AN ABSTRACT OF THE THESIS OF

Patrick E. Ramsing for the degree of <u>Honors Baccalaureate of Science in Chemical</u> <u>Engineering</u> presented on <u>May 27, 2011</u>. Title: Comparative studies of batch and continuous processes for the synthesis of copper nanoparticles.

Abstract approved:

Vincent T. Remcho

The cross over from batch nanoparticle synthesis to continuous synthesis processes is crucial to the commercialization of these materials. This project reports comparative studies of batch and continuous synthese of copper nanoparticles by the polyol method. Continuous synthesis of copper nanoparticles was done utilizing a stainless steel micro-mixer that yielded results comparable to batch synthesis. Characterization of copper nanoparticles was done using scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA). Continuous synthesis yielded 15% higher conversion of copper ions to copper nanoparticles than batch synthesis.

Keywords: copper nanoparticles, continuous, process, polyol, micro-mixer Corresponding email: ramsing.patrick@gmail.com ©Copyright by Patrick E. Ramsing May 27, 2011 All Rights Reserved Comparative studies of batch and continuous processes for the

synthesis of copper nanoparticles.

by

Patrick E. Ramsing

A PROJECT

submitted to

Oregon State University

University Honors College

in partial fulfillment of the requirements for the degree of

Honors Baccalaureate of Science in Chemical Engineering (Honors Associate)

Presented May 27, 2011 Commencement June 2011 Honors Baccalaureate of Science in Chemical Engineering project by Patrick E. Ramsing presented on May 27, 2011

APPROVED:

Mentor, representing Department of Chemistry

Committee Member, representing Pacific Northwest National Labs

Committee Member, representing School of Chemical, Biological and Environmental Engineering

Department Head, Chemical, Biological and Environmental Engineering

Dean, University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

Patrick E. Ramsing, Author

TABLE OF CONTENTS

Page
1. INTRODUCTION
1.1 Why copper nanoparticles?1
1.2 Copper nanoparticle batch synthesis methods1
1.3 Continuous synthesis of metal nanoparticles
1.4 Polyol method for the continuous synthesis of copper nanoparticles
2. EXPERIMENTAL DESIGN
2.1 Batch synthesis of copper nanoparticles
2.2 Continuous synthesis of copper nanoparticles7
2.3 Printing of synthesized copper nanoparticles
2.4 Characterization
2.4.1 Scanning electron microscopy11
2.4.2 Transmission electron microscopy and selected area
electron diffraction11
2.4.3 X-ray diffraction
2.4.4 Thermal Gravimetric Analysis12
2.4.5 Yield
2.4.6 Determining size distribution of synthesized
copper nanoparticles13

TABLE OF CONTENTS (Continued)

3. RESULTS14
3.1 Batch synthesis of copper nanoparticles14
3.2 Continuous synthesis of copper nanoparticles
3.3 Scanning electron microscope analysis of
synthesized copper nanoparticles15
3.4 Transmission electron microscope analysis of synthesized copper
nanoparticles16
3.5 Selected area electron diffraction of synthesized copper nanoparticles18
3.6 X-ray diffraction of synthesized copper nanoparticles
3.7 Thermal gravimetric analysis of synthesized copper nanoparticles21
3.8 Yield of synthesized copper nanoparticles
3.9 Size distribution data for synthesized copper nanoparticles
3.10 Printing of continuously synthesized copper nanoparticles
4. CONCLUSION/RECOMMENDATIONS
4.1 Conclusion of project results
4.2 Recommendations for future work27
Bibliography

