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SOLUTION-BASED MODIFICATIONS OF TEMPLATE-GROWN NANOWIRES

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Abstract

The synthesis and modifications of nanoscale solids, which underpin advances in nanoscience and nanotechnology, has been a rapidly growing field of chemistry. Nanoparticles, including nanowires, can be synthesized in a variety of ways. However, hard template electrodeposition has many advantages such as creating multi-segmented nanowires. This thesis research explores new strategies for modifying and expanding the complexity of nanowire materials, including protection/deprotection, crystallinity enhancement, creating a composition gradient, and performing galvanic replacement reactions. Ag nanowires were successfully protected by reacting them with sulfur to produce Ag_2S. Any excess sulfur was removed by either heating the sample in tetraethylene glycol (TEG) at 200°C or reacting the wires in toluene. To deprotect the wires, the sulfur was removed by heating the wires in TEG at 300° C for two thirty-minute periods. In other modifications, the crystallinity of Pt nanowires was slightly enhanced by annealing them in TEG at 300°C for 1 hour. Establishing a composition gradient in Au/Ag nanowires was attempted by annealing the wires in TEG at 250°C. However, it was concluded that annealing the Au/Ag nanowires had no effect on the gradient. The metal nanowires modified in these experiments were characterized using powder x-ray diffraction and/or scanning electron microscopy, including elemental mapping.

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Chapter 1: Introduction

1.1: Nanoscale Solids

Advances in the synthesis of nanoscale solids are being rapidly reported in both organic and inorganic chemistry. These nanoparticle materials, which have at least one dimension in the nanometer size range (10^{-9} m), tend to have unique properties. In the last decade, much progress has been made to connect these nanomaterial properties to real life applications in the areas of electronics, catalysis, drug delivery, medical diagnosis, and many others.[1,2]

For example, beta-emitting gold nanoparticles were studied for their ability to reduce human prostate tumors in-vivo in mice. These gold nanoparticles demonstrated a high affinity for the tumor cells. As a result, tumor volumes were reduced by 82% over three weeks.[3] Gold nanoparticles also have been studied as a synthetic high-density lipoprotein, which can protect against the buildup of plaque in arteries and therefore minimize the associated consequences such as stroke and heart disease.[4] Another biological use for nanoparticles is the bacteriostatic properties of polymer/silver nano-composites.[5] These characteristics of Ag nanoparticles have allowed Samsung to release their "Silver Nano" line of air-conditioners, refrigerators and washing machines, which use the silver nanoparticle surface for antibacterial and antifungal advantages. Research into semiconductor properties of nanoparticles is another expanding area within nanotechnolog. For example, CdSe has been used in quantum dot solar cells and Ag_2S coated Ag nanowires blended with Pt nanowires have been used as a quantized conductance atomic switch (QCAS).[6-8]

The development of diverse methods for synthesizing nanomaterials, their chemical reactivity, and their size, permits the realization of unique magnetic, optical, electronic, catalytic and energy conversion properties.[7,9] One-dimensional (1D) nanowires are particularly valuable

as nanoscale materials because they are easily synthesized and their characteristics can be modified through a variety of reactions. Specifically, nanowires can be synthesized via solution-phase synthesis, vapor-phase synthesis, or template-base synthesis.[10] Template-based metal nanowires are a topic of increased attention and they can be synthesized through either soft or hard-template methods. In the soft-template process, chemical or electrochemical reduction is used to construct the nanowires in a polymer, which allows for large bulk quantities. Soft-template methods include redox reactions, seeding prior to chemical reduction, and electrochemical reduction. However, in hard-template chemistry, the nanowires are electrochemically grown through a porous membrane, either track-etched polycarbonate or anodic aluminum oxide (AAO).[11] (figure 1)

Figure 1
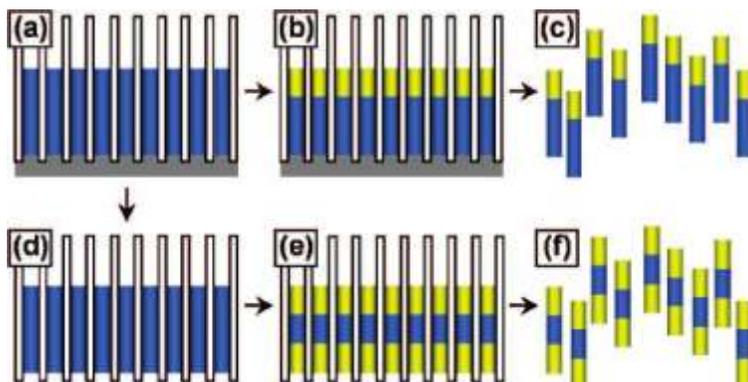
Figure 1. Nanowires reacted in the membrane before the Ag backing is removed (a and b) and after the backing is removed with HNO_3 (d and e). The wires are reacted (b and e) and then released from the membrane (c and f) by vortexing in NaOH.[9]

1.2: Electrodeposition

Electrodeposition produces 1D nanostructures with controlled aspect ratios (length-to-width) as large as 2000:1.[12] While semiconducting, molecular, and polymeric components can be deposited electrochemically, the deposition of metallic components are the focus of this project, specifically, metallic nanowires.[13] Electrodeposition is advantageous because it allows for a

regulated substrate deposition and the ability to control the growth length and elemental composition of the wires.[14] The nanowire structure is controlled by three variables: (1) the pore diameter of the membrane, which dictates the width of the wires; (2) the sequence of reagents used, which dictates the metallic sequence and pattern of the wires; and, (3) the charge that is applied, which controls the length of the wires.[15] The amount of negative charge passed through the system affects the length of the wires due to Faraday's Law of Electrolysis, which states that the element's equivalent weight is directly proportional to the amount of material deposited at an electrode.[12] In addition, reactions and modifications to template-grown nanowires can be explored either inside the membrane or in solution after removal from the membrane.[9]

One type of the template for electrochemical deposition of nanowires is the track-etched polycarbonate membrane, which is less commonly used due to the intersections of the membrane's pores. To prepare a polycarbonate membrane, nuclear fission fragment ions are forced to bombard a thin film of polycarbonate, creating damage tracks.[12,16] Then, these tracks are chemically etched into pores with uniform diameters, which can range from 10 to 2000 nm depending on the etching process. The pore density of the membrane can be as high as 10^9 pores per square centimeter. However, due to the nature of the damage tracks, which have entry angles as large as 34° with respect to the surface, many of the pores intersect. These intersecting pores affect not only the number of the wires but also their lengths and homogeneity. In addition, the wires cannot be modified while inside the membrane because the polycarbonate will dissolve under many of the solution-modification conditions. Due to these potentially detrimental consequences of the track-etched polycarbonate templates, anodic aluminum oxide (AAO) membranes are more frequently used in electrodeposition.[12,16]

The major advantage of using a porous AAO membrane is the unidirectional growth of the wires.[11] AAO membranes can be made with a pore density of up to 10^{11} pores per centimeter with pore diameters ranging from 5-200 nm.[12] These membranes are made by annealing and electropolishing a thin sheet of aluminum, which removes the top surface of aluminum oxide. Next, the sheet undergoes anodization, or oxidative coating, as it is placed into an acidic electrolyte solution. Then a chromate solution is applied to remove the oxide layer, and the sheet is placed back into the acidic electrolyte solution.[16] The resulting Al_2O_3 has a hexagonal array of uniformly cylindrical pores with little or no tilt, avoiding almost all pore intersection. The thickness of the template, and thus the upper boundary of wire length, is directly proportional to the time of anodization (longer anodization time results in a thicker template). In addition, the pore diameter can be controlled according to the acidic electrolyte solution used and the voltage of anodization. Once the template is synthesized, a metal film is deposited via ion sputtering or evaporation to coat one face of the template. This film substrate serves as the cathode for the electrodeposition and is usually composed of Ag or Cu.[12,16]

In addition to uniform wires, electrodeposition also allows for easy production of multisegmented nanowires. Varying the composition of hard-template grown nanowires can be established by using two different methods. The first, called pulsed electrodeposition, uses a single plating bath and takes advantage of the varying redox potentials of the two metals of interest.[10] The metal ions with the higher reduction potential (A) are kept at a low concentration while the metal ions with the lower reduction potential (B) are kept at a high concentration. The potential of the system is then set negative enough to deposit the metal A but not too negative to deposit the metal B. As a result, metal A will be deposited without any of metal B. Then, the potential is lowered in order to deposit metal B. Trace amounts of metal A will be deposited, but

because its concentration is so low, the segment will be primarily metal B. If pure segments are crucial for the experiment, the second method of using multiple plating baths for each different segment can be used. In this technique, one bath is used for a specific metal. Then, the bath is changed for the next metal.[10,12,14]

1.3: Electrodeposition Protocols

In this research, all cathode films were made from Ag, which was deposited via thermal evaporation to a thickness of about 300 nm. This side of the membrane was placed down on an Ag plate to act as the cathode (working electrode). Then, a rubber O-ring and glass flute were placed on the non-cathode side of the membrane. The glass flute was filled with water to make certain that the system did not leak. After the water was discarded, Pt mesh (counter electrode) attached to a Pt wire was submerged into an Ag solution without touching any other parts of the system (figure 2).

