LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-670921

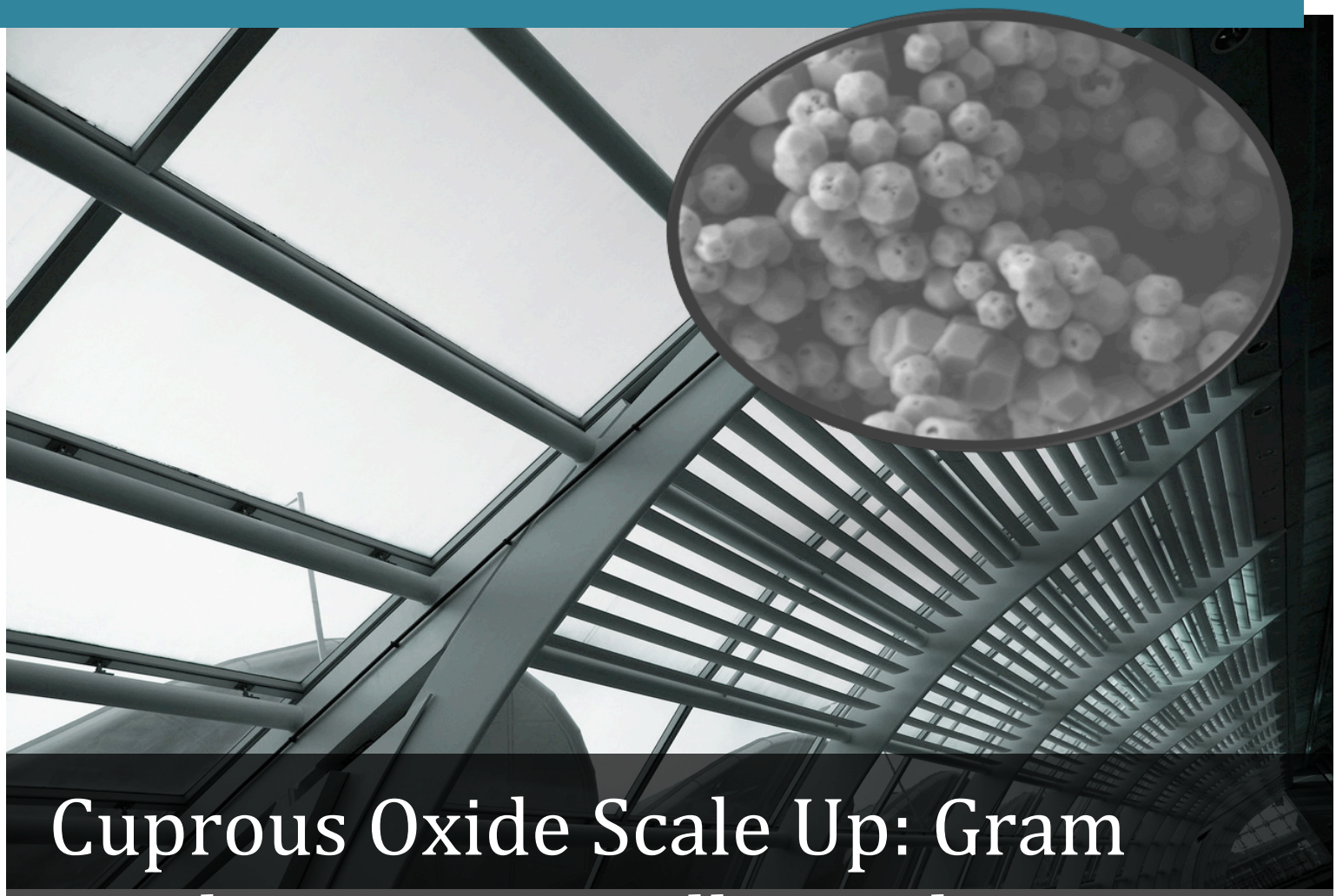
Cuprous Oxide Scale up: Gram Production via Bulk Synthesis using Classic Solvents at Low Temperatures

A. Hall, T. Y. Han

May 18, 2015

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.