LIST OF FIGURES

Figure

1.	Schematic of batch process for synthesis of copper nanoparticles by the polyol method. Solutions 1 and 2 were heated in a 120 °C glycol bath. 1.0 mL and 0.25 mL of solutions 1 and 2 respectively were then mixed in a preheated glass vial. After the reaction solution turned black in color signaling the reaction was completed, 2.5 mL of chilled analytical grade de-ionized water was added to quench and arrest the reaction	
2.	Process flow diagram for setup respectively, for the synthesis of copper nanoparticles. Solution 1 and 2 were fed at 0.5 mL/min and 0.125 mL/min to the micro-mixer using stainless steel tubing with an inner diameter of 2 mm. Following mixing the solution was heated to 120 °C in an 85 cm heating coil. Upon exiting the heating coil the copper nanoparticles solution was quenched in analytical grade de-ionized water	
3.	Setup used for jetting of the continuously synthesized copper nanoparticles. An animatics motor controlled a stage which moved the substrate	
4.	Scanned SEM images of continuously synthesized copper nanoparticles with hand traced particles (a) and solid particles(b) filled using MS Paint for further size analysis using ImageJ	
5.	SEM image of batch synthesized copper nanoparticles	
6.	SEM image of batch continuously copper nanoparticles	
7.	TEM images of synthesized copper nanoparticles for batch (a) and continuous (b) processes	
8.	High resolution TEM image of batch synthesized copper nanoparticle. Scale bar is 2nm.	
9.	SAED diffraction patterns of batch (a) and continuously (b) synthesized copper nanoparticles. FCC crystal structure is determined from spacing of the first three rings.	
10.	XRD profile for batch and continuous synthesized copper nanoparticles. Analysis was done at zero and 21 days after synthesis to determine if the particles are oxidizing	
11.	TGA profile for batch synthesized copper nanoparticles under a nitrogen atmosphere. The first weight loss is attributed to solvent evaporation, while the second is due to degradation of the polymer cap	
12.	2. TGA profile for continuously synthesized copper nanoparticles under a nitrogen atmosphere. The first weight loss is attributed to solvent evaporation, while the second is due to degradation of the polymer cap	
13.	Histograms of the synthesized copper nanoparticles data for batch (a) and continuous (b) processes	
14.	Copper nanoparticles printed using HP TIPS device on silicon wafer substrate. Substrate was at room temperature (a) and $100^{\circ}C$ (b).	

LIST OF TABLES

Table	Page	;
1.	Table 1: Parameters used for printing of continuously synthesized coppernanoparticles with HP TIPS device using type 21 print-heads.18	
2.	Comparison of yield results for the batch and continuous processes .Improved mixing during continuous synthesis increases the yield by nearly 15%	
3.	Particle diameter for batch and continuous copper nanoparticles synthesis processes	

Acknowledgements

The author would like to thank the following people for their help with this project:

-Prof. Vince Remcho for giving me the opportunity to work on this project and all the advice and direction given with experimentation.

-Sudhir Ramprasad for all the support and pushing me to be the best researcher that I can be.

-Prof. Greg Herman for serving on my committee and being an amazing professor.

-Todd Miller for providing the micromixer and direction for this project.

-Jack Rundel for always having time to help me with various areas of the project.

-Dan Palo for providing direction and advice throughout the project.

-Jair Lazarzo and Don Higgins for help in the design and construction of the continuous synthesis system.

-Shankar Krishnan for his help with the heat transfer calculations.

-Yi Liu and Teresa Sawyer for all their help with SEM and TEM analysis

-Dan Foster for all his help and patience with TGA analysis

-My wife Erica for all the support she gave me throughout the project

Comparative studies of batch and continuous processes for the synthesis of copper nanoparticles.

Chapter 1 Introduction

1.1 Why copper nanoparticles ?

Copper nanoparticle suspensions are gathering attention for use in inkjet printing applications as a more economical option to other noble metal nanoparticle conductors, such as gold and silver. Copper also do not exhibit the problem of ion migration at elevated temperatures and high humidity that are present with conductive silver contacts[1]. Nanocopper inks can be used for printing of flexible conductive surfaces in diodes, transistors, low-cost sensors, electrical circuits and radio frequency identification tags (RFID tags) [2]. Copper nanoparticles have also been shown to be an alternative to gold nanoparticle catalysts in fuel cells [3].

1.2 Copper Nanoparticle Batch Synthesis Methods

Many methods for batch synthesis of copper nanoparticles have been published using a variety of procedures and reagents. Work has been where the synthesis was conducted in an oxygen free environment to prevent the oxidation of the copper nanoparticles. Abdulla synthesized nanoparticles from copper nitrate in an argon [4] atmosphere, while Shan reduced copper chloride to copper nanoparticles under a nitrogen atmosphere [5]. These synthesis routes were not pursued for this project as one of the final objectives is to use a microfluidic device to manufacture copper nanoparticles under ambient conditions in large quantities for conductive inks. Work was also done using supercritical ethane and propane to synthesize copper nanoparticles [6], but the processes would not allow for integration to a polymeric device easily.

Other processes relied on more aggressive and toxic chemical agents such as hydrazine or borohydride to reduce various forms of copper salt (chloride, sulfate, nitrate and acetate) to copper nanoparticles [7-9]. These synthesis methods used polymers of various molecular weights (10-360K) such as N-vinylpyrrolidone (PVP) [9] and poly (vinyl alcohol) (PVA) [7] to prevent the copper from oxidization.