Figure 2

Pt Mesh

Glass Flute
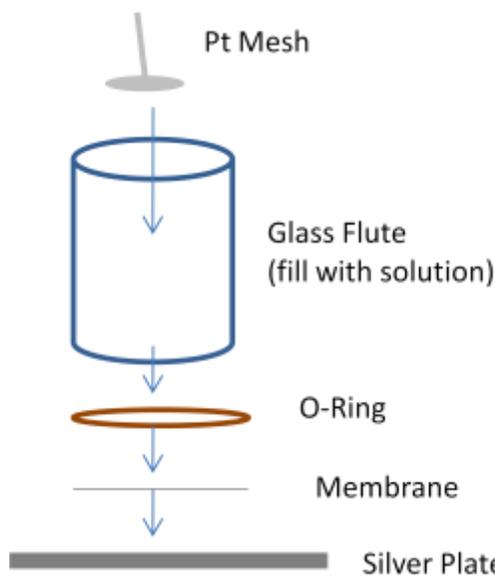(fill with solution)

O-Ring

Membrane

Silver Plate

Figure 2. Basic electrodeposition system set-up.

The potentiostat/galvanostat used in this research was the "VersaSTAT" by Princeton Applied Research. Along with the hardware, its respective computer software, "V^3 Studio" was used. The "Galvanostatic" experiment was selected on the software, the current (negative for reduction) was chosen based on the metal and its deposition rate, and the length of deposition was chosen based on the length of the wire desired.

First, Ag solution, with a pH between 8 and 10, was placed in the flute and Ag "plugs" were deposited to ensure that, if there was any branching of the pores, they were filled before the other metals were deposited. Next, the Ag solution was removed and the other metals were deposited. As shown in figure 1, once the metal or metals were deposited into the membrane, the Ag backing and plugs were removed by exposing the back of the membrane to 4M HNO_3. Then, the wires could either be removed from the membrane or kept in the membrane for modifications.[9] To remove the wires, the membrane and wires were vortexed in 5M NaOH for forty-five minutes and the polymer circle left from the membrane was removed.

Then, the wires were cleaned via centrifuging in 5M NaOH three times at 5000-7000 rpm for five minutes. Next, the supernatant was removed and the wires were centrifuged in distilled water three times at the same rate and time. If the wires were kept in water, they could oxidize. Therefore, after the water supernatant was removed, the wires were centrifuged in ethanol three times at the same conditions. Finally, the cleaned wires were kept in ethanol until ready for experimentation or analysis.

During this research, Au, Ag, Ni, Pt, Bi, Te, and Cu metals were deposited. Each metal deposited at different rates due to their reduction potentials. These deposition rates were calculated by dividing the length of the wires (evaluated by SEM) by the length of time

deposited (Table 1). Only Au, Ag, Ni, and Pt were analyzed by SEM, and, thus, the deposition

rates for only these metals were determined

Table 1

METAL	CURRENT (mA)	DEPOSITION RATE (micron/hr)
Ag	-1.65	4.5
Au	-1.65	2.5
Ni	-1.65	1.3
Pt	-5.00	1.5
Bi	-1.65	N/A
Te	-1.65	N/A
Cu	-2.00	N/A

The nanowires with segments of Au, Ag, Ni and Pt were synthesized by deposition of

Technic plating solutions (Au Orotemp 24-1, Ag Cyless R RTU, Nickel S, and Pt TP RTU). The

other solutions were made in enough distilled water to fill a 50 mL volumetric flask. The Bi

solution was made with 3.75 g $Bi(NO_3)_3 \cdot 5H_2O$, 3.25 g KOH, 6.25 g glycerol, and 2.50 g tartaric

acid. For the 2 mM Te solution, 18.7 mg TeO_2, 295.75 mg boric acid, 2 mL 8M HNO_3 and 6.25

g glycerol were added. Lastly, the Cu solution was made with 2.50 g $CuSO_4$ and 0.31 H_3BO_3.

Most of the electrodeposited wires were analyzed via powder x-ray diffraction (XRD),

which can assist in the identification of the structure and crystallinity of the wires. XRD analyzes

the arrangement of the atoms in a crystal by diffracting x-ray beams off of the crystal. First, the

incident ray strikes the crystal. Then, based on the angle and intensity of the reflected ray, the

two-dimensional electron density can be analyzed. This analysis can be measured by plotting the

intensity against the deflection of the incoming beam (2θ). As a result, the scan displays large

intensity peaks at the particular angle where the reflection was strong. In addition, the width of

the scan peaks can vary due to the size of the crystallite. For example, smaller crystal sizes yield

broader peaks. The diffraction pattern can then be compared to International Centre for

Diffraction Database (ICDD) reference patterns.

Although most wires that were synthesized via electrodeposition were multisegmented,

Ag wires and Pt wires were analyzed via XRD to ensure that the electrodeposition apparatus was

working correctly and that the metals were synthesized without impurities (figure 3 and 4).
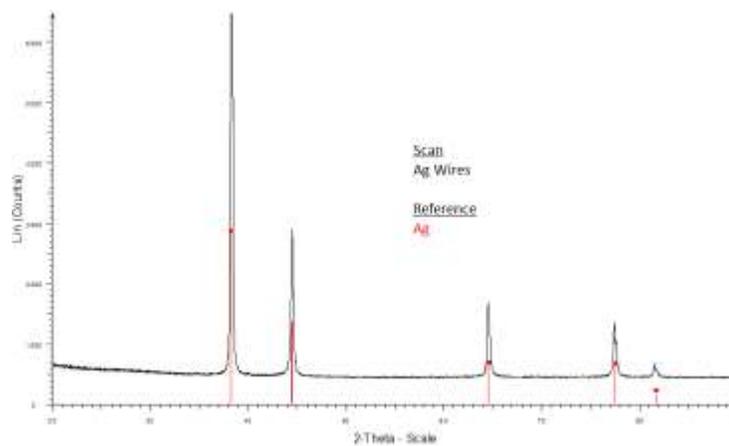
Figure 3

Figure 3. XRD pattern of Ag nanowires (black) synthesized via electrodeposition.
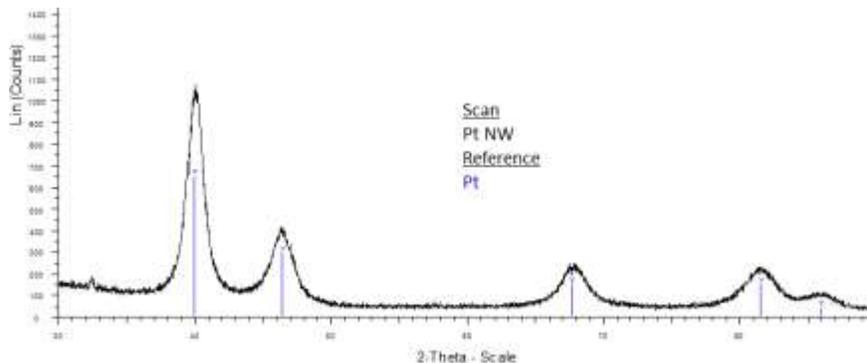It is compared to the Ag reference pattern (red).

Figure 4

Figure 4. XRD pattern of Pt nanowires (black) synthesized via electrodeposition.
It is compared to the Pt reference pattern (blue).

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As previously stated, most nanowires synthesized via electrodeposition are multisegmented because they offer unique properties. These characteristics can be applied to magnetic, electronic, biological, catalytic and optical operations. For example, due to their low dimensionality, both single-segment and multisegmented nanowires can possess magnetic anisotropy that varies whether the magnetic field is applied parallel or perpendicular to the wires. This characteristic allows the wires to exhibit giant magnetoresistance (GMR). For example, FeCu, NiCu, and CoCu demonstrate GMR because the magnetic properties of the Fe, Ni, and Co segments are separated by the non-magnetic Cu segments.[12] Multisegmented nanowires are also important in the development of electronics with their applications to resistors, transistors and switches. In biological applications, multisegmented nanowires, called nanobarcodes, can detect cell structures, such as proteins and DNA, while simultaneously separating the species for identification. One specific nanobarcode has Au and Ag segments to detect DNA while the other segment contains a twelve-nucleotide capture sequence that can bind to a twenty-four-nucleotide target sequence.[12]

