Nanotechnology
The Science of the Very Small

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A nanometer, one billionth of a meter! Can scientists see something this small? Can they manufacture devices at this small level? The answer is yes! Of course cells have been doing this for billions of years. They are nature's nanomachines and have perfected the science of manufacturing matter atom by atom. Now biologists, chemists, physicists, and engineers are collaborating to work at this nanoscale level as well.

Two high school science teachers were part of the NANORET (Nanotechnology Research Experience for Teachers) program this summer at the Center for Nanotechnology at the University of Washington. They got to see nanoscale research and learn more about this exciting scientific collaboration. Because many new advances in fundamental science, medicine and technology will come out of this research and due to the collaborative, interdisciplinary nature of the nanotech field, science teachers can use this fascinating "world of the small" to enhance students' learning of science. From these summer experiences, teachers learned that the basics taught to secondary high school students are important for keeping career options open to them. The field of nanotechnology will certainly interest not only the computer whiz kids, but also students interested in many diverse areas. Nanotechnology provides both a reason students should know about computers, biology, chemistry and physics, and a gateway to all of these area. Such areas as microscopy, optics, and molecular and atomic structure become meaningful and vital basics when considering nanoscience.

What is Nanotechnology?

Nanotechnology is the precision placement, measurement, manipulation and modeling of individual or small groups of atoms or molecules. Typically, such activities in the size range of 1-100 nanometers are considered as nanotechnology.

Importance of Nanotechnology

Almost every industry will be affected by nanotechnology. Many are already using it. Many applications include the creation of unique materials with desirable properties not attainable through bulk material processing. Nanotechnology can enable cheaper production methods, greater data storage and retrieval, designed drug discovery and delivery, more economical production of semiconductors, and creation of highly efficient nanofilters among a myriad of other uses.

Nanotechnology Program at the University of Washington

If you do not know much about nanotechnology, you are probably not alone. Building on ongoing research, nanotechnology at the University of Washington began in 1997 with the formation of the Center for Nanotechnology. This year the Center for

Nanotechnology became part of the National Nanotechnology Infrastructure Network (NNIN). The Nanotech User Facility located in Fluke Hall on the Seattle Campus has a scanning electron microscope (Fig. 1), an atomic force microscope (Fig. 2) and a fluorescent microscope (Fig. 3) for imaging and fabrication of nanoscale structures and devices. Dr. Dong Qin, Associate Director for the Center for Nanotechnology, can answer questions or show teachers and students these facilities upon request.

Lab Activities

Introducing students to nanotechnology is possible through some lab activities. *Cutting it Down to Nano* and *NanoSolutions*, two very inexpensive activities that are on the University of Wisconsin website (http://mrsec.wisc.edu/edetc/IPSE/educators/) are good introductions.

As a part of the NANORET program, the following lab activity was designed.

Title: The Water Race

Time: 50 minutes
Organization: Lab Stations
Level: High School

Purpose:

- Introduce students to the engineering of an interfacial surface at the nanoscale.
- Demonstrate the concepts of hydrophobic and hydrophilic behavior.
- Create a hydrophilic or hydrophobic surface using a 2 nanometer thick self assembled monolayer (SAM).

Lab Questions:

1. What do the terms hydrophobic and hydrophilic mean?
2. What is the definition of one nanometer?
3. What is a self assembled molecular (SAM) monolayer?
4. How does changing the surface of a substance affect its interaction with water?

Teacher Background:

1. In the water molecule, the hydrogen atoms tend to have a slightly positive charge and the oxygen atoms a slightly negative charge. Water molecules cling to each other through the hydrogen bond. No polar molecules form hydrogen bonds, so in the presence of water, the nonpolar molecules associate with one another while excluding the water molecules. This minimizes the overall free energy of the system. Nonpolar molecules that repel the water molecules are said to be hydrophobic and polar molecules forming ionic or a hydrogen bond with the water molecule are said to be hydrophilic. This property of water was important for the evolution of life. Hydrophobic interaction

plays the most critical roles in the formation of the lipid bilayer of the cell membrane and the folding of proteins and nucleic acids; therefore, hydrophobic interaction is the foundation for the existence of life.

