Teacher Preparatory Guide
Lesson 2: Synthesis of Nickel Nanowires

Overview: To produce nanowires, electrolysis can be used to plate metal ions into the pores of an inorganic alumina membrane (anodisc). At a high school level, the wires can be made using a AA battery supplying approximately 1.5 V. The following lab will expand upon the skills students have previously developed in the construction of electrolytic cells which allowed for the plating of metal ions on a surface in Lesson 1 (copper and zinc onto the surface of a toy dinosaur).

Purpose: This lab is designed to help students understand how nanowires can be created using a simple set up, and how this compares to the construction of nanowires in industry. There is also an emphasis in the questions on having students think about how a procedure can be modified to obtain different results. A lesson following the completion of the lab should cover current applications of nanowires and nanotechnology.

Time required: Two 45 minute class periods or one 90 minutes block period. The lab should take one period but can be extended into the second day for Section C if necessary. The second day will focus on discussion of nanotechnology applications.

Level: High School Chemistry

Materials per two student group

- Safety glasses
- Nitrile gloves
- Distilled water bottle
- Three 50 mL beakers per group
- One glass slide
- One small vial
- One thin stem pipette
- One pair of tweezers
- One strong magnet
- One AA battery with holder and +/- leads
- Two wires with alligator clips
- One Volt Meter (shared among groups)
- Electrical tape
- One cotton applicator (Q-tip)
- One piece of emory cloth
- One 3 x 10 copper strip
- One nickel wire
- One Whatman Anodisc (0.02 µm 25 mm) Cat. No. 6809-6022
- Gallium-Indium eutectic, 99.99+% (Sigma-Aldrich) (shared among groups)

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NNIN Document: NNIN-1209
Rev: 08/2010

- 50 mL of Watts nickel pure (nickel plating solution)
- 6.0 M Nitric acid (handled by teacher, NOT students)
- 5 mL of 3.0 M NaOH
- 50 mL of Acetone

Safety Information: Safety glasses should be worn at all times. Do not ingest the nickel plating solution, allow for ventilation, and avoid eye and skin contact. If eye contact is made, flush eyes with large amounts of water for 15 minutes and seek medical attention. Wash thoroughly with soap and cool water if contact is made with skin. **TEACHER** should perform step involving nitric acid, and this step should be done in a fume hood. If available, safety aprons can be worn to protect clothing.

Advance Preparation

Where to buy supplies:

- Five grams Gallium Indium Eutectic - Sigma-Aldrich, Product # 495425-5G
- Whatman Anodisc Alumina Filter 0.02 µm pore size – VWR, Product # 28138-067
- Nickel Wire 2 meters length 1.0 mm diameter - Alfa Aesar Stock, Product # 43133
- Watts Nickel Pure - Technic, Inc., 1 Spectacle St, Cranston, Rhode Island 02910, Product #130859

Teacher Background (additional information can be found in texts listed below)

Redox Reactions

Chemical reactions in which both oxidation (loss of electrons) and reduction (gain of electrons) occur. (ex. . $H_2 + F_2 \rightarrow 2\ HF$ Hydrogen is oxidized and Fluorine is reduced)

Single Displacement Reactions

A redox reaction in which an element replaces or displaces another from a compound. In these reactions, the element which replaces that which is in a compound is always oxidized. The element being displaced, is always reduced. The reaction shown below would occur if A is more reactive than B.

$$A + BX \rightarrow AX + B$$

Electrolytic Cells

There are three key components in an electrolytic cell: an electrolyte and two electrodes (a cathode and an anode). The electrolyte is usually a solution of water or other solvents in which ions are dissolved. An external voltage is applied to the electrodes, and the electrolyte provides ions that flow to and from the electrodes. A redox reaction takes place forming a solid at the cathode, while the mass of the anode decreases as metal atoms lose electrons and become ions in solution.

Applications of nanotechnology

Nanotechnology has already been used to improve existing products that may be in your home. Some examples include longer lasting tennis balls, lighter and stronger racquets, self-cleaning windows, odorless socks, dressings for wounds, and transition lenses for glasses. Nanomaterials such as carbon nanotubes and nanofibers can be added to products as a strengthening agent, and have been used for car bumpers, golf clubs, and bicycles. In 2006, around 200 products lay claim to have some nanotechnology connection and by 2010 that number exceeded 1,000.

