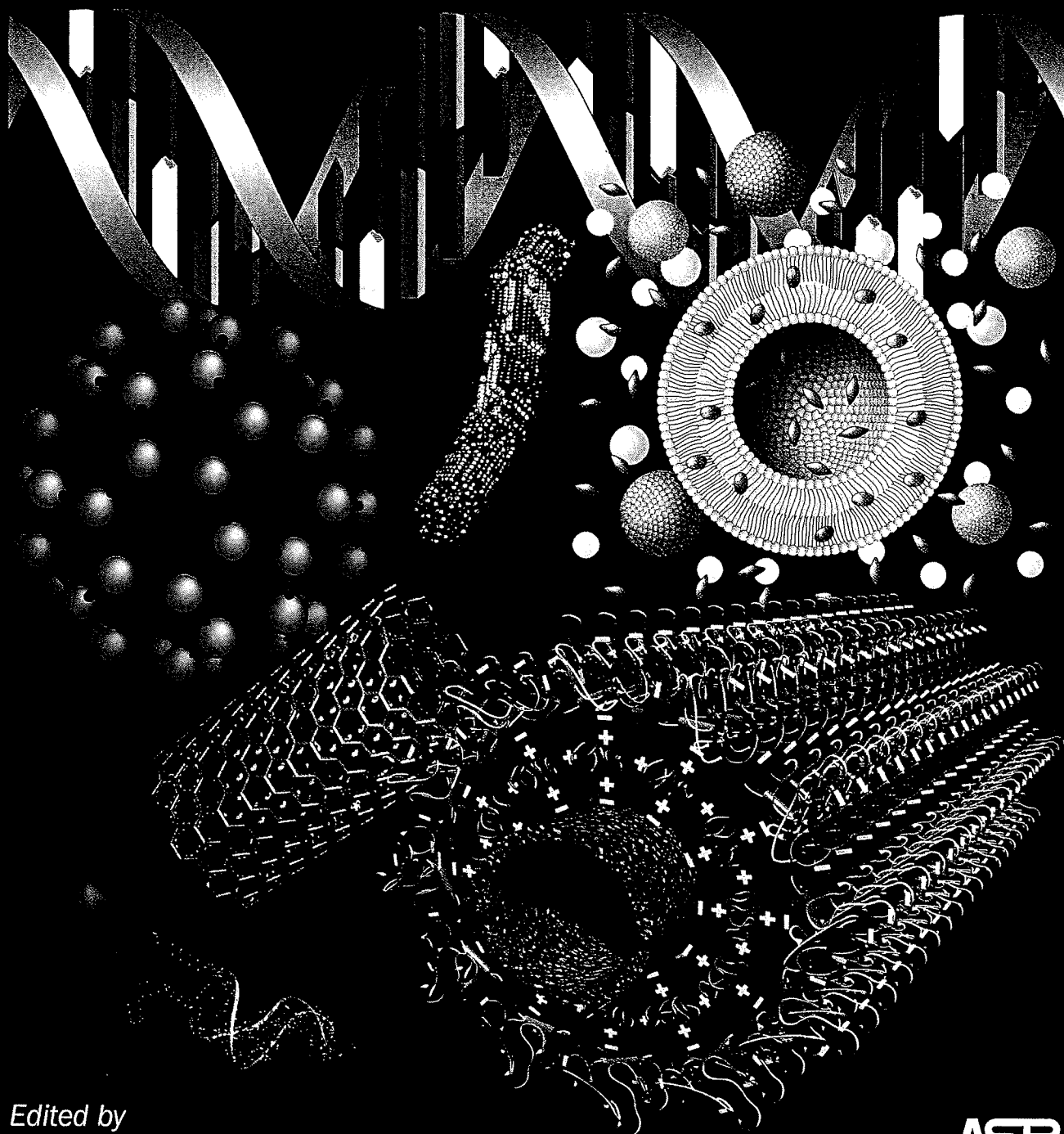


# NANOSCALE SCIENCE *and* ENGINEERING EDUCATION



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## CHAPTER

### Interdisciplinary Lab Course in Nanotechnology for Freshmen at the Florida Institute of Technology

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## 1 Introduction

Nanotechnology will continue to grow into the foreseeable future as a field of research and innovation throughout the world. Nanotech companies that want to remain competitive will need to attract workers who are highly trained in both science and technology. As a result of the interdisciplinary nature of nanotechnology, this workforce must have a cross-disciplinary awareness of current developments in nanotechnology and nanoscience. Students should be made aware of this field of study early in their education so that they can become better trained and more productive when they enter the workforce.

The Florida Institute of Technology (Florida Tech) offers Nanoscience and Nanotechnology, a laboratory course in nanotechnology for first-year undergraduate students. This course can serve as a model for other universities that are also dedicated to training future nanotech workers (also see chapter by Fonash, Fenwick, and Hallacher in this volume). Students are able to enroll in the nanotechnology laboratory as early as the second semester of their first year of college. The only course prerequisite is completion of one semester of general chemistry and its associated chemistry lab. The nanotech lab course was funded initially by the National Science Foundation and consists of lab modules that are developed by university faculty in such disciplines as physics, chemistry, chemical engineering, and biology. The course offers a unique, hands-on laboratory experience to first-year students of science and engineering that can potentially influence both their career choices as well as their future career success by providing them with early training in lab skills and techniques that they might use in an industrial or academic laboratory.

Among the desired outcomes of this laboratory course are: (i) introduce first-year students of all backgrounds to several material fabrication and characterization techniques currently in use in nanotechnology; (ii) provide a source of motivation for students to take additional courses in materials science and engineering at a later time in their education; (iii) reduce the amount of time that is needed to train an undergraduate student into becoming a productive member of a research team; and (iv) contribute to the broader goal of developing a more knowledgeable and productive workforce in nanotechnology.

The course is a 3-h lab that meets once per week for approximately 15 weeks. Depending on the number of students enrolled in the course, as well as the nature of a particular lab module, the students may be divided into sections that are taught by the participating faculty. The team-teaching format of the course allows for future growth in faculty participation from other science and engineering departments.

Relevant laboratory exercises from upper-level materials courses can be adapted to the freshman course, but primarily new experiments are developed specifically for the course. Students perform experiments in nanotechnology involving the fabrication of nanomaterials, such as carbon nanotubes, semiconducting CdS quantum dots, and metallic nanoparticles by chemical means or the growth of nanoscale thin films by sputter-coating and thermal evaporation. The students prepare their own samples for later characterization and/or testing. Students gain hands-on experience in imaging and manipulating the surface structure of nanomaterials using scanning tunneling and atomic force microscopes (STM and AFMs) and also learn about traditional electron microscopes, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The students receive grades for this one-credit course based on their reports and presentations.

Students who take this course acquire a broad understanding of the current goals of nanotechnology and a variety of experimental techniques. They develop a qualitative grasp of the principles underlying physical theories, such as electron tunneling but, more importantly, they learn to appreciate that they need to develop a deeper understanding of mathematics and physical science to fully understand those theories. This course provides students with skills needed for working in nanotechnology. It also helps them to achieve more as assistants in faculty-mentored research projects.

The overall success of the course can be seen by the number of students who continue to be interested and active in nanotechnology after they have taken the lab. The quality of their research productivity in faculty-mentored research projects is also apparent. Faculty members have been impressed by the students' ability to

operate probe microscopes and synthesize nanomaterials. This has sparked their interest in introducing nanotechnology concepts in upper level lecture and laboratory courses.

After a brief overview of other nanotechnology courses offered to first-year students at other institutions, this chapter describes Florida Tech's Nanoscience and Nanotechnology course in detail, including summaries of the experiments performed, a review of student feedback, and future plans for improving the course.

## 2 Overview of Nanotechnology Curricula for First-Year Students

Advances in fabrication and synthesis of new nanomaterials will create more goods and services that necessitate workers with knowledge of nanotechnology [1–3]. Colleges and universities play a leading role in preparing the workforce for this change. Various institutions teach nanotechnology within individual courses and through a series of classes that form an entire nanotechnology degree program at both the undergraduate and graduate levels.

Although degree programs specializing in nanoscience and nanotechnology are more common at the Masters and Ph.D. levels, undergraduate nanotechnology degree programs exist at universities in Australia (Flinders, Wollongong, and RMIT), Great Britain (Sussex and Leeds) and the United States (Louisiana Tech, University of Central Florida, Northwestern and Michigan Tech). Michigan Tech also offers a nanotechnology minor (see chapters by Shapter and Gooding; Hegab, Palmer, and Napper; and Jaszczak and Seely in this volume). A few schools, most notably Stanford University and Duke University, provide professional certification in nanotechnology. Most of these undergraduate and professional nanotechnology programs are interdisciplinary in nature and incorporate topics in science and engineering.

Undergraduates who study traditional fields of science and engineering can still learn about nanotechnology in individual courses. Many academic departments offer a capstone or upper-level elective courses in nanotechnology for their students. Prerequisites may include quantum mechanics, materials science, or chemical engineering courses. Sometimes these courses focus on one specific topic such as scanning probe microscopy, nanolithography, or carbon nanotubes. Students in these courses will have already studied science or engineering for several years and may possess general knowledge about nanotechnology from their outside reading.

Nanotechnology will impact more than just science and engineering. Students from any discipline, including the liberal arts, should be encouraged to learn about the ethical, economic, and sociological effects that may occur during the anticipated "nanotech revolution." Because these classes educate students from different majors and academic levels, many nanotechnology applications are touched upon but not treated in great depth. Discussions of current and future developments in nanotechnology are taken from popular culture, including science fiction. Students consider the role of governments to fund and regulate nanotechnology research (also see chapters by Abramson et al.; Berne; Jaszczak and Seely; Miller and Pfat- teicher; Porter; Toumey and Baird; and Zenner and Crone in this volume).

An increasing number of engineering and science programs offer introductory nanotechnology courses and seminars to freshman students. Although these classes lack the detail of an advanced course, they can benefit students and the university in other ways. Participating in such a course could encourage students who have not chosen their college major to study a field related to nanotechnology. Once they complete the course, students are better prepared to enroll in more advanced nanotechnology courses later in their college careers. Students can begin learning about cutting-edge science and engineering early, giving them an advantage when seeking internships and summer employment. Professors benefit by teaching curious students about subject matter that is often related to their own research, which in turn helps faculty members recruit undergraduate research assistants. Students who take courses of interest to them are more likely to remain in college and be academically successful [2; also see chapter by Walters, Hagelberg, and Shahbazyan in this volume].

Lectures and seminars are the most common types of introductory nanotechnology courses offered to first- and second-year students. No publisher—as yet—sells

a printed lab manual containing nanotechnology-related laboratory experiments, and investigating nanoscale materials can require advanced instrumentation that may only be available to researchers. However, these problems are becoming easier to overcome. Articles published in science and engineering education journals and educational websites, such as the one established by Materials Research Science and Engineering Center (MRSEC) at the University of Wisconsin-Madison, provide demonstration ideas and appropriate laboratory experiments [4; see chapter by Lisensky, Lux & Crone in this volume]. Nanoscience Instruments manufactures education-grade scanning probe microscopes that allow students to gain hands-on experience studying nanosized surface features [5]. With these resources, instructors have created a variety of introductory nanotechnology laboratory courses in physics, chemistry, and engineering. Many of these courses also explore the cultural and societal impacts of nanotechnology. Table 1 presents descriptions of their courses in order to provide an overview of the current (ca. 2005) state of the introductory nanotechnology curriculum for first-year students.

