# IPRO 348: Final Report

# Silver Nanorods as Indicators of Thermal History

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# Ag NANO

1. Executive Summary	2
2. Team Purpose	2
3. Objectives	2
4. Organization and Approach	3
4.1. Lab	3
4.2. Scale-Up	5
4.3. New Technology	5
4.4. Prototype	5
5. Analysis and Findings	5
5.1. Lab	5
5.2. Scale-Up	6
Figure 1: Silver Nanorod Production Process Flow Diagram	7
5.2.1. PFR:	7
Figure 2: Suggested PFR Synthesis Process	7
5.2.2. CSTR:	7
Figure 3: CSTR Synthesis Process	
Figure 4: Product Pump Calibration	
5.3. Toxicity and Disposal	9
5.4. Heat Transfer	
Figure 5: Heat Transfer Schematic for Silver Nanorod Thermal Indicator Label	
5.5. Prototype	11
6. Conclusions and Recommendations	
6.1. Lab Group	
6.2. Scale-Up	
6.3. Prototype	
6.4. Toxicity and Disposal	
7. Appendix	15
7.1. Appendix A (Figures):	15
Figure 6: Nanorod formation at 1 M NaOH and 25°C	
Figure 7: Nanorod Formation at 0.045 mL seed Solution and 25°C	
Figure 9: Nanorod Formation versus Time	
7.2. Appendix B (References)	17
7.3. Appendix C (Lab Protocol):	20
7.4. Appendix D (Scale-Up):	22
7.5. Appendix E (Research):	23
7.6. Appendix F (Prototype):	24
Table 2: Table of Competitors' Prices	
7.7. Appendix G (Business/Cost Analysis):	27
Table 3: Lab Purchases	
Table 4: Cost Analysis of Laboratory Materials	
7.8. Appendix H (Contact Information):	
7.9. Appendix I (Team Members):	29

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# 1. Executive Summary

Food borne illness is a major problem in the United States and around the world. A new report by The Centers for Disease Control (CDC) found that 88% of foodborne illness outbreaks result from thermophilic bacterial growth on foods that have been improperly kept at warm temperatures for extended periods of time.<sup>32</sup> IPRO 348, Silver Nanorods as Indicators of Thermal History, sought to gain a deeper understanding of how silver nanorods can be viably produced and investigated their application as thermal indicators for use in the food packaging industry.

The team developed a novel protocol by which viable silver nanorods could be consistently produced. This new, improved protocol was derived from laboratory experimentation on the original procedure. It was confirmed that the synthesized nanorods were dependent on both time and temperature and could be packaged as an indicator of food quality.

A prototype thermal indicator label was created using silver nanorods synthesized in the laboratory; the economic cost of producing these labels was investigated and compared against current commercial competitors. As the temperature of the food product increased, the nanorod label changed color, indicating spoilage. Silver nanorod labels were found to be competitive against existing thermal indicators based on production methods and scale-up design.

# 2. Team Purpose

IPRO 348 is a group brought together through a common interest in nanotechnology: we look to gain practical and professional experience in experimentation, scale-up design, academic research, prototype construction and project management. The team is striving to improve the process of producing silver nanorods while discovering, creating and evaluating potential applications for their future use.

# 3. Objectives

- a) Create a viable experimental procedure for the production of silver nanorods
- b) Consistently synthesize batches of well-formed silver nanorods in a laboratory environment
- c) Adjust the "half-lives" of silver nanorod batches to suit their intended applications
- d) Employ absorption spectroscopy to determine the quality of produced silver nanorods
- e) Determine optimal conditions for silver nanorod formation
- f) Research, design, and test processes to improve the effective production of silver nanorods
- g) Provide information regarding different processes used to facilitate silver nanorod formation
- h) Design, evaluate, and construct a working prototype incorporating use of a viable batch of silver nanorods
- i) Develop quantitative methods for controlling quality of produced silver nanorods
- j) Discover new technologies and applications relating to silver nanorods, such as medical applications, through academic research
- k) Compare existing technologies against discovered nanorod applications in terms of function, cost, economic demand, practicality and environmental impact
- I) Facilitate ChE 296 students' learning of the fundamentals in operating Aspen HYSYS software and in conducting laboratory research

2



- m) Promote cooperative teamwork towards achieving common goals while maintaining academic and behavioral integrity
- n) Gain greater knowledge regarding nanotechnology while participating in a positive teambuilding experience

# 4. Organization and Approach

To address the multifaceted issue of using silver nanorods to prevent food spoilage, subgroups dedicated to laboratory research, investigation of new technology, prototype creation, scale-up design and production, and ethics and environmental considerations were formed. Research was conducted through reading published articles, laboratory experimentation, contacting experts in the field, and mathematical simulation and analyses. Professor Perez-Luna also presented a lecture on the thermochromic behavior of silver nanorods, which explained their optical properties in correlation to light spectra.

The light absorbance wavelength of silver nanorods decreases as their aspect ratios also decrease when transitioning from rods to spheres. Information from the literature indicates that silver nanorods appear blue at 25° C and transition to purple, orange, and yellow when exposed to temperatures of 130° C, 155° C and 190° C, respectively.<sup>21</sup> This color gradient is a constant for silver nanorods—variations in the process occur only through changes in time and temperature. These discrepancies can be mostly attributed to the concentration of silver nanorods in solution.

Each subgroup made goals and a timeline of deadlines for achieving these objectives. iGroups was the primary source of communication between IPRO team members, who read pertinent articles and subsequently uploaded these articles to iGroups under appropriate folders established by each subgroup.

### 4.1. Lab

The laboratory group's first research topic dealt with the time-sensitivity and color-changing properties of silver nanorods. The first challenge to be addressed was the synthesis protocol needed to produce viable silver nanorods. Multiple methods can be employed in the production of silver nanorods: each procedure requires a significant number of chemical compounds, which may or may not be limited to those listed in the following table:

Compound	Use
Silver nitrate	Reduced to extract silver
Sodium Borohydride	Reducing agent
Ascorbic Acid	Reducing agent
Cetyltrimethylammonium Bromide (CTAB)	Stabilizer
Trisodium Citrate	Stabilizer
Polyvinyl Pyrrolidone (PVP)	Capping agent, stabilizer
Polyethylene Glycol	Promotes nanorod growth, stabilizer
Sodium Hydroxide	Controls pH, reaction rate

Table 1: Chemical Compounds used to Produce Ag Nanorods <sup>10, 21, 1</sup>
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Methods considered by the IPRO 348 laboratory team for the synthesis of silver nanorods included an electrochemical approach and a method utilizing seed-mediated growth.<sup>21</sup> The final method that was considered is known as Oblique Angle Deposition (OAD).<sup>11</sup> This method is geared specifically toward the production of optimally proportioned nanorods for the process of



Surface-Enhanced Raman Scattering (SERS).<sup>5, 10, 16, 34</sup> Further information regarding SERS and its applications can be found in Appendix E. The laboratory team elected to synthesize silver nanorods through a pre-formed seed mediated solution. This protocol has also been referred to as the "wet chemical synthesis" of silver nanorods.<sup>20</sup>

Safety is the number one priority in the laboratory at all times. Use of laboratory supplies and equipment should be done with the utmost concern for the safety of all people working in the laboratory. Disposal of chemicals should be done only after proper precautions have been accounted for. This can be done with the aid of peers and advisors; undergraduates cannot be expected to know how to dispose of all chemicals properly, so the lab group consulted with our advisor and listed all the chemicals used and how to properly dispose of each one.