Like with the Ag wires and Pt wires, Au/Bi/Au segmented wires were synthesized via electrodeposition by first depositing Ag plugs for ten minutes. Next, Au was deposited for 10 minutes, followed by 10 minutes of Bi and 10 minutes of Au. Then, the Ag backing was removed by exposing the back of the template to 4M HNO_3. Next, the wires were released from the membrane by vortexing them in 5M NaOH for one hour. Following the release, the wires were cleaned by centrifuging them for nine total cycles of 5 minutes each at 7000 RMP: 3 cycles in NaOH, 3 cycles in H_2O, and 3 cycles in ethanol. Finally, the wires were desiccated in a vacuum chamber and analyzed via powder XRD in order to test the reliability of the synthesis of

multi-segmented nanowires with our electrodeposition system. As expected, the XRD scan

showed both Bi and Au present when compared to the reference peaks (figure 5).
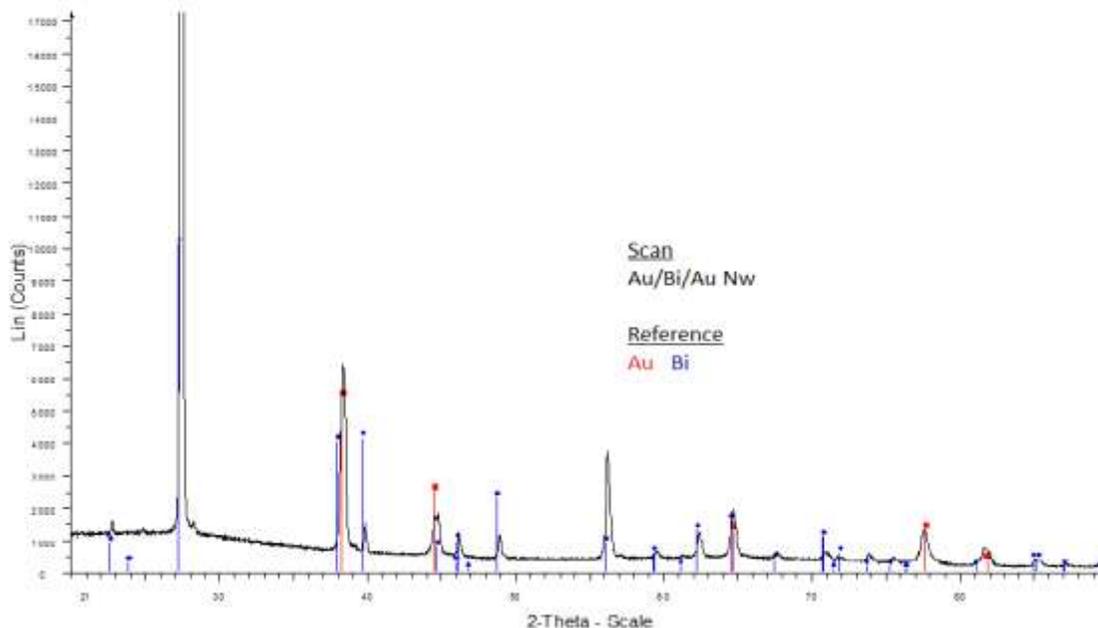
Figure 5

Figure 5. XRD pattern of Pt nanowires (black) synthesized via electrodeposition.
It is compared to the Au (red) and Bi (blue) reference patterns.

In addition to XRD analysis, the Au/Bi/Au wires were observed through scanning

electron microscopy (SEM) to insure that the wires were indeed striped. It was evident that the

wires contained three stripes, corresponding to the Au, Bi, and Au segments (figure 6).

Figure 6

Figure 6. SEM image of Au/Bi/Au nanowires

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In conclusion, the electrodeposition apparatus was used to successfully synthesize both single segment and multisegmented nanowires. Protocols for Ag, Au, Ni, Pt, Bi, Te, and Cu metal electrodeposition were established along with a majority of their deposition rates. As a result, these metals can be grown either as single-component nanowires or as multicomponent nanowires, which will allow for future solid-state modification experiments on electrodeposited nanowires systems. Such studies will be described in the chapters that follow.

Chapter 2: Solid-State Protection/Deprotection of Silver Nanowires

2.1: Introduction

Protection/deprotection strategies are important in the construction of complex molecules and are primarily used in organic chemistry experiments.[18] In these experiments, one functional group, for example, an amine, is rendered inert by protecting it from the reagent. To protect the amine, it is reacted with a protecting group, which is chosen based on its reactivity with the amine and non-reactivity with the remainder of the molecule. Then, the compound is exposed to, and reacts, with a reagent. Following the reaction, the amine is deprotected to its original state by removing the protection group, while the rest of the molecule has been reacted. While protection/deprotection methods are valuable in organic reactions, we hypothesized that an analogous concept can be applied to nanoscale inorganic solids.

Inorganic solid-state modifications, such as protection/deprotection, are important to the advancement of nanoparticle synthesis and modifications. The concepts discovered in this series of experiments can be generalized and applied to various types of multicomponent metal nanoparticle systems, thus expanding the methods and strategies needed to create complex nanoparticles. For example, A/B/A nanowires could be grown via electrodeposition. If the goal was to react only the A segments with a reagent (X) that would affect all of the segments (A and B), the B segment could be initially protected. To protect B, the compound would be reacted with a reagent (Y) that would only react with the B segments, yielding BY. Then, the entire wire would be exposed to the reagent of choice (X). Since the B would be protected, only the A segments would react to produce AX. Finally, the Y would be removed from the B segments (deprotected), yielding the desired AX/B/AX wires (figure 7).[19]
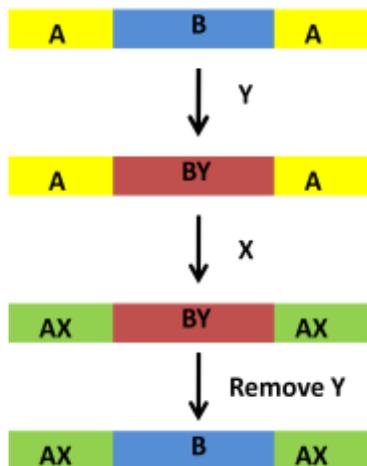
Figure 7

Figure 7 depicts the protection/deprotection reaction of A/B/A multisegmented nanowires. First, the B segment would be reacted with Y. Thus, protecting it from the next reagent, X. Then, the Y is removed or deprotected, leaving AX/B/AX nanowires.

In this series of experiments, Ag nanoparticles were grown using polyol synthesis, which involved the use of tetraethylene glycol (TEG) and $NaBH_4$ as reducing agents. Wires were chosen as the desired particle shape for these experiments because they are easily synthesized and modified. However, unlike with electrodeposition, it is more difficult to grow nanowires using solution-based strategies because the metal particles do not typically grow into high anisotropic 1-dimensional (1-D) wires in solution as they would inside the template pores. To aid in 1-D growth control, surface-capping reagents, such as polyvinyl pyrrolidone (PVP), were used.[20,21] It was important for these experiments to be performed on wires because these experiments were conducted with the expectation that the outcomes from the solution-phase nanoparticle reactions would be the same if conducted on multisegmented electrodeposited nanowires.

The goal of this series of experiments was to synthesize Ag nanowires, protect them by reacting them with sulfur, thereby producing silver sulfide (Ag_2S), then deprotect the Ag nanowires by removing the sulfur. The reagents chosen for these experiments were selected by

using the "likes dissolve likes" theory, which states that the solute will be most soluble in a solvent that has the closest polarity to itself. Therefore, it was hypothesized that water would not remove the sulfur from the Ag_2S nanowires because water is polar and sulfur is non-polar. However, it was expected that the toluene (non-polar) would remove the sulfur from the wires. In addition to the selected reagents, the amount of time the nanowires were heated in the reagents and the temperature at which they were heated were arbitrarily chosen as no conclusive literature concerning these conditions was found.

2.2: Experimental

The following reactions took place under normal atmospheric conditions unless stated otherwise. In addition, all particles were cleaned via centrifugation at 7,000 rpm for 5 minutes, followed by three 5-minute cycles in water and three cycles in ethanol under the same conditions. In addition, before each powder x-ray diffraction (XRD) measurement, the particles were dried via desiccation. A numbering system, from one to eleven, was given to all samples for easier organization and reference (tables 2 and 3).

2.2.1 Materials

Silver nitrate (99%), sulfur powder (99.5%), tetraethylene glycol (TEG, 99%), sodium borohydride (98%), and polyvinylpyrrolidone (PVP) were used as stock from Alfa Aesar.

2.2.2 Characterization

All analysis was completed on a Bruker Advance D8 X-Ray Diffractometer.

2.2.3 Synthesis of Ag₂S Nanoparticles

Ag nanoparticles were first grown via solution-phase synthesis; more specifically, modified polyol (TEG) synthesis with $NaBH_4$ as an additional reducing agent. The first step was reacting 1.0 mmol of $AgNO_3$ (170 mg) with 200 mg of $NaBH_4$. The solution was then heated in 5 ml of TEG to 180° C for 1hr to aid in reduction of the particles. The solution was then cooled, cleaned, and analyzed by powder XRD (sample 1). Next, in order to cap the particles into nanowires and prevent the wires from crashing out of solution, the nanoparticles along with 150 mg of 40K PVP (sample 2) were dissolved in TEG. Part of this sample was then reacted with 2 mol of S (64.13mg) to yield Ag_2S (protected). The nanowires were cleaned a second time and characterized via XRD (sample 3). Then, this batch was split into three samples to determine the best method to remove the excess sulfur from the Ag_2S nanowires. The first batch was heated in TEG for 3hrs at 200° C, cleaned, and analyzed by powder XRD (sample 4) with no change expected as TEG is simply the reducing agent. The second batch was cleaned again via centrifugation to wash off excess sulfur (sample 5). Finally, the third batch was washed with toluene for 15 minutes followed by a cleaning and XRD analysis (sample 6).