### 3 Florida Institute of Technology's Nanoscience and Nanotechnology Laboratory for First-Year Students

#### 3.1 Structure of Course

This interdisciplinary lab course is designed for undergraduates in the second semester of their freshman year. These students are majoring primarily in science or engineering disciplines, and have an interest in nanoscience research or in nanotechnology. It is not surprising that many students who enroll in the class have chosen to study chemical engineering, physics, or chemistry, because those are the disciplines of the current course instructors. However, it is worthwhile to note that biology students also choose to take the nanotechnology laboratory course despite the lack of biology-based experiments. So far, all the students have entered the course having already selected their degree major. Given the small number of students who have taken the course so far, there are no reliable data available to show that the course causes students to change majors.

The course introduces the students to techniques that involve nanomaterial fabrication by thin film deposition and chemical synthesis, as well as sample characterization techniques such as atomic force microscopy and scanning tunneling microscopy. The goals of the course are focused on learning experimental techniques that will allow students to better understand the underlying principles behind the concepts presented in more advanced courses in materials science, engineering, chemistry, and physics. Students who take this class will also be better prepared to contribute to research projects involving nanotechnology.

All instructors supervise approximately the same number of laboratory experiments. One faculty member coordinates miscellaneous tasks related to the course, such as contacting outside seminar speakers, creating a course web site, and submitting final grades to the university registrar. Each instructor designs his laboratory experiments independent of the others and instructors are free to introduce new activities each year. Instructors are responsible for writing the background material and instructions for the experiments also. For experiments that have been published online, such as those found at the University of Wisconsin-Madison MRSEC, the instructor also directs students to the appropriate website [4].

The course relies heavily on team teaching by faculty in science and engineering departments so as to distribute the faculty workload while exposing the students to many different perspectives of nanoscience and nanotechnology. The teaching faculty for the course initially consisted of faculty from the departments of physics and space sciences, chemistry, and chemical engineering. Biology faculty began participating during the course's second year of existence, and faculty members from other departments have been encouraged to participate by offering labs that add new content to the course. Qualified undergraduate or graduate students are selected as lab assistants, particularly those undergraduates who have taken the course in previous years. These students also help the instructors develop new laboratory experiments for the course.

Educational institution	Course title (type) and topics/objectives
Beloit College	Nanotechnology (lecture and lab) Introduction to nanotechnology, including synthesis of nanomaterials, their applications and the societal impact of nanotechnology.
Cornell University (see chapter by Plisch in this volume)	Nanotechnology (lecture) Design and manipulation of nanotechnology devices used in a wide variety of fields. Introduction to Nanoscience & Nanotechnology (lecture and lab) Broad overview of nanotechnology including fabrication techniques, probe microscopy, quantum phenomena, MEMS/NEMS and bionanotechnology.
Flinders University (Australia) (see chapter by Shapter & Gooding in this volume)	Nanotechnology I (lecture) Team projects involve relevant topics in nanotechnology, such as biosensors and molecular electronics. Course prepares students for additional nanotechnology classes.
Florida Institute of Technology	Nanoscience and Nanotechnology (lab) Synthesis of metal thin films, carbon nanotubes, metal and semiconductor nanoparticles and templated porous carbon foams; characterization using SEM, TEM, STM and AFM.
Lawrence University	Nanoscience and Nanotechnology (lecture and lab) Synthesis of nanomaterials and characterization using STM, biological nanoscience and discussion of ethical issues related to nanotechnology.
Michigan Technological University (see chapter by Jaszczak and Seely in this volume)	Fundamentals of Nanoscale Science and Technology (lecture) Scientific fundamentals, societal implications and applications of nanotechnology. Exploration: Exploring Nanoscale Science & Technology Through Carbon Nanotubes (lecture) Synthesis, processing, characterization and applications of carbon nanotubes.
Ohio State University	Fundamentals of Engineering (lecture and lab) Basic principles of engineering; students design and build a microfluidic lab-on-a-chip device.
Rice University	Nanotechnology: Context and Content (lecture) Basic technical aspects of nanotechnology and its societal and cultural significance.
University of California at Irvine	Nanotechnology - Present and Future (lecture) Introduction to nanotechnology with discussion of current state of research, future applications and risks.
University of Leeds (UK)	Top-down Nanofabrication (lecture and lab) Nano- and microfabrication methods, including chemical vapor deposition and lithography, and their uses in industry and research. Topics in Nanotechnology (lecture) Introduction to nanotechnology including fabrication, applications and societal implications. Practical Nanotechnology (lab) Synthesis and characterization of nanomaterials.
University of North Carolina at Chapel Hill	Handcrafting at the Nanoscale (lecture) Students build models of nanoscale objects, propose research projects based on their models and perform virtual experiments.
Utah State University (see chapter by Yang in this volume)	Nanotechnology-Materials Today (lecture) Fundamentals of nanotechnology with emphasis placed on the role of chemistry, biology, engineering and materials science.
Wabash College (see chapter by Porter in this volume)	Chemical Nanotechnology (lecture and lab) Introduction to nanotechnology, including class discussions of future developments in nanotechnology and laboratory experiments.
Washington University at St. Louis (see chapter by Agarwal in this volume)	Intermediate Nanotechnology (lecture) Basic scientific principles involved in nanotechnology, including computational methods used in modeling and simulation of nanoscale phenomena.
University of Wisconsin at Madison (see chapters by Zenner and Crone and Miller and Pfatteicher in this volume)	Nanotechnology and Society (lecture) Students discuss the influence of government policies and agencies on the development of nanotechnology and design social studies for evaluating topics related to nanotechnology.
University of Wisconsin at Stevens Point	Introduction to Nanotechnology (lecture) Tools used to characterize nanoscale phenomena, nanomaterial preparation techniques and potential applications.
University of Wollongong (Australia)	Current Perspectives in Nanotechnology (lecture and lab) Presentation of case studies of nanotechnology used in fields such as electronics, biomimetics, nanomaterials and devices. Design, synthesis, characterization and realization are addressed in each study.

\*Unless noted otherwise, schools are located in the United States. "Lecture" indicates a course in which information is conveyed primarily through seminars, lectures, discussions, and demonstrations. "Lab" indicates a course that requires students to gather scientific data by manipulating instrumentation and performing experiments.

Table 1: List of nanotechnology courses for first-year undergraduate students.\*

Course announcements are made to potential students while they are taking their introductory chemistry course in the first semester of their freshman year. The prerequisite for the nanotechnology laboratory course is completion of Chemistry 1 (CHM 1101), which includes a chemistry laboratory component. The Nanoscience and Nanotechnology Laboratory course has also been used effectively in the physics department as a means of recruiting high school students who are equally interested in nanotechnology and in attending Florida Tech.

The laboratory instructor evaluates student performances for each laboratory experiment. Satisfactory performance consists of the following: attendance and being on time for the lab, following instructions, completing the goals of the experiment (i.e., synthesizing a product, completing a sample analysis), cleaning up the work area after completing the lab, answering questions posed by the instructor, and participating in any discussions. Grades are assigned according to student performance in lab, a written assignment, and a final oral presentation.

During the first year of teaching the course (2004), the instructors assigned weekly laboratory reports. Students commented that the grading criteria of each instructor were different, as was the level of work expected for the reports. In subsequent years, students have written an in-depth (8–12 page) research paper that focuses on one area of nanotechnology that was covered during the course. Each student chooses a different topic after talking to the instructor about their selected topic. The students also present their work to the class during the final class meeting. Instructors provide information to each student regarding the details of how the report and presentation were graded. The participating faculty each grade the reports and presentations, and the student's grade is the average score assigned by each professor. Overall letter grades are based on the standard grading scale: 90–100% A, 80–89% B, 70–79% C, etc. On the basis of student evaluations, they prefer this method of evaluation.

To add this course to the Florida Tech curriculum in 2004, the instructors sought the approval of the university's Undergraduate Curriculum Committee. This required a description and justification for the course. Initially, the course was listed as a physics course (PHY 1091) since Dr. Mantovani of the Physics and Space Sciences Department was the Principal Investigator of the National Science Foundation grant that initially funded the course's development. Later, the course listing was changed so that it appeared in the Chemistry and Chemical Engineering sections of the catalog. This helped to emphasize to students that the course is truly interdisciplinary in nature. In the future, if faculty members from other departments contribute to the course, then the course will be listed in those catalog sections also. The current course description is as follows:

PHY / CHM / CHE 1091 introduces science/engineering freshmen interested in careers in nanoscience research/nanotechnology to techniques of nanomaterial fabrication by thin film deposition and chemical synthesis, and sample characterization techniques like atomic force and scanning tunneling microscopes. Requirement: Freshman status or instructor approval. Prerequisites: CHM 1101.

## 3.2 Laboratory Experiments

### 3.2.1 Scanning Probe Microscopy Experiments

Early in the course, an introductory lecture is presented to the students concerning the basic principles behind the operation of the STM, AFM, and other types of scanning probe microscopes (SPM), such as magnetic force microscopy, electrostatic force microscopy, and scanning capacitance microscopy [6]. Lecture topics include a discussion of the high resolution imaging capability of SPMs for imaging the surface topography of metals, semiconductors, and biological materials. Additional nonimaging lecture topics include the application of the STM to electronic and optical spectroscopy, the manipulation of atoms on surfaces using the AFM and STM, the potential application of SPMs in nanolithography, imaging of surfaces of insulators and biological materials, and the possible use of the AFM in data storage [7].

During the following week's class, the students are given hands-on training in the use of the educational STM and AFM systems, which were purchased specifically for imaging samples in this course [8]. This initial SPM lab activity allows each student to learn to use the STM to obtain atomic resolution images of highly oriented pyrolytic graphite (HOPG) as seen in Figure 1, and to image the slightly

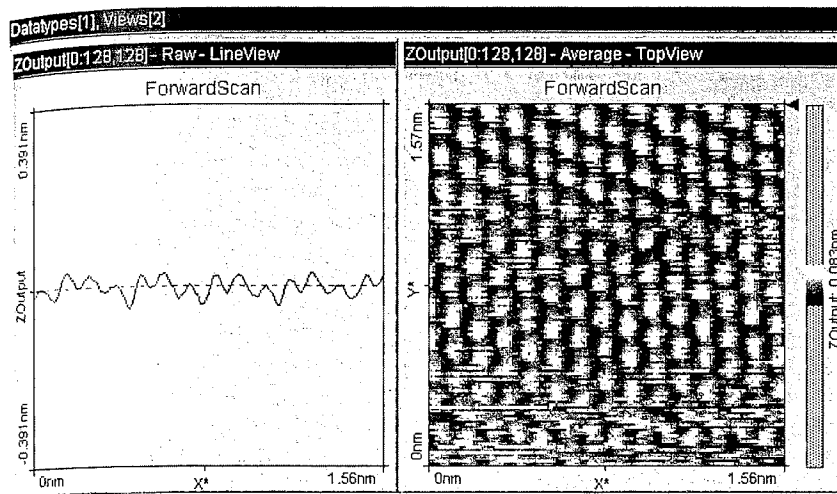


Figure 1: A typical atomic resolution STM image of HOPG illustrating an example of an atomically flat surface. The image on the right shows the surface topography in which bright regions represent high features, and dark colors represent low features. The line scan on the left is taken along a horizontal line in the image on the right where the left pointing arrow marker is located.

larger surface features of prepared sputtered gold samples. The students are shown how to fabricate STM tips and how to prepare the HOPG by cleaving it to obtain a clean surface which is atomically flat. In later labs, the students prepare their own samples and then use the STM or AFM to characterize their samples. They also learn to fabricate STM tips from gold wire using an electrochemical etching technique.