The silver nanorod growth solution was comprised of silver nitrate (AgNO<sub>3</sub>), ascorbic acid, CTAB, sodium hydroxide (NaOH). The silver nanorod seed solution was procured using silver nitrate (AgNO<sub>3</sub>), sodium borohydride (NaBH<sub>4</sub>), and ascorbic acid. Sodium borohydride functioned as a reducing agent for silver nitrate, while the presence of ascorbic acid ensured stability of the newly formed seeds.

Cetyltrimethylammonium Bromide (CTAB) solution was prepared as a component of the growth solution through suspension in water and continuous stirring while being kept at 30° C via water bath—this was performed to prevent re-crystallization of the CTAB solution, which would naturally occur at the ambient temperature in the laboratory. (see Appendix C)

It was necessary to observe a yellow change in solution color following the addition of sodium borohydride to ensure proper formation of the seed particles. The seed solution was then left for two hours before being ready for use in nanorod formation. It was assumed, from Professor Perez-Luna's experience and lack of experimental data, that the seed solution must be grown into nanorods within five hours of matriculation. Aluminum foil was employed to prevent light from altering the properties of the seed solution.

The seed and growth solutions were combined in varying ratios to yield batches of silver nanorods. To track the formation and decay of the silver nanorods, the absorption spectra were repeatedly measured at intervals throughout the experiment. Batches of silver nanorods were split into separate vials and stored at various temperatures.

Spectrographic analysis of these initially produced nanorods confirmed, from expectations, that they changed their length-to-diameter ratio and color with respect to the passage of time and ambient temperature. The shape of the nanorods transitioned from elliptical rods into spheres as the nanorods "decayed".

The first several weeks of experimental data were used to create an improved protocol. (see Appendix C) This new protocol was tested until nanorods were consistently created and was employed in the latter half of the semester to create many batches of nanorods. These new batches were used by other subgroups, including the scale-up and prototype subgroups.

To efficiently make use of lab availability and obtain sufficient data, the laboratory group was split into two smaller groups. The two teams went into the lab on different days to run experiments. Both groups were able to verify their results through repeated experiments which also provided more data for quantitative analysis.

Each team eventually ran different experiments to test more variables and obtain additional data. Laboratory research was performed under supervision of either the faculty advisor or graduate students and was executed using proper safety protocols. Findings, results, and observations were recorded in a lab notebook and in Microsoft Word and Excel formats to be shared via iGroups.

4



# 4.2. Scale-Up

The scale-up team's main objective was the increased production of silver nanorods using a continuous process. The previous IPRO attempted to create a continuous process by combining the reactants along a tube, similar to a plug flow reactor (PFR) but at laminar flow rates. This was done because the lab procedure required "gentle mixing" of the CTAB, seed, AgNO<sub>3</sub>, ascorbic acid, and NaOH solutions in order to produce quality nanorods.

The scale-up subgroup researched protocols that could accommodate these specifications and potentially result in better yields, which included methods that had already been implemented for continuous production of nanorods. After the lab group made a break-through in the protocol that allowed for more vigorous agitation, the scale-up group researched more common mixing methods and focused on creating a continuous scaled process in the laboratory through use of a continuously stirred tank reactor (CSTR).

# 4.3. New Technology

The New Technology subgroup's goal was to research different production methods of nanoparticles, the possibilities for commercialization of silver nanorods as a thermal indicator, and new technological applications for silver nanorods. The new technology subgroup also sought to gain professional insight on the active research of silver nanoparticles. Various team members communicated with professors from IIT and other institutions.

The Environmental Protection Agency's (EPA) website was searched extensively for information regarding regulations on nanotechnology. For regulations regarding the integration of nanotechnology with consumer products, as well as commercial nanotechnology approvals, students accessed the Food and Drug Administration's (FDA) official website.

# 4.4. Prototype

The prototype sub-group researched different types of plastics in the initial stages of design. Progress was achieved using trial and error in the laboratory. All prototype procedures attempted in the laboratory were suggested or approved by Professor Perez-Luna. (see Appendix F)

# 5. Analysis and Findings

### 5.1. Lab

The laboratory group generated spectrographic data over the course of the semester. The most powerful tool that we had for analyzing data was the model provided by the preceding IPRO. This model predicts how the ratio of a nanorod's width to its height (aspect ratio) will affect how it absorbs light across the spectrum of visible light. (see Appendix A)

A key feature in the model is that total light absorbed by a nanorod increases monotonically as the rod's aspect ratio increases. Thus, longer nanorods tend to absorb greater amounts of light. Additionally, as the aspect ratio increases, the single absorption peak resolves into two separate peaks and the distance between them increases. This transition correlates to the formation of a nanorod from a nanosphere.

Combining this information with the fact that absorption of a nanorod solution is linearly dependent on its concentration, this creates a framework by which nanorods can be evaluated. While working on developing rigorous and quantitative methods, our qualitative method relied



on the fact that higher peaks at higher wavelengths correlate to higher yields and higher aspect ratios. In other words, if we compare the spectral absorption of two samples and observe that one sample has a higher-amplitude peak than the other, then it must necessarily have either higher-aspect ratio nanorods or a higher concentration of nanorods, both of which are desirable.

Additionally, if one sample possesses a peak that is at a larger wavelength, it must have a greater concentration of high aspect-ratio nanorods. These statements can be simplified into a rule of thumb: a batch of nanorods may be considered to be of higher quality if its spectral absorbance peaks are "bigger and to the right".

High concentrations of reducing agent (10 M NaOH) resulted in the production of large amounts of short nanorods. At these high concentrations, lower amounts of seed solution generally produced lower concentrations of nanorods. At medium 5 M concentrations of NaOH, the lowest amount of seed solution produced the greatest concentration of nanorods, but no overall trend could be readily discerned.

At the lowest tested concentrations of reducing agent, 1 M NaOH, the least amount of seed solution promoted the greatest amount of nanorod concentration and length. While holding seed solution concentration constant, a strong trend was observed: by increasing the amount of reducing agent (NaOH) used, the nanorod length was reduced. Yield was also reduced in most trials, but no general trend was observed.

# 5.2. Scale-Up

The scale-up team researched alternative methods which included the polyvinyl pyrrolidone (PVP) method and the sodium dodecylsulfonate (SDSN) method.<sup>16, 19</sup> In the PVP method, the polyvinyl pyrrolidone acted as a reducing and capping agent. Literature showed that this reagent allows for the formation of silver nanorods without the need for seed crystals.<sup>16</sup> The PVP method was shown to create a high yield of nanorods, however this method of synthesis has already been patented, and therefore royalties would have to be paid to commercially utilize this method.<sup>43</sup> An additional method of creating silver nanorods examined the use of sodium dodecylsulfonate (SDSN) as a capping agent as opposed to using CTAB.<sup>16</sup> In being similar to the PVP method, the production of nanorods did not require a seed solution. However, it was concluded that the SDSN method resulted in higher yields of nanowires, an undesirable product. The original protocol was deemed sufficient for scale-up production.

Depicted below is the silver nanorod production process flow diagram which employs the use of a CSTR. Additionally, two methods were proposed for the synthesis of nanorods: a method in which CSTR was coupled with a proposed PFR and a method in which only CSTRs were used.

# AgNANO



Figure 1: Silver Nanorod Production Process Flow Diagram

#### 5.2.1. PFR:

As seen below, the PFR process only required a single pump for each stream of starting materials. In large scale production, it was determined that this process would require the least amount of materials and equipment. Under small-scale nanorod production, it was found that the size of equipment and slow flow rates resulted in insufficient mixing.



Figure 2: Suggested PFR Synthesis Process

### 5.2.2. CSTR:

The second method, depicted below, was tested in the laboratory and employed three CSTRs. This method provided adequate mixing of the reactants and resistance to disturbances.

