Dickinson College Dickinson Scholar

Student Honors Theses By Year

Student Honors Theses

5-20-2012

Synthesis and Characterization of Fluorescent Bio-Reduced Copper Oxide Nanoparticles

Katelyn Ann Cohen Dickinson College

Follow this and additional works at: http://scholar.dickinson.edu/student_honors Part of the <u>Chemistry Commons</u>

Recommended Citation

Cohen, Katelyn Ann, "Synthesis and Characterization of Fluorescent Bio-Reduced Copper Oxide Nanoparticles" (2012). Dickinson College Honors Theses. Paper 61.

This Honors Thesis is brought to you for free and open access by Dickinson Scholar. It has been accepted for inclusion by an authorized administrator. For more information, please contact scholar@dickinson.edu.

Synthesis and Characterization of Fluorescent Bio-reduced Copper Oxide Nanoparticles

By Katelyn A. Cohen

Submitted in partial fulfillment of Honors Requirements for the Department of Chemistry

Sarah K. St. Angelo Ph.D., Advisor

Rebecca E. Connor Ph.D., Reader Michael S. Holden Ph.D., Reader Kristi J. Humphreys Ph.D., Reader Cindy Samet Ph.D., Reader

May 4, 2012

Contents	Page Number
Abstract	3
Introduction	3
Experimental	6
Results	8
Discussion	15
Conclusion	20
Acknowledgements	21
References	21
Supplemental Information	22

Abstract

Cu₂O nanoparticles have become of growing interest for their applications in catalysis and electronics; however, few environmentally friendly and straightforward synthesis processes exist to produce these nanomaterials.¹⁻⁴ With the potential need for efficient nanoparticle syntheses in industry, the world of plant-based reducing agents has become of interest for their great availability and low environmental impact.⁵⁻⁸ Herein, I describe a onepot synthesis via the reducing agents in lemongrass to produce 1-10 nm spherical Cu₂O nanoparticles of a fluorescent nature. These particles have been characterized using UVvisible spectroscopy (UV-vis), fluorescence spectroscopy, high resolution transmission electron microscopy (HR-TEM), powder X-ray diffraction (XRD), and atomic absorption spectroscopy (AA). They display a small absorbance in the visible range and have a sizedependent fluorescence emission band near 453 nm. The relative quantum yield of these particles was found to be 0.0061±0.0019, an order of magnitude larger than some other Cu₂O nanoparticles.³ HR-TEM imaging reveals a lattice spacing of 2.4 Å, indicating the Cu₂O oxidation state. In addition, particle size control has been demonstrated by varying reactant ratios within the synthesis mixture. This room temperature, one-pot synthesis shows promising results for producing Cu₂O nanoparticles in a low cost, environmentally friendly process.

Introduction

Copper (I) oxide (Cu₂O) is a *p*-type metal semiconductor,¹⁻⁴ which has become of increasing interest with potential applications in solar energy conversion,¹ catalysis,^{1-3, 9} and optoelectronic devices.²⁻³ The natural abundance of its starting materials, its nontoxic nature,

and reasonably good electronic and optical properties make Cu₂O study attractive in the area of semiconductor science.¹ Cu₂O has a high optical absorption coefficient, low band gap energy (2.2 eV), and is thus, a good candidate for low-cost photovoltaics.¹⁻² In addition, Cu₂O has been recognized to have applications in catalysis, particularly in the area of water splitting for hydrogen production.⁹⁻¹⁰

Due to their increased surface area to volume ratio, Cu₂O nanomaterials in particular have shown unique properties, which differ from their bulk counterpart.²⁻³ The nanomaterials have optical absorption with observable blue-shift in absorbance or fluorescence emission upon decrease in diameter as a result of quantum size, morphology, and crystallinity effects.^{3,4} They also show increased stability and greater catalysis capacity since bulk materials are readily converted to CuO when exposed to air.^{3, 9-10} Thus, with an everincreasing list of applications, straightforward, environmentally friendly syntheses for Cu₂O nanoparticles are potentially desirable for translation to industry.