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At Penn State's Center for Nanoscale Science, researchers have developed arrays of microtubules that mimic some of the structures that are used within the cell to transport materials. Researchers are also currently working on the early detection of disease using nanotechnology, ultrasonic glucose monitoring for controlling diabetes, and molecular neurosensors that will measure the reaction to drugs in the brain. Nanowires are of interest in making connections in very small electrical components and medical devices.

For more information visit: http://www.gonano.psu.edu/
How Stuff Works – Nanowires http://science.howstuffworks.com/nanowire.htm

Teaching Strategies This lab should be performed in groups of 2-3 students. Redox reactions must be covered before the lab is started for students to understand what is occurring at the cathode and anode. Discussing nanowires and why researchers have an interest in them before the lab could be beneficial, or you could use the lab to introduce the topic of nanotechnology before exploring real world applications, which is the suggested format for this lesson.

Teacher Resources You may wish to use these resources as background information for the lesson preceding the lab activity.

Site	**Topics**
Finishing.com http://www.finishing.com/faqs/howworks.html	Defines and describes the electroplating process Provides alternative plating activities Explains why battery is important to plating
Britannica Encylopedia http://www.britannica.com/EBchecked/topic/183990/electroplating	Explains electrolytic cells and includes diagrams Provides historical context
University of Wisconsin MRSEC http://mrsec.wisc.edu/Edetc/nanotech/index.html http://mrsec.wisc.edu/Edetc/nanoscale/index.html	Defines nanotechnology and provides additional information Information on size and scale from kilometer to nanometer that may be useful when explaining how small nanowires are to students
Center for Nanoscale Science http://www.mrsec.psu.edu/education/teachers/demos/available_demos.asp	Nanoscale demonstrations are available both at Penn State and in your classroom

Additional resources

The following textbooks were used as resources in the preparation of this lesson as they include information along with pictures and diagrams of the electrolysis process. They are a good place to start, but any high school/college level chemistry text should have the necessary information.

1. Krimsley, V. S.; *Introductory Chemistry*, Second Edition; Brooks/Cole Publishing Company: California, 1995; 505-510
2. McQuarrie, D. A.; Rock, P. A. *General Chemistry*, Third Edition; W. H. Freeman and Company: New York, 1987; 812-840

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NNIN Document: NNIN-1209
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3. Zumdahl, S. S.; *Introductory Chemistry: A Foundation*, Fourth Edition; Houghton Mifflin Company: Boston, 2000; 550-574

Lesson 2, Day 1 – Instructional Procedure
Synthesis of Nickel Nanowires

Time (minutes)	Instructional Activity
10	Students will obtain lab materials, and prepare the anodisc for electroplating.
15	Students will test the battery, and then connect it to the electrodes for 10 minutes for plating. They will then clean up and prepare for the etching of the alumina membrane.
10	Students will use acetone to remove electrical tape, and will prepare their sample for the nitric acid.
10	Students will dissolve the membrane in NaOH for 5-10 minutes and after rinsing store the sample in a small vial

Lesson 2, Day 2 – Instructional Procedure
Synthesis of Nickel Nanowires

Time (minutes)	Instructional Activity
10-15	Students will finish *Section C* of the procedure if necessary. Students who are finished can discuss their answers for the lab questions before turning them in for grading.
5-10	Teacher will show videos of the alignment of nickel nanowires by a magnetic field under a 20x optical microscope. See the following website http://chemistry.beloit.edu/edetc/nanolab/nickel/index2.html If you have an optical microscope you may be able to have students examine their product. If they have difficulty distinguishing the nanowires, the importance of Scanning Electron Microscopes (SEM) can be discussed.
25	Teacher will give lesson on nanotechnology. Students should have had an introduction such as that in the unit on scaling (*How Big is Nano ?*on the NNIN educaton portal). If students have already discussed how small a nanometer is, the focus should be on potential applications, and how properties of certain materials differ on the nanoscale. For example, gold nanoparticles in solution will appear red as opposed to the yellow gold color they posses as bulk metal. Other properties affected include lower resistance to electricity, lower melting points, or faster chemical reactions. See nanotech resources listed above for additional information.

