IPRO317: Final Report

8 May 2009

Contents

List of Figures

1 Abstract

Metallic particles exhibit shape-dependent optical properties, allowing for the creation of materials exhibiting different colors without changing the chemical composition. Non-spherical nanoparticles are unstable and tend to revert to nanospheres over time. Thus, the colors exhibited change as the particles change shape to spheres. This color change as time goes on and as ambient temperature changes can be exploited in order to create thermal history indicators. However, before commercialization of silver nanorods can occur, a scalable and cost-effective method of synthesis must be designed and developed.

2 Background

2.1 Silver Nanorods

A nanoparticle is a particle no larger than 100 nanometers — a thousand times smaller than the width of a human hair and ten times smaller than a red blood cell. A nanorod is a type of nanoparticle where one side is typically 3–5 times longer than the others. Due to their shape, nanorods have special optical properties and change color due to their reversion to a more natural and physically stable spherical shape.

Silver nanorods have the unique characteristic of irreversibly changing color as the ambient temperature changes and as time goes on, making them suitable for commercial thermal history indicators. A simple label containing a small solution of these nanorods could be affixed to perishable food or medical products, for instance, allowing consumers to immediately tell at a glance the usability of a given product. Additionally, there is no feasible way for spherical nanoparticles to regress or be converted into the rod form — potentially changing a label's color to mark it as "safe" — making these labels essentially tamper-proof.

In addition to their use as thermal history indicators, silver nanorods have great potential for the creation of other innovative technologies. However, innovations in this field require the design of processes for continuous production of these silver nanorods. Currently, the best-known method of producing the nanorods is very labor-intensive and slow. Additionally, even in controlled lab environments, their synthesis is subject to high variability among batches and scientific groups. In order to be able to produce a commercial product utilizing silver nanorods, the production process must be error-free, scalable, and cost-effective.

Since the current method of silver nanorod production involves the manual synthesis of different solutions and the eventual mixing of these solutions, it lends itself nicely to a so-called continuous flow process. That is, the chemical reactions necessary to create silver nanorods would run in a continuously flowing stream of solution with no user intervention in the reaction. Two ways of creating such a continuous flow process involve the use of a continuous-stirred tank reactor (CSTR) or a plug flow reactor (PFR). A CSTR mixes solutions through continuous agitation while mixing in a PFR occurs through diffusion.

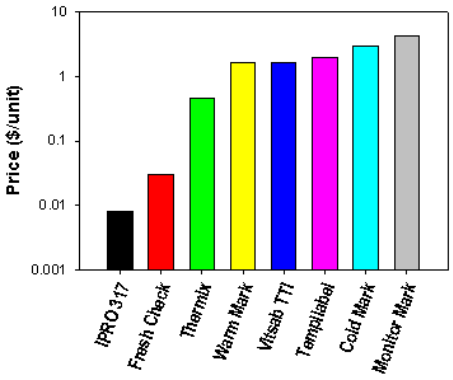


Figure 1: Prices of Competing Thermal Indicators

2.2 Economics

The economic viability of using silver nanorods for thermal history indicators needs to be addressed to determine whether they would be profitable. The potential market for thermal indicators is huge. In the 2008 alone, the USDA reported that the amount of exportation and importation of meat in the seven largest countries was over 27 million metric tons. Further, more than 33% of all red meat in the United States was wasted due to spoilage while in transit from producers to consumers. In addition to food, these thermal indicators could also be used for other temperature-sensitive products including pharmaceuticals and electronics.

There are a number of thermal history indicators currently on the market. Products such as Fresh-Check and CheckPoint use chemical reactions and special dyes to indicate whether a product is still usable. Compared to silver nanorod thermal indicators, these products only have a small spectrum of exhibited colors or patterns, leading to some ambiguity in the exact duration a product was left in non-optimal conditions.

Further, competing products are significantly more expensive than silver nanorod thermal indicators. Assuming that everything would be made by the same company, our thermal indicators could be as low as 0.8¢, over three times cheaper than the nearest competition, as shown in Figure 1 (p. 5).

3 Objectives

- optimize the existing batch process for creating silver nanorods
  - improve the reliability and consistency of the batch process by systematically varying parameters
- develop a continuous batch process for producing silver nanorods
  - time each of the batch steps

  - schedule each step such that a batch of nanorods is produced on a short interval

- explore the use of silver nanorods as thermal indicators
  - chart the colors the nanorods pass after time at given temperatures
- prove the economic viability of nanorods as thermal indicators
  - gather economic data pertaining to the competition
  - compare and contrast different packaging options pertaining to nanorod as thermal indicators and the involved costs and prices
- explore the storage of silver nanorods at different temperatures
  - store nanorods at 4°C, 39°C, and at room temperature
- design and build a microreactor for continuous nanorod production
  - apply chemical reaction engineering principles to build a prototype microreactor and determine the chemical reaction kinetics

4 Methodology

1. The primary problem that IPRO 317 faces is to prove the merit of using silver nanorods as a thermal history indicator. A further problem that IPRO 317 wishes to address is the conversion of the production of silver nanorods from a batch process to a continuous flow process.
2. Our group plans to do the following to address this task:
   (a) literature research concerning the production of silver nanorods;
   (b) literature research about processes employing the use of microreactors;
   (c) make silver nanorods in the lab through batch process to discover information about kinetics and thermodynamics of reactions;
   (d) develop preliminary designs for a microreactor using information from experiments;
   (e) use computer software to optimize design; and
   (f) build and test both CSTR and PFR microreactors.
3. Potential solutions will be tested by analyzing lab results.
4. The task of documentation will be delegated to two individuals.
   (a) One individual will be in charge of collecting, organizing, and compiling research regarding the production of silver nanorods, information about microreactors, and any other literature research that arises.

   (b) This individual will also be in charge of collecting, organizing and compiling any experimental data obtained from the lab. He will also work closely with the team leader to ensure that progress is being made.

