (1-5M) and concentration of H_2SeO_3 was fixed at 10mM at 23 °C and 24 hours of reaction. The lighter red color suggested Se structures were synthesized at lower density than those in Figure 3.1. Morphological transition from aggregation to globular structures was also observed in the SEM images. The density of globular structures is also higher in the more acidic solution as shown in Figure 3.4 B-C. The EDS spectra identified only Se and Ni were present on the samples and the fraction of Ni reduced as increasing the concentration of H_2SO_4 .

Another factor that affected the growth of Se structures was temperature. Two conditions that resulted in high density of Se structures at room temperature were chosen

to further study at 60°C. Furthermore, time-dependent experiments at two different time intervals (*i.e.*, 6 and 18 hours) were conducted to show the growth mechanism. As shown in Figure 3.6, Se aggregation was still synthesized at 1 mM H₂SeO₃ and 5 M H₂SO₄, but larger Se particles were formed at higher temperature. The Se particles grew in dimension and density as the reaction time was longer. In contrast, Se globular structures were changed to a mixture of nanoparticles and nanowires as the temperature increased from 23°C to 60°C at 10mM H₂SeO₃ and 5M H₂SO₄. Although Se nanoparticles and nanowires were observed at both time intervals, the density and dimension of nanoparticles and nanowires decreased and increased respectively. For the condition of 10 mM H₂SeO₃ and 5M H₂SO₄, the optical images for the samples synthesized at 60°C (Figure 3.5 B & D) do not show the red color which was observed for the samples at 23°C (Figure 3.1 C). This might be attributed to the transformation from non-crystalline amorphous to crystalline trigonal Se structures. Since trigonal Se has anisotropic structure, crystalline Se structures are one-dimensional. In addition, Gates et al. indicated that amorphous Se was mostly available in the spherical shape [16].

The change in deposited Se morphology could be explain by the nucleation and growth processes which were previously described in section 2.3.1. The higher the concentration of Se precursor and/or the concentration of H₂SO₄ resulted in more Se atoms available in solution. The density and dimension of Se structures thereby were larger as shown in Figure 3.1 and 3.2. The main difference between the growth of Se and Te structures at similar electrolyte composition was the formation of amorphous Se globular structures although Se has the anisotropic crystal structure. The globular structures were

then transformed into one-dimensional structures as shown in the time-dependent experiment. The phenomenon is typical for Se growth via dissolution and recrystallization mechanism and has been reported from different synthesis methods [12, 14-20]. The least stable phase (i.e. amorphous Se allotrope) is kinetically favored and commonly precipitates first owing to the Stranki's rule [14]. Since crystalline phase are thermodynamically more favorable than amorphous phase, the transformation occurs to reduce the free energy. The formation of amorphous globular structures could be attributed to the relatively fast reduction of Se by strong reducing agents. Xi et al. reported the red amorphous and trigonal Se particles were formed as sodium selenite was reduced by hydrazine and sodium formation respectively [13]. The effect of temperature at 10mM H_2SeO_3 and 5M H_2SO_4 might be owing to larger rate of Se reduction at higher temperature. In other word, the transformation to nanowires might need longer than 24 hours to occurs at room temperature. Chen et al. observed the formation of aggregated microsphere and one-dimensional nanostructures at 160°C while only 1-D nanostructures 180°C [14]. Furthermore, Wang et al. investigated the effect of various solvents on the transformation which was not observed in water at room temperature after a month [23].

3.4 Conclusion

Selenium globular nanostructures and nanowires were synthesized by galvanic displacement reactions of nickel in acidic sulfate bath. At the temperature of 23 °C, Se morphology transition from aggregation to globular structures were observed at different concentrations of H_2SeO_3 and H_2SO_4 . Furthermore, the density and dimension of Se structures were higher as increasing the H_2SeO_3 and H_2SO_4 concentrations. A different Se

morphology change from globular structures to wires exhibited at 60 °C, which might be attributed to the phase transformation from kinetically favored amorphous to thermodynamically favored crystalline Se.

3.5 References

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Figure 3.1. Optical images of Se deposited on Ni foam from (A) 0.1 mM, (B) 1 mM, and (C) 10 mM H_2SeO_3 with 5 M H_2SO_4 at 23°C for 24 hours. Scale bar 50 μm .

Figure 3.2. SEM images and corresponding EDS spectra of Se structures synthesized from (A) & (D) 0.1 mM, (B) & (E) 1 mM, and (C) & (F) 10 mM H_2SeO_3 with 5 M H_2SO_4 at 23°C for 24 hours respectively. Scale bar 2 μm

Figure 3.3. Optical images of Se deposited on Ni foam from (A) 1 M, (B) 2 M, and (C) 5 M H_2SO_4 with 10 mM H_2SeO_3 at 23°C for 24 hours. Scale bar 50 μm .

Figure 3.4. SEM images and corresponding EDS spectra of Se structures synthesized from (A) & (D) 1 M, (B) & (E) 2 M, and (C) & (F) 5 M H_2SO_4 with 10 mM H_2SeO_3 at 23°C for 24 hours respectively. Scale bar 2 μm

Figure 3.5. Optical images of deposited Se on Ni foams synthesized from (A) & (C) 1 mM and (B) & (D) 10 mM H_2SeO_3 with 5 M H_2SO_4 at 60°C for 6 and 18 hours respectively. Scale bar $50\mu\text{m}$

Figure 3.6. SEM images of Se structures synthesized from (A) & (C) 1 mM and (B) & (D) 10 mM H_2SeO_3 with 5 M H_2SO_4 at 60°C for 6 and 18 hours respectively. Scale bar 2 μm