Cetyltrimethylammonium bromide (CTAB) was also employed with and without polymers to prevent oxidation of the copper nanoparticles produced via reduction of copper salts[8,10]. Using these harsh reducing agents did not line up with the goals which were to find a synthesis pathway that relied on safer and more environmentally friendly reagents. One process was found that did fit the goals by using sodium hypophosphite to reduce copper sulfate in ethylene glycol which was capped by 40K molecular weight PVP polymer to prevent oxidation [1].

1.3 Continuous Synthesis of Metal Nanoparticles

The move from batch synthesis to continuous synthesis will allow for more efficient and economical scaling of processes for manufacturing of nanoparticles. The use of microfluidics is being investigated for these processes for several reasons. The main reason for using micro-mixers and fluidics is that the increased surface area to volume ratio increases rates of heat and mass transfer in the systems. This allows for efficient and even mixing, which then relates to a narrower particle size distribution when compared with batch synthesis techniques [11].

Several methods have been pursued for producing metal nanoparticles in continuous processes. Horikoshi utilized microwave radiation to synthesize silver nanoparticles continuously by reducing diaminesilver [12]. Supercritical pathways have also been used, for instance Veriansyah employed supercritical methanol to synthesize magnetite nanoparticles [13]. Copper nanoparticles were synthesized continuously by Zhang by reducing copper with hydrazine [14]. Zhang's process utilized mixing of two reagents in microchannels with the particles then suspended in a buffer solution to slow the rate of oxidation.

1.4 Polyol Method for the continuous synthesis of copper nanoparticles.

The polyol synthesis method developed by Lee [1] was selected for a starting point for the development of a process for the continuous synthesis of copper nanoparticles. The main objective for choosing a polyol method was that the synthesis is conducted in ambient conditions that will result in pure, metallic copper nanoparticles. The recipe that Lee developed was chosen over others as the reaction temperature was 90 °C which is considerably lower than other polyol recipes that required temperatures of 140 to 200 °C [15]. The lower temperature was desired so the process in the future can be transferred to polymeric microfluidic device. The reagents used by Lee are not as hazardous as what other processes require and also have the potential to be exchanged for more environmentally friendly reagents. Possibilities include but are not limited to finding alternatives to the capping agent or solvent, such swapping out ethylene glycol for propylene glycol.

Chapter 2: Experimental Design

2.1 Batch Synthesis of Copper Nanoparticles

Copper sulfate pentahydrate (CuSO₄·5H₂O), polyvinylpyrrolidone (PVP, MW = 10K), sodium hypophosphite monohydrate (NaH₂PO₂·H₂O), ethylene glycol, ethanol and de-ionized water were all of analytical grade and no further purification of reagents.

Solution 1 was prepared by mixing 1.0 g of PVP and 1.0 g of NaH₂PO₂·H₂O in 10 mL of ethylene glycol. A combination of vigorous mixing with a magnetic stir bar and sonication were used to thoroughly dissolve the PVP and reducing agent. A 1M solution of copper sulfate was prepared for solution 2 by adding 2.5 g of CuSO₄·5H₂O to 10 mL of ethylene glycol. Heating at 100 °C and vigorous stirring for one hour with a magnetic stir bar assisted in homogenizing the CuSO₄ solution.

Solution 1 and 2 were then heated for 10 minutes in a glycol bath maintained at 120 °C. A 15 mL glass scintillation vial was preheated to 120 °C on a hot plate while the reagents were being heated in the glycol bath. 1.0 mL of solution 1 at 120 °C was added to the vial followed by 0.25 mL of solution 2, and the solutions were mixed vigorously by a magnetic stir bar. The color of the solution changed as the reaction progressed, changing from a light green to rust, which progressed to chocolate brown and finally changed to a deep black at which point the reaction solution was quenched with 2.5 mL of de-ionized water and the vial removed from the hot plate and placed in an ice bath to ensure the reaction is arrested. The solution containing black copper nanoparticles was transferred to a 15 mL plastic centrifuge vial after 10 minutes of chilling and centrifuged

at 6000 rpm for 5 minutes using a Thermo Scientific(Asheville, US) Sorvall ST 16 centrifuge. The supernatant was decanted and the nanoparticles were resuspended in 5-8 mL of analytical de-ionized water. The nanoparticle solution was then sonicated to resuspend the nanoparticles to ensure thorough washing and then centrifuged. The rinsing process was repeated, after which the copper nanoparticles were resuspended in analytical grade ethanol and centrifuged. The supernatant was decanted and the copper nanoparticles suspended in 2-3 mL of ethanol for storage.