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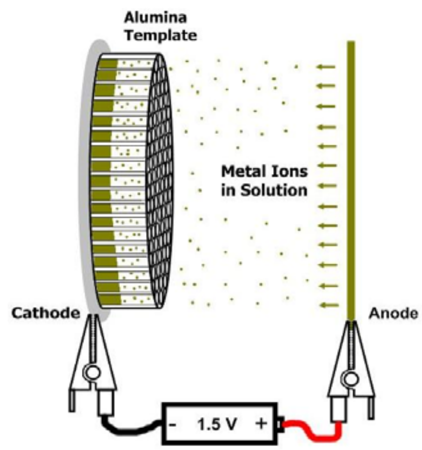
Name______________________________ Date_________________ Class_____________________

Synthesis of Nickel Nanowires
Student Worksheet (*with answers*)

Introduction

Figure 1: Model for synthesis of nickel nanowires. Figure developed by Paul Longwell (2009 NNIN-RET at Penn State)



Nanotechnology is the next big thing, and everyone is talking about it. Biosensors, nanomotors, and medical delivery systems are only a few of the many potential applications that scientists are currently working on. In a research lab nanowires can be produced by sputter coating or evaporating metals such as silver or gold onto the back of alumina membranes, which will make contact with the negative electrode in an electrolytic cell allowing various metals to form in the pores. This exact process can not be reproduced in the average high school, but by replacing the contact with a substance which can be applied easily; it may be possible to produce nanowires. In the following procedure you will use a liquid metal (Gallium Indium Eutectic) for contact and a AA battery to force the plating of nickel into the pores.

Purpose

1. To construct and study an electrolytic cell capable of plating metal ions (nickel) into alumina pores with a diameter of 20 nanometers.
2. To demonstrate how simple techniques can replicate the work done in a research level lab.
3. To consider possible applications of this process, and how further experiments could be performed using this procedure as framework.

Question

1. What applications can you think of for nanowires? What may also be needed for your potential application to become a reality?
   Answers will vary, and there is no "right" answer. Look for creativity and realistic applications.

Hypothesis Develop a hypothesis to answer one or both of the questions listed above.
Using a simple electrolysis set up, we will be able to synthesize and harvest nickel nanowires effectively when compared to a more complex method used in a research laboratory.

Key Terms

Oxidation: *A reaction in which the atoms in an element lose electrons and the valence of the element is* correspondingly *increased (postitive).*

Reduction: *A reaction in which the atoms in an element gain electrons and the valence of the element is correspondingly decreased (negative).*
Redox Reaction: *A reaction which combines oxidation and reduction half-reactions where one atom is gaining the electrons which another atom has lost.*

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Electroplating: *To coat with metal by electrolysis. A metal in its ionic state is stimulated with electrons to a non-ionic coating.*

Voltage: *The electromotive force or potential difference expressed in volts.*

Conductor: *A material through which an electrical current can pass. Metals are good conductors.*

Anodisc: *An alumina filter with pores of 20-200 nanometer diameter which can be used to create nanowires using electrolysis. The pores will eventually be etched away using NaOH, leaving only the nanowires behind in solution.*

Scanning Electron Microscope (SEM): *electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. SEM can achieve a better resolution than optical microscopes which are limited to the wavelength of light (400-700nm).*

Materials per student group

- Safety glasses
- Nitrile gloves
- Distilled water bottle
- Three 50 mL beakers per group
- One glass slide
- One small vial
- One thin stem pipette
- One pair of tweezers
- One strong magnet
- One AA battery with holder and +/- leads
- Two wires with alligator clips
- One Volt Meter (shared among groups)
- Electrical tape
- One cotton applicator (Q-tip)
- One piece of emory cloth
- One 3 x 10 copper strip
- One nickel wire
- One Whatman Anodisc (0.02 µm 25 mm)
- Gallium-Indium eutectic, 99.99+% (shared among groups)
- 50 mL of Watts nickel pure (nickel plating solution)
- 6.0 M Nitric acid (handled by teacher, NOT students)
- 5 mL of 3.0 M NaOH
- 50 mL of Acetone (can be shared among two groups if needed)

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Rev: 08/2010

Procedure

This procedure has been adapted from one developed by A. K. Bentley, M. Farhoud, A. B. Ellis, G. C. Lisensky, Ann-Marie Nickel, and G. Lisensky; *Template Synthesis and Magnetic Manipulation of Nickel Nanowires*; J. Chem. Ed. 82, 765-768 (2005).

A. Preparing the disc

Figure 2: GaIn coating of anodisc

1) Obtain a 0.02 micrometer Anodisc filter. The disc is quite brittle and is supported by a polymer ring. When handling, be sure that you are using tweezers to hold the support ring. **WITHOUT** turning the disc over, place on a glass slide and use a small piece of electrical tape to keep it in place.

