Template Synthesis and Magnetic Manipulation of Nickel Nanowires

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Nanotechnology, the study of materials having at least one dimension smaller than 100 nm, is a rapidly progressing field. Commercialization of nanotechnology using nanoscale particles can already be found in applications ranging from enhanced fabrics *(1)* to self-cleaning windows *(2).* Chemistry plays a central role in the development of nanoscale materials because it gives precise control over the composition of the nanostructures.

Despite the emerging emphasis on nanotechnology by the media, funding agencies, and academic and industrial research programs, its entry into the high school and college chemistry curricula has been slow *(3).* There is little opportunity in most undergraduate chemistry courses for students to prepare nanoscale materials and explore how these materials will be used in the technologies of the future. Experiments described in this *Journal* allow students to synthesize nanocrystalline Eu-doped yttria *(4),* watch the exciting behavior of a ferrofluid containing nanoparticles of magnetite *(5),* study the self-assembly of a monolayer of gold nanoparticles *(6),* and create their own carbon nanotubes *(7).* The experiment described in this article involves a fascinating area of current nanotechnology research: the synthesis and study of the properties of wires that are nanometers wide and micrometers long.

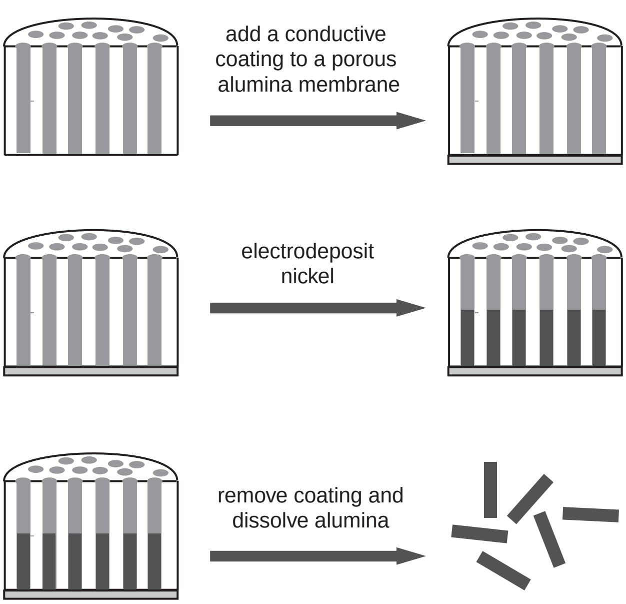

Figure 1. Schematic description of the template synthesis technique.

Nanowires are an intensively studied area of research owing to their potential applications in nanoscale electronic, magnetic, optical, and mechanical devices. One common approach to forming nanowires is the template synthesis technique, which was first popularized more than ten years ago and has become widely used *(8, 9).* Nanoporous alumina or polycarbonate membranes are used as templates to direct the growth of nanowires. Generally, a membrane's pores are filled with one or more metals via a technique such as electrodeposition. The membrane can be chemically removed, leaving metallic nanowires behind. A schematic description of the process is shown in Figure 1. The technique has been adapted to synthesize nanoscale semiconductor oxides *(10),* superconductors *(11),* magnetic structures *(12),* and giant magnetoresistance materials *(13).* Nickel nanowires are of particular interest to researchers because they could be employed to increase magnetic storage density *(14).* We present a straightforward electrochemical method to create nickel nanowires using an AA battery and observe them with an optical microscope.

A general problem with using nanowires in devices is the ability to control their position. Recently nickel nanowires have been manipulated using magnetic fields *(15).* In this experiment, students can watch the movement and alignment of their nickel nanowires through the lens of an optical microscope as they use common magnets to alter the applied magnetic field.

This experiment is an inexpensive, easy-to-understand introduction to nanowire synthesis. It especially highlights the role electrochemistry plays in the fabrication of nanoscale structures. The experiment is appropriate for introductory and advanced undergraduate chemistry students and could be used in the curriculum when redox chemistry, electrochemistry, materials chemistry, or magnetism are discussed.