Many methods of Cu₂O synthesis have been developed in recent years, including those to produce nanoparticles of varying shape and size. Methods have included techniques such as microemulsion,² thermal decomposition of copper (I) acetate in the presence of surfactant,¹ and reduction of cupric nitrate in the presence of fructose and ascorbic acid under alkaline conditions.³ The problem with many of these synthetic methods is that they often involve high temperature, multi-step preparation, or the use of toxic or environmentally harmful products. Thus, a one pot, mild reaction condition synthesis process to produce Cu₂O in large quantities may become of value in an industrial setting. The production of nanomaterials with simplified waste removal requirements could make a synthesis process of this nature even more valuable in industry.

Many nanotechnologists look to plant-based extracts and teas to create reducing agents capable of synthesizing various metal and semiconductor nanoparticles.^{5-8, 11-12} Many different phytochemicals,⁶⁻⁷ reducing proteins,⁸ and reducing sugars⁵ can be found in these plant-based materials, making them an attractive option for performing green synthesis techniques. As an added benefit, many of the reducing agents found in these materials not only act to reduce metals to create nanoparticles but also serve as capping agents. Capping helps to stabilize nanoparticles in solution to create homogeneous colloid mixtures.⁵⁻⁷ Thus, the use of plant-based agents may be not only more environmentally friendly and cost-effective, but also allows for long-term storage of these nanomaterials.

Within this thesis, I describe a one-pot synthesis of Cu₂O nanospheres of controlled diameter with a fluorescent character through the use of lemongrass as a reducing and capping agent. This method, developed from a previous method for gold nanotriangle production by Shankar *et al.*¹¹⁻¹² proceeds at room temperature with a lemongrass extract serving to reduce CuSO₄•5H₂O to Cu₂O nanoparticles. Size control was demonstrated by varying reducing agent ratios, and the quantum yield of these fluorescent particles was determined. Particles were imaged via high-resolution transmission electron microscopy and visualization of the lattice fringes allowed for Cu₂O identification via 2-D Fourier transformation. Initial attempts at isolating the size of the reducing agent within the lemongrass extract was achieved through the use of molecular weight cutoff filters.

Experimental

Nanoparticle Preparation

To create the extract, lemongrass (*Cymbopogon citratus*) was obtained from Wegman's grocery store and was thoroughly cleaned with house deionized water (diH₂O). 100 g of lemongrass was then chopped into 1-cm pieces and placed in 500 mL of boiling diH₂O. The mixture was allowed to boil for five minutes and then was cooled to room temperature. The mixture was filtered to a threshold of 0.2 μ m and stored as lemongrass extract (LGE) at 2° C.

To synthesize nanoparticles, a 0.001 M CuSO₄•5H₂O solution was made in diH₂O. CuSO₄•5H₂O (98%) was purchased from Acros Organics and used as received. To prepare 14 mL of nanoparticles, 10 mL of 0.001 M CuSO₄•5H₂O, 3.8 mL of LGE, and 0.2 mL of deionized water are combined in a flask, mixed well, and allowed to react at room temperature for one week. The solution produced is a cloudy, green-yellow color with a fluorescent appearance. Particles were stored at 2°C (If biological material was seen in solution, it was removed via filtration using 0.2 µm filters).

Characterization

UV-vis data was obtained on a HP 8453 UV-visible spectrometer thermostatted at 25°C and fluorescence emission data was obtained on a Jasco FP 6200 Fluorimeter at an excitation wavelength of 326 nm, at room temperature, using quartz cuvettes of 1 cm path length. High-resolution TEM images were obtained on a JEOL 2010 FE-TEM at The Pennsylvania State University Materials Research Institute. All samples were prepared by

placing a drop of Cu₂O nanoparticle solution on CF200-Ni-500 grids obtained from Electron Microscopy Sciences. Grids were allowed to dry for one hour at room temperature.