5. The following actions will be taken in order to analyze results.

   (a) Results will be collected and organized by the team archivist. These results will be analyzed by the Junior and Senior members of the group.

   (b) The consensus of the analysis will be brought to the advising professor with the intent of gaining insight and direction.

6. The IPRO deliverables will be generated by teams whose main foci are to coordinate the events and results of the team with the IPRO office deliverables.

   (a) These teams will work closely with the rest of the team in order to ensure that deliverables are generated in a timely manner.

   (b) The team leader will also work closely with the IPRO deliverable teams in order to ensure optimal results.

Due to the difficulty in nanorod synthesis, a lot of the optimization of the processes did not take place since the group was not able to completely determine the reaction kinetics. Further, the use of a CSTR for a continuous flow process was ruled out since stirring was determined to be detrimental to nanorod production.

5 Team Structure and Assignments

5.1 Team Structure

The team structure given in the Project Plan persisted for the majority of the semester until the last month or so when the IPRO team reorganized in order to produce the deliverables for the end of the semester. This change was effected for primarily two reasons: the CHE 296 students were in HYSYS training during one of the designated class times each week, thus reducing their ability to contribute to the lab teams they were a part of; and since the lab teams had very few successful experiments at the time, the prospect of researching, designing, and creating a working continuous production process by the end of the semester was diminished and the workload for the research team decreased.

As a result, three new subteams were created — the brochure team, the final report team, and the poster team — whose members were primarily CHE 296 students or from the research team. The purposes of these new teams were to complete and submit their respective deliverables. The lab teams remained the same aside from the removal of the CHE 296 students. The team leader and archivist retained their respective roles. The new divisions and their respective members were:

team leader Riju Konwar

archivist Marisa De Nicolo

brochure team Paul Adamczyk, *Ayokunle Apampa*, Mat Bednarz, Amaka Mbaegbu

final report team Aram Apyan, Malisa Ismail, Grant Justice, Evan Larkin, Joe Muchna, *Jason Petsod*

lab team Muhammad Darwish, Katherine Hammes, Riju Konwar, *Jennifer Peavler*, Mark Pyciak, Michael Schillaci, Russel Ucci, Amanda Wicker, Farouk Yaker

poster team Remi Adejinle, Brent Bijonowski, Muhammad Darwish, *Marisa De Nicolo*, Ryan Kyle

research team Aram Apyan, *Christian Arnoux*, Grant Justice, Evan Larkin, Joe Muchna, Jason Petsod

where the names in *italics* denote the respective team leader.

5.2 Individual Contributions

Paul Adamczyk Paul assisted the research and design teams acquire articles about silver nanoparticle applications. He was also part of the brochure team.

Remi Adejinle At the beginning of the semester, she worked in the lab with the rest of the lab team and when most of the lab work was done, she joined the poster team to design the poster for IPRO day.

Ayokunle Apampa During the course of the semester, he worked with the research team to find out and discover the adverse effects of silver nanorods. Basically, he dug for articles and when found, he summarized them for the team. Anyone wanting to know the adverse effects of silver nanorods had access to a summarized version and did not have to read the whole article again. Later in the semester, he was on the economics team and the brochure team and help designed the brochure and arrange contents. Also he found out the cost per label for the economic analysis section.

Aram Apyan Aram was part of the Research team working on data analysis using MATLAB and found and summarized articles about ongoing nanorod research. Later on, he worked on the final report as part of the final report team.

Christian Arnoux Christian Arnoux was the Research Team leader for IPRO 317. The semester was spent researching various articles on the background of silver nanorods in addition to developing a computer simulation that modeled how the optical properties of these materials change with shape. In turn, this simulation will be helpful analyzing the kinetics of the process.

Mathew Bednarz He was part of the lab team with Russel and Katherine and was co-group leader on the brochure team.

Brent Bijonowski Brent worked on the lab team with Jennifer, and was responsible for making silver nanorods. He also went in on occasion to clean lab equipment so that we would be ready to do further experiments. He later joined the poster team so that the team would be better prepared for IPRO day.

Muhammad Darwish Muhammad was on the lab team to start off and primarily worked on making the batch process work effectively. He worked on the actual batch, as well as spectrophometer graphs which relayed whether each batch was successful or not. Towards the end of the semester he worked with the poster group on putting the poster together and collaborating between the necessary groups to relay the most accurate information. He also worked a couple days on the channel design, running it, then looking at microscopic images to see if nanorods formed.

Marisa De Nicolo Marisa took the minutes for all the class periods, worked on the poster for IPRO day, and was the leader of the economic group. She was also a presenter at the final presentation and was present for the midterm presentation.

Katherine Hammes Katherine wrote the Project Plan at the beginning of the semester and also spent about 10 hours a week in the lab synthesizing nanorods. She and Russell Ucci were on lab team 3 and were usually there most of the day Thursdays and Fridays. Their main contribution was to be the first team to get an easily repeatable result because they had used lower concentrations than had been investigated earlier in the semester.

Malisa Ismail Malisa spent a couple weeks with the lab team, researched and gave ideas on how to coordinate the different teams and scheduling the lab sessions. Due to HYSIS labs, she could not work with the lab team, but worked on the Obstacles & Recommendations sections for the final report in the last 3 weeks of the semester. And on IPRO day, she manned the booth with other group members from 10:00 AM–12:30 PM and helped to explain to the judges and other interested parties about our project.

Grant Justice Grant assisted in the initial research as part of the research group and helped summarize the found journal articles. Later, he worked on the methodology section of the final report.

Riju Konwar As a team leader, Riju's responsibilities included the management and the organization of the IPRO 317. He distributed the members of the teams into their respective groups as per the interest shown by each individual. He also coordinated the week-to-week operation of the team to maximize the results required to validate the production of nanoparticles and its usability as a thermal indicators. He was also a part of the lab team and the research & development team. As a part of the lab team, he worked under the leadership of Farouk Yaker. Every week, Riju, along with his lab teammates, ran several runs of the experiment to produce nanorods in batches. Towards the end of the semester, he was successful in making nanorods in batches. He also ran several runs of the experiment using the microfluidics model with his lab team. The results of this part of the experiment were used to analyze the diffusion properties of the nanorod production in a continuous process. As a part of the research & development team, he also worked under the leadership of Christian Arnoux and researched to understand the kinetics behind the nanorod production and also to find new ways

of making the entire process continuous. He also helped work on the poster that was displayed on IPRO day and was a part of the final presentation.