Table 2

Sample #	Contents
1	Ag NP without PVP
2	Ag NW with PVP
3	Ag NW rx S
4	Ag NW rx S TEG 200°C
5	Ag NW rx S recleaned
6	Ag$_2$S toluene

Table 2 summarizes the experimental solutions used to synthesize Ag$_2$S from Ag

2.2.4 Removal of S from Ag Nanoparticles

The Ag was successfully reacted with S to form Ag$_2$S and the excess S was removed from the wires. Many experiments were performed in an attempt to remove the S from the Ag$_2$S (deprotect). First, the Ag$_2$S nanowires were boiled in water for 15 minutes, cleaned, and analyzed by powder XRD (sample 7). It was expected that the water would have no effect on the sulfur since they had opposite polarities. Next, the sample was placed in TEG at 200°C and stirred for 1 hr 40 min (sample 8). Then, half of the precipitate from sample 8 was reheated in TEG for 30 min at 300°C (sample 9) while the other half of the precipitate was washed with toluene then heated in TEG for 30 min at 300°C (sample 10). It was hypothesized that the TEG would have no effect and that the toluene would remove the sulfur due to their nonpolar characteristics. Finally, the supernatant from sample 9 was analyzed via powder XRD (sample 11) to ensure that all the wires were concentrated in the precipitate.

Table 3

Sample #	Contents
7	Ag_2S water boil
8	Ag_2S water boil and TEG 200°C
9	Ag_2S reheated in TEG 300°C
10	Ag_2S precipitate in toluene and TEG 300°C
11	Ag_2S supernatant

Table 3 summarizes the experimental solutions used to remove S from Ag_2S

2.3 Results

2.3.1 Synthesis of Ag_2S Nanoparticles

Before synthesizing Ag_2S, the Ag nanoparticles without PVP were compared to the Ag nanowires that were dissolved in TEG with PVP using powder x-ray diffraction. After analyzing both samples (1 and 2) against the Ag reference pattern, there was no significant difference between them (Figure 8 and 9). Since the PVP forced the particles into the wire shape and because there was substantially more Ag nanowires with PVP (sample 2), this sample was used for the remainder of the experiments.
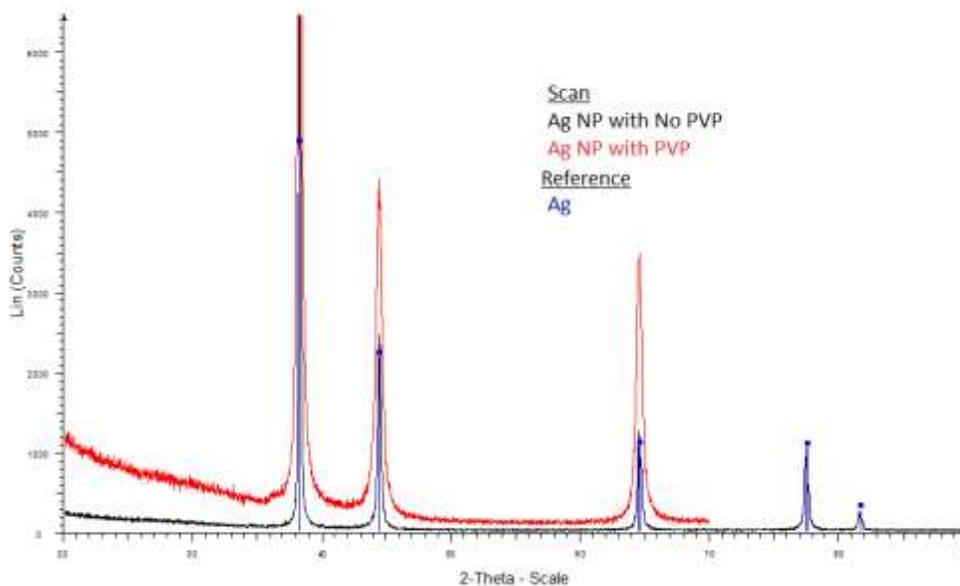
Figure 8

Figure 8. XRD patterns of Ag NP made without PVP (black) and Ag NP with PVP (red) compared to the Ag reference peaks (blue).

When the Ag nanowires (with PVP) were reacted with sulfur (sample 3), the x-ray analysis showed that Ag_2S was synthesized (Figure 9 and 11). However, indicated by the presence of peaks around 23 and 28° 2θ on the x-ray analysis, excess sulfur was also in the sample.
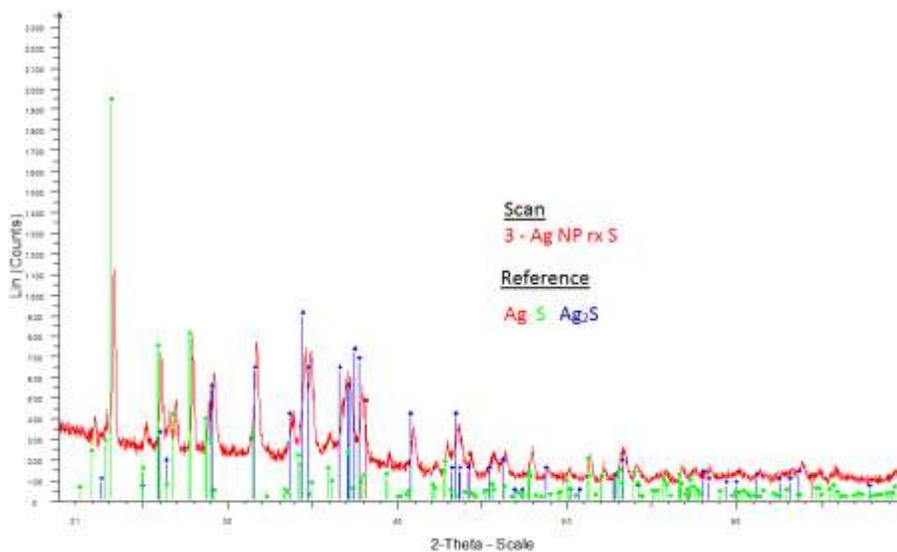
Figure 9

Figure 9. XRD pattern of Ag NP (with PVP) reacted with Sulfur (red). This scan is compared to the reference peaks of Ag (red), S (green) and Ag_2S (blue).

After heating the Ag nanowires that were reacted with S in TEG at 200°C (sample 4), the excess sulfur was removed as the peaks at 23 and 28° 2θ that corresponding to the sulfur reference peaks were absent (figure 10 and 11). Therefore, only Ag_2S was present. Using the "like dissolve likes" theory, TEG should not dissolve sulfur due to its polarity. However, we believed that high temperatures could remove excess sulfur, as it did.
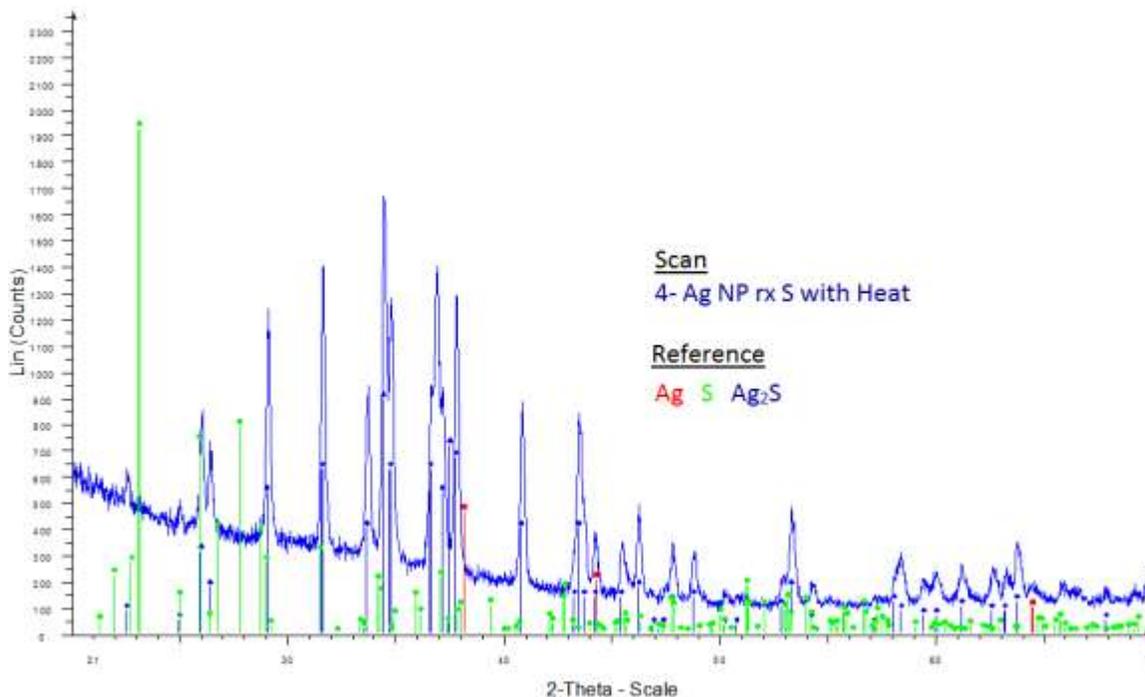
Figure 10

Figure 10. XRD pattern of Ag NP (with PVP) reacted with S and heated in TEG at 300°C (blue). This scan is compared to the reference peaks of Ag (red), S (green) and Ag_2S (blue).

Figure 11

Figure 11. XRD patterns of Ag NP (with PVP) (black), Ag NP (with PVP) reacted with S (red), and Ag NP (with PVP) reacted with S and heated in TEG at 300°C (blue). These scans are compared to the reference peaks of Ag (red), S (green) and Ag_2S (blue).