Cuprous Oxide Scale Up: Gram Production via Bulk Synthesis using Classic Solvents at Low temperatures

Office of Science, Science Undergraduate Laboratory Intnerhsip (SULI)

Ashley Hall | University of California, Merced
Lawrence Livermore National Laboratory
Livermore, CA

May 15,2015

Prepared in partial fulfillment of the requirements for the Office of Science, Department of Energy's Science Undergraduate Laboratory Internship under the direction of T.Y. Han and T. Olson in the Physical Life Science Division at Lawrence Livermore National Laboratory.

Table of Contents

Disclaimer

Abstract

Cuprous oxide is a p-type semiconducting material that has been highly researched for its interesting properties. Many small-scale syntheses have exhibited excellent control over size and morphology. As the demand for cuprous oxide grows, the synthesis method need to evolve to facilitate large-scale production. This paper supplies a facile bulk synthesis method for Cu_2O on average, 1-liter reaction volume can produce 1 gram of particles. In order to study the shape and size control mechanisms on such a scale, the reaction volume was diminished to 250 mL producing on average 0.3 grams of nanoparticles per batch. Well-shaped nanoparticles have been synthesized using an aqueous solution of $CuCl_2$, NaOH, SDS surfactant, and NH_2OH-HCl at mild temperatures. The time allotted between the addition of NaOH and NH_2OH-HCl was determined to be critical for $Cu(OH)_2$ production, an important precursor to the final produce The effects of stirring rates on a large scale was also analyzed during reagent addition and post reagent addition. A morphological change from rhombic dodecahedra to spheres occurred as the stirring speed was increased. The effects of NH_2OH-HCl concentration were also studied to control the etching effects of the final product.

1. Introduction

Cuprous oxide (Cu_2O) is a p-type semiconducting material with a theoretical direct band gap of ~2.2 eV [3]. This gives the oxide some unique semiconductor and optical properties. Research has been done on this oxide for its viability in applications such as usage in solar cells, nano-magnetic devices, biosensors, and as an antimicrobial [3].

Pervious efforts in cuprous oxide synthesis involved dangerous reducing reagents that were highly toxic such as hydrazine [5] and sodium borohydride [6]. The toxicity, flammability, and/or corrosiveness of the reagents made their synthesis unusable for industrial scale production. There is strong need for a synthesis that yields not only quality particles in good quantity but also in an environmentally conscious manner. There is a large amount of interest in the materials engineering and nanotechnology fields for the controlled fabrication of Cu_2O nanoparticles.

The synthesis provided by Huang et al. allowed for simple solvents to be used that does not require extensive or specialized handling outside of the standard laboratory safety procedures [7]. High temperatures or inert atmosphere were not necessary. These factors aid in the scalability of this synthesis. The objective of this research was to be able to scale up cuprous oxide nanoparticles to the gram scale with minimal defects, size variation, and uniform morphology.

2. Experimental

2.1 Materials

Sodium dodecyl sulfate (SDS), sodium hydroxide (NaOH), hydroxylamine hydrochloride (NH_2OH-HCl), and copper chloride ($CuCl_2$) were bought from Sigma Aldrich. All water used in this synthesis was passed through a Milli-Q filtration system. All materials were used without further purification. Sodium hydroxide and hydroxylamine hydrochloride were made into aqueous 1M solution mixed with water. Copper chloride was made into a 0.5M solution.