# Ag NANO



#### **Figure 3: CSTR Synthesis Process**

Aspects of the CSTR investigated in the laboratory included the reactor volume and the residence time. Based on the synthesis protocol and the amount of time the two solutions were stirred after mixing, it was determined that the 95% confidence interval for the residence time was 1 to 10 minutes. The residence time,  $\tau$ , remained the same as the process was scaled up. The flow rates and volume of the reactor were determined by equipment readily available in the laboratory which consisted of three peristaltic pumps and two voltmeters. According to the lab procedure, the optimal volume ratio of the CTAB solution to the ascorbic acid solution is 17:1; the best achievable ratio of the flow rates was 3:1. As a solution to this limitation, the concentrations of both solutions were altered so that each required a 1:1 flow rate ratio while a combined concentration constant was maintained.

In order to determine the flow rates, the two feed pumps were connected in parallel to a voltmeter and operated at 5 volts and 1.5 mA of combined current. The flow rates of the feed pumps were determined by recording the time taken to fill a graduated cylinder. As a result of the laboratory trials, the two feed rates were determined to be roughly equivalent, with about 3% deviation. The controller of the product pump had a dial to control the pump speed, and the dial was calibrated to different flow rates using the same test as that which was used to measure the flow rates of the feed pumps.



Figure 4: Product Pump Calibration

8



The total flow rate used was approximately 0.006mL/sec; each feed flow rate was measured to be around 0.003mL/sec. A 3% difference between experimental flow rate values was observed, and by using the values of residence time and product flow rate determined in the laboratory, the calculated volume of the reactor was found to vary from 0.3 mL to 10 mL. Under these parameters, a trial was performed in which feeds were pumped from a 40 mL beaker into the reactor, which was a 50mL glass beaker with a stirring rod. The product was pumped from the bottom of the beaker using a third peristaltic pump. The rate of the pump was adjusted until a steady level of 7 mL was observed in the reactor. Once the system remained at steady state for 15 minutes, a sample was collected and studied. The resulting spectrum was analyzed, and it was determined that few nanorods had been created; the product included more nanospheres than the desired nanorods. It was suggested that a better yield could be achieved by increasing the concentration of AgNO<sub>3</sub> tenfold while maintaining a low seed concentration.

# 5.3. Toxicity and Disposal

The generally accepted medical range for elemental silver concentration in human urine is 0.4 to 1.4  $\mu$ g/L—prolonged exposure to fluids of either concentrated aerosolized or colloidal silver can result in an epidermal condition known as argyria, where urine concentrations of silver can be over 200 times greater than the norm.<sup>6</sup> Argyria is usually characterized by a blue-gray discoloration of facial cutaneous tissue, and on a microscopic level, argyria can be visualized (via histologically-stained light microscopy or scanning electron microscopy) by the deposition of silver granules in the basal membrane layer of epithelial tissue, such as hair follicles.<sup>25</sup> Although silver concentrations can build up within the liver, kidneys, corneas, gingival, mucus membranes, nails, and spleen, no serious health complications have been recorded in argyria cases, outside of [apparently permanent] cosmetic damage.<sup>6, 25</sup>

The cellular cytotoxic effects of silver nanoparticles have been recently well-documented: exposure produced gross, radical alterations in the cellular morphologies of epithelial tissue, indicating that integrity of the cytoskeletal structures within these cells had been compromised. Additionally, the majority of exposed cells failed to float in solution under light microscopy, leading to the conclusion that these cells had died from widespread necrosis.<sup>1</sup> Preliminary examination of energy (ATP) levels in the mitochondria of exposed cells revealed that silver nanoparticles exhibited both a time- and dose-dependent inhibitory relationship on the cellular metabolic cycle: ATP production inactivity peaked between 2 and 3 days' time and exhibited linear behavior with respect to the concentration of the silver nanoparticle exposure solution.<sup>1</sup>

Genotoxic effects from exposure to silver nanoparticles on the intracellular level have also been investigated: dose-dependent damage to DNA in cells exposed to silver nanoparticles slowed the cell-cycle by forcing the cell to stop at the  $G_2/M$  checkpoint in order to effect DNA repairs, and this effect was even more pronounced in tumor cells, which exhibited a greater propensity to engage in apoptosis than that which was observed in healthy cells exposed to silver nanoparticles.<sup>1</sup> A separate study found that silver nanoparticles possess the capability to bind and form a complex with DNA, raising its  $T_m$  (melting) temperature—this indicated that the conformation of the superhelical DNA structure had been altered by re-adjusting the non-planar and tilted orientation of DNA bases from their natural positions.<sup>35</sup>

While clinical data has shown that an excess of gaseous or colloidal elemental silver in the body does not present serious medical complications from argyria, the consequences of a large concentration of silver nanoparticles on the cellular level from biological laboratory research has implied otherwise: in order to avoid either of these societally undesirable outcomes, effective disposal methods will need to be developed and enforced to minimize hazardous exposure to



elemental silver or silver nanomaterials in commercially-available products and healthcarerelated devices.

The commercialization of nanotechnology has displayed an exponential growth pattern over the past several years: given that nanomaterial applications are not confined to the limits of any single industry, research data estimates indicate that up to half a dozen nanotechnology-based products may be entering commercial markets per week by the end of 2010.<sup>37</sup> MSDS safety reports discussing the physical properties, chemical hazards, and disposal practices of two types of silver-based nanomaterials list that silver nanoparticles are considered and disposed of by the American Environmental Protection Agency (EPA) and the Canadian Domestic Substances List (DSL) as hazardous waste, yet specific disposal methodologies for these nanomaterials are neither clearly defined nor readily available.<sup>29, 30</sup> Hazards associated with elemental silver or CTAB include inflammation if absorbed through the skin and irritation if ingested, inhaled, or if brought into contact with the eyes.<sup>29, 30</sup>

Previous research has shown that silver nanoparticles exhibit potent cytotoxic and genotoxic effects on healthy epithelial tissue, and general case studies examining argyria, which is characterized by permanent blue discoloration of the epithelium, investigated the gross physiological effects resulting from elemental silver over-exposure.<sup>1, 6</sup> Further speculation has postulated that nanoparticles, when disposed of in wastewater treatment, will either dissolve in water or agglomerate through a net attractive Van der Waals force that exceeds the nanomaterials' repulsive electrostatic force.<sup>37</sup> Agglomeration of silver nanoparticles represents a serious health concern for aquatic species that may inadvertently ingest the substance<sup>29, 30</sup>, and while no currently widespread and comprehensive solution exists for the treatment and safe disposal of silver nanomaterials, creation and optimization of disposal methodologies will be of great importance over the next decade as nanotechnology proliferates throughout global commercial markets. (Further information regarding the organizations that the American government has established to deal with potential environmentally-toxic nanomaterials may be found in Appendix E)

# 5.4. Heat Transfer



Figure 5: Heat Transfer Schematic for Silver Nanorod Thermal Indicator Label

Since the basis of a thermal indicator is that it can accurately monitor the temperature of the environment, understanding the heat transfer throughout the device is essential. For the heat



transfer model of the thermal indicator, the silver nanorod solution was assumed to be encapsulated in a capillary tube, as this allows for established heat transfer equations to be used. Steady state heat transfer was assumed at every instant so as to simplify the model for calculating the values of heat transfer as opposed to changes in temperature per unit time. Because there is a greater temperature difference between  $T_{out}$  and  $T_1$ , there will be greater heat transfer in this region than in the contact area with the food packaging. This indicator did not take the ends of the capillary tube into account. The resulting equation is depicted below.<sup>12</sup>

$$q = \frac{T_1 - T_4}{\frac{1}{(h_o A_o)} + \frac{r_o - r_i}{k \frac{A_o - A_i}{\ln(A_o/A_i)}} + \frac{1}{h_i A_i}}$$