2. A nanometer is one billionth of a meter. The field of nanotechnology works with materials and measurements 100 nanometers or smaller.

3. A self-assembled monolayer (SAM) is a layer of organic molecules formed spontaneously on a solid substrate. One end of the organic molecule binds to the solid surface via a covalent bond while the other end points outwards. There are many ways to form SAMs on different solid substrates. Two most commonly used methods are using thiol containing organic molecules to form a packed SAM on coinage metals such as gold, silver, copper, or using various silane molecules to form SAM on silicon or insulating glass surfaces. Because the exposed end of the SAM determines the surface properties of the SAM modified substrate, we can alter a hydrophobic surface (a surface that expels water) into a hydrophilic surface (a surface that attracts water) by carefully selecting the SAM forming molecules.

However, the application of SAM is not restricted to modification of surface properties.

For example, if an electrically conducting chemical group is added to the exposed end of SAM, a nano-conducting wire or sheet can be formed[1]. In this experiment, we will focus on modifying the copper surface properties using SAM of 1-hexadecanethiol and 16-mercaptohexadecanoic acid. Both of these molecules contain a thiol group that forms a covalent bond to the copper surface. However, the exposed ends of these two molecules have completely different chemical properties. 1-hexadecanethiol has a highly hydrophobic $C_{18}H_{38}$- tail while 16-mercaptohexadecanoic acid has a hydrophilic carboxyl group pointing outwards. So you can imagine that grafting 1-hexadecanethiol SAM on the copper surface renders a more hydrophobic surface while formation of 16-mercaptohexadecanoic acid SAM on copper surface will make it more hydrophilic.

4. Water is repelled more by a surface when the hydrophobicity of the surface is increased. The contact angle of a water droplet is larger on a more hydrophobic surface.

<u>Materials:</u>

- Copper Dual-sided PC Board 114 x 161 mm (276-1499A Radio Shack)
- Chemicals
    - PCB Etchant Solution (276-1534 Radio Shack)
    - 1-Hexadecanethiol (448303-1G Sigma Aldrich Corporation)
    - 16-mercaptohexadecanoic acid (52270-100ml Sigma Aldrich Corporation)
    - Ethanol
    - Acetone
    - Distilled water
- 4 100 ml beakers
- 3 watch glasses
- timers
- hot plate
- air source (or hair dryer)
- micropipettes and tips

- wash bottles with distilled water for students

Safety equipment: gloves, aprons, goggles, Material Safety Data Sheets (MSDS) for all chemicals.

Teacher Preparation:

Clean and thoroughly dry 4 beakers.
Make solutions:

- 1 beaker of 1-hexadecanethiol solution (100 microliters in 40 ml ethanol) – Label $-CH_3$ and cover with a watch glass.
- 1 beaker of 16-mercaptohexadecanoic acid (10 millimoles [.114 grams] in 40 ml ethanol) – heat at 30 Celsius to dissolve. Label -COOH and cover with a watch glass.
- 1 beaker with 40 ml. PCB Etchant Solution. Label Ferric Chloride and cover with a watch glass.
- 1 beaker with distilled water for rinse.

Prepare one wash bottle with ethanol and one with acetone.
Set up beakers on a counter at 6 labeled stations for student teams to rotate.
Station 1: Copper pieces, acetone, ethanol
Station 2: Air source for drying
Station 3: Ferric Chloride, timer
Station 4: Distilled Water rinse
Station 5: $-CH_3$ solution, timer
Station 6: -COOH solution, timer

Cut copper into segments to fit into the beakers. Each lab group needs 2 pieces.
Review MSDS and all safety rules with students prior to the start of the experiment.