2) With gloves on, use a cotton applicator (Q-tip) to paint liquid Gallium Indium (GaIn) on the surface of the disc. Only dip the applicator into the metal once as it spreads very thin and addition GaIn will not be needed. Check for gaps in the coating by holding the glass slide up to the light. If there are any holes, continue to cover the surface. When you are finished it should look like the disc in figure 2.

3) Obtain a copper strip and sand down both sides using an emory cloth. Then rinse it off with distilled water and dry with a paper towel.

4) Remove the disc from the glass plate and flip it upside down so that the GaIn side is making contact with the **copper** strip that you have just cleaned.

5) Use electrical tape to fasten the disc to the copper electrode. Tape all sides of the disc so that the solution can not leak behind the disc, and tape the back of the copper strip. When in solution none of the copper should be exposed. When you are done your electrode should look similar to figure 3, except for the color of the disc.

Figure 3: A completed copper electrode

B. Plating the nanowires

1) Use a volt meter to test the voltage of a AA battery in a holder. The voltage should be at least 1.3 V. If less, set the battery aside and obtain a new one.

2) Fill the 50 mL beaker with the nickel plating solution. Insert your copper electrode so that the anode disc is completely submerged. If necessary use tape to fasten it to the side of the beaker. Then fasten a nickel wire to the opposite side of the beaker with tape.

3) Connect the **negative** lead of the battery to the **copper** electrode, and the **positive** lead to the **nickel** wire. Make note of the time that you started in your lab notebook. Disconnect the battery after 10 minutes have passed.

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4) Remove the copper electrode from solution. Record your observations in your lab notebook.

5) The nickel solution can be reused for this experiment, so pour it back into the small storage bottle provided by your teacher. **DO NOT** pour it back into the stock solution. Then answer the following question in your lab book.
    a. What happened to the nickel ions which were in solution? *The nickel ions which were in solution joined with electrons at the cathode and were reduced. This reduction occurred inside of the pores of the alumina membrane, forming nickel nanowires.*
    b. If you believe they were depleted, then how can the solution be reused? *The solution can be reused because the nickel wire which was taped to the side of the beaker (anode) provided additional nickel ions to the solution as electrons were removed. Overall, the mass of the anode should have decreased.*

C. Harvesting the nanowires

1) Rinse the copper electrode with distilled water.

2) Fill a 50 mL beaker with acetone and soak the electrode for up to 15 minutes. This will remove the adhesive from the tape. When the tape begins to curl, gently peal it off using tweezers.

3) Once the tape is removed, using tweezers remove the anode disc and flip it over so that the shiny GaIn side is facing up. Then place it on a glass slide and tape it down.

4) Take the slide to your teacher who will use nitric acid on a cotton swab to remove the GaIn in a fume hood. The teacher will soak the cotton swab in water before disposal, and rinse off both sides of the disc with distilled water.

5) Pour 5 mL of NaOH in a clean 50 mL beaker, and place the disc inside. The ceramic material will begin to dissolve after 5-10 minutes. When the polymer support ring has separated, use a stirring rod to detach the remaining nickel from the inside, and then discard the ring in a solid waste container.

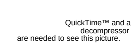

Figure 4: Removal of GaIn with nitric acid

6) Place the beaker on a strong magnet and move it from side to side. The nickel nanowires should follow the magnet.

7) Use the magnet to pull the nanowires to one side of the beaker. Then use a pipette on the opposite side to suck up and remove the NaOH. Add distilled water to the nanowires, and repeat the last step using the magnet and pipette several times to clean the wires.

8) When the wires have been cleaned make sure they are suspended in distilled water, and transfer them to a small vial. Label the vial with the names of your group members, and the contents. Answer the following questions in your lab notebook.