### 5.5. Prototype

Before beginning production of a physical model, several thermal indicator concepts were drafted. (see Appendix F) At the start of the prototype production, several types of materials were obtained to prepare different design concepts. These materials include Nalgene labware vials, Plexiglas, styrene sheets, Silicone Elastomer Base, Silicone Elastomer Curing Agent, plastic lab wrap, and glass pipettes. After careful consideration of the drafted designs and the available supplies, the prototype team decided that silicone rubber would be the optimal material to encapsulate the nanorods due to its capacity to be cast in a mold of desired specifications. (see Appendix F) The molds needed to form the silicone rubber were created using Lego pieces, small glass trays and plastic lab wrap. Materials used to make the label were double stick tape, packing tape, and white printing labels. After some trial and error, a general procedure was created for producing the plastic to encapsulate the silver nanorod solution. (see Appendix F)

The team members have worked throughout the semester to develop a prototype that is cheaper and more reliable than current commercial competitors. After making the needed calculations, the groups determined the cost to be \$0.20: this figure includes the price of chemicals, the materials used to make the prototype and the label upon which the nanorods' color gradient will be printed. Other manufactured thermal indicators on the market include Time Strip, All Living Things Liquid Crystal Thermometer, Tip Temp and Warm Mark. A comparison of the prices and features of these thermal indicators can be found in Appendix F.

### 6. <u>Conclusions and Recommendations</u>

The production process of silver nanorods must be refined before commercialization can occur. The existence of several production methods further complicates this goal. However, as different technological applications emerge, optimal dimensions for silver nanorods can be specified, and thus their creation can be directed to meet those specifications. The nanoparticles' thermochromic behavior makes them competitive against current commercial thermal indicators. Silver nanorod thermal history indicators will fare well on the market because of their irreversible color change, expansive color gradient, and ease of production through a small number of readily available chemicals. In terms of diagnostic applications, funding should continue to be allocated for silver nanorod production. The destructive nature of many viruses makes early detection a priority for the healthcare industry and for the greater community; silver nanorods show great promise as an aid in virus detection.<sup>36</sup>



The next IPRO should attempt different methods of silver nanorod production, namely the OAD method that prepares favorable SERS substrates. In addition, students should develop a method to measure the accuracy of the time/temperature dependency of the silver nanorods. Despite the fact that the IPRO 348 members experienced difficulty contacting nanotechnology professionals, continued correspondence with these individuals is necessary to gain deeper insight on the topic.

#### 6.1. Lab Group

The lab team began with limited information on silver nanorod formation and little to no knowledge about the lab protocol but was able to create consistent, high quality batches of silver nanorods via seed-mediated growth. This protocol was designed by the lab team and includes the major finding that mixing order was critical to the formation of nanorods. Using this lab protocol, the group was able to repeat experiments to not only verify the ability to produce nanorods, but to also test other variables that affect nanorod formation and properties. In order to properly create silver nanorods, the lab protocol (see Appendix C) must be followed with these key points: use 1 M NaOH in the intermediate solution, add the solutions in the proper order, and shake the final solution to ensure proper mixing.

The lab group concluded that the optical phenomena of silver nanorods are time and temperature dependent. Reactant concentrations have an impact on the lifetime and quality of silver nanorods. Color change of the solution indicates the decay of the nanorods into nanospheres. Nanorods left in warmer conditions tend to form nanospheres more quickly than those left in cooler conditions. Applications of this project rely heavily on the temperature dependence of the silver nanorods; therefore, it is very important to determine exactly how to control the temperature dependence properties. The lab group found that nanorods do indeed have temperature dependence but did not go into further detail regarding how this sensitivity could be properly controlled. Many additional experiments must be performed to fully determine the temperature-based properties of silver nanorods and how these qualities can be effectively controlled for use in commercial applications.

Time dependence studies can be performed by creating consistent, high quality batches of nanorods and monitoring them over time. Spectrographs should be taken during routinely spaced time intervals along the nanorods' lifetime. This data will be critical for analysis of the nanorods. Temperature dependence experiments can be completed by placing nanorods in environments with various ambient temperatures; more spectrographic data should be periodically taken to determine nanorod temperature dependence. As greater amounts of high-quality data become available, more insightful conclusions can be made and verified.

For the continuation of this project, it will be necessary to further verify the laboratory protocol created and used through this semester. While many experiments have been run, the laboratory protocol should be the most important aspect in nanorod formation experiments. Once the protocol has been verified, many different experiments can be performed. These include time dependence, temperature dependence, and reactant concentration experiments. Changing the reactant concentrations will further verify the laboratory protocol and test how the properties of nanorods can be effectively controlled. Silver nanorod formation is a new procedure, and it is critical to understand how the input variables affect the performance of the nanorods in potential commercial applications.



All of this information can be used to detail exactly how nanorods are formed and for which applications they can be utilized. Alternatively, the needs of the application can be taken into account, and nanorods can be formed to meet these standards. Application requirements and data analysis will merge in the creation of competitive commercial applications for silver nanorods.

Future IPRO teams should account for the importance of laboratory safety when creating silver nanorods. It is costly to waste materials, break equipment, and it can be very time-consuming if certain precautions are not taken. Nanorods can be created and used for testing but not created for the sole purpose of taking up lab time. Every experiment should have a purpose such that data can be taken efficiently and analysis can be effectively performed. The project should continue as long as the application of nanorods can be shown to be safe, cost effective, and beneficial to society.

#### 6.2. Scale-Up

The scale-up subgroup designed, created, and tested a continuous method of producing nanorods using a CSTR. While the scaled process resulted in the successful production of silver nanorods, the yield could be improved. In order to improve the yield of nanorods, future IPROs would benefit from using pumps with a greater range of variable speeds. This would allow the continuous process to more closely mimic the protocol developed by the laboratory team. For larger scale equipment, a 17:1 ratio of the CTAB to ascorbic acid flow rates would be more appropriate in the scale-up of the lab procedure.

## 6.3. Prototype

The prototype team created two thermal indicators containing the silver nanorods. One of these designs used a Nalgene vial to contain the silver nanoparticles; the other used silicone rubber to encapsulate the nanomaterials. Both designs used the same label design.

It is clear that the advantages of IPRO 348's prototype outweigh its potential setbacks. The team's thermal indicator is cheaper by an average of \$0.50, while its expansive color gradient suggests the device is more accurate. Comparatively, the temperatures to which the silver nanorods are sensitive vary more than that of the competitive products (see Appendix F). Recommendations for future prototype developments should further capitalize on the characteristics of the silver nanorods. It is also recommended that future team members expand on a thermal indicator design in terms of materials used as well as the possible packaging and shipping of the devices.

Prototype designs incorporating a hydrogel to suspend the nanorods should also be considered, as this would potentially allow better containment of the nanorods in the case of a broken label, which would minimize the risk to the environment and human health.