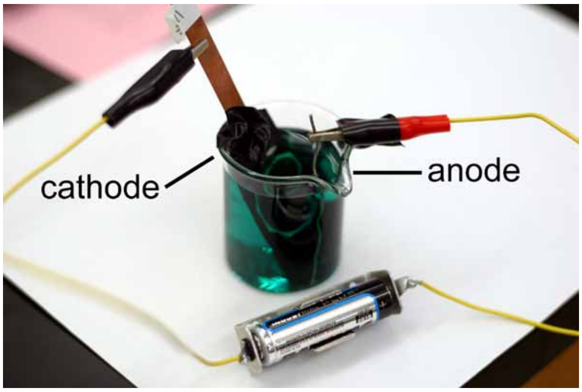

Figure 2. The electrochemical cell showing the membrane taped to a copper plate as the cathode, the nickel wire as the anode, the Ni plating solution, and an AA battery.

Figure 3. The nanowires in ethylene glycol respond to a cow magnet set at one side of the vial.

Experimental Procedure

The alumina membranes are available commercially from Whatman, Inc. (Detailed lab instructions and information on supplies can be found in the Supplemental Material.W) One side of the alumina membrane is first sputtered with silver metal or painted with GaIn eutectic to block the pores and form a conductive layer that serves as the cathode. The membrane is mounted on a copper plate using insulating electrical tape. The tape covers the copper plate and prevents the nickel from electrodepositing on it. The assembly is placed in a 50-mL beaker, a nickel wire is added as the anode, and both electrodes are connected to an AA battery. Adding commercial Ni plating solution (available from Technic, Inc.) completes the circuit and Ni^{2+} is reduced to Ni inside the pores of the membrane while the Ni wire is oxidized to Ni^{2+}. The plating solution can be reused many times. The battery provides a potential of −1.5 V, which is well negative of nickel's standard reduction potential of −0.257 V. The electrochemical setup is shown in Figure 2.

The electrodeposition is allowed to continue for 10–50 minutes, depending on the length of wires desired. The membrane is removed from the copper plate, the Ag metal or GaIn eutectic is dissolved using concentrated nitric acid, and the alumina is dissolved using 6 M sodium hydroxide. As the alumina dissolves, the nanowires are liberated and float freely in the sodium hydroxide solution. A series of washing steps dilutes the base and the nanowires can be suspended in a number of solvents indefinitely for storage.

Hazards

This experiment requires the handling of concentrated nitric acid and 6 M sodium hydroxide. Both will burn skin and eyes. Exposure to nickel (through skin or oral absorption) can cause skin rashes. GaIn eutectic may cause skin irritation. The hazards of nickel nanowires due to inhalation are unknown, so nanowires should be kept and handled in solution. Goggles must be worn at all times during the preparation of the nanowires and gloves must be worn when handling the GaIn eutectic, nickel solution, and strong acids and bases.

Results and Discussion

Magnetic Manipulation

To test the magnetic response of the liberated nickel nanowires, set a magnet at the side of a vial containing the nanowire suspension and allow it to sit for a few minutes. Spikes in the nanowire material will become visible. These spikes follow the magnetic field lines similar to the behavior observed in ferrofluid *(5)*. This effect can be seen in Figure 3.

To observe the magnetic response of individual nanowires, place one drop of nanowire suspension on a clean microscope slide and cover with a cover slip. (The nanowires can be suspended in water or ethylene glycol.) Place the slide on the stage of an optical microscope. Wires can be seen with as little as 10× magnification. By holding a rectangular magnet on one side of the microscope slide while examining the nanowires, students can align the nanowires with the magnetic field. Nanowires can be aligned horizontally or vertically as shown in Figure 4. Additionally, if a magnet is spun on one side of the slide, the nanowires will spin like small stir bars. Movies of the magnetic behavior of the nanowires are included as part of the Supplemental MaterialW and online video lab manual *(16)*.