Synthesis Variation

To test synthesis size control, the previously described procedure was altered by varying reducing agent and 0.001 M CuSO₄•5H₂O relative volumes. The total volume was always kept to 14 mL, with the ratios tested shown in Table 1. Samples were then

Sample	Volume LGE (mL)	Volume 0.001 M CuSO ₄ •5H ₂ O (mL)
1	1.8	12
2	3.8	10
3	5.8	8
4	7.8	6
5	9.8	4
6	11.8	2

Table 1. Reactant volume ratios for size variation syntheses. Samples were allowed to react in the same manner as the standard synthesis process with the 3.8:10 (LGE:CuSO₄•5H₂O v/v) solution taken as the standard nanoparticle sample. All samples included 0.2 mL of deionized H₂O.

Quantum Yield

The relative quantum yield (QY) of the Cu₂O nanoparticles was determined using a previously published method.¹³ A standard curve was generated using a quinine sulfate reference standard¹⁴ that was purchased from Anaspec Inc. The quinine sulfate was dissolved in 0.1 M H₂SO₄, and the emission spectra of quinine sulfate solutions of various concentrations were recorded with an excitation wavelength of 326 nm. The absorbance spectrum of each solution was also recorded at 326 nm. The procedure was repeated for the Cu₂O nanoparticles, which were diluted in diH₂O to generate a nanoparticle curve.

Atomic Absorption Spectroscopy

To determine the copper content within the Cu₂O particles, a Varian 55B atomic absorption spectrometer was fitted with a Cu hollow cathode lamp. The atomic absorption of CuSO₄•5H₂O solutions ranging from 1 μ g/mL to 10 μ g/mL was recorded along with the absorption of the concentrated nanoparticles obtained by aggregating particles in a KCl salt solution and dissolving in nitric acid. A calibration curve was constructed and the copper content of the nanoparticles was determined based on a line of best fit.

X-ray Diffraction

XRD data was obtained on a Philips APD 37207 X-Ray Diffractometer using powder samples. To prepare samples for XRD analysis, multiple attempts at isolating the particles were made. Particles were spun at high RPM for multiple hours, aggregated using KCl, made into gelatin samples via a method described by Chen and Carroll,¹⁵ and lyophilized using a Lab-Conco 4.5 Freeze-Dry system.¹⁶

Reducing Agent Characterization

In an attempt to identify the reducing agent present in the lemongrass extract, Amicon Ultracel regenerated cellulose molecular weight cutoff filters were utilized with thresholds of 50 kDa, 30 kDa, 10 kDa, and 3 kDa. Samples of the lemongrass extract were centrifuged for 45 minutes at 4000 RPM and 4°C in an Eppendorf 5804 centrifuge fitted with a A-4-44 swing arm rotor. The isolated samples were allowed to react using the previously described synthesis process to determine approximate size of the reducing agent.

Results

By modifying the methods of Shankar *et al.*¹¹⁻¹² fluorescent nanoparticles were successfully synthesized. Figure 1 shows the progression of the synthesis process, from

creating the lemongrass extract through final nanoparticle production. It can be seen that all solutions display a slight yellow-green tint, with the final synthesized nanoparticles displaying fluorescent nature, giving the solution a luminous appearance.





Fluorescence data obtained from the synthesis variation experiments can be seen in Figure 2. As the amount of reducing agent in solution was increased (i.e. the LGE), particle solutions have a greater emission intensity and also experience a $\lambda_{em max}$ shift to shorter wavelengths. The solution of nanoparticles which contained 2 mL of 0.001 M CuSO₄•5H₂O and 11.8 mL of LGE (2:12) deviates from the shape of all other emission spectra, with emission between 400-425 nm going below the 4:10 sample and lacking the shoulder displayed by all other samples.

TEM images of the 12:2 and 8:6 samples shows particles of diameter 4.7 ± 1.5 nm in the 12:2 sample and a bimodal population of diameter 2.0 ± 0.4 nm and 3.2 ± 0.7 nm in the 8:6 sample (Figure 3). These two populations are statistically different to the 99% confidence level based on a student's t-test with a sample size of 80 and 133 particles for each population.



Figure 2. Fluorescence emission spectra of Cu₂O nanoparticles produced by varying relative volumes of reagent. With increasing volume of LGE, an increase in intensity and shift to shorter $\lambda_{em max}$ wavelengths is observed. The legend denotes simplified volume ratios of the form "LGE volume-0.001 M CuSO₄•5H₂O volume" rounded to the nearest milliliter.