As an initial lab activity using the AFM, the students image the indentations on a piece of an uncoated CD-ROM (Fig. 2), and a prefabricated microstructure pattern (Fig. 3). In subsequent labs, the students use the AFM to image carbon nanotubes deposited on cleaved mica (see Figs. 19–22 in Section 3.2.2). They use the AFM to re-image the surface topography of HOPG and sputtered gold samples that they had previously imaged using the STM the week before, and they obtain new images of nonconductive samples.

It is expected that each student will understand the basic principles of the STM and AFM after completing this experiment. They should be able to operate both instruments and know how to use the instrument software to acquire and process images. After completion of this experiment, it is our expectation that they also understand how to prepare STM tips that are used to image atomically flat samples, such as HOPG, as well as rougher surfaces, such as sputtered gold samples.

### 3.2.2 Nanomaterial Syntheses

Approximately half of the laboratory activities performed in Florida Tech's Nanoscience and Nanotechnology Laboratory course involve synthesizing nanomaterials and observing their chemical and physical properties. The synthesis methods include heterogeneous catalysis, electrochemical reactions and the use of emulsions,

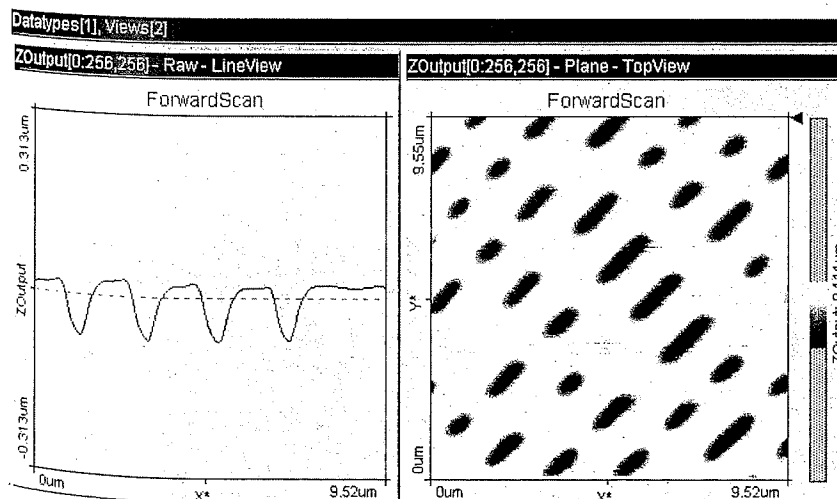


Figure 2: A typical AFM image of an uncoated CD-ROM surface.



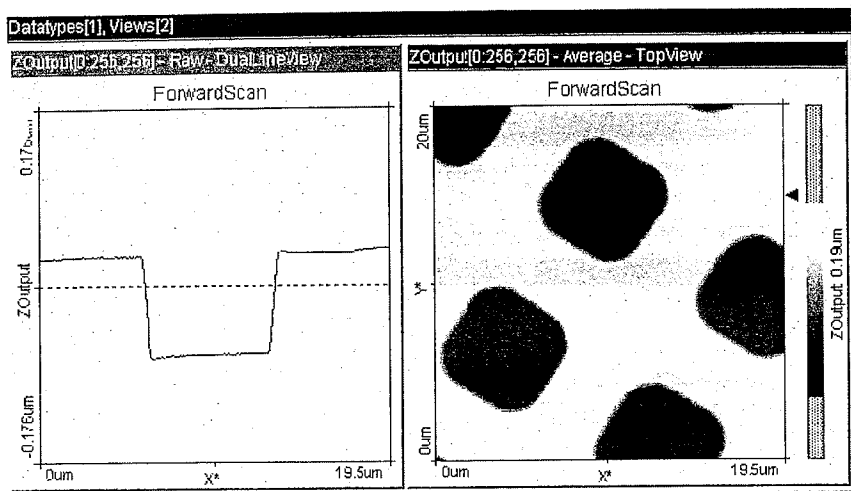


Figure 3: A typical AFM image of a microstructure patterned sample.

colloids, and templates. Each experiment has current or near-future applications. Some were adapted from the literature and several were designed by the course instructors. More detailed procedures for these lab experiments can be found in the references. Because of the interdisciplinary nature of the subject, these experiments often illustrate nanoscale phenomena along with concepts learned in general chemistry, chemical engineering, and physics.

**3.2.2.1 Thin Film Deposition Techniques and the Preparation of Samples** After a brief lecture on the principles underlying thin film vacuum deposition techniques such as chemical vapor deposition, thermal evaporation, and sputtering, the students learn to use a sputter coating system to fabricate thin film samples consisting of nanoscale gold particulates. Other deposition methods, such as electron-beam evaporation and electrodeposition, are presented to the students via a computer and Internet resources. Standard substrate cleaning procedures are presented for making polished silicon wafers, glass microscope slides, cleaved mica, and HOPG. The students fabricate monolayer and submonolayer thin metal films using the sputter coater. Metal particulates that are grown as a submonolayer on a silicon wafer and then heat-treated are known to have oblate spheroidal shapes with typical diameters in the 10–30 nanometer range. The students use the STM and AFM systems to image the thin metal films that they have fabricated themselves (Fig. 4).

**3.2.2.2 Preparation of an Aqueous Ferrofluid** Preparation of ferrofluids is the students' favorite activity in Florida Tech's nanotechnology laboratory. The procedure is straightforward, and the only item not commonly found in a chemistry

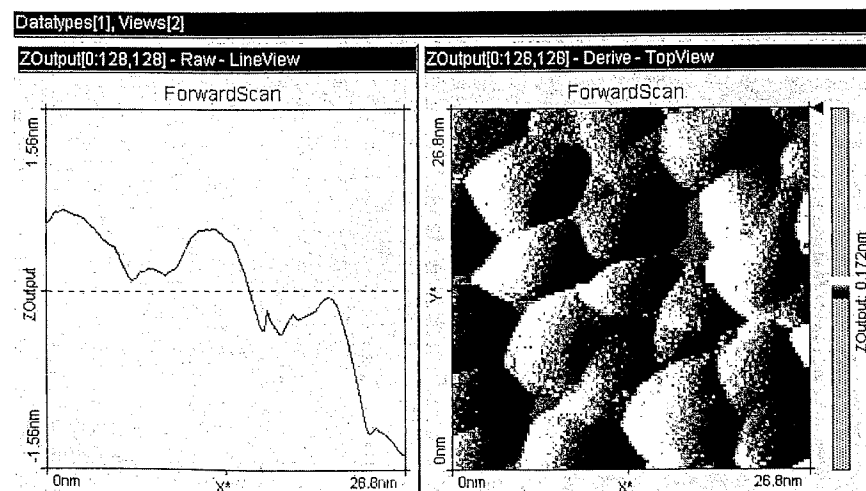


Figure 4: An STM image of a gold thin film deposited on a cleaved mica substrate.

teaching laboratory is a strong magnet that students use to manipulate the fluid [9, 10]. Necessary chemicals include iron(II) and iron(III) chloride salts, hydrochloric acid, ammonia and tetramethylammonium hydroxide. Because only a small amount of ferrofluid needs to be synthesized for students to observe its magnetic properties, the consumption of reagents and waste production are minimal. Students read a lab procedure and view online video instructions at the MRSEC website prior to attending lab [10]. The experiment provides the instructor with an opportunity to discuss surfactants and magnetism—subjects often overlooked in a general chemistry class.

Stock solutions of HCl and  $\text{NH}_3$  are prepared prior to the laboratory session. Students dissolve iron(II) and iron(III) chloride in separate HCl solutions and then mix them together. The slow addition of an ammonia solution causes magnetite ( $\text{Fe}_3\text{O}_4$ ) particles to precipitate. Tetramethylammonium hydroxide surfactant is added to prevent agglomeration of the magnetite particles and then the solvent is removed. This creates a ferrofluid consisting of approximately 10-nm diameter  $\text{Fe}_3\text{O}_4$  particles that is stable for several hours. After completing the synthesis, students observe the behavior of the magnetite colloid in the presence of a magnetic field created by a strong magnet.

A ferrofluid contains nanometer-sized particles, in this case magnetite ( $\text{Fe}_3\text{O}_4$ ), that are ferromagnetic. That is, groups of electrons with the same quantum spin state form domains within the particle's lattice. Each domain has a magnetic moment and the moments in all domains align with each other in the presence of a magnetic field. This causes the particles to be attracted by a magnetic field. The attraction of the colloidal particles is so strong that the viscosity of the solution changes. The ferrofluid does not flow when a magnet is brought close and the fluid follows the movement of the magnet. Therefore, a ferrofluid is a solution whose position and rate of flow can be controlled by a magnetic field. The interaction between the particles and the magnetic field is so strong that the surface of the suspension "spikes" when a strong magnet is placed underneath the ferrofluid (Fig. 5). The spikes form as the suspended magnetite particles follow the magnetic field lines. This behavior is not observed if a ferromagnetic metal is melted since the high temperature provides sufficient thermal energy to cause the magnetic moments to become randomly oriented [9].

Ferrofluids have many applications in the aerospace, automotive, medical, and audio-electronics fields. Commercially manufactured ferrofluids often use a low volatility organic solvent instead of water and the experimental parameters are customized for different applications. The most common use of ferrofluids is as a seal between moving machine parts, such as a rotating shaft [11]. A magnetic field, created by a ring of permanent magnets placed around the seal, holds the ferrofluid in place. Advantages of ferrofluid-based seals (FFS) are their long operational lifetime (10–20 years), consistent behavior over a range of applied pressures, ease of manufacture, and low leakage of gases and contaminants. Satellites, automobiles, oil refineries, computer hard drives, and various manufacturing processes in the chemical, textile, and biotechnology industries take advantage of the superior properties of FFS. Perhaps more relevant to college students is its use as a magnetically driven damper and a heat sink in audio speakers [12; also see chapter by Bowles in this volume]. The damping ability of a substance is proportional to its viscosity, and so a ferrofluid is an ideal choice since its viscosity is easy to control with a magnetic field. Ferrofluids also conduct heat five times more efficiently than air.