Figure 1: Schematic of batch process for synthesis of copper nanoparticles by the polyol method. Solutions 1 and 2 were heated in a 120 °C glycol bath. 1.0 mL and 0.25 mL of solutions 1 and 2 respectively were then mixed in a preheated glass vial. After the reaction solution turned black in color signaling the reaction was completed, 2.5 mL of chilled analytical grade de-ionized water was added to quench and arrest the reaction.

2.2 Continuous Synthesis of Copper Nanoparticles

Solutions 1 and 2 (as described in section 2.1) were used in toward the synthesis of copper nanoparticles in a continuous process. Harvard Apparatus (Holliston, USA) PHD 2000 syringe pumps were used along with 10 mL plastic syringes to supply the reagent solutions. Stainless steel tubing with an inner diameter of 2 mm was used with Swagelok (Solon, US) fittings to circulate the reagent streams to the stainless steel micromixer. Channels within the mixer were 200 to 300 μ m wide with critical dimensions of 25 to 50 μ m, which was setup to interleave thin layers of reagent to maximize diffusion and thus more efficient mixing. The syringes containing reagents were connected to the inlet stainless steel lines using PEEK Idex(Oak Harbor, US) fittings. The micro-mixer was placed outside of the heating bath to prevent clogging by copper nanoparticles, which was observed when the reagents were mixed above room temperature. A heating coil of a predetermined length of 85 cm with a residence time of 260 seconds was used to ensure the solution was heated to the desired temperature of 120 °C. A thermocouple at the end of the heating coil measured the temperature in the glycol bath to ensure the solution was at 120 °C. Upon exiting the stainless steel tubing the copper nanoparticles were collected in a 15 mL VWR plastic centrifuge tube containing 8-10 mL of chilled analytical grade de-ionized water. The copper nanoparticles were then purified as described in section 2.1.



Figure 2: Process flow diagram for setup respectively, for the synthesis of copper nanoparticles. Solution 1 and 2 were fed at 0.5 mL/min and 0.125 mL/min to the micro-mixer using stainless steel tubing with an inner diameter of 2 mm. Following mixing the solution was heated to 120 °C in an 85 cm heating coil. Upon exiting the heating coil the copper nanoparticles solution was quenched in analytical grade deionized water.

Solution 1 was pumped at 0.5 mL/min, while solution 2 was pumped at 0.125 mL/min. Before feeding the reagent solutions, ethylene glycol was fed to the micro-mixer for 7-10 minutes at the above flow rates to bring fluid flow through the mixer to a steady-state. The syringes on the pumps were then quickly swapped with syringes containing the reagent solution. Priming the system with glycol was done to minimize the effect of the reagents mixing when flow through the mixer is not yet fully developed. The syringe pumps were calibrated before experimentation using reagent solutions with stainless steel of the appropriate diameter.

2.3 Printing of Synthesized Copper Nanoparticles

Printing of the continuously synthesized copper nanoparticles was performed with an HP TIPS (Thermal Inkjet Picojet System) device. Type 21 TIPS print-heads which use standard inkjet technology were used. These print-heads contain ten nozzles which are 80 microns in diameter. One, two or five of the ten available nozzles were used for printing of the nanoparticles in an effort to print thin discrete electrical contacts. The parameters used for printing the nanoparticles in ethanol are listed in Table 1. Values for voltage and pulse width were taken from recommendations provided by HP for when ethanol is used as the solvent.

TIP ID#: 21				
Back Pressure	1100-1200 Pa	Voltage	29.25 V	
Nozzles Used	1,2 or 5	Period	5000 µseconds	
Pulse Energy	40-60 μJ	Frequency	200 Hz	
Precursor	0.02 µseconds	Pulses	1000-100000	
Gap	0.14 µseconds	Drop per	10000	
Pulse Width	2.5 µseconds	Nozzle	10000	

 Table 1: Parameters used for printing of continuously synthesized copper nanoparticles with HP TIPS device using type 21 print-heads.

Substrates to be printed on to were placed on an automated stage while the TIPS device remained stationary, so that reproducible results could be obtained. The platform was powered by an animatics smart motor (model SM2320SQ-VRE) which was controlled by a desktop computer using smart select interface v. 2004 software made available by animatics. Figure 3 illustrates this setup which facilitated multiple passes to

be made on the same location on a substrate at a constant speed. The height of the printhead above the substrate was kept as small as possible, without contacting the substrate (~1mm). Silicon wafers, glass slides and several polymers (polyimide, polycarbonate and polysulfone) were used for substrates, while most experimentation focused on silicon wafers. Testing was done with substrates at both room temperature and preheated to 100 to 120° C.