Sample 5, which was cleaned a second time after being reacted with sulfur, matched the Ag_2S reference peaks. However, as with sample 3, excess sulfur was still present, indicated by the peaks at 23 and 28° 2θ (figure 12). Therefore, to remove the excess sulfur, this sample was reacted with toluene (sample 6). According to the x-ray diffraction analysis, the excess the sulfur was removed from sample 6, leaving just Ag_2S (figure 12). Therefore, to synthesize Ag_2S NP from Ag nanowires, one must react the nanowires with sulfur and then either heat the solution in TEG to around 200°C or wash the sample with toluene to remove the excess sulfur.
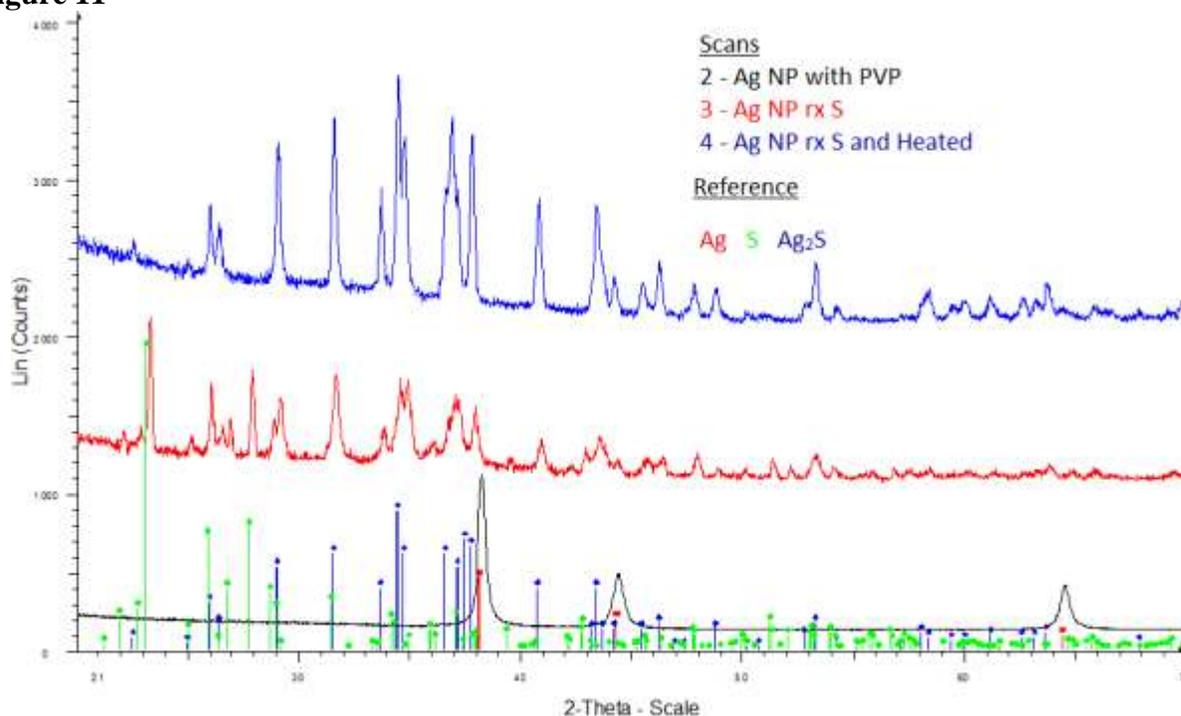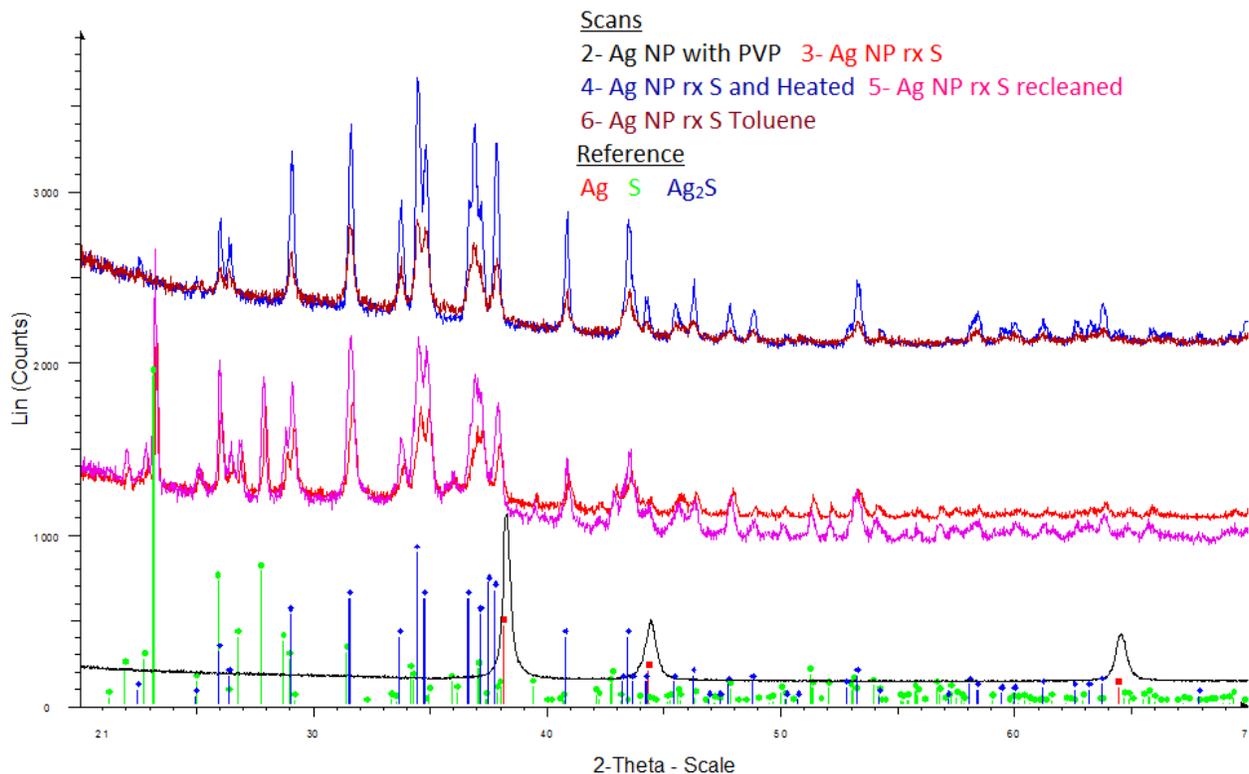
Figure 12

Figure 12. XRD patterns of Ag NP (with PVP) (black), Ag NP (with PVP) reacted with S (red), Ag NP (with PVP) reacted with S and heated in TEG at 300°C (blue), Ag NP (with PVP) reacted with S and cleaned twice (pink), and Ag NP (with PVP) reacted with S followed by toluene (maroon). These scans are compared to the reference peaks of Ag (red), S (green) and Ag_2S (blue).

2.3.2 Removal of S from Ag_2S Nanoparticles

The next step was to remove the sulfur from the Ag_2S nanowires, thus, "deprotecting" them. As expected, the sulfur was not removed when the wires were boiled in water for 15 minutes (sample 7). This was indicated by the scan match with the Ag_2S reference peaks (figure 13 and 14). When these wires were heated in TEG at 200°C (sample 8), the scan still matched the reference peaks of the Ag_2S but also had peaks corresponding to the Ag reference peaks (figure 13 and 14).
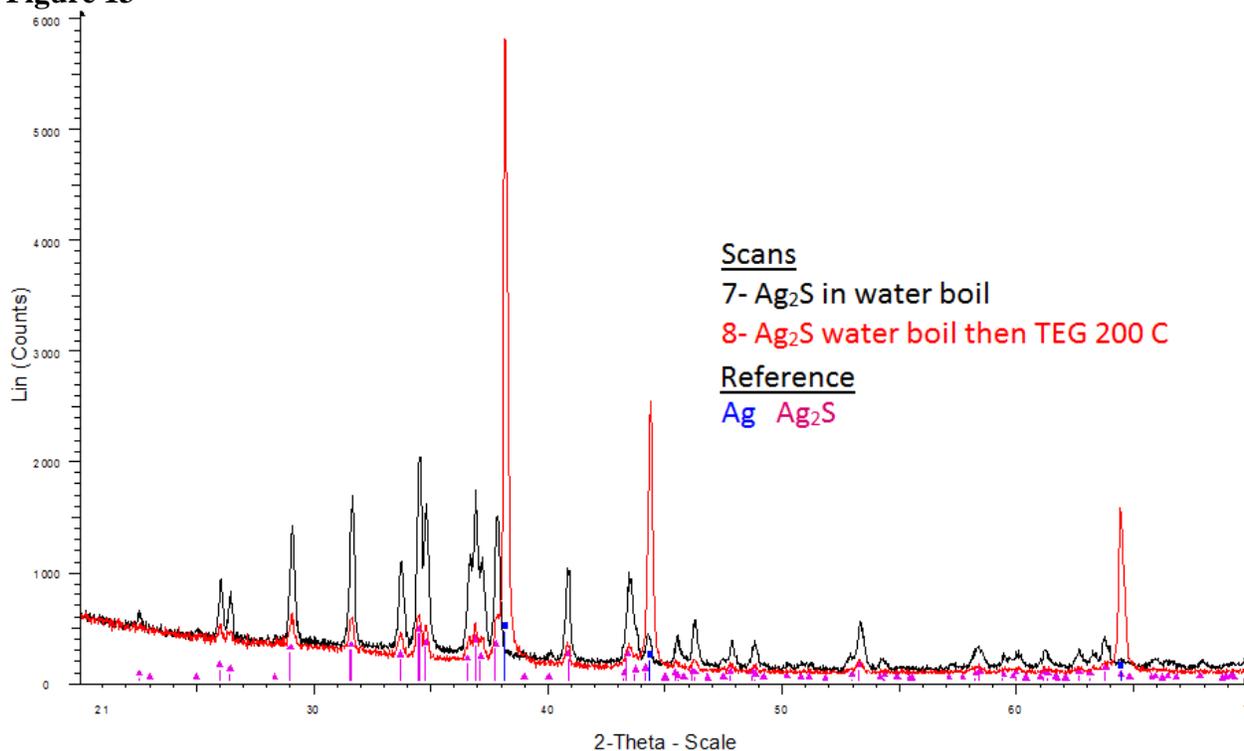
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Figure 13

Figure 13. XRD patterns of Ag_2S NP after boiling in water (black) and Ag_2S NP after the water boil and heat up in TEG at 200°C (red). These scans are compared to the reference peaks of Ag (blue) and Ag_2S (magenta).