Ryan Kyle Ryan was a part of the lab and poster teams.

Evan Larkin Evan worked with the research team for the majority of the semester, then later composed the abstract, background, and objectives sections of the final report.

Amaka Mbaegbu Amaka was a part of the lab and brochure teams.

Joseph Muchna Joe was a part of the research team and near the end of the semester worked on the ethics portion of the final report.

Jennifer Peavler Jennifer Peavler was the lab team leader. She familiarized all the lab members with the procedure for making nanorods. She also made several batches of silver nanorods.

Jason Petsod As part of the research team, Jason helped find journal articles on silver nanorods and helped develop MATLAB simulations used for modelling nanorods' absorption and aspect ratio correlation. Near the end of the semester, he led the final report team and he developed the team's web site.

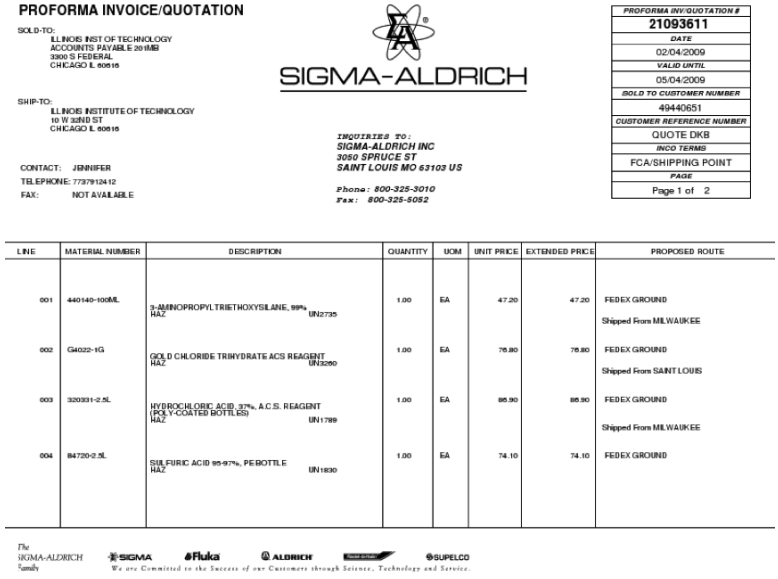
Mark Pyciak Throughout the semester, Mark worked with lab group 2 in the laboratory trying to determine the optimal batch conditions for obtaining the best yield of nanorods. Subsequently, he conducted a couple preliminary continuous process runs using the microfluidics reactor. He made significant contributions to the technical portion of the final report and was involved with editing the IPRO day poster. Finally, he also helped set up the exhibit table on IPRO Day.

Michael Schillaci Michael did extensive lab experiments with lab group 2, helped write the technical portion of report, and helped set-up for IPRO day.

Russel Ucci Russel was part of the project plan team working on the project milestones and worked in the lab.

Amanda Wicker Amanda worked on the project plan at first, then in the lab during the majority of the semester, and some economics analysis at the end.

Farouk Yaker Farouk was the group leader of Lab Group 2. His duties consisted of being in charge of three team members in the laboratory throughout the semester as well as personally conducting research on optimizing the batch process of nanorod production. As the group leader, he routinely met with Professor Perez-Luna along with other team leaders to discuss progress, issues and the direction of the lab teams. He was also in charge of scheduling the lab teams in the lab. He made significant contributions in poster layout and he helped set up the IPRO Day exhibit.



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LINE	MATERIAL NUMBER	DESCRIPTION	QUANTITY	UOM	UNIT PRICE	EXTENDED PRICE	PROPOSED ROUTE
001	440140-100ML	3-AMINOPROPYLTRIETHOXYSILANE, 99% HAZ UN2735	1.00	EA	47.20	47.20	FEDEX GROUND Shipped From MILWAUKEE
002	G4022-1G	GOLD CHLORIDE TRIHYDRATE ACS REAGENT HAZ UN3260	1.00	EA	76.80	76.80	FEDEX GROUND Shipped From SAINT LOUIS
003	320331-2.5L	HYDROCHLORIC ACID, 37%, A.C.S. REAGENT (POLY-COATED BOTTLES) HAZ UN1789	1.00	EA	86.90	86.90	FEDEX GROUND Shipped From MILWAUKEE
004	84720-2.5L	SULFURIC ACID 95-97%, PE BOTTLE HAZ UN1830	1.00	EA	74.10	74.10	FEDEX GROUND

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Figure 2: Chemical Expenditures

6 Budget

The chemicals required for the synthesis of silver nanorods were the only expenditures for this IPRO and are shown in Figure 2 (p. 11).

7 Code of Ethics

Overarching Standard Help to make a safe, cheaper, and more effective thermal indicator using silver nanorods to benefit the use of temperature dependent products, including foods and medicines, in order to protect the consumer from unusable products.

7.1 Law

The team will be knowledgeable of laws that govern the use of thermal indicators and be sure the products works before use is permitted.

Pressure The team may attempt to complete the project before sufficient data is provided.

Risk An unsafe, unusable product will be released to the consumers.

Risk Insufficient data will be obtained by the group which will lead to a product without evidence supporting it.

Measure The team will meet and establish the goals on a regular basis, keeping all members informed of the progress and set-backs of the product.

7.2 Contracts and Agreements

The team will be sure that the product works to standards promised to the customer before marketing will occur.

Pressure The team may attempt to rush the testing or production of the product.

Risk The team will overlook a vital attribute of the product.

Risk The team will miss important testing information.

Measure The team will spread tests and lab work amongst several different groups in order to assure the data received is an accurate description of what occurred.