#### 6.4. Toxicity and Disposal

A significant amount of research is still needed to reach a final conclusion on the implementation of nanotechnology in commercial products. Government organizations are recognizing nanotechnology as a viable pursuit but are taking necessary precautions before deeming such products safe for consumers.<sup>31</sup> It is important to develop emergency protocols in the event of accidental contact with potentially toxic materials. The FDA and EPA have encouraged the production of nanomaterials but stress the importance of performing quality control and safety trials prior to commercial distribution.<sup>7, 31</sup> Though no specific regulations



currently exist for the mass production of nanomaterials, the EPA has a basic procedure in place. This procedure requires manufacturers to provide the EPA with comprehensive information concerning the specific nanomaterial so the EPA can determine its potential environmental effect.<sup>7</sup>

While clinical data has shown that an excess of gaseous or colloidal silver in the body does not present serious medical complications, biological research has shown that silver nanoparticles possess cytotoxic and genotoxic properties on a cellular level.<sup>1, 35</sup> Agglomeration and inadvertent ingestion of silver nanoparticles in bodies of water also represents a serious health concern for aquatic species.<sup>29, 30</sup> In order to avoid undesirable outcomes, effective disposal methods will need to be developed to minimize hazardous environmental exposure to silver nanomaterials in commercially-available products.

The next IPRO should keep in mind that as more information becomes available about the effect of nanoparticles on the environment, the EPA will release new regulations concerning nanoparticle production. It is important that future plans for production remain flexible to change in order to accommodate for these new regulations. Our successors should also continue studying the toxicity of silver nanomaterials. If team members can develop protocols that effectively gauge and protect against the hazards of silver and CTAB, the technology will take another step towards commercial production.

Suggestions for future work include developing a methodology for detecting silver nanoparticles in the atmosphere and pursuing a deeper understanding of how silver nanoparticles are absorbed and transported in the human body.



# 7. Appendix

7.1. Appendix A (Figures):



Figure 6: Nanorod formation at 1 M NaOH and 25°C



Figure 7: Nanorod Formation at 0.045 mL Seed Solution and 25°C

# AgNANO



Figure 8: Nanorod Formation at 5 M NaOH and 25°C



Figure 9: Nanorod Formation versus Time



# 7.2. Appendix B (References)

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# 7.3. Appendix C (Lab Protocol):

# 7.3.1. Purpose:

- 1) To make silver nanoparticles on a lab-scale using a continuous process
- 2) To test the differences between a CSTR and PFR reactor for this process

# 7.3.2. Materials:

- 1) AgNO<sub>3</sub>
- 2) Trisodium citrate
- 3) NaBH<sub>4</sub>
- 4) Ascorbic acid
- 5) Hexadecyltrimethylammonium bromide (cetyltrimethylammonium bromide or CTAB)
- 6) 3 peristaltic pumps, rubber tubing, regular tubing (dimensions TBD)
- 7) 4 Beakers
- 8) PFR with a 'Y' connector

# 7.3.3. Method:

- 1) All glassware used for these experiments should be clean and free of particulate materials. If the experiments show aggregation of the seed solution (see below) it may be necessary to clean the glassware with aqua regia (3:1 concentrated HCL to HNO<sub>3</sub>) and the solutions may need to be filtered.
- 2) The experiment will last about 2 to 5 hours, for within that timeframe must the silver seed must be used due to a thin film or particles appearing at the surface after 5 hours.
- 3) 20 mL of solution will be prepared with a final concentration of 0.25 mM AgNO<sub>3</sub> and 0.25 mM trisodium citrate in water. To improve accuracy it may be necessary to prepare 10X solutions (i.e. 2.5 mM AgNO<sub>3</sub> and 2.5 mM trisodium citrate) so they can be diluted 1:10 in water prior to synthesis.
- 4) Heat the previous solution to 50-60°C first. While stirring vigorously [small stirring rod], 0.6 mL of 10 mM NaBH₄ is added and stirring is stopped after 30 seconds. The solution should change color from transparent to yellow (sometimes green but this is not desired). Wrap the vial in aluminum foil.
- 5) Measure the optical absorption spectrum of the seed solution (obtained in the previous step). There should be a strong absorption peak centered around 390-395 nm. If the peak appears at wavelengths larger than 400 nm or if it shows a shoulder extending to larger wavelengths this may indicate partial aggregation of the nanoparticles, which is not desired for further nanorod synthesis. If the solution is aggregated repeat the synthesis again.
- 6) The seed may be used between 2 to 5 hours after preparation.



# 7.3.4. Nanorods:

- In order to make the nanorods themselves, first a solution will be prepared containing 0.25 mL of 10 mM AgNO3 and 10 mL of 80 mM CTAB. Use a larger pipette when measuring out CTAB in order to avoid foaming.
- Then, 4 nm seed solution in amounts of 0.25 mL, can be added to the previous solution. Longer and shorter nanorods can be made with lower or larger amounts of seed solution respectively.
- 3) In a separate solution, mix 0.50 mL of 100 mM ascorbic acid with 0.10 mL of 1 M NaOH. (0.025)
- 4) Each solution should be pumped into the reactor (either the CSTR or the PFR reactor) using peristaltic pumps. There should be thorough mixing.
- The flow rate ratio should be 10.5 to 0.6 AgNO3/CTAB/Seed to Ascorbic Acid/NaOH. (Different flow rates and reactor volumes will be tested for the two types of reactors). The target residence time is 1 to 10 minutes.
- 6) The outlet stream will exhibit a color change from red, to brown, to green depending on seed concentration.
- 7) Measure the optical absorption spectrum of the formed nanorods. There should be two peaks present.

# 7.3.5. Separating and Quality Testing:

- 1) Each solution contains a mixture of rods and spheres. Separate the nanorods from the spheres by centrifugation. The centrifugation speed and duration will depend on the aspect ratio of the nanorods formed.
- 2) Measure the optical absorption spectra in order to determine the quality of the nanorods.
- 3) The aspect ratio of the rods increases with decreasing seed concentration.
- 4) If the nanorods are of good quality, centrifuge them again and resuspend in CTAB solutions of concentrations 80 mM, 10 mM and 1 mM. Split the nanorod solutions in three vials and incubate each at room temperature, 4 °C and 37 °C. Take photographs periodically to record color changes. Also measure the optical absorption spectra in order to record the changes quantitatively.



# 7.4. Appendix D (Scale-Up):

The first step required in making the nanorods is the production of a silver seed solution. The production of seed solution takes about 2 to 5 hours. Within that timeframe (2 to 5 hours), the silver seed must be used due to a thin film or particles appearing at the surface after 5 hours. To begin production of the seed solution, all glassware used for these experiments must be clean and free of particulate materials. If the experiments show aggregation of the seed solution, it may be necessary to clean the glassware with aqua regia (3:1 concentrated HCL to HNO<sub>3</sub>) and the solutions may need to be filtered.

First, 20 mL of a solution is prepared with a final concentration of  $0.25 \text{ mM AgNO}_3$  and 0.25 mM trisodium citrate in water. To improve accuracy, it may be necessary to prepare 10x solutions (i.e. 2.5 mM AgNO<sub>3</sub> and 2.5 mM trisodium citrate), so they can be diluted 1:10 in water prior to synthesis. Next, the previous solution is heated to about 50 to 60°C. While stirring vigorously with a small stirring rod, 0.6 mL of 10 mM NaBH<sub>4</sub> is added and stirring is stopped after 30 seconds. The solution should change color from transparent to yellow (sometimes green but this is not desired). The vial is wrapped in aluminum foil.

The optical absorption spectrum of the seed solution (obtained in the previous step) is then measured. There should be a strong absorption peak centered around 390-395 nm. If the peak appears at wavelengths larger than 400 nm or if it shows a shoulder extending to larger wavelengths, this may indicate partial aggregation of the nanoparticles, which is not desired for further nanorod synthesis. If the solution is aggregated, repeat the synthesis again.

The next step is to produce the nanorods. In order to do this, four solutions need to be made in addition to the seed. The four solutions are, .25 mL of 10mM AgNO<sub>3</sub>, .50 mL of 100 mM ascorbic acid, 10 mL of 80 mM CTAB, and .10 mL of 1 M NaOH. These solutions then need to be mixed in the correct order. First, the AgNO<sub>3</sub> solution, the CTAB solution, and 180  $\mu$ L of seed solution are mixed in a 20 mL vial.