After washing the precipitate with toluene then heating the wires in TEG at 300°C (sample 10), the x-ray analysis still showed Ag_2S with excess sulfur, as seen in solution 8. However, after reheating solution 8 in TEG at 300°C (sample 9), both the precipitate and supernatant (sample 11) showed only Ag, as indicated by their diffraction patterns (figure 14). We believe the long exposure to high temperatures was the main reason why the sulfur was removed rather than the TEG solvent.
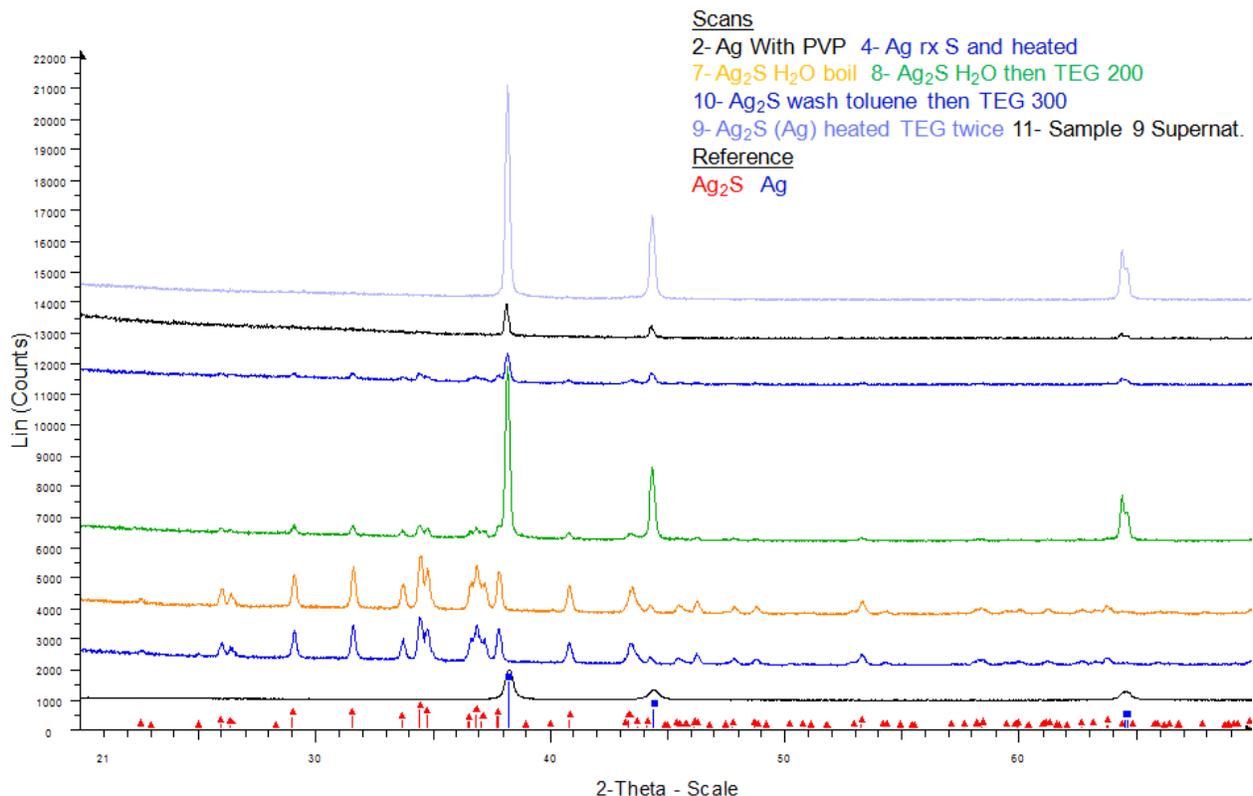
Figure 14

Figure 14. XRD patterns of Ag NP (with PVP) (black),, Ag NP reacted with S and heated in TEG at 200°C (blue), Ag2S NP following a water boil (orange), Ag2S NP following a water boil and heated in TEG at 200°C (green), Ag2S NP precipitate heated in TEG at 300°C (periwinkle), Ag2S NP precipitate reacted in toluene and heated in TEG at 300°C (blue), and Ag2S NP supernatant (black). These scans are compared to the reference peaks of Ag (blue) and Ag2S (red).

In conclusion, it was possible to protect and deprotect the Ag wires with sulfur. However, additional experiments are required to determine why TEG and heat are able to both remove excess sulfur and deprotect the Ag wires by removing the sulfur. While these experiments focused on single-component nanowires, the goal was to successfully protect and deprotect nanowires so that the methods could be used as a platform for other experiments, including protecting and deprotecting A/B/A multisegmented nanowires.

Chapter 3: Additional Modification of Electrodeposited Nanowires

3.1: Introduction

Modifications to enhance nanowire crystallinity, introduce a composition gradient via interdiffusion, and galvanically replace metals on electrodeposited nanowires were attempted in order to provide an experimental basis for further research in those areas. It is important for basic protocols to be established for such solid-state modifications, as they can be useful in complex systems where additional methods are needed to produce the desired results.

The crystallinity of multisegmented nanowires has been enhanced through pulse electrodeposition with increased relaxation times between deposition pulses.[22] In Henry's experiments, he attempted to form single crystalline areas on Si nanowires. To increase the crystallinity, the wires were self-heated by applying an electrical current. The current increased the temperature of the wires and allowed the Si atoms to rearrange into a more ordered structure. In addition to applying electrical current, electro-migration, which is the erosion by electrons, directed the path of crystallization.[23] In our research, the goal of these experiments was to increase the crystallinity of Pt electrodeposited wires by annealing them to high temperatures in TEG.

The interdiffusion between two metals of a multisegmented nanowire system can be quite complex. Kline was able to analyze Au/Sn/Au diffusion patterns via electron microscopy. He concluded that the Au diffuses faster than Sn because the Au gets thinner as it nears the Sn segment, transitioning from AuSn to $AuSn_4.$ However, it was observed that the Au diffusion was blocked by SnO_2 between the $AuSn_4$ and the Sn segments. He found that oxide layers often form around noble metal segments, such as Au, Ag, and Pt, and thus prevent interdiffusion. [11]

Due to this oxide layer formation, single-bath electrodeposition, also known as pulse electrodeposition, would be advantageous over multi-bath deposition. As mentioned before, the more noble metal (low concentration) is deposited first by using a potential that is negative enough to deposit this metal but not too negative to deposit the less noble metal . Then, the less noble metal (high concentration) is deposited by making the potential even more negative.[11] While this technique may prevent oxide formation, the goal of our gradient modification experiments was to introduce interdiffusion between Au and Ag segments of multisegmented nanowires that were grown using multiple bath techniques. The potential problem with this strategy would be the formation of an oxide layer between the Au and Ag segments due the wire's exposure to air while changing deposition solutions.

Another nanowire modification of interest involves the use of galvanic replacement reactions, in which host templating particles are replaced by a cationic metal with a higher reduction potential. The host particles are oxidized while the cations are reduced, and, as a result, the cations are deposited in place of the host.[24] In a technique referred to as templating via galvanic replacement, hollow nanotubes or nanorings are created by utilizing galvanic replacement reactions around nanowires. By synthesizing nanoparticles in this fashion, the diameter of the tubes or rings can be controlled by changing the nanowire diameter and the chemical composition can be controlled by analyzing the reduction potentials of both the host and cation metals. It is critical that the nanowires are grown in a uniform manner, as galvanic replacement reactions tend to occur at places with higher surface area such as wire tips, twinning boundaries, and stacking faults.[25]

One example of templating using galvanic replacement reactions is Luisman's synthesis of hollow nanorings via on-wire lithography (OWL). Luisman used electrodeposited Ni/Au

striped nanowires as the sacrificial host. These wires were reacted with $HAuCl_4$ to form an Au/Ag alloy on the Ag segments, leaving the Ni segments unaffected. Next, the Ni and Ag metals were dissolved by wet chemical etching, using HCl and HNO_3.[26] As a result, Au nanoporous rings were synthesized with uniform diameters. Similar methods have also been used to create Pt and Pd nanoporous rings.[27,28] In our experiments, the goal was to galvanically replace the Ag, Ni, and Cu segments of Au/Ag/Au/Ni/Au/Cu/Au with Pt.