Figure 3: Setup used for jetting of the continuously synthesized copper nanoparticles. An animatics motor controlled a stage which moved the substrate to obtain reproducible printing data.

2.4 Characterization

2.4.1 Scanning Electron Microscopy

Characterization of synthesized nanoparticles by scanning electron microscopy was performed using a FEI (Hillsboro, US) Quanta 3D Dual Beam scanning electron microscope at the Oregon State Electron Microscopy Facility. Copper nanoparticles suspended in ethanol were placed onto 1 cm² silicon coupons that were cleaned with analytical grade acetone. Sample coupons were then placed in a vacuum desiccator overnight to thoroughly dry the samples. Platinum and gold was sputtered onto the samples with a Cressington (Watford, UK) sputter coater for 30 seconds before imaging. Imaging was done with accelerating voltages of 15-30 kV in high vacuum (~10⁻⁴ Pa).

2.4.2 Transmission Electron Microscopy and Selected Area Electron Diffraction

Characterization of synthesized copper nanoparticles by TEM was done using a Philips (Hillsboro, US) CM12 Scanning Transmission Electron Microscope (Oregon State Electron Microscopy Facility) and FEI Titan FEG Transmission Electron Microscope (CAMCOR at University of Oregon). Copper nanoparticles suspended in ethanol were placed on molybdenum grids and dried. Operating voltage of 120 kV was used. The FEI Titan was used for high resolution TEM images. SAED was conducted with a camera length of 530 mm.

2.4.3 X-ray Diffraction

Dried copper nanoparticles were placed on a glass substrate. A D8 Discover Bruker instrument was used at 40 kV and 40 kA. Sweep rate was 5 degrees per min $(20^{\circ} \text{ to } 80^{\circ})$ with copper k α radiation.

2.4.4 Thermal Gravimetric Analysis

Thermal gravimetric analysis of synthesized copper nanoparticles was done using a TA Instruments 2950 TGA. 10 mg of dried copper nanoparticles were placed in an aluminum pan and run under a nitrogen atmosphere to prevent oxidation of the copper nanoparticles at a heating rate of 15 $^{\circ}$ C per minute to a maximum temperature of 600 $^{\circ}$ C.

2.4.5 Yield

The yield for batch and continuous copper nanoparticles was determined by gravimetric analysis using a Acculab (Chicago, US) AL-104 analytical balance. Yield was calculated from the mass of nanoparticles synthesized when compared to the mass of copper that was available to react. 90% confidence intervals were calculated using Student t statistics.

2.4.6 Determining Size Distribution of Synthesized Copper Nanoparticles

SEM images of synthesized copper nanoparticle were printed on to standard copy paper. Tracing was done by placing a sheet of carbon paper between the SEM image and a blank sheet of paper. Particles were then traced onto the blank paper along with the scale bar from the SEM image. The paper with the traced particles was then scanned into a tif. file where the particles were filled in using MS Paint. Figure 4 is the scanned traced images after tracing and using Paint to make the particles solid.



Figure 4: Scanned SEM images of continuously synthesized copper nanoparticles with hand traced particles (a) and solid particles filled using MS Paint for further size analysis using ImageJ.

Images with solid particles were analyzed using ImageJ software by defining the scale from the scale given by the SEM and then calculating area by counting pixels. The data was then exported to Excel for calculation of particle diameters.

Chapter 3: Results and Discussion

3.1 Batch copper nanoparticle synthesis

The batch recipe was adapted from a copper nanoparticle recipe published by Lee¹. Adjustments to the recipe were decreasing the molecular weight of the PVP polymer and increasing the reaction temperature from 90°C to 120 °C [16]. The molecular weight of the polymer was decreased from 30k to 10k to minimize the amount of PVP polymer that would need to be decomposed during sintering of the printed nanoparticles into conductive contacts. Lowering the molecular weight of PVP polymer lowered the viscosity of solution 2, allowing it to be used in the continuous process. Scanning (SEM) and transmission (TEM) electron microscopy was used to characterize particle size and shape, while x-ray diffraction (XRD), selected area electron diffraction (SAED) and thermal gravimetric analysis (TGA) was done to characterize particle morphology. Yield and size distribution data was also collected.