7.3 Professional Codes of Ethics

The team will know the National Society of Professional Engineers code of ethics and be sure to follow them.

Pressure The team may rush the product to complete it within a limited time span.

Risk The team will rush the product without proper testing, violating the code's policy to "avoid deceptive acts."

Risk The team will feel rushed and use unqualified members to do tasks.

Measure The team will divide tasks according to expertise and be sure that several groups prepare and test the products.

7.4 Industry Standards

The team will be sure that its product falls within or exceeds the industry standard for thermal indicators and has a minimum amount of failure.

Pressure The product may be rushed through production or testing.

Risk The product will fail to perform to the standards required by the consumer.

Risk The product will fail to meet what it is marketed as.

Measure The members of the team will know how the product works and the specifications for it and the product will not be released without each member agreeing to the standards set forth.

7.5 Social, Civic, and Geographic Communities

The team will be sure to test the thermal indicator to assure the safety of the community and the consumers who will use it.

Pressure The team may feel obligated to have a product completed by a certain deadline.

Risk The product will not be tested for its environmental risks.

Risk The product will fail and lead to hazardous conditions to the consumer.

Measure The team will investigate all potential risks in the use of the product before it is released to the public. The team will assign members to investigate such hazards, far before the production is started.

7.6 Personal Relations

The members of the team will be sure to submit honest data to the other members and stakeholders so as not to invalidate the final product.

Pressure Team members may feel obligate to rush their portions of production or testing.

Risk Team members will feel the pressure of deadlines and rush to complete their individual sections.

Risk Team members will fabricate evidence to streamline production.

Measure Several team members are assigned to each task with the ability to overlook the evidence of the associates. The team member must then submit his data to a sub-team leader, who in turn, submits to the team leader. This chain of command and the involvement of several members helps to eliminate fraudulent data.

7.7 Moral and Spiritual Values

The team will be sure not to use, prepare or test the product in any way that may offend one's moral or spiritual views.

Pressure The team may feel rushed in the testing of their products.

Risk The team will feel the need to allow the products to be tested with their team members, thus possibly infringing on one's moral or spiritual values.

Risk The team will require extra meetings which may infringe on an individual's moral or spiritual values.

Measure The team leader will be sure to make all meetings outside the given time blocks optional, and be sure not to force anything upon individuals, who are unable to do such.

8 Experimental Procedure

8.1 Silver Nanorods

Silver nanorod synthesis can be characterized by three distinct steps: preparation of seed solution, preparation of growth solution, and a subsequent mixing of the growth and seed solutions with NaOH. The silver seeds are prepared by reducing $AgNO_3$ using $NaBH_4$, with trisodium citrate acting as a stabilizing agent for the nanoparticles. The following procedure was tailored to yield a high concentration of 4 nm seed. The seed solution has an incubation period of two hours and a shelf life of five hours. After five hours the seed solution can no longer be used as it develops a thin film of particles on the liquid surface. It is prepared in 20 mL batches with a final concentration of 0.25 mM silver nitrate and 0.25 mM trisodium citrate mixed in aqueous solution. The mixture is stirred vigorously while 0.6 mL of 10 mM $NaBH_4$ is added. After 30 seconds of stirring, the solution is set aside for two hours.

Preparation of the growth solution consists of mixing 0.25 mL of 10 mM silver nitrate with 0.50 mL of 100 mM ascorbic acid and 10 mL of 80 mM CTAB. It can be used immediately after mixing. The growth solution lasts indefinitely therefore larger quantities can be made ahead of time and stored for future use.

After two hours elapse, the seed solution is ready to be used. According to literature, varying the seed concentration in the growth solution will have an effect on the aspect ratio of the rods that will form. The rod aspect ratio will increase as the seed concentration decreases. Seed growth was observed by others in the range of seed concentrations varying between 0.06 mL and 2 mL. The concentrations tested were 0.06 mL, 0.125 mL, 0.25 mL, 0.5 mL, 1 mL, and 2 mL. Experiments performed by this IPRO group however did not yield any nanorods at the 2 mL seed solution concentration. The best results were obtained at the 0.25 mL seed solution concentration. The procedure for making rods consists of taking one batch of growth solution and introducing to it the appropriate volume of seed solution. The final step consists of adding 0.10 mL of 1 M NaOH solution. Most references in literature state that a gentle shaking is required to promote good mixing; however this IPRO group has found that a gentle 45° tilt of the reaction vessel and its subsequent return to an upright position is all that is required. Gentle shaking has the potential of disrupting seed formation and is not recommended. Within 1 to 10 minutes, an observable color change signals the successful formation of silver nanorods. This is verified by using UV-vis absorption spectroscopy.

8.2 Microfluidics Channel

A major focus of this IPRO was understanding the process of producing nanorods in batches in order to determine the most important variables that hinder or promote acceptable yields of nanorods. After succeeding in this regard, the next step was to apply these results to a continuous flow process. However, because the scope of adapting the whole process to continuous flow is quite extensive, this IPRO decided to focus on only one of the three steps which is the final step of mixing the seed and growth solution with NaOH. A major obstacle that was encountered consisted of determining

the proper mixing dynamics. The issue with this is that there has to be some mixing but not too much as this will hinder nanorod production. Initially, it was believed that a CSTR could be used to mix the growth and seed solutions with NaOH, however, each lab group noticed that the amount of mixing necessary to promote nanorod growth was actually quite small. It was also deduced that most of the mixing occurs via diffusion. In this regard, it was decided that a CSTR would produce excessive agitation that would probably hinder nanorod production.

Consequently, a PFR system was chosen in favor of the CSTR in order to keep the mixing dynamics confined to diffusive type dynamics. One important constraint that needed to be addressed was that the Reynolds number needed to remain small to keep the flow in the PFR in the laminar regime. To accomplish this, the velocity would have to be scaled appropriately due to the fact that the PFR diameter is on the order of $200\,\mu$m. A variable speed peristaltic pump will be used to achieve the proper flow rate.