3.2: Experimental

The following reactions took place under normal atmospheric conditions unless stated otherwise.

3.2.1 Materials

Unless stated otherwise, anodic aluminum oxide membranes (Anodisc 25, Whatman Scientific, 0.2 µm) were used as the template for nanowire electrodeposition. The following metal reagents were used as received from Alfa Aesar: $Bi(NO_3)_3 \cdot 5H_2O$, $CuSO_4$, H_3BO_3 and H_2PtCl_6. Nanowires containing Ag, Au, Ni, or Pt segments were fabricated by deposition from Technic plating solutions (Ag Cyless R RTU, Au Orotemp 24-1, Nickel S, and Pt TP RTU).

3.2.2 Characterization

Powder X-ray diffraction (XRD) data was collected using a Bruker Advance D8 X-Ray Diffractometer and microscope images were collected using a FEI Quanta 200 environmental SEM with EDS element mapping.

3.2.3 Enhancing Nanowire Crystallinity

One goal of the modification experiments was to improve the crystallinity of electrodeposited nanowire structures. It was hypothesized that, by annealing the Pt nanowires in high heat, the nanowire's crystallinity would be enhanced. First, short silver (Ag) plugs were deposited for 1 hr (~4.5 μm in length) to fill in any branching of the pores, and then Pt was deposited for 1 hr (~6 μm in length). Then, the Ag back was removed with 4M HNO_3 and the membrane was then split in half. One-half was kept as a control for the x-ray analysis while the other half was annealed for 1 hr in TEG at 300°C with an argon sparge and dried for powder XRD.

3.2.4 Establishing a Composition Gradient on Au/Ag Nanowires

A second goal of the modification experiments was to establish a composition gradient between the metal segments on an electrodeposited nanowire. The first attempts were performed on Ag/Au segmented nanowires. Ag plugs were deposited for 1 hr followed by a one μm long Pt segment (40 min), which was later used as a marker for the SEM analysis. Next, the following sequence of metals was deposited: 5 min Au (0.208 μm), 2.78 min Ag (0.208 μm), 10 min Au (0.42 μm), 5.6 min Ag (0.42 μm), 20 min Au (0.83 μm), 11 min Ag (0.83 μm), 30 min Au (1.25 μm), and 16.7 min Ag (1.25 μm). The last segment deposited was a short Au (10 min) tip to prevent the 1.25 μm Ag segment from being removed when the membrane was exposed to the HNO_3. Then, the Ag back was dissolved with 4M HNO_3 and the wires were removed from the membrane by vortexing it in 5M NaOH for 30 min. Next, the released wires were washed via centrifugation for five-minute cycles at 7000 rpm: three cycles in 5M NaOH, three cycles in H_2O, and three cycles in ethanol. Then, the wires were refluxed for 1hr in TEG at 250°C with an

argon sparge. Following the reflux, the wires were prepared for SEM by diluting the sample and mounting the wires on a SEM grid.

3.2.5 Galvanic Replacement on Nanowires

The goal of this modification experiment was to replace specific metal segments of electrodeposited nanowires with another metal using galvanic replacement reactions. First, Au/Ag/Au/Ni/Au/Cu/Au nanowires were synthesized via electrodeposition. All of the metal solutions were used from stock solutions except the 50 mL of 0.2M Cu solution, which was made by sonicating 2.5g of $CuSO_4$ with 0.31g of H_3BO_3 in distilled water. Then, 4M HNO_3 was added until the pH was 1.

First, Ag plugs were deposited for 1hr. Then, the following sequence was deposited: 20min Au, 30min Ag, 20min Au, 30min Ni, 20min Au, 30min Cu, and 20min Au. Then, the Ag back was removed using 4M HNO_3 and the wires were released from the membrane by vortexing it in 5M NaOH for 1hr. The wires were then cleaned via centrifugation for five-minute cycles at 4000 rpm: three cycles in 5M NaOH, three cycles in H_2O, and three cycles in ethanol.

Platinum, with a reduction potential of 1.18v, was chosen as the reagent for this experiment because we expected that it would be deposited on all of the segments that were composed of metals with lower reduction potentials: Ag (0.7996v), Cu (0.3419v), and Ni (-0.257). The Au segment would not react with Pt because its reduction potential (1.498v) was higher than that of Pt. First, the wires were washed by centrifugation them in H_2O for two cycles at 4000 rpm for 5min each. Next, 3ml of H_2O was added to the wires along with 1ml of 1.0mmol H_2PtCl_6. This solution was stirred for 2hr 30 min. Then 15ml of saturated NaCl solution was added to the wires to remove any AgCl byproduct that may have formed. Finally, the wires were

cleaned via centrifugation for two cycles in H_2O followed by two cycles in ethanol for five

minutes each at 4000 rpm and mounted on a SEM grid.

3.3 Results

3.3.1 Enhancing Nanowires Crystallinity

Following the wire anneal, the crystallinity of the control (non-annealed) wires was

compared with the experimental (annealed) wires. The crystallinity of the wires can be measured

via powder XRD by observing diffraction pattern peak broadening, which is explained by the

Scherrer equation. From this equation, peak broadening is inversely proportional to crystallite

size. Therefore, it was hypothesized that the annealed nanowires would have a larger crystallinity

pattern and thus sharper peaks on an x-ray diffraction analysis.

After reviewing the XRD characterization, the experimental scan had slightly sharper

peaks than the control (figure 15), indicating an enhanced crystallinity. Although the difference

in the scans peak sharpness was not extremely significant, it was concluded that the crystallinity

could be improved by annealing the wires. However, the use of a heat furnace or the application

of heat for a longer duration of time may be better strategies for enhancing nanowire
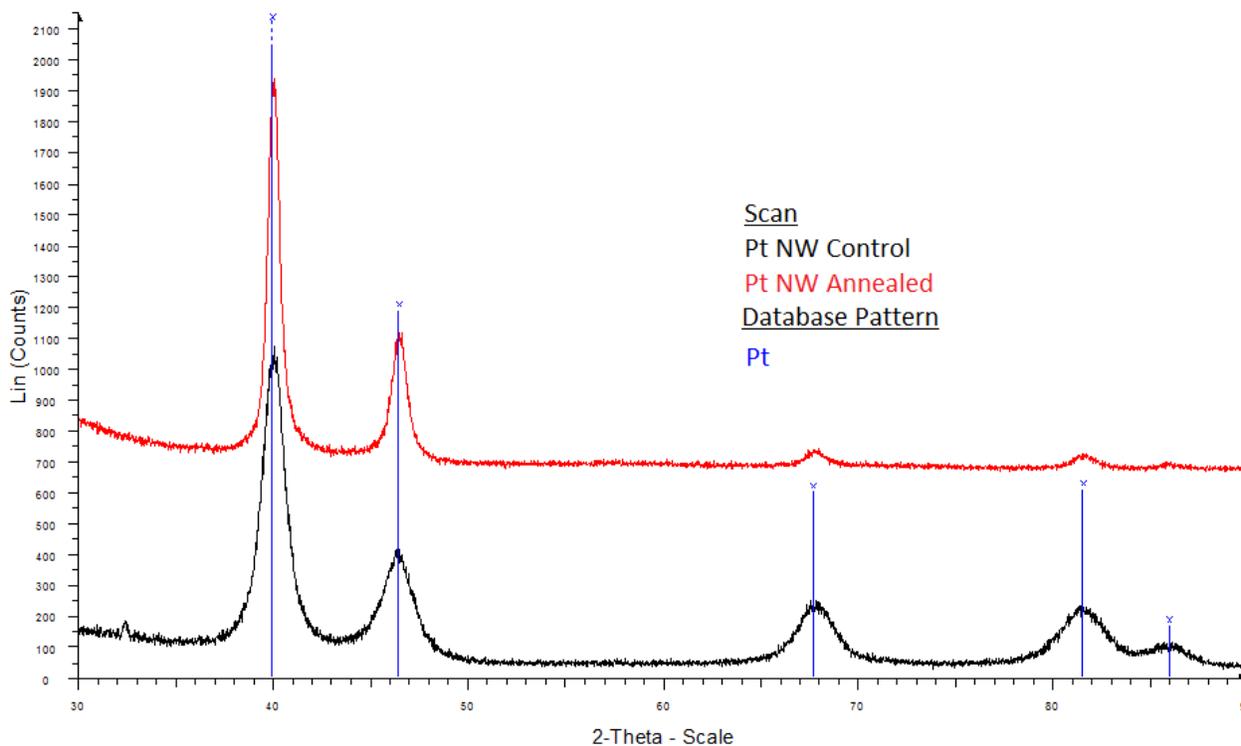
crystallinity.

Figure 15

Figure 15. XRD patterns of Pt NW control (black) and Pt NW after annealing (red) compared to the Pt database reference patterns (blue).