In the near future, researchers envision using ferrofluids in medicine. Ferrofluids can help deliver pharmaceutical drugs to a specific region of the body by

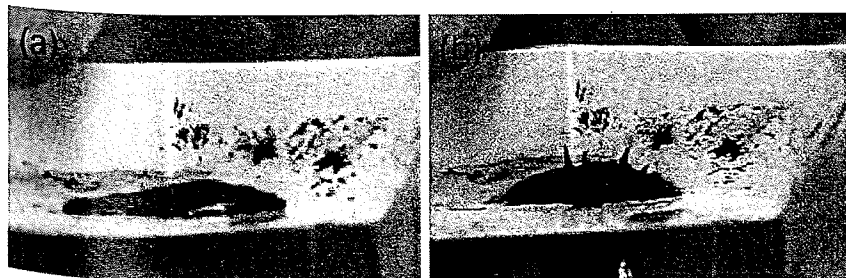


Figure 5: Picture of ferrofluid in the absence (a) and presence (b) of a magnetic field created by holding a magnet below the weigh boat.

applying an external magnetic field concentrated at the desired location [13]. Scientists have found that the encapsulating material around the iron oxide core of ferrofluid nanoparticles can be toxic to cancer cells [14]. Again, the particles are directed to the cells by applying a magnetic field. Ferrofluid hyperthermia is being tested to destroy tumor cells [15]. In this treatment, the ferrofluid particles are introduced into the malignant cells. The magnetic field causes the iron oxide particles to vibrate, generating heat. The temperature of the particles within the tumor cell increases until the cell is destroyed.

**3.2.2.3 Synthesis of Colloidal Cadmium Sulfide Nanoparticles** Dr. Kurt Winkelmann adapted this experiment from research conducted by Angela Agostiano et al. [16]. The procedure was modified to allow first-year students to prepare cadmium sulfide (CdS) nanoparticles using inexpensive reagents and common laboratory equipment [17]. Much of the lab's development was performed by a student who had completed the nanotechnology laboratory. A UV/visible spectrophotometer is required to characterize the CdS nanoparticles and determine their diameter. However, this is used only once by each lab group and so only a single instrument is necessary. This experiment illustrates quantum confinement that alters the color of CdS particles. In addition, students learn to calculate particle size, operate a spectrophotometer, and understand the intermolecular forces that exist among solute, solvent, and surfactant molecules.

Color is one of the most easily observable properties that changes due to the small dimensions of nanomaterials (also see chapter by Larsen, Pienta, and Larsen in this volume). Cadmium sulfide is a semiconductor that absorbs light in the visible region of the electromagnetic spectrum ( $\lambda \leq 513$  nm). Absorption of a sufficiently energetic photon excites an electron from the valence band to the conduction band of the semiconductor. A hole is created in the valence band as well. Electrons and holes move through the semiconductor lattice and around each other. If the CdS particle's diameter is less than the distance between the electron and hole, the energy required to form the electron-hole pair increases. Thus, bulk CdS particles absorb light at longer wavelengths (lower energies) than nanometer-sized particles. This shift in absorption wavelength is observed as a change in color from orange to yellow and even to green for the smallest of CdS nanoparticles. The particle diameter can be determined from the particles' UV/visible absorption spectrum using the Brus equation [18]. A spectrum typical of 5.2-nm diameter CdS particles is shown in Figure 6.

Because of the large ratio of surface to interior atoms, nanoparticles are inherently less stable than their bulk analogues. As in the case of all nanoparticle preparations, precautions must be taken to avoid particle agglomeration. Micelle solutions provide one effective method to prepare nanosized particles and prevent them from precipitating as the bulk material. In this experiment, students add a small amount of aqueous  $\text{CdCl}_2$  to a mixture of hexane, pentanol, and cetyltrimethylammonium bromide (CTAB) surfactant. A water-in-oil micelle solution forms with the aqueous phase surrounded by CTAB molecules which are dispersed within the pentanol-hexane solvent mixture. A second micelle solution is prepared containing an aqueous sodium sulfide solution instead of cadmium chloride. Students mix these two colorless solutions to create a translucent yellow solution that is stable for many hours. CdS nanoparticles are typically 5–6 nm in diameter and show a shift of approximately 40 nm in their absorbance spectrum compared to bulk cadmium sulfide.

Many applications of nanometer-sized cadmium sulfide particles are based on their high surface area and absorption of visible light. A collection of small particles has a greater total surface area than the same mass of larger particles, and so catalytic reactions that occur on the CdS particle surface are enhanced by their greater surface area. The band gap of CdS is small enough for the absorption of some visible light. Because the solar spectrum at sea level contains much more visible than ultraviolet light, materials such as CdS are well-suited for using solar energy to drive chemical reactions that generate electricity.

Cadmium sulfide nanoparticles are being studied for use in environmental remediation and production of alternative fuels. They have been studied extensively as photocatalysts for the degradation of many organic pollutants [19–22]. Composites that include CdS nanoparticles can generate  $\text{H}_2$  gas from water during irradiation [23–25]. Photogenerated electrons in cadmium sulfide nanoparticles are

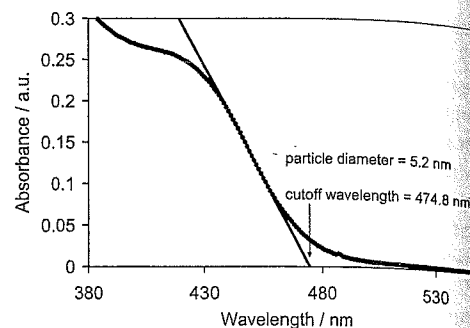


Figure 6: Absorbance spectrum of cadmium sulfide nanoparticles prepared in a water-in-oil emulsion. The cutoff wavelength is used to calculate the particle size.

capable of reducing carbon dioxide to produce small organic molecules [26]. This consumes a greenhouse gas and produces compounds that could be converted into fuel. Photovoltaic devices, which convert solar energy into electricity, often take advantage of the properties of cadmium sulfide nanoparticles [27].

Generally, nanoparticles with varied sizes not only have different colors, they also emit light of different wavelengths when irradiated. This property is used in medicine [28] as follows. Molecules that interact with tumors or viruses can be attached to the nanoparticle surface, which, in turn, allows the particles to accumulate around a target, such as a virus. Their fluorescence emission can be observed when the biological sample is irradiated with UV light. Because nanoparticles with different sizes emit different colors of light, a variety of particles with different molecules attached can be used to detect many targets at the same time. They are a preferable replacement for the organic dyes currently used because dyes degrade quickly in the body, providing doctors with only a short period of time to observe the presence of the tumor or virus.

**3.2.2.4 Preparation of STM Tips by Electrochemical Etching** One of the mottos in the field of scanning tunneling microscopy is “The tip and the sample are everything.” This means that the instrument will not record a high-quality image if either the sample or tip is not suitable for imaging. Therefore, one of the challenges in operating an STM is the reliable and reproducible fabrication of the probe tips. There are several requirements for STM tips. They must be sharp to an atomic point meaning that the apex of the tip must consist of a single atom. Depending on the flatness of the surface, different surfaces require tips of different aspect ratios—rougher surfaces require sharper tips. If a tip’s aspect ratio is too low, then multiple sites on the tip will interact with the surface, leading to the occurrence of so called “tip imaging.”

Tip imaging caused the repetitive features observed in Figure 7 that show the shape of the tip rather than the shape of the surface. STM tips must be free from any sort of oxide coating that would form an electrically resistive layer and thereby jeopardize the flow of electrons between the sample and the tip. This requirement limits the variety of tip materials, at least for tips that are used to analyze surfaces in air. Finally, STM tips should be easy to prepare, requiring low cost equipment and relatively short preparation times. The method of fabrication should allow a high percentage of success (also see chapter by Yang in this volume).

One method of STM tip fabrication that has been shown to work well is the electrochemical etching of gold wire [29]. The procedure for this laboratory activity was developed by Dr. Joel Olson of Florida Tech’s Department of Chemistry. In addition to showing students how to prepare STM tips, the laboratory experiment illustrates the principles of electrochemistry that they learn in their general chemistry course.

Students assemble the experimental setup shown in Figure 8. A graphite rod from a number 2 pencil and a piece of gold wire serve as the electrodes. A 1 M HCl solution oxidizes the gold and helps the gold cations to dissolve in the solution. The electrodes are connected to a Variac variable transformer. The AC voltage is set to 2.5 V using a digital voltmeter. Etching the gold begins when the Variac is turned on and should continue for 20 to 30 min. Small bubbles of chlorine gas form during the reaction, so students should perform this experiment in a fume hood. The wire breaks when all the gold is etched away at the solution-air interface. At this point, the Variac should be turned off and the piece of gold wire that is attached to the gator clips can be cut in half, making two atomically sharp STM tips. Students should rinse their STM tips in deionized water, making sure that they do not bend them. Tips can be stored in a protective box. Viewing tips with an optical microscope can reveal if they are damaged. Figure 9 shows an undamaged tip and a bent, unusable tip.

**3.2.2.5 Synthesis of Nickel Nanowires** The preparation of nickel nanowires illustrates how a template can be used to design nanostructures [30]. As in the case of the STM tip preparation, it is preferable that students perform this lab after being introduced to electrochemistry so that they understand the components of an electrochemical cell. The first-year students find this experiment to be the most challenging because of the number of steps involved. Inattention to details can lead to unsuccessful results, but students who successfully complete this experiment find it very rewarding.

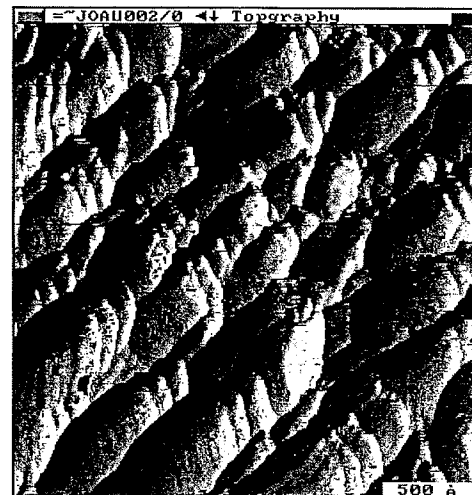


Figure 7: An STM micrograph of a gold film. The repetitive shapes evident in various parts of the image (peaks pointing up and to the right) are indicative of tip imaging. (Image provided courtesy of Dr. Joel Olson, Florida Institute of Technology).

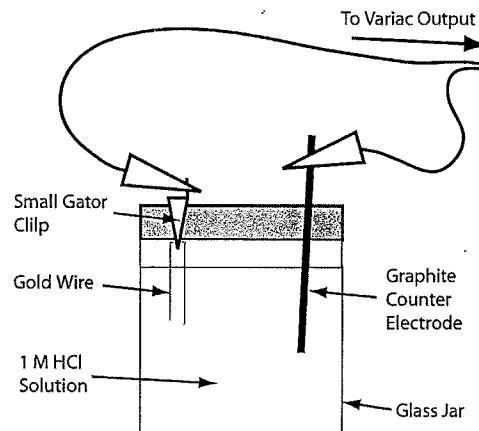


Figure 8: Diagram of experimental set-up to electrochemically prepare gold STM tips.

The procedure requires students to construct an electrochemical cell, disassemble it without damaging the delicate template material, and then separate the nanowires from the template. Students should wear goggles, lab coats, and gloves and use extra caution when handling the concentrated acid and base solutions. Steps involving those solutions are performed in a fume hood.

Students assemble an electrochemical cell that deposits nickel atoms within a commercially available aluminum oxide filter with 20-nm pores. The first step is to prepare the electrode for the reduction of  $\text{Ni}^{2+}_{(\text{aq})}$  to  $\text{Ni}_{(\text{s})}$  within the filter pores. One side of the filter is coated with gallium indium eutectic paint. With the painted side of the filter pressed against a flat piece of copper metal, the edges of the filter are taped to the copper with electrical tape to prevent the nickel plating solution from seeping between the filter and the copper cathode. The anode consists of a piece of nickel wire. Alligator clips connect an AA battery to the electrodes which are immersed in the solution.