The plug flow reactor in this case is the microfluidic channel. The design of the PFR is such that there are two feed streams: one containing the growth and seed solution and the other the NaOH solution. Both streams are then fed into one main line. As the streams flow through this line, diffusion occurs down a concentration gradient. However, to maximize the diffusion process, the residence time was increased by stopping the flow of the fluid in the main line. The formation of the nanorods is directly proportional to the residence time. Hence, the residence time needs to be fluctuated to generate the appropriate parameters to isolate the ideal conditions for nanorod production.

The microfluidics channel (Figure 3) is fabricated from the elastomeric polymer polydimethylsiloxane (PDMS). The first step in the fabrication of a microfluidics stamp consists of making a negative mask. The pattern is laid out and drawn using Canvas 8 software and printed on a transparency using a laser printer. Next, using a photoresist, a master is fabricated using optical lithography. This is done by first cutting a silicon wafer, called the substrate, into the appropriate size. The cut substrate is then washed using a piranha solution and baked on a hotplate at 200°C for 5 minutes in order to dehydrate the surface of the substrate.

The substrate is then spin-coated using the SU-8 100 photoresist. A two stage spin procedure is used which at low speeds, about 900 rpm for 6 seconds, allows the dispensing of the photoresist. At high speeds, 2500 rpm for 30 seconds, the coating is homogenized on the substrate. In order to remove the solvent from the coated substrate and facilitate the process of congealing the film, the substrate is covered with aluminum foil and baked at 60°C for 5 minutes. Next, a negative mask is placed on the photoresist-coated substrate and exposed to UV radiation in the range of 350–400 nm. SU-8 is well suited to be exposed in this range. It is unaffected at wavelengths above 400 nm; however, it has high actinic absorption below 350 nm. The amount of exposure is dependent on various process parameters along with film thickness. At this time, another 5 minute bake is required at 60°C in order to selectively cross-link the exposed portions of the film. The mask is then peeled off and the sample is washed in acetone using the spin coater to remove any remaining photoresist from the substrate.

The next step involves fabricating the inlet and outlet ports for channel. This is accomplished using 3–4 mm lengths of copper wire. One end of the cut piece of wire is then file down to make it flat and this flat end is then crazy-glued to the master. Six

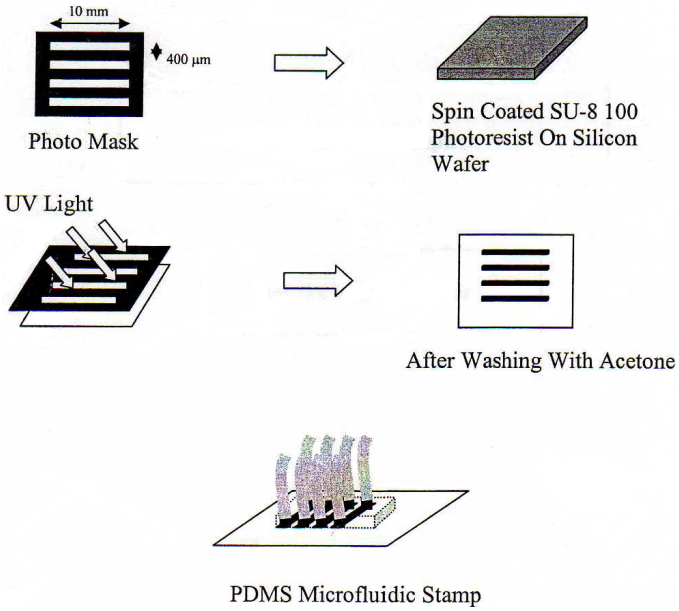

Figure 3: Microfluidics Channel Design

hours of curing are required to insure proper adhesion. Next, silicone tubing is connected to copper posts to form an inlet and an outlet for the channel. Finally, the PDMS stamp is replicated from the master. This is done by mixing the polydimethylsiloxane prepolymer with a curing agent in a 10 to 1 ratio by weight or volume. The mixture is stirred thoroughly and poured over the master and placed in a Petri dish and allowed to cure overnight at ambient conditions. A second curing is required at a temperature of 65°C for two hours. The microreactor is now ready. All that remains is to remove the replica from the master with care along with the copper rods. The stamp can now be tested for leaks by pressing it against a glass slide and flowing deionized water through the channel. The fabrication of the PDMS Microfluidic Stamp is a two day process. Its fabrication requires skill and considerable patience. Due to its size, configuration, and material out of which it is constructed it is quite delicate and must be handled with care. The very first microreactor prepared for a trial run was inadvertently damaged because of these limitations.

9 Results

9.1 Overview

Despite severe setbacks due to systemic problems encountered with the batch creation of nanorods, we were eventually able to design and construct a continuous flow reactor. For the majority of the semester, our lab teams were unable to replicate the procedure described in [9] to produce silver nanorods. However, by varying different steps and

variables in the process, a working procedure was eventually found near the end of the semester and development of a continuous flow process started in earnest.

Meanwhile, the research group conducted research into scaling up the batch process into a continuous flow process. In order to devise such a process, the chemical reaction kinetics of silver nanorod production needed to be determined and analyzed. However, due to the difficulties in producing viable batches of nanorods, actual experimental data for analysis was not available for much of the semester and the group instead developed computer simulations to model the reactions.

Once silver nanorods were being reliably produced in the laboratory, their color-changing thermal properties were immediately evident. Further, as described in §2.2, the chemicals used to produce a single thermal history indicator would cost 1–2 cents, significantly less than that of other products on the market, thus demonstrating the economic viability of the use of silver nanorods in commercial indicators. The major technical obstacle in commercialization would be the development of a continuous flow process to quickly and accurately produce the silver nanorods.

Development of the continuous flow process began immediately after a working batch process was established and the reaction kinetics could be analyzed. Due to the difficulties of adapting the entire procedure to continuous production, this IPRO only focused on making the final mixing of seed and growth solutions into a continuous process. An initial prototype microfluidics model was created in order to determine the parameters and kinetics necessary for the construction of a working microreactor. However, steady production of nanorods was not achieved with the model.