To examine the nanowires using a scanning electron microscope (SEM), a drop of water containing the nanowires is allowed to dry. Samples of nanowires imaged using a LEO 1530 FE-SEM are shown in Figure 5. If a magnetic field is applied to the drop as it dries, the nanowires will align along the direction of the magnetic field, as shown in Figure 5B.

Length of Nanowires versus Deposition Time

A variation of the synthesis is to assign different deposition times to groups of students and use SEM to measure the average length of nanowires produced by each pair of students. Data compiled by students at UW–Madison and Beloit College using GaIn eutectic as the cathode are shown in Figure 6. As expected, longer deposition times produce longer nanowires. The nanowires grow at a rate of approximately 1 μm/min under the laboratory conditions described; no special effort was made to control the experimental geometry. Nanowires formed using the sputtered silver cathode grew approximately twice as fast as those formed using the GaIn eutectic cathode.

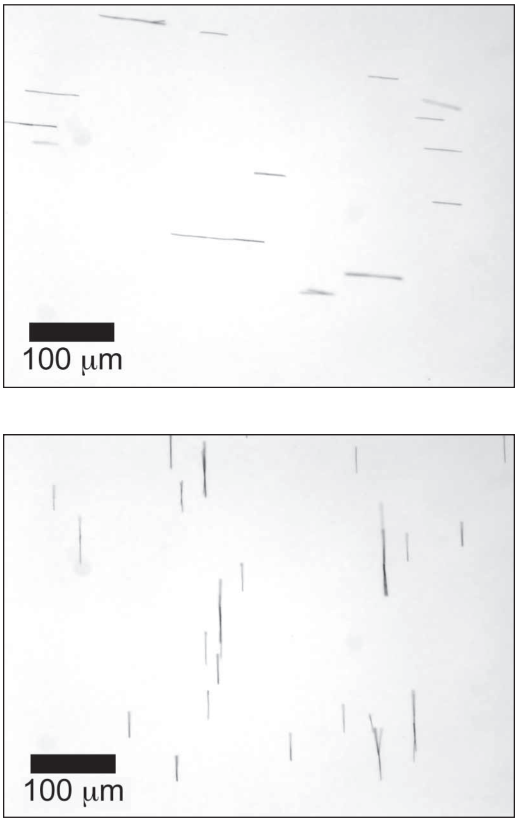

Figure 4. Optical microscope images (20x magnification) of the nanowires aligning horizontally (top) and vertically (bottom).