After 30 min, the clips are disconnected, and the cathode is removed from the solution. Metal is clearly visible within the filter. The electrical tape is removed by soaking the copper electrode in acetone. After cleaning the gallium indium paint from the filter with concentrated nitric acid, students dissolve the aluminum oxide filter in a sodium hydroxide solution. This releases the nanometer-sized nickel wires from the filter pores. Using a magnet, students collect the nanowires while decanting the NaOH solution. The nanowires are then washed with deionized water and stored in a glass vial. As in the case of the ferrofluid synthesis, students can study the magnetic properties of the nanowires. The wires can be observed using a scanning electron microscope or even an optical microscope since they agglomerate into larger, rod-shaped clusters.

Template synthesis is a common route for the preparation of nanomaterials [31] and will be a likely method for the production of parts for nanomachines developed in the future. In this activity, nanowires are built by depositing atoms within the pores of a filter. The pore size limits the dimensions of the resulting nanowire. Longer deposition times result in longer wires.

Nanowires have uses as chemical sensors and as a medium for information storage. When grown between two electrodes, a nanowire can detect the presence of nanogram quantities of solutes [32]. As molecules or ions in solution adsorb to the surface of the nanowire, the conductance between the electrodes decreases by an amount related to the adsorption strength of the molecule or ion. The manner in which the conductance changes with the applied voltage can identify the adsorbed solute. As students discover during this experiment, nickel nanowires respond to an applied magnetic field. Their small size makes them an attractive recording material for magnetic storage devices such as a computer hard drive [33].

**3.2.2.6 Guided Inquiry Laboratory Involving Gold Nanoparticles** In a guided inquiry activity, students prepare a solution containing 13-nm diameter gold particles [34]. The solution color depends on the type of solute added to the gold colloid solution. Students are challenged to determine what causes the color change of a gold colloid solution in the presence of different solutes.

A stock solution of  $\text{HAuCl}_4$  is prepared before the laboratory session. Each laboratory group takes a small portion of this solution, dilutes it, and brings it to a boil. Students then add sodium citrate to reduce the gold(III) ions to gold nanoparticles and form a citrate-gold complex on the particle surface. The resulting solution has a deep red color. Students pour 2–3 mL of the gold colloid solution into six plastic cuvettes. To these solutions, they add several drops of different types of strong, weak, and nonelectrolyte solutions. There are a dozen different solutions, so all the lab groups test different samples.

The gold nanoparticles remain separated due to electrostatic repulsion caused by the negatively charged citrate ions on their surfaces. Addition of soluble ionic compounds increases the solution's ionic strength, allowing the citrate-complexed nanoparticles to approach each other more closely. Agglomeration of the gold particles changes their absorbance spectrum and consequently makes the red solution turn blue. Figure 10 depicts the different absorbance spectra for solutions containing various amounts of sodium chloride. The color difference is clearly visible without the use of a spectrophotometer.

Each laboratory group records any color changes that occurred in their cuvettes. At the end of the laboratory session, the groups combine their data. On the basis of their tabulated results, it is clear that electrolyte solutions cause the gold colloid to

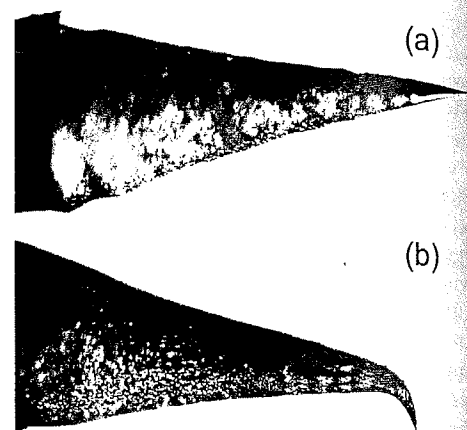


Figure 9: Images of an undamaged tip (a) and a tip that has been bent (b) as the result of improper handling or use. (Image provided courtesy of Dr. Joel Olson, Florida Institute of Technology.)

change color from red to blue and that nonelectrolytes have no effect. The instructor then asks students to supply an explanation for this phenomenon. With some help, students attempt to correctly describe why the gold nanoparticle solution changed color.

The easily observed color change of the gold particles can be used to detect a specific sequence of DNA in an aqueous solution [28]. Gold nanoparticles are prepared in the same manner as described above. Portions of a specific sequence of DNA, called probe DNA, selected by the analyst are attached to the gold particles. A different probe DNA sequence is bound to a second batch of gold nanoparticles. The choice of probe DNA sequences is based on their ability to bind to a target strand of DNA that may be in solution. If both probe DNA portions attach to the target DNA, the gold particles will be drawn close together, turning the solution's color from red to blue. If only one probe or neither probe DNA binds to the target DNA in solution, then no color change occurs.

**3.2.2.7 Templated Porous Carbon Synthesis and Characterization** A method for the preparation of a family of silica-templated porous carbons is described. In most cases, a carbon material with a bimodal distribution of pore sizes is generated. The nanoscale pores are consistent with the diameter of the templating agent's features; in addition, a pore structure in the 10- to 1000- $\mu\text{m}$  range is also observed.

Fuel cell performance is typically plotted as voltage vs. current density, with power density being the product of voltage and current density. Currently, there are several factors limiting fuel cell use in vehicular applications on a widespread basis (also see chapter by Cabrera and Tryk in this volume). The first factor is cost. The second factor is the weight of the fuel cell relative to the weight of the vehicle. A third important factor is that the power density of fuel cells is limited by mass transfer resistances in the fuel cell gas diffusion layers, which are similar to a thin sheet of carbon paper. The goal of the research project that inspired this experiment in the Nanoscience and Nanotechnology Laboratory course is to minimize these mass transfer resistances by developing replacements for the fuel cell gas diffusion layers. To achieve this goal, a matrix of porous carbons for eventual use in fuel cell gas diffusion layers are prepared by systematically varying carbon precursors and templating agents. The students in the course use one of three carbon precursors and one templating agent to prepare three templated porous carbons. Other applications for the templated porous carbons include use as catalyst supports [35, 36], adsorbents [37, 38], and electrode materials [39].

Numerous investigators [40–53] have prepared templated and untemplated porous carbons using the generic scheme shown below (Fig. 11). Resorcinol (1,3-dihydroxybenzene) combines with formaldehyde to generate a mixture of products, all with two  $-\text{CH}_2\text{OH}$  groups at various positions around the aromatic ring. These multi-substituted aromatic alcohols are readily polymerized in the presence of an acid (in this case, sulfuric acid) to form hyperbranched, porous polymeric networks. The porosity in Figure 11 is typically on the order of 1–1000  $\mu\text{m}$  [53].

The key difference between the synthesis procedure used in this experiment and the general procedure shown in Figure 11 is the use of a well-defined silica templating agent which yields a carbon material with a highly ordered porosity on

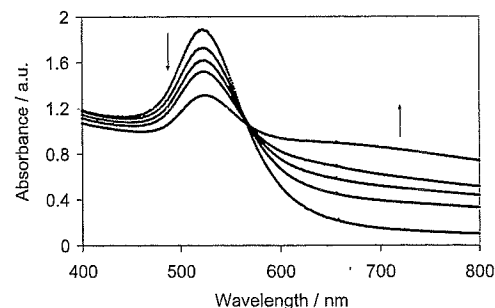


Figure 10: Absorbance spectra of Au nanoparticle solution with various amounts of NaCl added. The absorbance at 525 nm (red solution) decreases and absorbance at longer wavelengths increases as more NaCl is added, creating a blue solution.

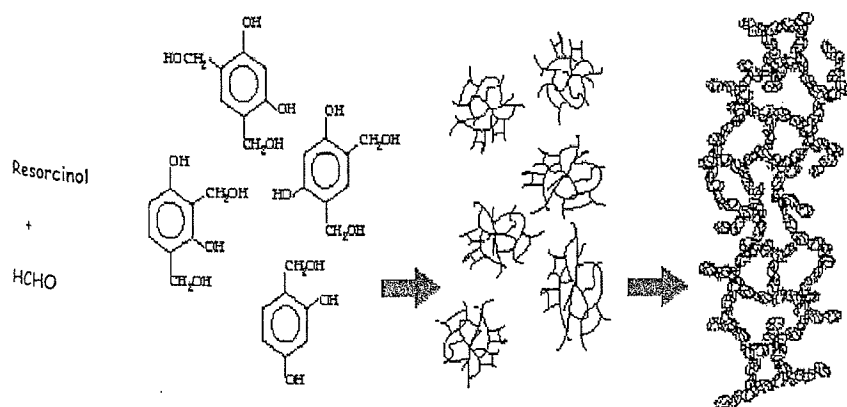


Figure 11: Generic procedure for preparing porous carbons [53].

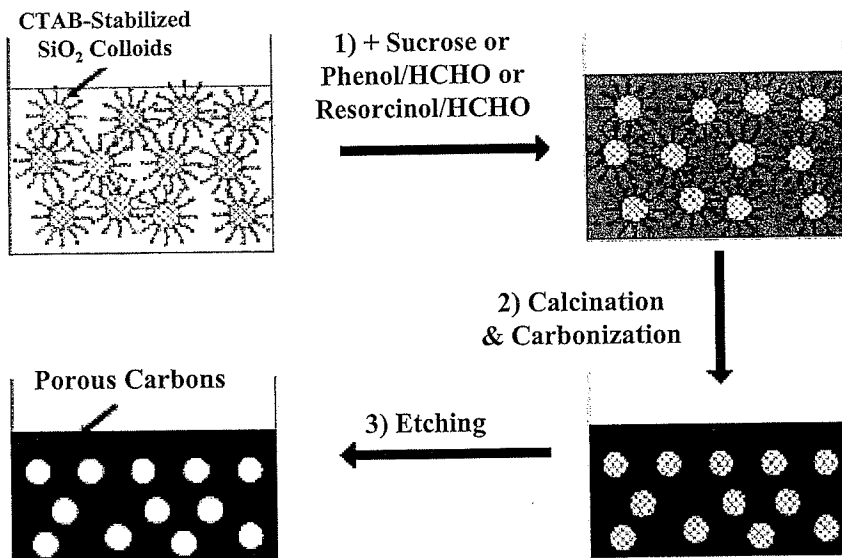


Figure 12: Generic synthesis procedure for templated carbon foams.

the nanometer scale. This is critical to the fuel cell gas diffusion layer application, as one of the objectives in the parallel research work is to assess the effect of pore size on the fuel cell gas diffusion layer performance. This nanoscale porosity is achieved by etching the silica template out of the carbon/silica composite shown in the bottom left hand corner of Figure 12. Students in the nanotechnology course are responsible for completing step 1 in Figure 12 [53]. The rest of the procedure is explained after the sol/gel chemistry portion of the laboratory in step 1 is completed.