Next the NaOH solution and the ascorbic acid solution are mixed in a separate vial. From there, the mixed NaOH and ascorbic acid solution is added to the AgNO<sub>3</sub>, CTAB, and seed solution. Then proceed to shake the vial to mix it. There should be a color change first seen instantly and then continuing to change over the next 10 minutes. The color should go from a yellow, to red, to purple, to a final color of blue. The absorption spectrum from 300 nm to 800 nm should then be measured and if the procedure was followed correctly, there should be two peaks, one between 400 and 500 nm and the other larger peak between 500 and 600 nm.

This procedure can be done with varying volumes of seed solution used and varying concentrations of NaOH used. Varying the volumes and concentrations where modify the final color achieved and absorption spectrum achieved. After the solution has finished changing colors, approximately 10 minutes, 2 mL of the solution was transferred into a 2 mL eppendorf vial and put into the centrifuge for 3 minutes at 16,000 RCF. Coming out of the centrifuge, all the nanorods should be at the bottom of the eppendorf.

If the nanorods are collected on the sides of the vial, re-suspended the nanorods by shaking the solution and re-centrifuge them for a shorter time. Using a pipette, the nanorods are resuspended in a second eppendorf vial with 1 mM CTAB. The concentration of the CTAB can be modified to vary the decay time of the nanorods; the larger the concentration of CTAB, the slower the decay. As the nanorods decay, the absorption spectrum can be taken at various points to show how both the peaks change.



### 7.5. Appendix E (Research):

One of the most promising applications for silver nanorods is the diagnostic capabilities associated with Surface-Enhanced Raman Scattering (SERS). In this technique, the surface of a material is bombarded on a molecular level by photons, which scatter the surface plasmon at a particular frequency or energy, permitting for the specific identification of biological constituents.<sup>34</sup>

SERS has been used to identify common virus strains (through their miRNA) through the unique scattering properties of these virus strains' surfaces.<sup>10</sup> This phenomenon is simply known as Raman Scattering: the surface-enhanced prefix implies that with the aid of a particular substrate, the spectroscopic signal can be greatly enhanced. It has been found that when silver nanorod arrays are placed on top of viral RNA-coated glass slides, the Raman spectra can be enhanced to the order of ten to the eighth power.<sup>5</sup>

The OAD method of production is employed to produce nanorods of desirable length, diameter and density (nanorods per square micrometer).<sup>11</sup> Information from the literature has indicated that these dimensions can be approximated to 900 nm, 100 nm, and 13 nanorods per  $\mu$ m<sup>2</sup> of area.<sup>11</sup> From a diagnostic standpoint, this technology possesses the capacity to become extremely beneficial. SERS could play an integral part by aiding in the early detection of Human Immunodeficiency Virus (HIV).

The time required to obtain results could be shortened to days, compared with weeks or even months through traditional techniques such as the polymerase chain reaction (PCR), antibody detection or Western Blot assays.<sup>38</sup> Additionally, SERS may also lessen risks for obtaining false positive/negative results since its accuracy is grounded in genetic screening and is not implemented through mass DNA amplification or protein identification.<sup>38</sup>

The government agency that is most concerned with the incorporation of nanomaterials into consumer products is the FDA; to that end, the FDA commissioned the Nanotechnology Task Force. This task force strives to encourage the development of nanotechnology while ensuring that the proper guidelines be followed throughout the process.<sup>31</sup> Furthermore, the representatives of the task force desire to keep the public as informed as is necessary on the topic of nanoparticles and the possibilities of the chemicals becoming part of everyday life in the near future.<sup>31</sup> The task force, established in August of 2006, seeks to continue to promote and protect public health but realize that technology is taking science and medicine in the direction of nanoparticles integration.<sup>31</sup>

The EPA's website specified the current regulations of the manufacture of nanoparticles: anyone considering manufacturing new nanoparticles, which are those not already listed in the TSCA Chemical Substances Inventory, must provide the EPA with necessary information concerning the nanoparticles.<sup>7</sup> The EPA will use this information to make sure that the new chemical will not endanger the environment or human health. For the manufacture of existing nanoparticles, the EPA requires a Significant New Use Notice, in order to ensure that the manufacture of the product follows environmental and safety procedures.<sup>7</sup>

The National Nanotechnology Initiative is an ongoing project that was created to task different government organizations to conduct as much vital information as possible on the topic of nanotechnology. Its first conference on October 6-7, 2009, had an agenda that involved creating research strategies, communicating with organizations about the environmental effects of nanoparticles and assessing the overall progress of nanotechnology.<sup>40</sup>



# 7.6. Appendix F (Prototype):

### 7.6.1. Thermal Indicator Label Construction

- 1) **Note:** It is prudent that no curing agent be mixed into the container of pure base, and vice versa. Use caution when using the UV light, as looking directly into it can cause irreparable vision damage.
- 2) Remove the lid of the container of Silicone Elastomer Base and add it to a small, disposable cup. The base is very viscous, and so the easiest way to take it out of the original container is by using a disposable pipette tip to scrape the base onto the sides and drip it into the cup. Leave enough room in the cup to add the curing agent. These must be added together in a 10:1 volumetric ratio of base to curing agent.
- 3) Once enough base has been added to the cup, replace the lid on the base container, and place the pipette tip to the side to be used later. Remove the cap on the Silicone Elastomer Curing Agent, and pour enough into the disposable cup to create the 10:1 ratio. Recap the bottle of pure curing agent.
- 4) Mix the base and curing agent vigorously using the pipette tip until well-mixed. This occurs when bubbles can be seen throughout the mixture.
- 5) Pour the mixture into the mold. For the prototype, two pieces are needed. One is the part with the cavity for the nanorods to be placed, and the other is the flat backing to seal in the cavity. Both pieces start out as a flat backing.
- 6) For the flat backing, a small glass tray is used, and only one batch of silicon is needed per tray. After pouring the silicone mixture into the tray, it is set aside until the bubbles have all disappeared.
- 7) After the bubbles have disappeared, the mixture can then be left to harden overnight, or placed under a UV light to speed up the process.
- 8) Use the UV light with caution. Do not look directly into the light. It has a delay after turning the switch to ensure there is no accidental blinding. Do not look directly at light to check if it's working. Use a white sheet to find highest intensity of the light, and place the tray underneath it. Remove the silicone mixture from the UV light once it has hardened.
- 9) To produce the cavity, start with a hardened silicone mixture in a small glass tray. Make two more batches of silicone mixture and pour them on top of the hardened mixture in the tray. Once the bubble have disappeared, gently place a Lego piece facedown into the mixture until the wet silicone rises along the sides of the Lego piece. Leave it to harden overnight.
- 10) Once pieces are hardened, carefully separate the silicone rubber from the glass tray and Lego piece.
- 11) Use a pipette pump to measure and place 30  $\mu$ L into each cavity in the silicone rubber created by the Lego piece.
- 12) Spread wet silicone mixture along the hardened flat piece and stick to the piece of silicone rubber with the cavity, sealing the cavity with the wet silicone mixture. Place under the UV light until hardened.



#### 7.6.2. Specifications of Materials

Nalgene labware vials were originally considered for encapsulating the silver nanoparticles. Upon seeing the sample vials, however, they were determined to be too large and bulky for a practical label. The next idea was to use sheets of clear styrene that could be melted into a desired form and then sealed. One of the major concerns with this method was using of heat to seal the plastic so close to the nanoparticles which are heat sensitive. This method could potentially shorten the life of the thermal indicators, or even ruin their effectiveness altogether.