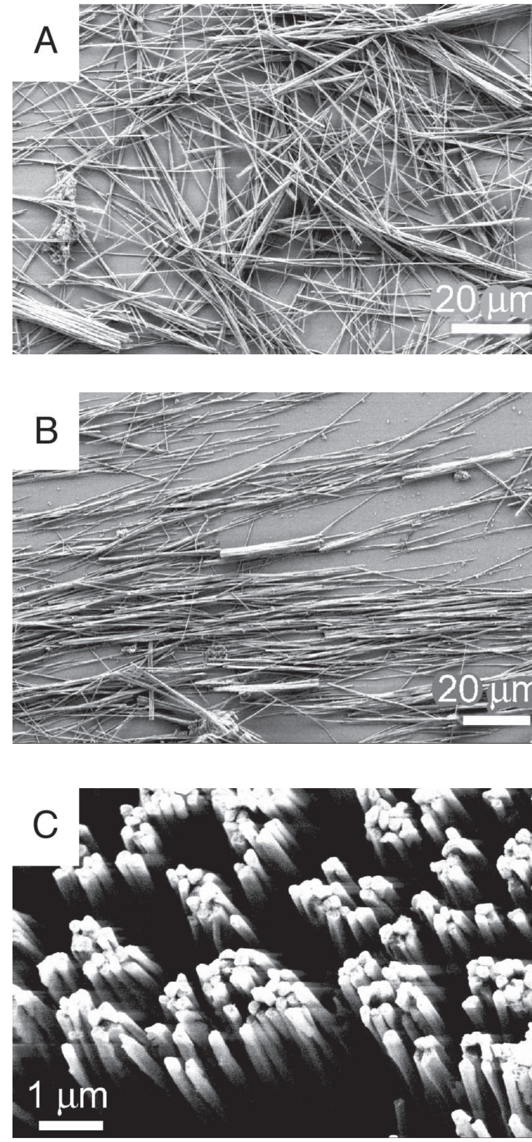

Figure 5. SEM images of (A) a random arrangement of nanowires; (B) nanowires aligned using a magnet as the drop dried; and (C) upright nanowires on the silver backing after dissolving only the alumina membrane.

X-Ray Diffraction

X-ray powder diffraction patterns of the nanowires taken both before and after the nanowires are liberated from the membrane are shown in Figure 7. While the wires are still embedded in the membrane, the nickel(220) peak is most intense. This implies that the nanowires are growing with a preferential orientation of the (220) plane in the direction of growth. After the wires are liberated and dispersed randomly on a microscope slide, the XRD intensities closely match the Ni standard pattern.

Use and Assessment

The lab has been included in courses at the University of Wisconsin–Madison, Milwaukee School of Engineering, and Beloit College. Students have ranged in background from first-year nonmajors enrolled in a colloquium course on nanotechnology to materials science and physics graduate students. Students usually work in pairs to create the nanowires. The nanowire synthesis takes approximately 90 minutes to complete if less than 30 minutes are used for deposition; the remaining time is used for experiments with the nanowires. Alternatively, the laboratory can be divided into two shorter lab periods. Following the written procedure (available in the Supplemental Material[W]), 23 of 24 pairs of students were successful in making and observing nickel nanowires. Some courses used an online video lab manual instead of the written procedure, which provided videos of each step in the experiment alongside simplified written instructions *(16).* Seventeen of nineteen lab teams using the Web-based video lab manual were successful.

Students were asked for their comments regarding both the clarity of the written or online instructions and the effectiveness a of the lab a teaching tool for the topics of electrochemistry and nanotechnology. Most students said they had never heard of nanotechnology or nanowires before the lab. The “downtime” during nanowire deposition was often used for a brief introductory lecture about nanoscale materials. Students reported that this lecture was helpful in their understanding of the lab. In addition to appreciating the

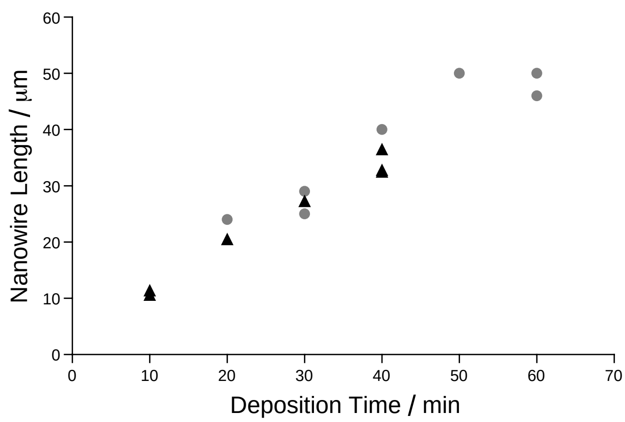

Figure 6. The relationship between nickel deposition time and length of the nanowires recovered from the membrane. Triangles represent data from UW–Madison and circles represent data from Beloit College.

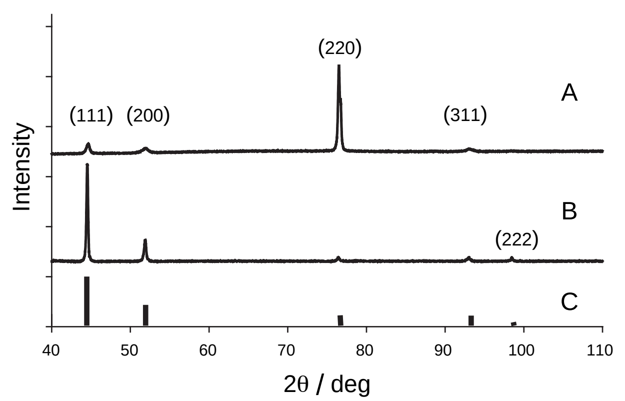

Figure 7. X-ray powder diffraction pattern of (A) nanowires still embedded in the alumina membrane, (B) liberated nanowires dispersed on a microscope slide, and (C) the JCPDS standard file #4-850 for nickel.