Because this is the first lab of the semester, Dr. Brenner gives a hands-on demonstration of sol/gel synthesis and a 10-min lecture using Jell-O as the sol. Each student is given a Styrofoam cup, a plastic spoon, and half a box of Jell-O. The students ladle ~120 mL of hot, preboiled water into the cup, dissolve the Jell-O powder, and put their Jell-O into a very cold (-50°F) freezer. By the end of class, the Jell-O has gelled, and the students have a tasty introduction to nanotechnology. The gelatin preparation is followed by the templated porous carbon synthesis, which students can easily complete in 90 min while the Jell-O is in the freezer.

Although in principle, any silica could be used as a template for porous carbon synthesis, Dr. Brenner has found that, among the silicas available from Aldrich (see [www.sigmaaldrich.com](http://www.sigmaaldrich.com)), Davisil 633 silica is the easiest to suspend properly as a colloid. However, the data presented here use MCM-48 (a porous silica with 48 Å pores) and HMS silica with pore diameters of 3–4 nm. For the nanotechnology laboratory, a colloidal suspension is prepared as follows. Davisil 633 silica (0.10 g) is added to distilled, deionized water (0.520 mL measured using an Eppendorf pipette) followed by the addition of 0.10 g of CTAB or cetyltrimethylammoniumchloride (CTAC) surfactants and carbon precursors. One of several precursors could be used: either sucrose (0.25 g) or mixtures of formaldehyde (~0.70 g) and aryl alcohols (~1.00 g) such as furfuryl alcohol, phenol, and resorcinol. (Furfuryl alcohol is not used by the students in the nanotechnology course because of its stench.) A gel forms via the addition of H<sub>2</sub>SO<sub>4</sub> (0.34 g) as a catalyst. Technical-grade sulfuric acid is acceptable, as is table sugar instead of the sucrose. All reagents except for the MCM-48, which was synthesized by Dr. Brenner according to a published procedure [54], can be purchased from Aldrich. The gelation can occur without the addition of the surfactant, but the degree of order in the nanoscale pores would not be as uniform as desired.

The remaining steps of the procedure are explained to students after the sol/gel chemistry portion of the synthesis is completed. The same sol/gel procedure is carried out in an alumina boat, which is then placed into a tube furnace. This is followed by drying in flowing dry air at 100°C for 6 h, curing in flowing dry air at 160°C for at least 6 h, and finally carbonization in flowing N<sub>2</sub> at 3°C/min up to 900°C with a 1 h hold at 900°C. The final step involves extraction of the templating agent. This is done in Dr. Brenner's laboratory with KOH, although HF works

as well. This process is similar to several syntheses found in the literature [40–52]. Microstructural analysis by SEM and TEM is performed during the following week's session of the nanotechnology laboratory class.

The micron-scale (SEM) and nanoscale (TEM) characterization results from some of the templated porous carbons and carbon/silica composite precursors are shown below. The SEM photo in Figure 13(a) was collected by a student in the nanotechnology course and shows a microstructure at 3000X similar to that shown schematically in Figure 11. Obviously, the large pores shown in Figure 13 lack order and were not those that were templated by the Davisil 633 silica, which has a much smaller particle size. In fact, the phenol/formaldehyde/Davisil 633 silica-derived samples in Figure 13 still have the silica in them, as shown by the submicron bumps seen in Figure 13(b). The TEM photo in Figure 14 for a sucrose-derived carbon whose MCM-48 template has been removed reveals an array of ordered pores of approximately 48 Å, as expected.

**3.2.2.8 Preparation of Carbon Nanotubes** Students synthesize aluminum oxide substrates with pores containing transition metal particles to be used as catalysts for the growth of multi-walled carbon nanotubes. The catalyst materials are dried, calcined, and reduced so that they might be active for the preparation of carbon nanotubes via the catalytic decomposition of  $\text{CH}_4$  at 600°C and 1 atm. The catalysts and nanotubes are then analyzed by AFM and TEM.

Carbon nanotubes have been prepared by a multitude of investigators [55–73]. The different synthesis methods that have been used to prepare nanotubes is remarkable, as summarized in Table 2. Of these, arc discharge, microwave plasma-assisted chemical vapor deposition (CVD), and catalytic or noncatalytic CVD have been the most popular. One of the more common approaches, and the method employed in this laboratory, is the decomposition of methane or methane/hydrogen mixtures over Fe, Co, or Ni on  $\gamma\text{-Al}_2\text{O}_3$  catalysts at temperatures ranging from 600–900°C – a technique first developed by Rodriguez [69, 70]. The metal particles act as seeds for the nucleation of the nanotubes and are eventually encapsulated by the nanotubes. A modification of the catalytic CVD method uses Anopore™ Anodisc alumina as a templating agent to prepare highly uniform, rigid rods, unlike the tangled tubes produced by most synthesis methods.

Nanotubes are being proposed for applications in molecular electronics [74, 75], molecular motors [76], microelectromechanical systems [77], and purifications of chiral molecules [77, 78], as well as in a variety of structural composites. A series of nominally 5 wt.% metal ( $M = \text{Ni}, \text{Fe}, \text{Co}, \text{or Pt}$ ) on activated basic gamma aluminum oxide (also called alumina and subsequently denoted as  $\gamma\text{-Al}_2\text{O}_3$ ) catalysts are prepared via incipient wetness impregnation. However, the first step is to determine the point of incipient wetness for  $\gamma\text{-Al}_2\text{O}_3$  for an aqueous solution that does not contain the metal salts.

The alumina powder is sieved such that its particle diameter range was between 20 and 40 mesh using sieve trays. Each student weighs 5.0 g of  $\gamma\text{-Al}_2\text{O}_3$  into separate vials, then adds water drop-wise using a disposable glass pipette into the alumina, and counts the number of drops of water required to reach the point of incipient wetness. The point of incipient wetness is defined as the point at which the pore volume of the alumina support material is completely filled. With each subsequent water droplet, some of the alumina becomes wetted (i.e., forms clumps). Stirring distributes the water evenly throughout the entire powder sample. After each drop (or several drops at the beginning of the impregnation) is added, students stir the alumina using a glass stirring rod until its granular texture is restored, as indicated by a lack of clumps and the absence of any powder sticking to the sides of the vial. Granular texture is defined as easily flowing when poured or tipped. Gradually, it becomes more difficult to stir the water into the powder, and the alumina powder becomes fluffier. From a practical standpoint, the point of incipient wetness can also be defined as the point at which one more drop of water produces a powder that no longer flows when tipped, no matter how long the powder is stirred.

The results of one group of students' determination of the point of incipient wetness are summarized in Table 3. Students perform the calculations during the lab session so that they can carry out the next step in the procedure. Results of other student groups were quite similar. With assistance from Dr. Brenner, students use Microsoft Excel spreadsheets to calculate the average, the standard deviation,

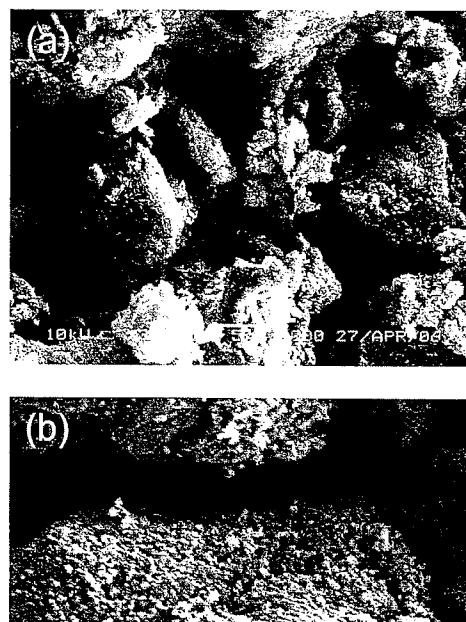


Figure 13: Phenol/HCHO/Davisil 633-derived porous carbon/silica composites at 3000X (a) and 10,000X (b), respectively.

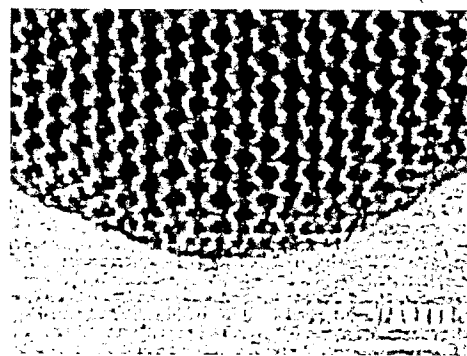


Figure 14: Templated porous carbon derived from a sucrose carbon precursor and an MCM-48 silica templating agent.



Synthesis method	Ref.
Membrane-templating	[55]
Arc discharge	[56-61]
Microwave plasma-assisted chemical vapor deposition (CVD)	[61-63]
Evaporation of C <sub>60</sub> , then use heat (950°C), Ni catalyst, and magnetic field	[64]
Catalytic CVD with H <sub>2</sub> and thiophene	[65]
Catalytic CVD with CH <sub>4</sub> and perhaps H <sub>2</sub>	[66-70]
High pressure decomposition of CO (HiPCO)	[71]
Diffusion flame synthesis	[72]
Arc discharge, followed by injection through a capillary tube in surfactant solution	[73]

Table 2: Methods used to synthesize carbon nanotubes.

and the 95% confidence interval of the pore volume in mL of H<sub>2</sub>O per gram of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support material. On the basis of these data, it is determined that 0.45 mL of H<sub>2</sub>O per gram of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support would be a conservative underestimate of the pore volume of the alumina support. A conservative underestimate of the pore volume is used to avoid formation of large metal particles which can form if the pore volume is exceeded. Larger metal particles are less effective as catalysts.

Table 4 shows that students filled the lower limit of the distribution of pore volumes (0.45 mL of H<sub>2</sub>O per gram of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support material) with one of a series of aqueous metal salt solutions. Students prepare the metal salt solutions and add each solution to separate vials of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> so that the concentration of solution is 0.45 mL solution per gram of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the support material contains 5 wt.% of metal (not metal salt) after the sample is dried and calcined. The final weight percentages of metals in the catalyst samples are shown in the lower right of Table 4. Using this simple method of adding solution drop-wise to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> yields satisfactory results. The loading in student E's Pt catalyst was limited both by a desire to limit cost and the low solubility of the hexachloroplatinic acid salt precursor. While students C, D, and F got the correct amount of metal in the catalyst, students A, B, and G found that they could not add as many drops of the metal salt solution as they had with the distilled water. This was most likely caused by agglomeration of the metal salt precursors at the mouths of some of the pores, thereby occluding some of the pore volume. This happened despite the students being forewarned about filling the pores with metal salt solution too quickly.

The experimental apparatus for the drying, calcination, and reduction of the metal/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, as well as for the nanotubes synthesis, is shown schematically in Figure 15. All gases used are ultrahigh purity grade (99.999%; Boggs

Student	g Al <sub>2</sub> O <sub>3</sub>	Drops H <sub>2</sub> O added	mL H <sub>2</sub> O/g Al <sub>2</sub> O <sub>3</sub> (~15 drops/mL)
A	4.9	34	0.46
B	5.0	34	0.45
C	5.1	38	0.50
D	5.0	36	0.48
E	4.9	36	0.49
F	5.1	40	0.52
G	5.0	35	0.47
		Average	0.48
		Std. Dev.	0.02
		95% Lower Limit	0.46
		95% Upper Limit	0.50

Data recorded by students to determine the amount of metal salt solution needed to fill the pores of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

Table 3: Students' incipient wetness impregnation results.