9.2 Research

The research group of IPRO 317 was formulated to scale-up the batch nanorod synthesis to a continuous flow process. Before any considerable goals could be met it was imperative to develop a strong knowledge base behind silver nanoparticle synthesis and the various applications they have in modern science. Therefore, considerable time was spent researching and summarizing various journal articles that covered the topic. To delegate this task efficiently, each member of the research group was designated a certain topic to research and summarize. Summaries were then posted on the iGroups web site to enhance each team member's understanding of nanoparticle synthesis, applications, and adverse effects.

Once a solid background was obtained, research shifted to study batch and microreactor processes that are utilized in the synthesis of silver nanorods. Considering that most of the group had backgrounds in areas other than chemistry and chemical engineering, considerable time was spent in the familiarization of chemical reaction engineering principles for use in the scale-up of the batch process. The usual procedure in reactor scale-up from a laboratory-scale batch process to a full-scale continuous process is to determine the chemical kinetics of the particular reaction. However, silver nanorod synthesis does not follow any known reaction rate law. Therefore, separate lab experiments needed to be analyzed to obtain the rate law of the particular reaction. In batch reactor experiments, concentration, pressure, and/or volume are typically recorded at different times throughout the reaction. However, the reaction unique to nanorod growth is analyzed using wavelength time data. Therefore, correlations be-

tween wavelength and concentration needed to be determined. The graph in Figure 4 illustrates the growth of the nanorods over time where the kinetics of the reaction can be analyzed.

Correlations between wavelength and concentration were obtained by creating a MATLAB simulation for different aspect ratios (Appendix B). The increase in aspect ratio was directly proportional to the increase in concentration of silver nanorods in solution. The correlation was determined by simulating the optical absorption spectrum of a silver nanorod solution with the aspect ratio R. This spectrum can be modeled using an extension to Mie's theory that sums over all electric and magnetic multipole oscillations that contribute to the absorption. The extinction coefficient κ for N particles in a volume V is given by [12] and [13] as:

$$\kappa = \frac{2\pi N V \varepsilon_m^{3/2}}{3\lambda} \sum_j \frac{(1/P_j^2)\varepsilon_2}{\left(\varepsilon_1 + \dfrac{1-P_j}{P_j}\varepsilon_m\right)^2 + \varepsilon_2^2} \tag{9.1}$$

where ε_1 and ε_2 are the dielectric constants for silver found from the CRC Handbook of Chemistry and Physics. P_j are the depolarization factors for each of the three axes A, B, and C of the nanorod and are:

$$P_A = \frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right) - 1\right] \tag{9.2a}$$

$$P_B = P_C = \frac{1-P_A}{2} \tag{9.2b}$$

where

$$e = \sqrt{1 - \left(\frac{B}{A}\right)^2} = \sqrt{1 - \frac{1}{R^2}}. \tag{9.3}$$

The dielectric constants are functions of wavelength determined by fitting the data from the tables in the Handbook of Chemistry and Physics to a curve. The tables give dielectric constants as a function of photon energy E in electron volts (eV). To convert the energy in eV to wavelength, the relation $\lambda = 1240/E$ was used (λ in nm). Fitting the experimental data in MATLAB yielded the correlations:

$$e_1 = (1.634 \times 10^{-5})\exp(2.917\lambda) - 391.5\exp(-1.581\lambda) \tag{9.4}$$

and

$$e_2 = (3.661 \times 10^{-10})\exp(5.484\lambda) + 12.29\exp(-0.8866\lambda). \tag{9.5}$$

The above equations were incorporated in the computer program attached to the report. The dependence of the absorption maximum of the longitudinal plasmon resonance on the nanorod aspect ratio was determined from the simulation:

$$\lambda_{\max} = 85.011R + 337.89. \tag{9.6}$$

This correlation helps to convert the wavelength time data from the lab experiment to concentration time data for help in the kinetics analysis. The aspect ratio defined as the

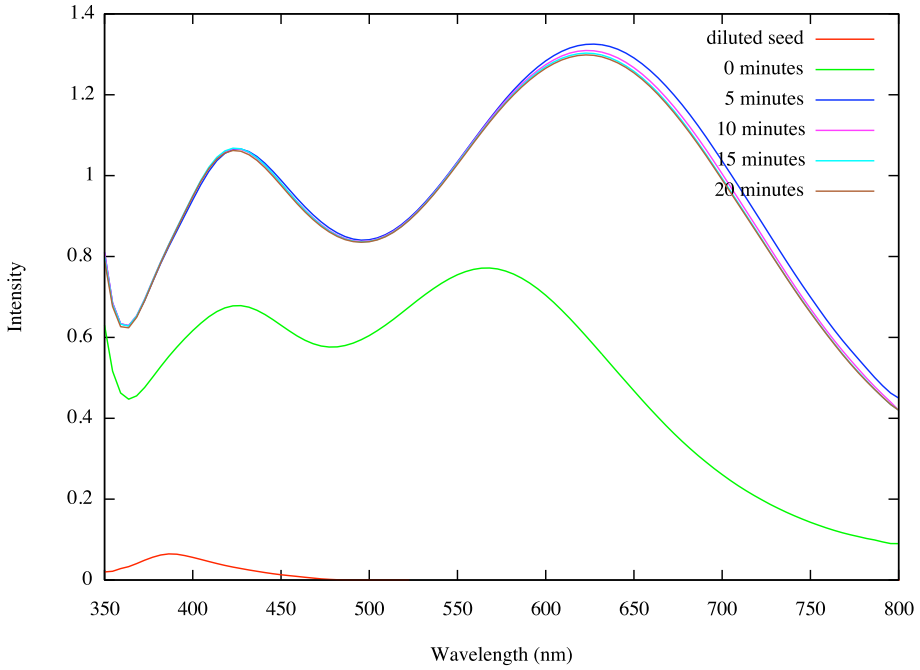

Figure 4: Nanorod Growth over Time

ratio of the length to the radius of a nanorod can directly determine the concentration increase of silver for all nanorods in solution. As the aspect ratio increases the concentration increases directly. Assuming the radius stays constant as the rods increase in length, the change in volume of the nanorods could be determined. The increase in concentration could then be obtained given the density and molecular weight of silver. Various experiments were attempted that monitored nanorod growth over time. Success was found with one growth solution to which the research group is currently in the process of replicating.