nearly 100% success rate of the lab, the students liked the relevance to current research and emerging technologies. One student said, “I felt like I was contributing to science and not just doing a lab that’s been done a thousand times.” Another said the lab demonstrated that “it isn’t that hard to make nanowires.” Many enjoyed seeing their nanowires using the optical microscope: “It was neat because we got a visible product that has potential technological uses in the world.”

Conclusion

This experiment gives students a unique opportunity to create and manipulate their own nanoscale materials. It brings nanotechnology into the teaching lab and shows students how electrochemistry can be used to make nanoscale structures. The lab is applicable across the undergraduate curriculum (from general chemistry to engineering to materials science) and may also be appropriate for high school chemistry courses.

Acknowledgments

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[W]Supplemental Material

Instructions for the students, including lab questions, notes for the instructor and videos of the magnetic behavior are available in this issue of *JCE Online*.

Literature Cited

1. Nano-Tex. *http://www.nano-tex.com* (accessed Feb 2005).
2. PPG SunClean Self-Cleaning Glass. *http://www.ppg.com/gls_residential/gls_sunclean* (accessed Feb 2005).
3. National Nanotechnology Initiative. *http://www.nano.gov* (accessed Feb 2005).
4. Bolstad, D. B.; Diaz, A. L. *J. Chem. Educ.* **2002,** *79,* 1101–1104.
5. Berger, P.; Adelman, N. B.; Beckman, K. J.; Campbell, D. J.; Ellis, A. B.; Lisensky, G. C. *J. Chem. Educ.* **1999,** *76,* 943–948.
6. Keating, C. D.; Musick, M. D.; Keefe, M. H.; Natan, M. J. *J. Chem. Educ.* **1999,** *76,* 949–955.
7. Fahlman, B. D. *J. Chem. Educ.* **2002,** *79,* 203–206.
8. Penner, R. M.; Martin, C. R. *Anal. Chem.* **1987,** *59,* 2625–2630.
9. Hulteen, J. C.; Martin, C. R. *J. Mater. Chem.* **1997,** *7,* 1075–1087.
10. Lakshmi, B. B.; Patrissi, C. J.; Martin, C. R. *Chem. Mater.* **1997,** *9,* 2544–2550.
11. Yi, G.; Schwarzacher, W. *Appl. Phys. Lett.* **1999,** *74,* 1746–1748.
12. AlMawlawi, D.; Coombs, N.; Moskovits, M. *J. Appl. Phys.* **1991,** *70,* 4421–4425.
13. Evans, P. R.; Yi, G.; Schwarzacher, W. *Appl. Phys. Lett.* **2000,** *76,* 481–483.
14. Pignard, S.; Goglio, G.; Radulescu, A.; Piraux, L.; Dubois, S.; Declemy, A.; Duvail, J. L. *J. Appl. Phys.* **2000,** *87,* 824–829.
15. Tanase, M.; Bauer, L. A.; Hultgren, A.; Silevitch, D. M.; Sun, L.; Reich, D. H.; Searson, P. C.; Meyer, G. J. *Nano Lett.* **2001,** *1,* 155–158. Bentley, A. K.; Trethewey, J. S.; Ellis, A. B.; Crone, W. C. *Nano Lett.* **2004,** *4,* 487–490.
16. Nickel Nanowires. *http://mrsec.wisc.edu/edetc/nanolab/nickel/index.html* (accessed Feb 2005).

Editor’s Note

For more information about electrochemical fabrication of nanowires, see pp 720–726 in this issue.