Student	Formula of metal salt	Formula weight (g/mol)	Metal	Atomic mass (g/mol)
A	Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	403.99	Fe	55.847
B	Co(NO <sub>3</sub> ) <sub>2</sub> · 9H <sub>2</sub> O	291.04	Co	58.9332
C	Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	291.04	Co	58.9332
D	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	290.81	Ni	58.6934
E	H <sub>2</sub> PtCl <sub>6</sub> · 6H <sub>2</sub> O	517.9	Pt	195.08
F	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	290.81	Ni	58.6934
G	Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	403.99	Fe	55.847
	Mass of Al <sub>2</sub> O <sub>3</sub> for catalyst, g	5.00		
	mL H <sub>2</sub> O/g Al <sub>2</sub> O <sub>3</sub> (conservative)	0.45		
	mL metal salt solution	2.25		
	g metal/(g metal + g Al <sub>2</sub> O <sub>3</sub> )	0.05		
	g metal/5.0 g Al <sub>2</sub> O <sub>3</sub>	0.26		

Student	g Metal Salt in 2.25 mL	g Metal Salt in 20 mL	Actual Metal Salt Dissolved per 20 mL, g	# of Drops Added to Al <sub>2</sub> O <sub>3</sub>
A	1.90	16.92	16.7	27
B	1.30	11.55	11.4	32
C	1.30	11.55	11.4	34
D	1.30	11.59	11.5	34
E	0.99	8.82	1.0	24
F	1.30	11.59	11.5	34
G	1.90	16.92	16.7	31

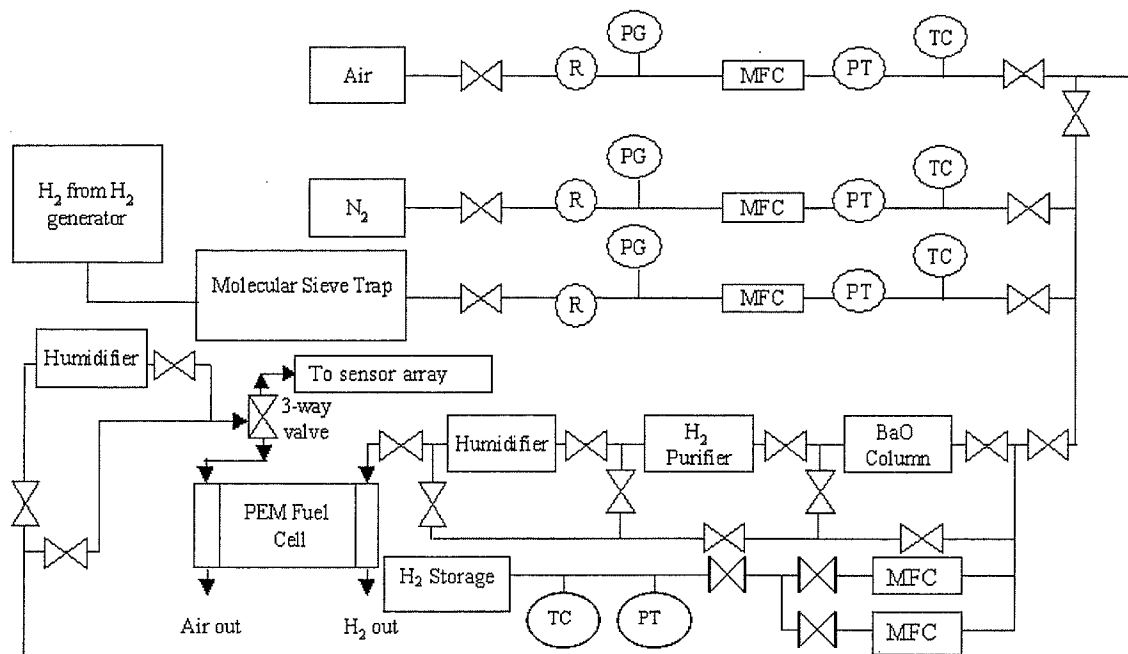
Student	mL metal salt solution added to Al <sub>2</sub> O <sub>3</sub>	g metal salt added per 5 g Al <sub>2</sub> O <sub>3</sub>	g metal added per 5 g Al <sub>2</sub> O <sub>3</sub>	Wt.% metal in Catalyst
A	1.80	1.50	0.21	3.99
B	2.13	1.22	0.25	4.69
C	2.27	1.29	0.26	4.97
D	2.27	1.30	0.26	5.00
E	1.60	0.08	0.02	0.42
F	2.27	1.30	0.26	5.00
G	2.07	1.73	0.24	4.55

Table 4: Data recorded by students to calculate the weight percentage of metal in their metal/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst samples.

Gases). The mass flow controllers are Tylan FC-280 (H<sub>2</sub>) or Unit Instruments UFC-1100A, and the NTT-205 series Span Instruments pressure transducers range from 0 to 250 psia. Data acquisition and control are achieved via National Instruments LabView software and a 12-bit AT-MIO-16E DAQ card connected to an AMUX-64T multiplexer for analog to digital input conversion.

Loading of the nanotube synthesis reactor (Fig. 16) is accomplished by adding the following materials in sequential order: (i) vermiculite up to a small lip about two thirds of the way down the 1.27 cm OD inner tube, (ii) a plug of quartz wool on top of the small lip, (iii) all of one batch of the metal salt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst precursor, (iv) another plug of quartz wool on top of the catalyst precursor and, finally, (v) a 5-cm high bed of vermiculite to ensure that any incoming gas is at the same temperature as the catalyst prior to catalyst contact. A thermocouple is inserted into the bed from the bottom and positioned within the catalyst. The Cajon VCR connections on both ends are next sealed, and then the reactor is leak-tested with nitrogen gas by looking for a pressure drop of <0.6 atm over a period of 10 min. The reactor then is purged with 200 standard cubic centimeters per minute (sccm) nitrogen at room temperature.

While still at room temperature, the gas supply is switched to 200 sccm of dry air. The reactor is next heated at 10°C/minute to 120°C and held at that temperature for an hour to dry the catalyst precursor. It was heated at 10°C/min to 600°C and held there for an hour to calcine the catalyst precursor to its fully oxidized state. Following this, the reactor is cooled in dry air down to room temperature, purged with dry nitrogen for an hour at room temperature and then heated to 400°C under 200 sccm nitrogen at 10°C/min. At 400°C, 10 sccm of H<sub>2</sub> is added to reduce the metal oxide to



the metal. The flow is then switched to a 50:50 mixture of methane and hydrogen at a total flow rate of 10 sccm and the temperature is increased to 600°C. After holding at 10 sccm at 600°C under the methane/hydrogen mixture for two hours and then cooling under this gas mixture down to room temperature, the flow is switched to nitrogen at 200 sccm for 30 min to purge the system.

If necessary, the nanotubes can be passivated using a mixture of 20 sccm of dry air and 180 sccm of pure nitrogen. The samples are unloaded from the synthesis reactor onto a set of sieve trays, over which the vermiculite is easily separated from the mixture. The remaining nanotubes and catalyst powder are then poured into a vial and weighed. The nanotube/catalyst powder mixture is washed with nitric acid in an attempt to dissolve the catalyst powder from the nanotubes. The purified nanotubes are placed in an open vial, dried at 110°C in a convection oven for 1 h, capped and stored in a desiccator.

Once the carbon nanotubes have been obtained, approximately 0.01 g of the nanotubes are dispersed in a vial containing several milliliters of isopropanol. The resulting suspension is then shaken, and one drop from the middle of the suspension is pipetted onto a Quantifoil holey carbon on Cu TEM grid. After allowing several minutes for the isopropanol to evaporate, the nanotube powder is ready to examine via TEM. Because the density of dispersed nanotubes and any undissolved catalyst particles is too low for AFM measurements, two droplets from the bottom of an unshaken mixture of the same nanotubes/isopropanol suspension are placed on each of the following surfaces: HOPG, mica and gold for the next week's AFM study. TEM is accomplished using a 80 kV Zeiss TEM while digital image analysis is achieved using ImageJ software [79].

Figures 17–20 are AFM images of nanotubes dispersed on highly oriented pyrolytic graphite derived using the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Students estimate the lengths, heights, and diameters, of the individual fibers to be 0.2–0.5 μm, 0.06–0.10 μm, and ~0.01 μm (10 nm), respectively. By contrast, as seen in the TEM micrograph (Fig. 21), the nanotubes derived from the Co/Al<sub>2</sub>O<sub>3</sub> catalyst appear to be non-rigid tubes with diameters ranging between 5–8 nm and lengths between 0.2 and 0.5 μm.

The nanotube/catalyst powder mixture is washed with nitric acid to dissolve the catalyst powder away from the nanotubes. However, the TEM photo shown in Figure 21 shows that not all of the nanotubes could be separated from the Co catalyst powder. The dark, round features of the metal from the catalyst indicate that the metal is incorporated into the nanotubes, a result routinely seen by nanotube investigators.

Figure 15: Portable gas/vapor handling system used for the drying, calcination and reduction of the metal/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and for the synthesis of the nanotubes.

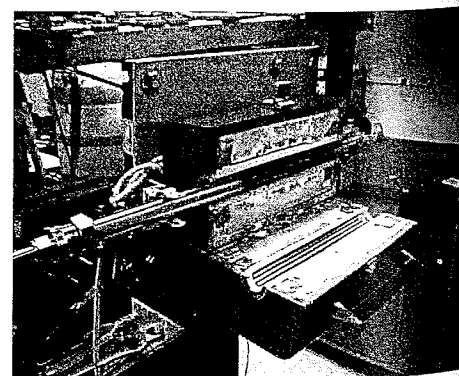


Figure 16: Nanotube synthesis reactor inside tube furnace.

### 3.2.3 Other Activities

In addition to the characterization and synthesis experiments, students also participate in lab tours and seminars. Each year, students tour Florida Tech's Imaging Laboratory, managed by Dr. Michael Grace of the Department of Biological Sciences. Dr. Shaohua Xu from the Florida Space Research Institute gives a presentation of the biological applications of AFM. These events are particularly educational to the students because no experiments in the Nanoscience and Nanotechnology lab as yet focus on biology-related topics in nanotechnology. Students have also taken a field trip to tour the research laboratories at NASA's Kennedy Space Center (45 min north of Florida Tech). The seminars and tours provide opportunities for students to learn about many nanotechnology topics that are not covered by the weekly experiments.

### 3.3 Student Feedback

During the last meeting of the Nanoscience and Nanotechnology Laboratory course, students are asked to complete Florida Tech's official class evaluation form and an additional survey created by the instructors. The latter evaluation tool asks more detailed questions about the course in general and aspects of each week's activity. The results discussed here are drawn from that survey. From these results, the instructors can improve the experiments that they teach or replace those activities that students do not find worthwhile. Students who enrolled in the nanotechnology laboratory in 2004 and 2005 were requested to fill out another questionnaire that focused on how their experiences in the nanotechnology laboratory affected them in subsequent years of their college education. Results of this survey are discussed at the end of this section.

Students rated (using a 3-point scale) each experiment based on the helpfulness of assigned reading material and the organization of the lab experiment itself. When students completed lab reports for each experiment in 2004, they gave their opinions of the instructors' requirements for the reports. In subsequent years, students evaluated the research report assignment. Students also mark their top three favorite activities.