3.2 Continuous copper nanoparticle synthesis

The batch recipe for copper nanoparticle synthesis was successfully translated to a continuous process. Process details are outlined in section 2.2. The same instruments and methods used for characterizing batch synthesized copper nanoparticles were employed for the continuously synthesized copper nanoparticles.

3.3 Scanning electron microscopy (SEM) of synthesized copper nanoparticles

SEM images of synthesized copper nanoparticles are shown in Figure 5 and 6 for batch and continuous processes, respectively. Imaged copper nanoparticles have comparable size and shape between the SEM images.



Figure 5: SEM image of batch synthesized copper nanoparticles.



Figure 6: SEM image of continuously synthesized copper nanoparticles.

3.4 Transmission electron microscopy (TEM) of synthesized copper nanoparticles

TEM images of synthesized copper nanoparticles are shown in Figure 7 for both batch and continuous processes. Figure 8 is a high resolution TEM image of batch synthesized nanoparticles where the crystal lattice of the pure copper core is shown with the amorphous polymer cap.





Figure 7: TEM images of synthesized copper nanoparticles for batch (a) and continuous (b) processes.



Figure 8: High resolution TEM image of batch synthesized copper nanoparticle. Scale bar is 2nm.

3.5 Selected area electron diffraction (SAED) of synthesized copper nanoparticles

The lattice structure of the copper nanoparticle core was determined to be facecentered cubic (FCC) for both processes. This was determined using the distance between the center of each image to the first three rings of the SAED pattern. Figure 9 shows the SAED diffraction patterns for the batch and continuous processes.



Figure 9: SAED diffraction patterns of batch (a) and continuously (b) synthesized copper nanoparticles. FCC crystal structure is determined from spacing of the first three rings.

The rings from the SAED patterns were determined to be the (111), (200), and (220) planes using a standard SAED pattern for an FCC gold sample. The planes are identified by the plane spacing (d) which is calculated using Eq. 3.1 where K is 1.598 mm-nm, the camera constant, and R is the radius of the diffraction pattern in millimeters.

$$Rd = K$$
 Eq. 3.1

3.6 X-ray diffraction (XRD) of synthesized copper nanoparticles

X-ray diffraction was used to characterize both batch and continuously synthesized copper nanoparticles. XRD analysis was performed on "as-prepared" synthesized copper nanoparticles. Aliquots of the same samples were then aged for 21 days and analyzed to observe any changes in the crystal structure. Changes to the crystal structure could be due to oxidation of the copper to Cu_2O . Copper oxide is undesired as it increases the electrical resistivity of any sintered copper surfaces. Figure 10 shows the xray diffraction profile for both batch and continuously synthesized copper nanoparticles.



Figure 10: XRD profile for batch and continuous synthesized copper nanoparticles. Analysis was done at zero and 21 days after synthesis to determine if the particles are oxidizing.

There are two forms of copper oxide. Cupric oxide (CuO) is a higher oxide of copper, while cuprous oxide (Cu₂O) is the principal form of the oxide and is the form that is present in the synthesized copper nanoparticles. One way for the amount of copper oxide to be decreased is to increase the molecular weight of the capping polymer, PVP [17]. This is due to interactions between the Cu^{2+} ions in solution and lone pair electrons on the oxygen atom present in the PVP during the nucleation and growth phases of

copper nanoparticle synthesis. The oxygen lone pair electrons are donated to a hybrid orbit of the Cu^{2+} ion, which reduces the susceptibility of the copper ions to oxidation during synthesis. The reduced intensity of the copper oxide peaks for the continuously synthesized nanoparticles may be attributed to more complete coating with PVP due to more efficient mixing that is present in the micro-mixer.

3.7 Thermal gravimetric analysis (TGA) of synthesized copper nanoparticles

Thermal gravimetric analysis was used to estimate the amount of polymer that was coated on the metallic copper core. The mass change vs. temperature profiles for both batch and continuous processes are shown in Figure 11 and 12, respectively. TGA analysis was performed under a nitrogen atmosphere to prevent the oxidation of the metallic copper core. The first drop in the mass of the sample ended near 200 °C and was attributed to the evaporation of the storage solvent. The second drop in mass of the sample tails off near 600 °C, which is associated with the decomposition of the polymer that was coating the copper core of the nanoparticles. This data can then be used to estimate the mass of polymer that was utilized to coat the copper core of the nanoparticles.



Figure 11: TGA profile for batch synthesized copper nanoparticles under a nitrogen atmosphere. The first weight loss is attributed to solvent evaporation, while the second is due to degradation of the polymer cap.