The actual transparency of the styrene sheeting was also a concern with this design. Another design idea was to carve wells into sheets Plexiglas for the silver nanoparticles to be placed, and then seal them together. The drawback to this idea was the thickness of Plexiglas made it impractical to stick on a container such as a milk carton. Finally, the prototype team decided to try using silicone rubber to encapsulate the silver nanoparticles due to the ability to control the thickness of the product and the transparency of the material.

After reviewing the five designs, the first to be tested was the cylindrical cavity. A silicone rubber base and curing agent were mixed to create a viscous liquid that sets into rubber over time. When mixing, one volume unit of the base should be added to ten volume units of the curing agent. The mixture, when poured into a mold, will spread out to create a thin flat layer. It can then be left alone to dry or placed under UV light to quicken the process. To create the cavity, three layers were used.

The first was a flat layer, the second used the top of a large square Lego piece to form the cylindrical cavities. The last layer which has yet to be attached to the other two was another flat layer to cover the cavities. So far, one three-layer label has created 36 cavities, however, only one label has been made. This first label was made to test the durability and appearance of silicone rubber, not to create an efficient label. Efficiency will be tested on the next label model to be made. This shows hope for one label to have more than 36 cavities, and for less silicon rubber to be wasted in the process.



#### 7.6.3. Discussion of Designs

There were five main designs for the prototype to be created. The first option consisted of a flat adhesive label. It was hoped that the silver nanorods would be applied as if it were dye to a section of the label. However, without extensive testing, it is still unsure if the nanorods would be able to function over time as dye.

The second option was a cylindrical cavity within a plastic to encapsulate the nanorods. This model stood out because it was small, simple, and appeared efficient in cost. Also, because of the small size it may be difficult to see the color of the nanorods.

The third option would use a section of the product itself as a cavity to place the nanorods and rest of the label with a piece of plastic to seal the opening. Although this would eliminate extra material protruding from the product, it would be very costly to change the manufacture of each container only to be used for nanorods.

In the fourth option, a thin tube would serve to encapsulate the nanorods. The tube and the label would then be attached to the product. Our team could not find many advantages for this design.

The last option included a thin plastic cavity large enough to hold a packet of nanorods and the label which would be attached to the product. This product was appealing because not only would the shape of the product not have to be altered, but the plastic cavity would be able to form to curved and flat products.

Indicator Name	Visible Characteristics	Time/ Temperature Dependence	Reversible?	Product Focus/Target	Comparison to Ag Nano	Price
Ag Nano	Color change: blue – purple – orange – yellow	Primarily Time – Temp quickens process	No	Food Label	N/A	\$0.21
Time Strip	Red dye only; Numbers	Time with singular temp. threshold	No	—Food (Baby food, defrost watch) —Cosmetics	<ul> <li>Only time dependent</li> <li>Must be activated</li> <li>Disposable</li> </ul>	\$4.99 (for 16 pack)
Warm Mark	Red dye only; "Brief", "Moderate", and "Profound"	Time; single temp. focus only	No (Can be stopped)	—Food —Medical Supplies	—Exposure to temp. higher than threshold —Range: 18°-37°C (8-48 hours)	\$1.44
Thermax	Label	Temp. Violation Indication	No	—Food —Other industrial products	<ul> <li>—Automatic activation</li> <li>once temp is surpassed</li> <li>—Range: 84°-108°F</li> </ul>	\$1.75
All Living Things	Wide ranging color gradient	Temp. only	Yes	Animal Tanks – Mostly reptilian	—Liquid Crystal technology	\$3.99
Tip Temp	Change from white to black	Temp. only	No	—Food —Other industrial products	—Range: 35°-140°F	\$0.50 (Must buy 100)
3M Monitor Mark	Blue moves across window	Time and Temp.	No	—Food	<ul> <li>—Choose one time</li> <li>—Higher temps move</li> <li>blue quicker</li> </ul>	\$4.20 (Must buy 20)
T100 Temp Label	"OK", "Over/Under Conditions", Indicators Light up one color	Temp.	No	—Food —Pharmaceuticals	<ul> <li>Measure temp. at 1</li> <li>min. increments</li> <li>Range: -18°- 55°C</li> <li>Battery Operated</li> </ul>	\$16.27

#### Table 2: Table of Competitors' Prices

# 7.7. Appendix G (Business/Cost Analysis):

# 7.7.1. Project Budget

Items needed in the laboratory were purchased from Sigma Aldrich®, Millipore ®, and Lab Safety Supply.

Table 3: Lab Purchases						
Vendor	Item Number	Item Name	Quantity	Price		
Millipore <sup>®</sup>	UFC503024	Centrifugal Filter	1	\$92.00	\$110.00 <sup>+</sup>	
Sigma Aldrich®	Z239119	Pour Boats	1	\$40.10	6212 G1 <sup>‡</sup>	
Sigma Aldrich®	Z190543	Scintillation Vials	1	\$239.50	\$313.64	
Lab Safety Supply ®	144166L	Best <sup>®</sup> Powder-Free Nitrile Gloves	1	\$10.20	\$20.67	
Total Price				\$ 381.80	\$444.31 <sup>§</sup>	

### 7.7.2. Total Budget

The expenditure for laboratory materials totaled to \$444.31.

Table 4: Cost Analysis o	f Laboratory Materials

		Price/Bottle	Amount/Bottle	Amount/Batch	Price/Batch
Item Number	Seed Solution	(\$)	(g)	(mg)	(\$)
204390	AgNO <sub>3</sub>	250	1250	8.4	0.00168
S1804	TSC	330	5000	14.7	0.00097
213462	NaBH <sub>4</sub>	100	139.5	3.1	0.00222
	Nanorod Solution				
204390	AgNO <sub>3</sub>	250	1250	1.91	0.00038
A5960	Ascorbic Acid	500	269	176.52	0.32810
H9151	СТАВ	195	250	293.7	0.22908
S8045	NaOH	1000	119	7.9931	0.06717
	Total				0.62961

 <sup>&</sup>lt;sup>†</sup> Invoice was not received, approximated total cost
 <sup>‡</sup> Items were shipped together from vendor
 <sup>§</sup> Total Price including the shipping and handling



# 7.8. Appendix H (Contact Information):

- 1) Dr. Yiping Zhao. University of Georgia. 221 Riverbend Research South Laboratory, 220 Riverbend Road, Athens, Georgia. <u>zhaoy@physast.uga.edu</u>. (706) 542-2843.
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- 3) Dr. Sandra Bishnoi. Illinois Institute of Technology. 3105 South Dearborn Street, Chicago, Illinois. <u>bishnoi@iit.edu</u>. (312) 567-8922.



# 7.9. Appendix I (Team Members):

#### **James Cheever**

James is a senior majoring in chemical engineering. As the leader of the ethics sub-group, James studied the seven layers of ethics and focused on the ethical issues surrounding the IPRO project throughout the course of the semester, while also participating in weekly meetings with the new technology sub-group. Towards the end of the semester, James assisted the poster and brochure groups through minor input, advice, and oversight.

#### **Edward Chiem**

Edward is a CHE 296 student. For the majority of the semester Edward was part of the lab team working on silver nanorod synthesis. He helped create a new protocol for making silver nanorods. When the teams were re-organized, Edward joined the final presentation team and assisted in creating the PowerPoint for the IPRO day presentation.