Student feedback overall was positive for each of the experiments with regard to both the usefulness of pre-lab reading material and the organization of the experiments. Student feedback has led the instructors to rearrange the order of some activities and remove some experiments from the curriculum, such as the preparation of nickel nanowires.

Students exhibited a slight preference for the synthesis experiments over the characterization experiments. The ferrofluids synthesis was the students' favorite activity. However, it is difficult to draw detailed conclusions about students' preferences since the sample size (12 students per year) is very small. For instance, the SEM demonstration received as much positive feedback as any other activity, but did not receive any ratings as being one of the top three activities in 2006. Among the characterization experiments, the STM and AFM-related experiments were preferred more consistently because each of the student groups were able to use the instrument independently for much of the laboratory session, rather than listen to longer lectures as was done much more for the TEM and SEM characterization sessions. Too much lecturing or preparatory reading was required for students to grasp the theory needed to understand those characterization methods. Provision of an excess of supplemental material was viewed negatively by the students. For example, Prof. Brenner instructed students to read literature articles recorded on CD-ROMs from his graduate nanotechnology and materials characterization courses as background material. Students found all the information to be overwhelming, even though some of this supplemental material was necessary for the end of semester presentations and reports.

In the portion of the survey that dealt with their overall views of the course, students rated the course as very interesting and beneficial to their education. They appreciated the close interaction with faculty members since many of Florida Tech's first-year laboratory courses are taught by graduate students. Opinions concerning the usefulness of the course website and the scheduled time of the course (6–9 p.m. Mondays) were mixed.

Results of the long-term survey of previous nanotechnology laboratory students showed that most (85%) agreed that the lab course helped them better understand topics in subsequent classes. Of the students who gained undergraduate research,

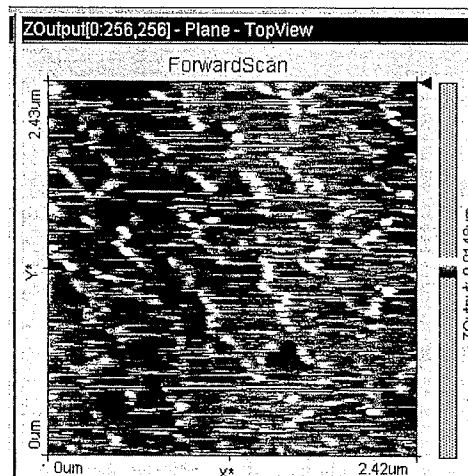


Figure 17: Nanotubes on HOPG derived using Ni catalyst (2.4  $\mu\text{m}$   $\times$  2.4  $\mu\text{m}$  area scanned).

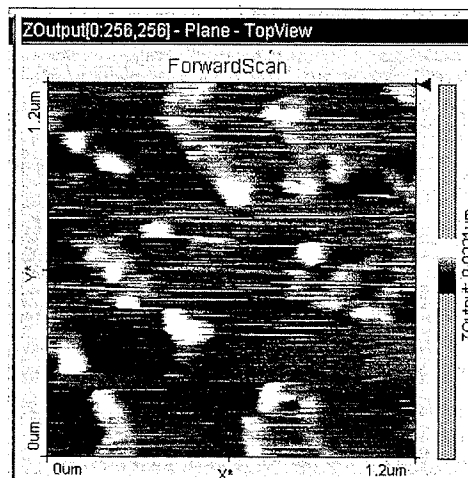


Figure 18: Nanotubes on HOPG derived using Ni catalyst (1.2  $\mu\text{m}$   $\times$  1.2  $\mu\text{m}$  area scanned).

co-op, or internship positions, 64% agreed that the nanotechnology course influenced their decision to pursue such opportunities. Almost all of the students surveyed (85%) would recommend the course to a friend.

## 4 Future Course Improvements

Science education journals publish many new nanotechnology laboratory experiments each year. The Nanoscience and Nanotechnology Laboratory instructors try to keep abreast of the latest articles and also develop their own experiments. As the general public becomes more familiar with nanotechnology, it is increasingly important that students learn about the societal impact of nanotechnology. Activities such as a class debate regarding a nanotechnology-related issue of public interest could be introduced in future course offerings. As mentioned previously, the course lacks a strong nanobiology component. It is hoped that this deficiency will be corrected soon with the involvement of faculty from Florida Tech's Department of Biological Sciences. Students could use fluorescent nanoparticles to image features of biological cells and study the toxicological effects of nanomaterials on cell cultures. These and other ideas will be explored over the next few years. The instructors wish to expand the course so that more students can enroll. This will require additional STM and AFM instruments and assistance from graduate teaching assistants.

## 5 Concluding Remarks

Florida Tech faculty involved with this course agree that it has been a success. Students enjoy learning about nanotechnology and the instructors enjoy helping the students perform these experiments. In closing, the authors wish to present evidence showing the impact of the course at Florida Tech and beyond, provide some hints to successfully implement a similar course and finally to give some personal thoughts about the course.

After teaching the Nanoscience and Nanotechnology course for 3 years, the instructors are beginning to see its impact on the broader science and engineering curriculum. Other faculty members have observed how easy it is for students to operate the STM and AFM, and so they are now interested in using the instruments in upper-level laboratory courses, such as physical and analytical chemistry. The instructors' familiarity with the synthesis and characterization of various nanomaterials has motivated them to include these topics in other courses. For instance, Dr. Winkelmann now uses ferrofluids as an in-class demonstration when discussing magnetism in general chemistry. It is expected that this course will continue to influence the science and engineering curriculum at Florida Tech. With increased publicity, the instructors hope that the Nanoscience and Nanotechnology Laboratory course can serve as a model to help educators at other schools to begin similar endeavors. The authors have been invited to speak at other colleges and scientific conferences, so there is clearly an interest in this course outside of Florida Tech.

Although nanotechnology is a new topic for the undergraduate curriculum, successfully implementing a nanotechnology course is not unlike introducing any new course. The university should support the endeavor by giving faculty time to create new curriculum materials and teach the course. The professors who teach a similar nanotechnology laboratory course should expect to spend additional time to make sure that the course runs smoothly, especially during its first year. Obviously, financial support through the school or an outside funding source is necessary to purchase instrumentation and supplies. The Nanoscience and Nanotechnology Laboratory instructors have found that annual costs of consumable laboratory supplies are low as long as the class size remains small.

Team-teaching a course obviously requires that the instructors work well together. Although each faculty member teaches his own experiments without the involvement of the other instructors, all use the same grading system and course syllabus. This allows each professor the opportunity to work somewhat independently, but provides consistent course structure and system of grading which the students desire. The involvement of faculty from several disciplines helps to attract students

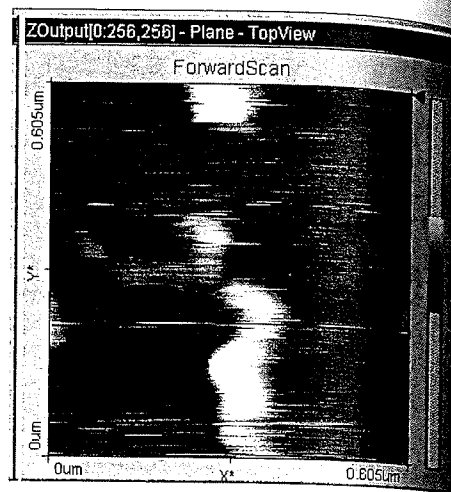


Figure 19: Nanotubes on HOPG derived using Ni catalyst ( $0.6 \mu\text{m} \times 0.6 \mu\text{m}$  area scanned).

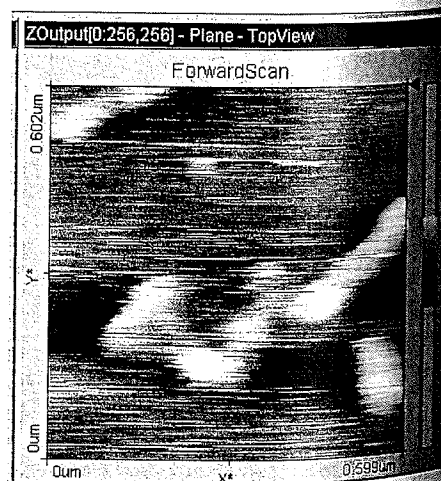


Figure 20: Nanotubes on HOPG derived using Ni catalyst ( $0.6 \mu\text{m} \times 0.6 \mu\text{m}$  area scanned).

with different academic majors and provides the students with a more balanced view of important nanotechnology topics.

Dr. Winkelmann has enjoyed the opportunity to work closely with students who have a strong interest in the subject matter. Several of the most talented students return to help the instructors develop new nanotechnology laboratory experiments for first-year students. There is a great need for the development of more curriculum materials for undergraduate nanotechnology courses, especially laboratory experiments. Undergraduate students are particularly well-suited to perform such work. Participating in teaching this course has also provided many opportunities for Dr. Winkelmann to collaborate with other scientists outside the field of chemistry.

Dr. Brenner was surprised at how much more difficult teaching these labs was as compared to his Introduction to Materials Science and Engineering course. This was particularly true with regard to the TEM practical training since it was difficult to maintain students' interest in a darkened room. Too much explanation of how to operate equipment is of far less educational value than the design of experiments that require more active learning techniques, such as synthesis. Perhaps the most effective year for teaching TEM was the first year (2004), when Dr. Brenner split the class into two six-student subsections that met for 1.5–2 h each, instead of one twelve-student class for 2.5 h. Expanding experiments that require expensive equipment, for which a university may only have one or two, is definitely not recommended.

Dr. Mantovani was generally pleased with the ability of students to learn to use the scanning tunneling and atomic force microscopes. Of course, some students are more careful in operating delicate instrumentation than are others. Care is especially required when handling the STM and AFM tips. It is recommended that the instructor be readily available to assist the students when they encounter a difficult situation or have questions. The instructor should always be responsible for replacing the AFM tips due to their extremely delicate nature. However, once the students have overcome their initial apprehension in using an unfamiliar piece of equipment, they are usually able to become somewhat proficient in its use rather quickly. The skills and knowledge that the students acquire during these lab activities by fabricating tips for the STM, or by preparing substrates for thin film vacuum deposition, are immediately useful to the students in the laboratory course, and these experiences will be undoubtedly useful to them in the future. One difficulty that can be encountered during the laboratory session is the limited access to the STM and AFM instruments. At most, two students should use each instrument at any time, which means that it is important to make sure that all of the students are engaged in some relevant activity when they are not using the STM or AFM. Usually, having the students be involved in some background reading of articles or book sections when they are not using the microscopes provides a good solution.

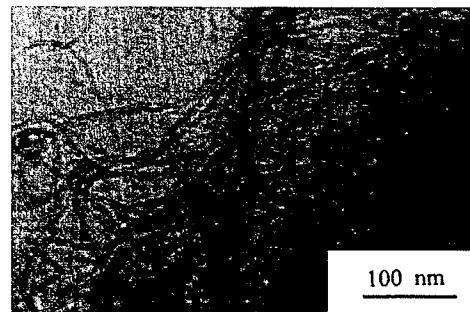


Figure 21: TEM image of 5–8 nm diameter carbon nanotubes derived using Co catalyst.

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