Figure 12: TGA profile for continuously synthesized copper nanoparticles under a nitrogen atmosphere. The first section of mass loss is attributed to solvent evaporation while the second drop in mass is due to degradation of the polymer cap.

The TGA analysis showed that the continuously synthesized particles were coated with more polymer than the batch synthesized particles. For 11 mg of continuously synthesized particles roughly 1.5 mg of the total mass was PVP polymer, while for 16.7 mg of batch synthesized particles the PVP mass was 0.7 mg This result is most likely due to the more efficient reagent mixing in the micro-mixer that then allows for more thorough coverage of the metallic copper core by the PVP polymer.

3.8 Yield for batch and continuous copper nanoparticle synthesis

Yields for copper nanoparticles synthesized by both batch and continuous

processes were calculated. The yield was calculated using Eq. 3.2.

$$Yield = \frac{Mass of copper nanoparticles synth esized}{Mass of copper available during synt esis} \times 100\%$$
 Eq. 3.2

Table 2 shows the results for both processes with 90% confidence intervals. Continuous synthesis gives higher yields by nearly 15%, which is correlated to more efficient mixing of reagents so that more copper ions are converted to nanoparticles.

Process	Yield	Number of samples (n)
Batch	20 ± 1 %	3
Continuous	34 ± 9 %	2

Table 2: Comparison of yield results for the batch and continuous processes .Improved mixing during continuous synthesis increases the yield by nearly 15%.

3.9 Synthesized copper nanoparticle size distribution data

Using SEM images, the size distribution for the synthesized copper nanoparticles was estimated. Histograms for batch and continuous synthesis are shown in Figure 13. The average, standard deviation, maximum and minimum particle diameters are given in Table 3.



Figure 13: Histograms of the synthesized copper nanoparticles data for batch (a) and continuous (b) processes.

Table 3: Particle diameter for batch and continuous copper nanoparticles synthesis processes.

	Batch Process	Continuous Process
Average Diameter [nm]	62	85
Standard Deviaton [nm]	23	25
Particles Mearsured [n]	43	211
Min/Max Diameters [nm]	27 / 126	36 / 195

The difference between the continuous and batch size distributions is minimal, with both samples following the basic Gaussian curve. The analysis shows that continuously synthesized copper nanoparticles are on average 20 nm larger in diameter than batch synthesized copper nanoparticles, but that standard deviations are the same for both sample populations. The results from this data can be used as qualitative data due to collection method described in Section 2.4.6. The collected results were done in an attempt to sample the entire population, but bias contributed by human collection means this data cannot be used quantitatively.

3.10 Printing of continuously synthesized copper nanoparticles

Printing was done as described in section 2.3, with the following results shown below using silicon wafer substrates. Figure 14 shows when 1 nozzle was used with a type 21 print-head and 5 printing passes were done consecutively on the substrate. The substrate in Figure 14a was at room temperature when printed on and for Figure 14b the substrate was preheated to 100-120 $^{\circ}$ C.



Figure 14: Copper nanoparticles printed using HP TIPS device on silicon wafer substrate. Substrate was at room temperature (a) and $100^{\circ}C$ (b).

In Figure 14a, the majority of the printed nanoparticles are seen at the edge of the printed line. This is caused by the rapid evaporation of solvent at the edges due to surface tension. The suspended nanoparticles migrate with the solvent to the edge where the evaporation is occurring and are deposited there. The substrate was heated in Figure 14b with the goal of getting the PVP surrounding the copper to melt onto the substrate and stick to prevent migration of the copper nanoparticles to the line edge. Comparing the spread of nanoparticles across the printed line width in Figure 14, heating the substrate minimized the migration of the printed nanoparticles.

4.1 Conclusion of project results

Copper nanoparticles were continuously synthesized successfully using a micromixer with similar results to batch synthesized copper nanoparticles. SEM, TEM, SAED, TGA and XRD characterization methods were employed to compare the synthesis processes. Continuously synthesized copper nanoparticles showed a lower presence of the unwanted copper oxide from the XRD analysis. TGA results supported these findings by showing that more protective polymer coated the nanoparticles synthesized in the continuous process. Higher conversion (+15%) of copper ions to copper nanoparticles was accomplished with the continuous process. Improved oxidation protection and conversion are due to more efficient mixing of reagents by the micro mixer.