9.3 Experimental Results

The graph in Figure 4 displays the growth of the silver nanorods (using a 250 μL seed) over time in intervals of approximately five minutes each. The first peak which appears around 400 nm wavelength represents silver nanoparticles (spheres) and the second peak between 600 and 650 nm represents the silver nanorods. As the peaks become broad (stretch), the length of the nanorods increases. Initially, as each interval passes the intensity (peak) increases thus representing an increased number of nanorods growing over time. As in comparison with the initial time the final time interval has shown a great rise in intensity and thus shows a greater number of rods formed. There are a finite number of nanorods that can be made using set amount of solution thus the second peak will reach a relative max peak and length for the concentrations used.

9.4 Laboratory Observations

Making nanorods is considered by some to be more of an art than a science. The reason for this is simply that the mechanism of the production process is not completely understood due to the interaction of many different variables. In keeping with the scientific approach of engineering processes, IPRO 317 attempted to create a deterministic nanorod production process. There are a number of variables that need to be taken into account during the synthesis of silver nanorods:

- volume of seed
- residence time
- impurities
- temperature effects
- pH
- diffusion effects
- reactor type
- choice of reducing agents

This list is by no means exhaustive, yet it illustrates the degree of complexity in attempting to determine the optimum conditions for producing nanorods.

As was previously mentioned, the process of producing nanorods can be broken down into three distinct steps: preparation of seed solution, preparation of growth solution and a subsequent mixing of the growth and seed solutions with NaOH. Each step is performed at a different point in time, characterising the process as a semi-batch process. In order to adapt this process to continuous flow, it is necessary to address each of these steps and integrate them into one system. The difficulty that arises in the implementation of the continuous process is at least partially the result of the long residence time necessary for the formation of the seed solution. The volume of the seed solution used in the batch process was also critical to the formation of nanorods. The initial volume used to form nanorods was 2 mL. However, upon further examination, the ideal range for seed solution was experimentally determined to be 0.06–1.0 mL. The best results were obtained by using 0.25 mL of the seed solution. Initially, impurities in the source ingredients were also considered as a deterrent in the formation of nanorods. However, this was quickly resolved by further experimentation and maintaining a strict cleanliness regime in the laboratory process. Temperature also seemed to be a factor as nanorod production was further enhanced when the seed solution was heated to approximately 40–50°C in order to stop the reducing agent ($NaBH_4$) from hindering the formation of nanorods by reacting with the growth solution. With respect to pH, reactor type and the choice of reducing agents, further testing is required to determine their effects on the formation of nanorods. A completely continuous process would inevitably involve multiple reactors to address this issue.

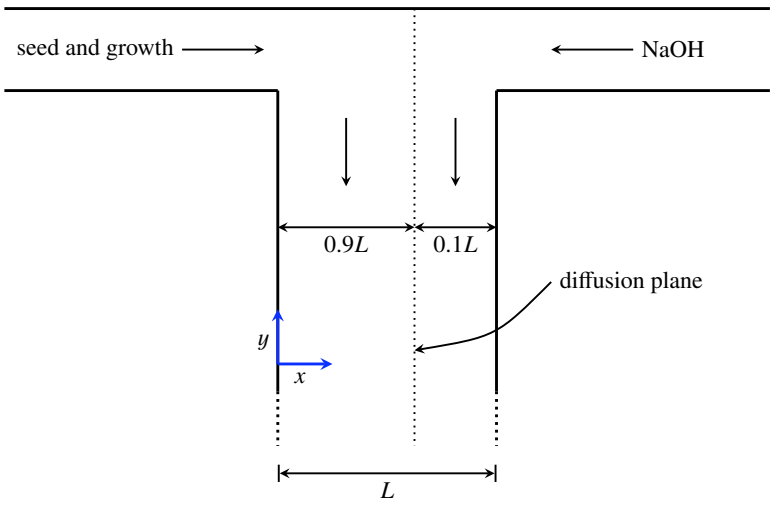

Figure 5: Experimental Setup for Diffusion Analysis

9.5 Mathematical Model

Conservation of mass can be used to generate an initial mathematical model for the microtubule setup in the laboratory. This setup was the first step towards developing a continuous process for the production of silver nanorods. Two inlet microtubules, one containing the seed and the growth solution mixture and the other containing the sodium hydroxide (NaOH) would be pumped through a micro-channel and then collected at the other end.

The experimental setup shown in Figure 5 will be used for determining the relationship of diffusion to the flow rates of the respective inlet streams. The flow rate of the seed and the growth solution was set at a higher rate than the inlet flow rate of the NaOH. As these two streams flows through a common duct, they form two parallel layers of laminar flow with a very distinct diffusion plane determined by the flow rates of the inlet streams. Diffusion occurs along a concentration gradient along the x-direction while convection occurs along the y-direction along length of the microtubule.