Figure 3. TEM imaging and sizing histograms for 12:2 (a) and 8:6 (b) relative volume ratio variation samples. The 8:6 sample showed a bimodal population with two diameters of nanoparticles present.

To characterize the Cu₂O nanoparticles, multiple methods were employed. Figure 4 shows the UV-visible absorbance spectrum of the Cu₂O nanoparticles. In examining the visible spectrum a slight shoulder between 350-400 nm can be seen. With the exception of this shoulder, the particles show little absorbance in the visible spectrum, which can be attributed to the fact that these nanoparticle solutions are not highly colored. Figure 5 shows the fluorescence emission spectrum of the Cu₂O nanoparticles at an excitation wavelength of 326 nm, a wavelength determined via an excitation survey scan. The nanoparticles display a $\lambda_{em max}$ at 453 nm with a wide, broad peak observed between 350-600 nm with a shoulder at approximately 410 nm. The nanoparticles display a relatively low emission intensity, reaching a maximum around an intensity of approximately 155, indicating that the particles are fluorescent, but not intensely fluorescent.



Figure 4. UV-visible absorbance spectrum of the Cu₂O nanoparticles. The black arrow shown indicates a small absorbance shoulder between 350-400 nm.



Figure 5. Fluorescence emission spectrum of Cu₂O nanoparticles at an excitation of 326 nm. A peak with a $\lambda_{em max}$ of 453 nm is observed with a slight shoulder at approximately 410 nm.

To further understand the fluorescent nature of the nanoparticles, a relative quantum yield of the particles was determined in comparison with a quinine sulfate reference standard of QY=0.54.¹⁴ Curves for both the reference standard and the nanoparticles were generated by plotting the integrated intensity (defined as the area under the fluorescence emission spectrum between 350-600 nm) versus the absorbance at 326 nm (Figure 6).¹³ Using the curves generated in duplicate for quinine sulfate and the Cu₂O nanoparticles the quantum yield of the particles was calculated using Equation 1:

[Eq.1]
$$\Phi_x = \Phi_{ST} \left(\frac{Grad_x}{Grad_{ST}} \right) \left(\frac{\eta^2 x}{\eta^2 s r} \right)$$

where Φ is the quantum yield of a particular sample (for this equation X denotes the nanoparticles and *ST* denotes the standard), *Grad* is the slope of the generated calibration curve, and η^2 is the refractive index of the solvent. The refractive index of the quinine sulfate solutions was taken to be the refractive index of 0.1 M H₂SO₄ (1.3336) and the refractive index of the nanoparticles solution to be the refractive index of water (1.42424). The average



Figure 6. Calibration curves of the quinine sulfate reference standard (2-left) and the Cu₂O nanoparticles (2-right). Curves were generated by plotting the integrated intensity of the fluorescence emission spectrum versus the absorbance of the solution at 326 nm (the excitation wavelength).

HR-TEM imaging shows approximately spherical particles with high resolution imaging revealing lattice fringes (see supplemental information). A 2-D Fourier transform (FT) of the lattice fringes have 4 spots at high frequency, which, when converted from Fourier space to real space, give a lattice spacing of 2.4 Å (Figure 7). Other TEM images show particles as bright or black spots with an average size of 2.32±0.61 nm across one synthesis and 2.20±0.60 nm across another. The sizing histogram for the 2.20 nm particles can be seen in Figure 8. The 2.32 nm particles were sized using ImageJ over 300 particles across the horizontal axis and the 2.20 nm sizing was performed over 66 particles. Images show a matrix of biological material surrounding the particles, which has proved difficult to

remove.



Figure 7. HR-TEM image of Cu₂O nanoparticles (left) and 2-D Fourier transform (right) with simulated lattice fringe cartoon. Particles are indicated in the HR image by the white circles. The Fourier transform of two of these particles is seen and shows a central region of high frequency with four surrounding regions of high frequency, used to find the distance between the lattice, as seen in the cartoon, in real space.