#### **Andre Colmenares**

Andre is a CHE 296 student. At the beginning of the project, Andre was part of the New Technologies research group. As the project progressed and became more focused on the implementation of silver nanorods as thermal indicators, he was responsible for creating the heat transfer model that determined that the silver nanorod solution, would use the outside temperature as the cause for color change. During the final preparations for the project, he was a member of the presentation group and also color corrected the lab photographs for use in the final project.

#### **Matthew Dado**

Mat worked in the lab group. He contributed to writing a lab protocol based on academic research. Mat was the leader of one of the lab groups that created nanorods in the second week of class. Mat worked extensively with the Midterm Presentation group to prepare and give the Midterm Presentation. After the midterm, Mat continued to work with the lab group and also focused efforts on the final report. Near the end of the semester, his efforts were focused on the Final Report, Final Presentation, and helping the group to understand the results of the lab work. Mat also was on the Final Presentation team and presented on IPRO Day.

#### Elena Dorr

As team leader, Elena's responsibilities included the management and the organization of IPRO 347. She led class meetings and coordinated with sub-group leaders. She worked hard preparing meeting agendas and leading the group toward collective decision making. She conducted research in the lab with Mat and Dan, where they successfully synthesized and tested batches of silver nanorods. In addition, she completed academic research concerning scale-up, creating the first scale-up designs with Fernando, Mat, and James. Much of her research during the semester was focused on the applicability of the product and the concerns and causes of food borne illness around the world. She also worked hard to prepare deliverables and to mentor her peers in project management skills and report writing. She worked extensively on all of the deliverables.

#### Fernando Gomez

For this semester's IPRO Fernando worked with the scale up team. For the first part of the semester he focused on alternative methods of creating silver nanorods. He researched different mixing strategies in an attempt to scale-up the original lab protocol. After the lab protocol was changed in a way that strong mixing was acceptable, he focused on creating a continuous method of the new lab protocol. He determined the flow rates of the reactors, and the volume of the reactor. For the last part of the IPRO he worked to find other commercial uses for silver nanoparticles. He determined competitor thermal label costs in comparison to IPRO 348's prototype label.



#### Joshua James

Josh was part of the lab and presentation sub-groups. He focused on the production of pre-seed solutions, the collection of UV-VIS spectra of nanorod solutions, and the IPRO day presentation.

#### **Madeline Jensen**

Madeline worked with the scale-up group at the beginning of the semester. She investigated alternative methods for the production of silver nanorods that would be better suited to a continuous process. She worked with the design and testing of the CSTR continuous process. Additionally, she helped the new technology group determine aspects of the safety and the disposal of silver nanorods. Finally, she contributed to the editing of the final report.

#### Katherine Lazicki

Katherine was a member of the Ethics subgroup, the New Technology subgroup, and the Prototype subgroup. This semester, she made a presentation summarizing the 7 layers of ethics for the IPRO team and researched the EPA regulations concerning the production of nanoparticles. She also helped to develop a prototype thermal indicator using the silver nanorods.

#### **Matthew Lumnitzer**

Matt was an IPRO 296 student who was a member of the scale-up team. During the first few months, Matt helped the scale-up team determine the best method for producing silver nanorods continuously on a large scale. He researched current commercial suppliers of silver nanorods, alternate methods of producing silver nanorods, and plug-flow reactor technology. Later in the semester, Matt worked in the lab to build and test a continuous flow process model. Matt also researched safe applications of colloidal silver for the ethics group and helped write and revise the conclusions in the final report.

#### **Emmanuel Marcha**

Emmanuel was part of the Business Team and primarily focused on graphic design throughout the semester. Being one of the few that had knowledge of Adobe Illustrator and Photoshop, Emmanuel decided to dedicate his time tediously working on the poster and brochure for IPRO Day. Emmanuel also designed the poster used for a competition sponsored by the American Institute of Chemical Engineers (AIChE), as well as another competition sponsored by the Society of Women Engineers (SWE). Emmanuel was able to hone his design skills and learn more about Chemical Engineering throughout the course of this IPRO.

#### **Daniel McClelland**

Dan is a CHE 296 student. Dan initially was on the Lab Team and worked on the synthesis of silver nanorods. Later on when the teams were changed, Dan was on the presentation team where he helped the presenters create and edit the presentation.

#### Aurash Mohaimani

As a member of the ethics, new technology (research), and prototype sub-groups, Aurash participated in major phases of the writing and editorial revisions regarding the project plan, abstract, and final report deliverables, in addition to suggesting the original concept behind the milk gallon/carton for the thermal indicator label's placement.

#### Ngozi Nwangwa

As leader of the new technology sub-group, Ngozi primarily conducted research. Over the course of the semester, she scheduled and led regular sub-group meetings. She suggested the technology of SERS (Surface-Enhanced Raman Scattering) to be what the group identified as the most promising application of silver nanorods. Once this designation was made, the group moved to gather information related to the toxicity of silver nanorods, seeing as this step was vital to the initiation of its future commercialization. She took the initiative to contact faculty actively conducting any relevant research. She compiled and edited significant portions of the final report.



#### Erica Payne

During her first IPRO, Erica was able to participate in a preview of what she will be doing when she begins her career. She learned a lot from being in the prototype team and was able to merge her artistic skills with design efficiency to create a group of feasible ideas for the final prototype. By communicating with the team, Erica learned that every team member is capable of contributing valuable input towards achieving common project goals.

#### Amber Purcell

Amber was in the New Technology group. She assisted in researching applications of silver nanorods, and writing up the product specifications for the prototype. She worked on the final prototype with Katie by trying to create the silicone rubber wells. She also helped edit the final paper.

#### Andrew Raddatz

Andy was a part of the business team and focused on the formatting of the various deliverables. He used his knowledge of Microsoft Word to make things look nice. He produced an animation that was played continuously during IPRO day. He made minor contributions to the poster and brochure teams.

#### **Michael Server**

Michael was part of the lab team with Matt and Charlie and part of the poster/brochure team. He prepared solutions and made nanorods for the Monday/Tuesday lab group.

#### **Charles Sizer**

Charlie contributed to the lab group by interpreting the data produced from a mathematical point of view. He organized the data into forms usable by the rest of the team and future IPROs. In the build up to IPRO day, he worked with the poster, presentation and final report group to provide graphics and rigorous interpretations of the data.

#### Willy Taracena

Willy was the leader of the business team, a member of the prototype team and the poster/brochure team. As part of the business team, he developed and maintained a budget for the IPRO. Willy also oversaw any tasks that were assigned to the business team. He assisted with the edits and finalization of the Project Plan and the Poster. As part of the prototype group he investigated the toxicity of the silver nanorods. As part of the poster group he helped with visual aspects and edits.

#### **Ryan Tillman**

As a sophomore in this IPRO, he was introduced to the IPRO system. He was a member of the scale-up team, and also worked a little bit in the lab. As a member of the scale up team, he helped develop the continuous process that was used to produce nanorods. Ryan was also a part of the poster and brochure team.

#### Anna Vassi

Anna is a ChE496 student. In the beginning and for the greater part of IPRO, Anna was the leader of the Lab subgroup which focused on nanorod synthesis and data analysis. She also performed research to aid the scale-up team and worked briefly with the prototype subgroup. She assisted with the formation of the project plan and then towards the end of the semester, Anna was part of the Poster & Brochure team and assisted with designing the visual aids and handouts for IPRO Day.

#### **Meghan Wiebe**

At the beginning of the semester, as part of the scale-up team, Meghan went to the weekly meetings and worked toward subgroup goals. She focused her research on the PVP method. Later in the semester, Meghan went into the lab with the scale-up team where they participated in further research into the continuous process. Finally, at the end of the semester, she joined the final paper team where she worked toward completing the goals set forth by that team. Meghan also helped the group leader with poster design.