4.2 Recommendations for future work

Future project work should investigate the following items to optimize the synthesis of copper nanoparticles. Experimentation with oleic acid as a capping agent while using propylene glycol as the solvent in an attempt to make the synthesis a greener process. Lower the process temperature to Lee's synthesis temperature of 90°C to allow easier integration of the process to a polymer based microfluidic device. A microfluidic device should be adopted for synthesis to narrow the size distribution of the nanoparticles. Utilization of functionalized TEM grids to image single nanoparticles, so

qualitative data can be gathered regarding nanoparticle size. Development of an improved separation/purification process of the synthesized nanoparticles to increase the yield, while decreasing the amount of solvent waste generated from washing. Sintering of printed copper nanoparticles also needs to be conducted to determine the conductivity of the conductive surfaces and then compare it with the conductivity of bulk copper. Adjustment of reagent flow rates and concentrations to optimize the yield of synthesized nanoparticles and decrease the amount of waste generated.

Bibliography

- [1] Lee et al, Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics, Nanotechnology 19 (2008)
- [2] Jang et al, Sintering of Inkjet printed copper nanoparticles for flexible electronics, Scripta Materialia 62 (2010) 258-261
- [3] http://www.sciencedaily.com/releases/2007/03/070328111145.htm Accessed 05/20/2011
- [4] Abdulla-Al-Mamun et al, Simple new synthesis of copper nanoparticles in water/acetonitrile mixed solvent and their characterization, Mat. Letters 63 (2009) 2007-2009
- [5] Shan et al, Synthesis and characterization of copper sulfide nanocrystallites with low sintering temperatures, J. Mat. Chem. 18 (2008) 3200-3208
- [6] Kitchens and Roberts, Copper Nanoparticle Synthesis in compressed liquids and supercritical fluid reverse micelle systems, Ind. Eng. Chem. Res 43 (2004) 6070-6081
- [7] Khanna et al, Synthesis and characterization of copper nanoparticles, Mat. Letters 61 (2007) 4711-4714
- [8] Wu and Chen, Synthesis of high-concentration copper nanoparticles in aqueous CTAB solutions, J Colloid and Interface Science 273 (2004) 165-169
- [9] Sarkar et al, PVP-Stabilized Copper Nanoparticles, J. Phys. Chem. 112 (2008) 3334-3340
- [10] Tang et al, A simple way of preparing high-concentration and high purity nano copper colloid for conductive ink in inkjet printing technology, Colloids and Surfaces, 360 (2010) 99-104
- [11] Zhao et al, Nanoparticle synthesis in microreactors, Chem. Engr. Science 66 (2011) 1463-1479
- [12] Horikoshi et al, Formation of Ag nanoparticles in aqueous carboxymethlcellulose solutions in batch and continuous-flow reactors, Nanoscale, 2 (2010) 1441-1447
- [13] Veriansyah et al, Continuous synthesis of magnetite nanoparticles in supercritical methanol, Mat. Letters 64 (2010) 2197-2200
- [14] Zhang et al, Microfluidic synthesis of copper nanofluids, Microfluid Nanofluid, 9 (2010) 727-735
- [15] Park et al, Synthesis and size control of monodisperse copper nanoparticles by polyol method, J Colloid and Interface Science, 311 (2007) 417-424
- [16] Vanheusen et al, Production of Metal Nanoparticles, US Patent Application #20080034921A1
- [17] Jeong et al, Controlling the Thickness of the Surface Oxide layer on copper nanoparticle, Adv. Func.

APPENDIX: Heat transfer derivation and calculations.

Starting with the following equations

$$Q = mC_{p}\Delta T (1)$$

$$Nu = \frac{hD}{k_{f}} (2)$$

$$Q = UA\Delta T (3)$$

$$l = \frac{A}{D} (4)$$

First rearrange eqn. 3 to solve for A and insert into eqn. 4

$$l = \frac{Q}{UD\Delta T}(5)$$

Next rearrange eqn. 2 for h and substitute in for U in Eqn. 5

$$l = \frac{Q}{Nuk_f \Delta T}(6)$$

Finally inset eqn. 1 into eqn. 6 and simplify

$$l = \frac{hmCp\Delta T_{lm}}{UNuk_f\Delta T}$$
(7)

From this derivation, calculations were done to find the length of tubing required for heating which was ~8 cm. However this length needed to be 3.5x longer since some of the assumptions made in the heat transfer calculations for the Nusselt (Nu) number, which affects U and h were for ideal conditions. Small changes in these numbers, especially U have large impacts because it is located in the denominator. A final length of 28 cm was used to ensure the solution was heated to the desired temperature.