Student Procedure (see Fig. 4)

1. Put on gloves, goggles and lab aprons.
2. Clean copper PC board first with acetone and then with ethanol at Station 1 and dry with air at Station 2.
3. Using a wash bottle or micropipette, place a drop of distilled water on the surface of the copper to test the surface properties of the copper. (Water will stick to the surface when the surface is tilted on a hydrophilic surface and will run off of a hydrophobic surface.) Record your observations in your lab notebook.
4. At Station 3, place copper PC board so that one half the board is in the Ferric Chloride solution for 30 seconds. This will etch the surface to remove the copper oxide.
5. At Station 4, rinse the ferric chloride off the copper in distilled water.
6. Air dry at Station 2.
7. At Station 5, place copper board so the etched surface is in the $–CH_3$ solution for 5 minutes. Then take out the board and wash with ethanol at Station 1.
8. Air dry at Station 2.

9. At your lab table, add one drop of distilled water using a micropipette (or wash bottle) to the untreated copper half and one drop of distilled water to the side treated with –CH_3.
10. Tilt the surface of the copper board to determine if the water sticks to the surface (hydrophilic) or runs off the surface (hydrophobic).
11. Record your observations in your lab notebook.
12. Clean a second copper PC board with acetone and ethanol at Station 1 and air dry at Station 2.
13. At Station 3, place copper PC board so that one half the board is in the Ferric Chloride solution for 30 seconds. This will etch the surface.
14. At Station 4, rinse the ferric chloride off the copper in distilled water.
15. Air dry at Station 2.
16. At Station 6, place copper board so the etched surface is in the –COOH solution for 5 minutes and then wash with ethanol.
17. Air dry at Station 2.
18. At your lab table, add one drop of distilled water using a micropipette (or wash bottle) to the untreated copper half and one drop of distilled water to the side treated with –COOH.
19. Tilt the surface of the copper board to determine if the water sticks to the surface (hydrophilic) or runs off the surface (hydrophobic).
20. Record your observations in your lab notebook.

Data and Observation:

Substance	Observations	Hydrophobic or hydrophilic
Clean copper PC board		
1-hexadecanethiol solution (-CH_3)		
16-mercaptohexadecanoic acid (-COOH)		

<u>Conclusion:</u> Write a paragraph to describe the results of the experiment and your reflections on your experiences during this lab.

<u>Summary Questions:</u>

1. Can the properties of a surface be changed? What is your evidence?
2. What happens to water on a hydrophobic surface?
3. What happens to water on a hydrophilic surface?

<u>Assessment:</u>

- Lab Notebook Entry
- Typed Lab Abstract: Purpose, materials and procedures, results, and conclusions.

Reference

1. S. Hong, R. Reifenberger, W. Tian, S. Datta, J. I. Henderson, and C. P. Kubiak, "Molecular conductance spectroscopy of conjugated, phenylbased molecules on Au(111): the effect of end groups on molecular conduction," *Superlattices Microstruct.*, Vol. **28**, pp. 289–303, 2000.

Resources for teachers

The following people at the University of Washington in Seattle, WA are great resources for information on nanotechnology: Dr. Ethan Allen, Education & Outreach Manager, Center for Nanotechnology; Amy Leslie, Lead Teacher, University of Washington Engineered Biomaterials; Dong Qin, Associate Director, Center for Nanotechnology.

To learn more about nanotechnology, here are a few great web sites:

http://www.nano.gov – This site gives information on the National Nanotechnology Initiative. There is a section for K-12 students and teacher resources.
www.howstuffworks.com.nanotechnology.htm – A great site for students to learn about nanotechnology as well as other devices.
http://mrsec.wisc.edu/edetc/ - This site has great lab activities.
http://www.tntg.org/id46.htm - This site has links to other nanotech sites.
www.nano.washington.edu – This site gives information on the programs at the University of Washington in Seattle.

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