Figure 8. TEM images of Cu_2O nanoparticles (left and center) and a particle-sizing histogram (right). Particles appear as contrasting spheres on the TEM background and are surround by a biological matrix. Based on the sizing displayed in this histogram, average particle diameter is 2.20 ± 0.6 nm.

AA spectroscopy results show that the overall copper recovered from the nanoparticles is $1.875 \ \mu g/mL$ based on a calibration curve generated using CuSO₄•5H₂O standards (see supplemental information). Original copper concentration within the reactant solution was 5.670 $\mu g/mL$, indicating that 33.07% of copper in solution was converted into nanoparticles. Based on this conversion rate, nanoparticle diameter, lattice spacing, and unit cell calculations reported by Yin *et al.*,¹ the overall nanoparticle concentration in solution was calculated to be 1.27×10^{13} nanoparticles per milliliter of solution or 62 nM.

Preliminary powder X-ray Diffraction results can be seen in Figure 9. Small diffraction patterns are seen at 2 θ angles of approximately 31° and 38°, although the overall spectrum shows little diffraction to noise contrast. In addition, diffraction patterns are difficult to discern due to their overall shape.

Attempts at isolating the reducing agent within the lemongrass showed that all syntheses, <50 kDa, <30 kDa, <10 kDa, and <3 kDa, produced nanoparticles. It was noted that the <50 kDa and <30kDa solutions produced particles before others based upon visual inspection, but all solutions were converted to nanoparticles within the following day.



Figure 9. XRD diffraction pattern of lyophilized nanoparticles. Small diffraction patters of a broad nature can be seen at 31° and 38°, although the overall spectrum shows little diffraction to noise contrast.

Discussion

Based on obtained fluorescence and TEM data, the synthesis described herein appears to be successful for producing similar size, fluorescent nanoparticles. While some particles display a more oval shape, all particles show a relatively spherical nature with an aspect ratio approaching 1 based on visual inspection of the micrographs. In addition, the clear fluorescence maxima seen in the emission spectra show that these particles do in fact display fluorescent characteristics, with emission of light seen at approximately 450 nm when excited at 326 nm. Wang *et al.*¹⁷ also report that Cu₂O nanoparticles produced through reduction of cupric nitrate with hydrazine have a light-yellow appearance, an initial indication that the synthesized nanoparticles were, in fact, Cu₂O.

By observing the fluorescence data obtained for nanoparticles synthesized through varying reactant ratios, a clear increase in $\lambda_{em max}$ with changing ratios of reducing agent and 0.001 M CuSO₄•5H₂O is evident. This result highly supports the idea that increasing or

decreasing the amount of reducing agent changes the size of the particle. In quantum dots of a similar size, $\lambda_{em max}$ has been shown to move to longer wavelengths with increasing particles diameter,¹⁸ supporting that increasing the relative amount of lemongrass extract in solution creates particles of a smaller average diameter. In addition, Shankar *et al.* found that decreasing the amount of lemongrass extract in their solution caused a λ_{max} shift to longer wavelengths and created anisotropic gold nanotriangles of increasing edge length.¹² This directly corresponds to the fluorescence emission results obtained, however, the TEM sizing contradicts this finding.

Based on the obtained TEM data, nanoparticle size appears to have increased with a greater volume of reducing agent in solution. This is opposed to the common trend seen with nanomaterials: a greater amount of reducing agent creates particles of smaller diameter.^{12, 18} Because the populations seen in the 8:6 LGE: CuSO₄•5H₂O sample were bimodal, it is highly likely that the nature of the reducing agent may be the cause of this unexpected trend, particularly with respect to growth versus nucleation. It may be that two elements in the LGE are responsible for these two stages of nanoparticle production. Yang *et al.*³ saw that when larger amounts of fructose (one of the reducing agents within their reaction) were utilized in the synthesis of Cu₂O nanocubes, several of their samples experienced greater growth rate than nucleation rate, and thus, larger particles were formed. However, with increasing fructose concentrations, the usual trend was eventually observed, and smaller particles were seen. The ratio of reducing agent at which this return occurred was 266.4:1, much higher than the ratios studied here of 12:2. It may be necessary in further experiments to explore if this type of trend returns with our own nanoparticles. It will also be necessary to examine the

remaining reactant ratio samples (6:8. 4:10. 2:12) via TEM to absolutely confirm the trend that greater amounts of reducing agent produce particles of greater diameter.