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a. What kind of microscope would allow you to see the nanowires in greater detail, an optical microscope or a scanning electron microscope? *A scanning electron microscope would allow for much better resolution than an optical microscope. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm.*

b. Could you create copper or zinc nanowires? If so, how would you do it? *If your students have performed Lesson 2 (electroplating of dinosaurs) they may mention that a copper electrode (instead of nickel) along with copper sulfate would plate copper ions into the pores of the anodisc. The same could be done with zinc using a zinc anode, and zinc salt solution.*

c. Could you produce nanowires consisting of two different metals? If so, how could you do this? Would the wire be uniform (ex. Copper and nickel throughout) or would it have two distinct ends (ex. One copper and one nickel)? *Nanowires can be produced with two or more metals and would have two distinct ends. This could be done by stopping the plating process with one metal solution, and then finishing with another. For example, you could use a copper plating set up for the first five minutes, and a nickel plating set up for the next five minutes.*

Cleanup

Plating solutions are replenished through the metal wire or strips connected to the positive end of the battery, so they can be used indefinitely. Collect the solutions from the students in separate bottles or containers, just incase there is a contamination. This will prevent the loss of the stock solution if a procedural error was performed resulting in depletion of ions in solution. The metal strips can be reused. Emory cloth can be used to clean the surface and provide better contact. Small quantities of NaOH can be poured down the drain with excess water, and the nitric acid from the cotton swab can be diluted in water of the course of a few hours.

Assessment

Assessments *for* Learning

Following the lab, students will submit their lab notebook for grading. Once returned to the students, the teacher should allow for a class discussion on the results and the significance of the lab. Allow students to ask questions that were not addressed during the activity. Write all of these questions up on the board, and then go through each one together as a class. If a question or scenario comes up which you do not know the answer to, allow the students to develop a procedure to find the answer. Ask questions which change the procedure slightly. For example, what would happen if the anodisc was not fully coated with GaIn? Would some metal still form in the pores of the disc? Would none form at all? Is there a way to make hybrid wires which have nickel on one half and copper on the other? What are potential applications for nanowires with two different ends (think about properties of metals, magnetism for alignment, etc)?

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Assessments *of* Learning

Description	What is Assessed	Feedback
The students will perform the lab for the electroplating nickel in the synthesis of nanowires. The lab requires students to define key terms, answer questions about the process, and keep their notes organized in a lab notebook. While there is no data or graphs to analyze, students must rely on their previous knowledge involving multiple concepts to form conclusions.	The students' notebooks allow for assessment regarding their organization of thoughts and ideas. The lesson itself assesses the students' ability to understand and make connections between different concepts. The class discussion allows the teacher to asses a students ability to go beyond what is taught and to imagine how new technology can be applied to current problems.	Students receive a score according to the completeness and accuracy of their answers, and the organization of their notes. They also receive comments when the wrong answer or explanation is provided which both challenges the misconception, and provides further explanation of the correct concept.

National Science Content Standard: Level 9-12

A. Science as Inquiry

- Identify questions that can be answered through scientific investigations
- Design and conduct a scientific investigation
- Use appropriate tools and techniques to gather, analyze, and interpret data
- Develop descriptions, explanations, predictions, and models using evidence
- Think critically and logically to make the relationships between evidence and explanations
- Communicate scientific procedures and explanations

B. Physical Science – Structure and Property of Matter section

- Structure and properties of matter
- Chemical reactions
- Interactions of energy and matter

E. Science and Technology – Abilities of Technological Design section

- Identify appropriate problems for technological design
- Design a solution or product
- Implement a proposed design
- Evaluate completed technological designs or products
- Communicate the process of technological design

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Pennsylvania Science Education Standards

3.2 Inquiry and Design

10.A Apply knowledge and understanding about the nature of scientific and technological knowledge.

- Know that science uses both direct and indirect observation means to study the world and the universe.
- Describe various types of chemical reactions by applying the laws of conservation of mass and energy.

10 B. Apply process knowledge and organize scientific and technological phenomena in varied ways.

- Describe materials using precise quantitative and qualitative skills based on observations.
- Develop appropriate scientific experiments: raising questions, formulating hypotheses, testing, controlled experiments, recognizing variables, manipulating variables, interpreting data, and producing solutions.

10 C. Apply the elements of scientific inquiry to solve problems.

- Generate questions about objects, organisms and/or events that can be answered through scientific investigations.
- Evaluate the appropriateness of questions.
- Design an investigation with adequate control and limited variables to investigate a question.
- Conduct a multiple step experiment.
- Organize experimental information using a variety of analytic methods.
- Judge the significance of experimental information in answering the question.

12 A. Evaluate the nature of scientific and technological knowledge.

- Know and use the ongoing scientific processes to continually improve and better understand how things work.

3.4 Physical Science, Chemistry, and Physics

10.B Apply process knowledge and organize scientific and technological phenomena in varied ways.

- Use knowledge of chemical reactions to generate an electrical current.
- Explain resistance, current and electro-motive force (Ohm's Law).

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