The equation of motion in such a continuous process can be written as:

$$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C = D\,\nabla^2 C + R \tag{9.7}$$

where C is the concentration, $\mathbf{v}$ is the velocity, D is the diffusivity, and R is the rate of reaction. The terms in this equation model the accumulation, convection, conduction, and generation, respectively. Convection was assumed to be negligible since there was no flow in the y-direction and the contribution due to the reaction was also ignored. Therefore, (9.7) can be rewritten as:

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \tag{9.8}$$

with C denoting the concentration of NaOH. If we let $\varphi = C/C_0$, we have:

$$\frac{\partial \varphi}{\partial t} = D\frac{\partial^2 \varphi}{\partial x^2}. \tag{9.9}$$

Since $\varphi = \varphi(\eta)$, using the chain rule on both sides yields:

$$\frac{\partial \varphi}{\partial \eta}\frac{\partial \eta}{\partial t} = D\frac{\partial}{\partial \eta}\left[\frac{\partial \varphi}{\partial \eta}\frac{\partial \eta}{\partial x}\right] \tag{9.10}$$

where $\eta = x/\sqrt{4Dt}$:

$$-\frac{\eta}{2t}\frac{\partial \varphi}{\partial \eta} = D\frac{\partial}{\partial \eta}\left[\frac{1}{\sqrt{4Dt}}\frac{\partial \varphi}{\partial \eta}\right]. \tag{9.11}$$

$$-\frac{\eta}{2t}\frac{\partial \varphi}{\partial \eta} = \frac{1}{4t}\frac{\partial^2 \varphi}{\partial \eta^2} \tag{9.12}$$

$$\frac{\partial^2 \varphi}{\partial \eta^2} + 2\eta\frac{\partial \varphi}{\partial \eta} = 0 \tag{9.13}$$

Letting $\psi = \partial\varphi/\partial\eta$, the resulting first-order differential equation can be solved using separation of variables, yielding:

$$\frac{\partial \varphi}{\partial \eta} = c_1 \exp(-\eta^2) \tag{9.14}$$

where c_1 is an arbitrary constant. Integrating again results in:

$$\varphi = c_2 + c_1 \int_0^{\eta} \exp(-\eta'^2)\, d\eta' \tag{9.15}$$

where η' is a dummy variable of integration and c_2 is another constant.

10 Obstacles

10.1 Scheduling Conflicts

First, there were scheduling conflicts. The batch reaction in producing the silver nanorods involves a lengthy process time and ran longer than the designated IPRO class times. Also, there were three separate groups conducting the experiments; whose team members had different schedules outside of class times, thus increasing the scuffle for lab time.

In resolving the scheduling conflict, the experiments were conducted in a sort of segmented fashion. The experiments were conducted at times when the majority of team members could meet instead of at times when all members could meet. And the experiment tasks were further delegated; a member would make the seed solution and someone else or the other members would continue the experiment to the end.

10.2 Logistical Issues

Second, there were issues with limited laboratory access, inconsistent growth solutions and lack of clean vials used to conduct the experiments, as well as a poor initial yield of silver nanorods.

The team leaders of the laboratory groups had to apply in advance for access key cards from the Chemical Engineering department to enter the laboratory building. This affected some groups because the team leaders had no key access cards so initially, they relied on graduate students who work in the same lab for entry. Teams also shared access key cards to resolve the issue. Later, the team leaders all had access key cards and groups had fewer issues with gaining entry to the laboratory.

The wrong growth solutions used at the start-up experiments yielded inconsistent data and results. But early note of this error resolved the issue quickly and new growth solutions were made and more careful measurements were subsequently taken. Additionally, because there were three separate lab teams, too many vials were being used up at any given time. This led to a shortage of clean vials available for use. Jennifer Peavler asked for assistance to clean the used vials so the lab teams can progress with more experiments. Further, so that this issue would not recur, used vials were regularly cleaned out after completed experiments.

There was a poor yield of silver nanorods in the initial experiment runs. This affected data analyzing for the reaction kinetics, hence also affected the modeling and designing of a continuous reactor for the project.

11 Recommendations

Given that the production of nanorods via the batch process is time consuming, some stock solutions can be made ahead of time in bulk so that failed experiments can be repeated easily. In particular, the growth solutions used in this process, CTAB, and NaOH, can be kept for an indefinite period of time. Made in bulk, a desired amount can be measured and extracted from this supply at each experiment run. Thus, there would be fewer numbers of vials used. As stated above, good laboratory practice dictates the regular cleaning of used vials after completed experiments.

Future IPRO teams should bear in mind that experiments often can run longer than the allocated class times. Extra time will be required in cases when there are errors in measuring raw materials or when equipment breaks down. Those within the IPRO team who wish to contribute in the lab should have flexibility in their schedules. Also, the laboratory team leaders should apply for access to the lab at the very start of the term. This will ultimately ease the lab entry for their team members and therefore, will increase the project management efficiency.

In regards to more technical issues, future IPROs also need to focus on the effects of pH, reactor type and the choice of reducing agents on the formation of nanorods. Scale-up for the microfluidics flow design will also be pivotal in furthering the cause of continuous silver nanorods production. Additives like iodine which enhance the production of nanorods need to be analyzed under experimental conditions. This will increase the efficiency of the future continuous design.

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13 Resources

From the time sheets submitted on iGroups, our team members spent over 300 hours in the lab conducting nanorod synthesis and 150 hours on nanorod research outside of the designated class time. Further, the team's expenditures are described in Section 6.

14 Acknowledgements

We are grateful to Professor Victor Perez-Luna and Supdito Chakraborty for their guidance, helpful discussions, and the use of their laboratory facilities.

A Web Site

IPRO 317's web site is located at `http://quicksilver47.org`.

B MATLAB Nanorods Simulation

```
function k=nanorods(w)

for j=1:.1:4
    R=j;

l=200:.1:900;
w=1240./l;
e1=1.634*10^-5*exp(2.917*w)-391.5*exp(-1.581*w);
e2=3.661e-010*exp(5.484*w)+12.29*exp(-0.8866*w);
em=1.33^2;

e=sqrt(1-1/R^2);
P(1)=(1-e^2)/e^2*(1/2/e*log((1+e)/(1-e))-1);
P(2)=(1-P(1))/2;
P(3)=P(2);

    k=0;
    for i=1:3
        k=k+1/P(i)^2*e2./((e1+(1-P(i))/P(i)*em).^2+e2.^2);
    end
    k=k*2*pi*em^1.5/3./l;

plot(l,k)
xlabel('wavelength (nm)')
ylabel('absorbance (AU)')
title(['R=',num2str(R)])
pause on
pause
end
```