When examining characteristics other than overall size dispersion and general fluorescence, it becomes imperative to examine the quantum yield of these particles, defined as the ratio of photons emitted to photons absorbed. Yang *et al.*³ have observed a quantum yield an order of magnitude smaller than that observed here (0.61%). However, Yang's obtained quantum yield of 0.066% was obtained in the study of Cu₂O nanocrystals with an average length of 28 nm. Because the Cu₂O particles studied here are of different shape and size, it may be that the quantum effects of such a small particle change the way in which the particle emits radiation, allowing for overall greater fluorescence efficiency.³ In addition, the Cu₂O nanoparticles synthesized here may be of greater crystallinity than the Cu₂O nanocubes of Yang, affecting the QY. However, it should be noted that, though these particles display greater quantum yield than other Cu₂O nanoparticles, a quantum yield of 0.61% is still relatively small for fluorescent materials. For example, the quinine sulfate used as a reference standard has a quantum yield of 54%, well in excess of the QY of the Cu₂O nanoparticles, and Daboussi et al.²¹ observed quantum yield of 30-50% for CdSe quantum dots with a ZnS shell with average diameter of 2.3-5.5 nm.

HR-TEM imaging provides the most definitive evidence of the Cu₂O oxidation state. Urban *et al.*¹⁹ found a lattice spacing of 2.46 Å for Cu₂O nanoparticles of a similar size and shape, pointing to similar lattice structure, and thus, overall composition for the particles studied herein. Yang *et al.*³ also found a lattice spacing of 2.4 Å in their Cu₂O nanocubes through the use of FT, increasing the likelihood that the particles synthesized were in fact Cu₂O, as opposed with CuO. Skarman *et al.*²⁰ also found a lattice spacing of 2.4 ± 0.1 Å for

Cu₂O thin films, noting that this spacing length excludes the possibility of metallic copper (spacing of 2.09-2.12 Å).

Obtaining XRD data for these particles proved more difficult than expected. Attempts to aggregate the particles via centrifugation proved fruitless, and attempts to obtain data through gelatin slides showed no discernible diffraction pattern. Analysis of samples aggregated via KCl showed diffraction patterns for the salt materials, and no nanoparticle diffraction patters could be obtained. Lyophilization of the particles proved the best method for sample production and produced clumps of what appeared to be nanoparticles and dried plant-based material. The observed Bragg peaks at 20 angles of 31° and 38° may correspond to the Cu₂O (110) diffraction and the Cu (111) diffraction patterns respectively. Yin et al.¹ saw the Cu₂O (110) diffraction of their Cu₂O nanocrystals at a 20 of 29° and the Cu (111) diffraction at a 20 of 36°. Because of the broad nature and high signal to noise ratio of our observed Bragg peaks, it is difficult to isolate at exactly what angle these diffraction patterns occur. The small size of the particles and the high amount of plant-based material in solution make it difficult to achieve a highly defined diffraction pattern. Because the data obtained herein is highly preliminary, it can be said that the obtained diffraction pattern may show evidence of Cu₂O lattice structure, however, further experimentation will be necessary to fully confirm this hypothesis.

AA Spectroscopy results show a Cu concentration of $1.875 \ \mu g/mL$ in the nitric acid dissolved nanoparticles and based on this information the nanoparticle concentration was determined to be 1.27×10^{13} nanoparticles/mL of solution, leading to an overall concentration of 21 nM. This concentration explains why isolation of these particles was extremely difficult and lyophilization of large volumes of nanoparticle solution was necessary to produce

enough material for XRD analysis. It may also explain why the nanoparticle solution is not intensely colored and shows little absorbance in the visible range.