3.3.2 Establishing a Composition Gradient on Au/Ag Nanowires

Au/Ag nanowires were annealed and the gradient between the segments was observed through an SEM (figure 16-18). The elemental sequence was mapped in figure 16, showing the Pt marker tip in blue along with the Ag (green) and Au (red) stripes. When comparing the wires prior to annealing (figure 17) with the wires after annealing (figure 18), there seemed to be no significant change or diffusion between the metals. Therefore, it was concluded that annealing Au/Ag segmented wires in TEG at 250°C does not cause any interdiffusion of metals on these wires. However, future experiments with increased temperatures and heat exposure times may lead to diffusion. In addition, an oxide layer could have prohibited interdiffusion between the segments and therefore, pulsed electrodeposition could be another alternative.
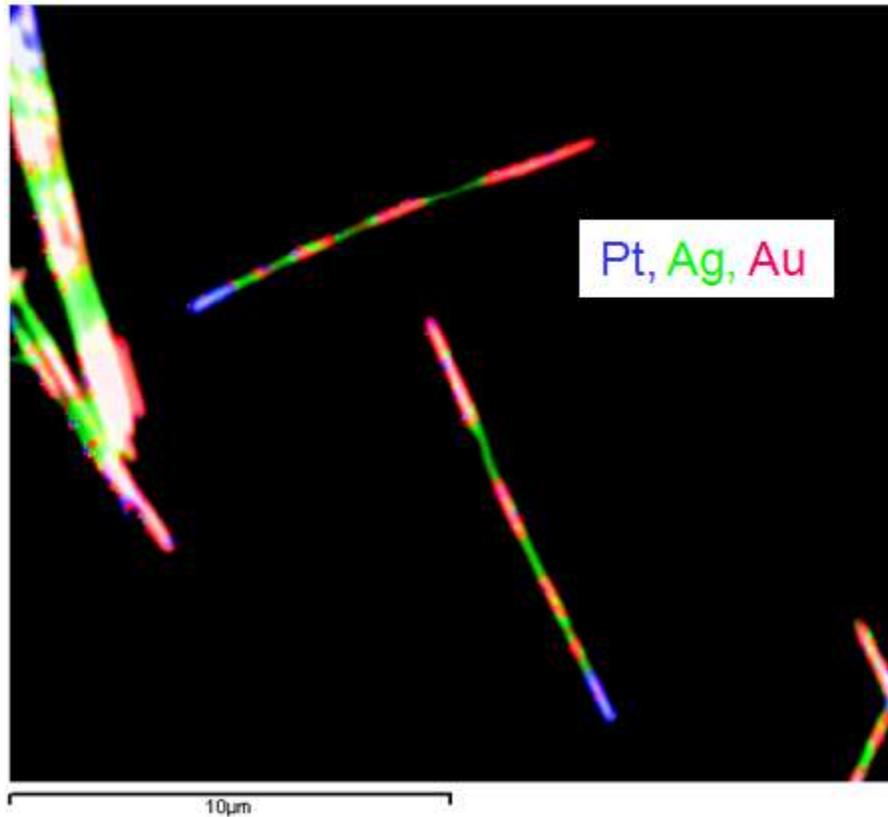
30

Figure 16

Figure 16. SEM image of the Au/Ag segmented wires with the Pt marker tip after annealing. The Pt is colored blue, the Ag is green, and the Au is red.
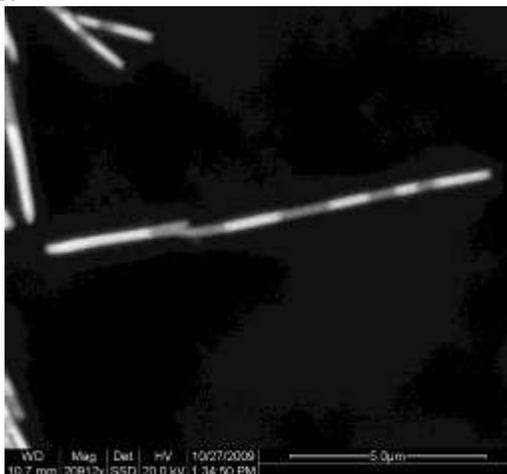
Figure 17   **Figure 18**

Figure 17. SEM image of the
Au/Ag NW before annealing.

Figure 18. SEM image of the annealed
Au/Ag NW after annealing.

3.3.3 Galvanic Replacement on Nanowires

Due to the reduction potentials of the Ag, Ni, and Cu segments of the

Au/Ag/Au/Ni/Au/Cu/Au nanowires, it was expected that they would be replaced by Pt when they

were submerged in the H_2PtCl_6. An SEM image was taken of the wires prior to exposing them to

H_2PtCl_6 (figure 19). This image showed distinct Au, Ag, and Ni segments. However, the Cu

segment was very thin and could only be seen in some of the wires due to the wire tips breaking.
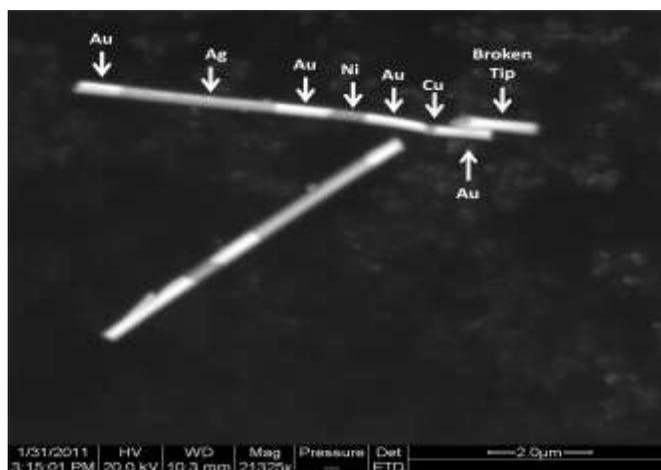
Figure 19

Figure 19. SEM image of Au/Ag/Au/Ni/Au/Cu/Au NW prior to the H_2PtCl_6 reaction.

The wires were also observed via SEM and elemental mapping following the reaction

betweent the nanowires and the H_2PtCl_6 (figures 20 and 21). Contrary to the hypothesis, only

trace amounts of Pt were found through elemental mapping. In the SEM image, the Ag segment

of the nanowires had a bumpy appearance not seen in the wires prior to the reaction. This

deposition on the Ag surface was thought to be Pt; however, it was not substantial enough to

show on the mapping (figure 21).

Figure 20

Figure 20. SEM image of the Au/Ag/Au/Ni/Au/Cu/Au NW following the H_2PtCl_6 reaction.
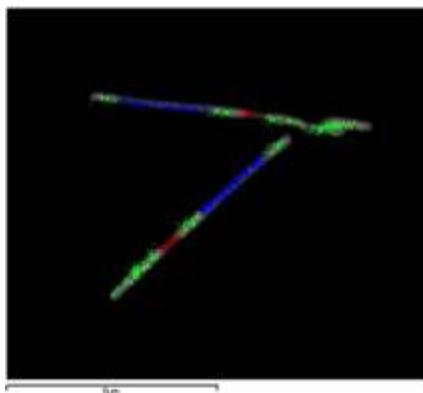
Figure 21

Figure 21. Elemental mapping of the SEM image of the Au/Ag/Au/Ni/Au/Cu/Au NW following the H_2PtCl_6 reaction. The green segments are Au, the blue is Ag, and the red is Ni. The Cu segment did not have enough trace points to mapped.

In conclusion, the Ag, Ni, and Cu segments were not successfully replaced by the Pt.

However, the experimental methods of the galvanic replacement could be altered by adding heat

to the reaction. In Alia's experiments, he successfully synthesized Pt nanotubes around Ag

nanowires by using galvanic replacement. First, the Ag NWs were refluxed with H_2PtCl_6 at

100°C in water. Finally, the solution was quenched in an ice bath and the silver chloride

precipitate was removed with saturated sodium chloride.[29] The addition of heat may be an

important factor to facilitate Pt deposition on the wires since the diffusion coefficients heavily depend on the reaction temperature. Therefore, in future experiments, it is recommended that the reaction are performed under heat with an argon sparge.

Conclusions

The electrodeposition protocols were successfully established for Au, Ag, Ni, Pt, Bi, Te, and Cu. The electrodeposition set-up deposited single-segment nanowires, which was demonstrated by powder XRD analysis of Ag wires and Pt wires. In addition, Au/Bi/Au multi-segmented nanowires were synthesized through our electrodeposition set-up and confirmed via powder XRD.

Ag nanoparticles were grown via solution-phase polyol synthesis. These wires were reacted, and therefore protected, with sulfur to form Ag_2S and any excess sulfur was removed by heating the wires in TEG at 200°C or by washing the nanowires with toluene. In addition, the Ag nanowires were deprotected by removing the sulfur through two periods of heating in TEG at 300°C.

The crystallinity of the Pt nanowires was successfully enhanced by annealing the wires in TEG at 300°C for 30 minutes. However, the Pt nanowire crystallinity may be further enhanced by applying an electric current to the wires and/or heating the wires to higher temperatures for a longer period of time. The methods taken to introduce a composition gradient on Au/Ag striped nanowires through galvanic replacement reactions on Au/Ag/Au/Ni/Au/Cu/Au multisegmented nanowires with Pt did not work as expected.

However, additional experiments could be performed. For example, the interdiffusion of Au and Ag metals could have been prohibited by the formation of an oxide layer between the segments. Therefore, pulse electrodeposition may be a better strategy to prepare the nanowires. In addition, the galvanic replacement of the Ag, Ni, and Cu with Pt may be facilitated if the nanowires and cationic solution were reacted under heat.

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Penn State Dance Marathon (THON) - *Special Events Committee Member*
Penn State's Pre-Dental Society - *Webmaster*
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Red Cross Blood Drive, Penn State University
Homecoming Parade AED Honors Society. Penn State University
Playground Construction Adventure Zone. Mechanicsburg, PA