Because all reaction mixtures containing molecular weight separations of the lemongrass extract reacted to produce nanoparticles, this indicates that the reducing agent responsible for nanoparticle production is of molecular weight lower than 3,000 Da. Shankar et al. hypothesize that reducing sugars present in the lemongrass extract, in particular aldoses, cause reduction of gold nanotriangles.¹¹ It is likely that these reducing sugars act in a similar manner on the CuSO₄•5H₂O present in solution. Shankar et al. also indicated that their nanotriangles were stabilized via the aldehydes and ketones present in solution, allowing for a highly homogenous colloid mixture, which was also seen with the Cu₂O nanoparticles.¹¹ If in fact aldoses in the LGE do serve as the reducing agent for nanoparticle production, this confirms the results seen in the synthesis experiments performed. Because aldoses are monosaccharides with small molecular weights, they pass through the cutoff filters with ease and produce nanoparticles in all reaction mixtures. In addition, Panigrahi et al.⁵ have shown that several simple aldoses can be used as reducing agents to synthesize common metal nanoparticles. While further investigation will be necessary to determine if aldoses are indeed the reducing agent in the LGE, the results obtained herein point to the idea that the reducing agent is not a protein, as average protein mass lies well in excess of 3 kDa.

As mentioned previously, there is also the possibility that two reducing agents exist in solution, one responsible for nucleation and another for growth. This may explain why a bimodal population was seen in the 8:6 sample of the synthesis variation experiment. One population experienced nucleation with a longer growth period and the other a shorter growth period (i.e. the growth causing agent was either less effective or concentrated for this second

population). This may also explain why some samples produced nanoparticles in the MW cutoff experiments before others, as some sample may have had greater nucleation causing reducing agent in solution than others, causing nanoparticle to happen earlier in time in these solutions. Again, further experimentation will be necessary to either confirm or deny this hypothesis.

Conclusions & Future Work

Cu₂O nanoparticles of a fluorescent nature were successfully synthesized via reduction of CuSO₄•5H₂O by extract of the lemongrass plant. This reduction behavior of this plant-based extract may be the result of aldoses present in solution. Size control may have been demonstrated through changes in the experimental conditions, and nanoparticles of larger diameter were synthesized with greater volumes of the reducing agent in solution. Particles show a relative fluorescence quantum yield of 0.61% and a lattice spacing of 2.4 Å with an average diameter of about 2.5 nm for one set of conditions.

Further TEM analysis to confirm the size-control hypothesis will be necessary to definitively demonstrate size control and more extensive XRD analysis will be necessary to fully elucidate the crystal lattice structure and confirm Cu₂O as indicated by the lattice spacing experiments. In addition, definitive identification of the reducing agent will prove helpful in understanding other possible uses for this plant-based reducing agent; organic extraction of the LGE will be employed. In addition, synthesis process changes may be explored in future experiments, possibly in the direction of microwave-mediated synthesis. Understanding the kinetics of this synthesis is also desirable via UV-vis or florescence monitoring, particularly if microwave-mediated synthesis proves fruitful and produces nanoparticles under an even shorter time frame. The Cu₂O particles described herein demonstrate traits which may prove useful in future applications. The simple, one-pot and environmentally friendly synthesis process described should be easily translated to large-scale production. The synthesized Cu₂O nanoparticles also have small diameter, indicating a high surface area: volume ratio, a highly desired trait for catalysis.⁹⁻¹⁰ As CuO nanomaterials are high contenders in the cataysis of hydrogen production via water splitting, these nanoparticles may prove useful in this venue.⁹ The fluorescent nature of these particles also points to possible future applications in optoelectronics and photovoltaics,¹⁻³ another common application for Cu₂O nanomaterials.

Acknowledgements

I must first and foremost thank Professor St. Angelo for her amazing guidance throughout this entire process, this thesis would never have come to fruition without her. I would also like to thank Professor Humphreys for use of her centrifuge, Professor Connor for assistance with lyophilization of the nanoparticles and autoclaving of glassware, and Robert Dean for assistance with the XRD. I would like to thank Dr. Joseph Kulik and Xiaojun Wen for their assistance in obtaining HR-TEM images. I would like to thank Dickinson College and the Chemistry Department for supporting this research along with the CES and SFR grants for providing funding for HR-TEM imaging.

References

- 1) Yin, M.; Wu, C.; Lou, Y.; Burda, C.; Koberstein, J.; Zhu, Y.; O'Brien, S.; J. Am. Chem. Soc. 2005, 127, 9506-9511.
- Suzuki, K.; Tanaka, N.; Ando, A.; Takagi, H.; J. Am. Ceram. Soc. 2011, 94, 2379-2385.
- 3) Yang, Z.; Chiang, C.; Chang, H., Nanotechnology, 2008, 19, 1-7.
- 4) Zahmakiran, M.; Ozkar, S.; Kodaira, T.; Shiomi, T.; Mater. Lett. 2009, 63, 400-402.
- 5) Panigrahi, S.; Kundu, S.; Ghosh, S.; Nath, S.; Pal, T., J. Nanopart. Res., 2004, 6, 411-414.
- Nune, S.; Chanda, N.; Shukla, R.; Katti, K.; Kulkarni, R.; Thilakavathy, S.; Mekapothula, S.; Kannan, R.; Katti, K.; J. Mater. Chem. 2009, 19, 2912-2920.

- Moulton, M.; Braydich-Stolle, L.; Nadagouda, M.; Kunzelman, S.; Hussain, S.; Varma, R., *Nanoscale*, 2010, 2, 763-770.
- 8) Song, J.; Kim, B., Bioprocess Biosyst. Eng., 2009, 32, 79-84.
- 9) Zhu, P.; Li, J.; Zuo, S.; Renxian, Z., Appl. Surf. Sci., 2008, 255, 2903-2909.
- 10) Huang, Z.; Cui, F.; Kang, H.; Chen, J.; Zhang, X.; Xia, C.; Chem. Mater. 2008, 20, 5090-5099.
- Shankar, S.; Akilesh, R.; Ankamwar, B.; Singh, A.; Ahmad, A.; Sastry, M., Nat. Mater., 2004, 3, 482-488.
- 12) Shankar, S.; Rai, A.; Ahmad, A.; Sastry, M., Chem. Mater., 2005, 17, 566-572.
- Jobin Yvon, "A Guide to Recording Fluorescence Quantum Yields," www.jyhoriba.co.uk, (accessed 2/15/2011).
- 14) Fletcher, A.; Photochem. Photobiol. 1969, 9, 439-444.
- 15) Chen, S.; Carroll, D.; Nano. Lett., 2002, 2, 1003-1007.
- 16) Magdassi, S.; Bassa, A.; Vinetsky, Y.; Kamyshny. A.; Chem. Mater. 2003, 15, 2208-2217.
- 17) Wang, L.; Wei, G.; Qi, B.; Zhou, H.; Liu, Z.; Song, Y.; Yang, X.; Li, Z.; Appl. Surf. Sci. 2006, 252, 2711-2716.
- 18) Mutavdžić, D.; Xu, J.; Thakur, G.; Trilulzi, R.; Kasas, S.; Jeremic, M.; LeBlanc, R.; Radotic, K., Analyst, 2011, 136, 2391-2396.
- 19) Urban, J.; Sack-Kongehl, H.; Weiss, K., Z. Phys. D., 1996, 36, 73-83.
- 20) Skarman, B.; Wallenberg, L.; Larsson, P.; Andersson, A.; Bovin, J.; Jacobsen, S.; Helmersson, U.; J. Catal. 1999, 181, 6-15.
- 21) Dabbousi, B.; Viejo, J.; Mikulac, F.; Heine, J.; Mattoussi, H.; Ober, R.; Jensen, K.; Bawendi, M. J. Phys. Chem. B. 1997, 101, 9463-9475.

Supplemental Information



Figure 10. CuSO₄•5H₂O calibration curve for AA spectroscopy experiment. Absorbance values were obtained using a Cu hollow cathode lamp.



Figure 11. HR-TEM image of Cu₂O nanoparticles. Lattice fringes can be seen in the nanoparticles indicated by the white circles.