2.2 Synthesis of Cu_2O Nanoparticles

In a typical synthesis a 500 mL round bottom flask was used. One hundred and eighty milliliters of water was added and brought to 34°C in a water bath. SDS, 9.375g, was then added to the solution under rigorous stirring. The remaining 12.75mL of water was added after to help wash the SDS powder out of the flask's neck for a total of 192.75mL water added. A period of 30 minutes was allotted for solution to come to temperature. No particulates from the SDS were observed. Under moderate stirring, 10 mL of 0.5M $CuCl_2$ was added

followed by 22.5 mL of 1M NaOH. As soon as the pouring of the sodium hydroxide began, counting started up to 30 seconds. Once 30 seconds have passed, 20 mL of 1M NH_2OH-HCl was added. The solution was allowed to stir for half a minute before stirring was turned off and allowed to age for 60 minutes. There was a distinct color change to aqua blue (from addition of $CuCl_2$ to water / SDS solution) followed by a royal blue (from addition of NaOH), then a hunter green (from addition of NH_2OH-HCl), which led to the final color change to a carrot orange after age occurs from the formation of cuprous oxide. See figure 1 for reaction sequence and respective color change.

The reaction did not require an inert atmosphere. Throughout the reaction the flask was capped. For purification, particles were centrifuged at 5000 RPM for 3 minutes. The supernatant was decanted and the particles went through seven ethanol washes followed by two water washes following the same procedure. Particles were then suspended in 40 mL ethanol for storage.

2.3 Characterization

Sample preparation for SEM consisted of taking an aliquot of nanoparticles while they were thoroughly dispersed in ethanol and dripping it onto a pretreated silicon substrate. It was left out in the fume hood to let the ethanol evaporate followed by imaging.

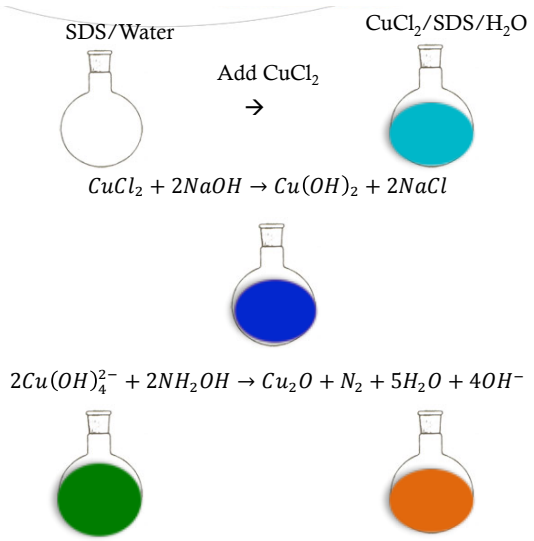


Figure 1: Solution color scheme change with corresponding reaction.

3. Results and Discussion

Size and shape control have been demonstrated on a small scale [1-3]. By just increasing the reaction volume from 50mL to 250mL lessens the control of such features. The synthesis method from Ho and coauthors yielded particles with a high order of shape and size regularity in a small reaction (10 mL) but the yield was low [1]. After increasing the concentrations of the chemicals to ten times the original concentration, the yield was increased enough to be viable for scale up. Scaling up to 1 liter greatly increased defects (facet deformation), polydisperisty, decreased shape uniformity, and increased multiple nucleations on single seeds. This led to the assumption that the reagent amounts used in small scale are not linearly transferable to the large scale, 1-liter production. However it does, on average, produce 1 gram of Cu_2O nanoparticles. In order to combat this disconnect with scale up, the 1-liter reaction volume was quartered to a 250mL volume. Three factors were tested in an attempt to understand what small interplaying factors emerge as scaling increases.

3.1 The Hydroxylamine Hydrochloride Effect

The role of hydroxylamine was to act as a reducing agent for the copper hydroxide in the following reaction below.

Eq1. $$2Cu(OH)_4^{2-} + 2NH_2OH \rightarrow Cu_2O + N_2 + 5H_2O + 4OH^-$$

The hydroxylamine source for this experiment was hydroxylamine hydrochloride (NH_2OH-HCl). Though the HCl did not interfere with the chemical reaction in formation of cuprous oxide, it did affect the surface chemistry of the particle facets. When an attempt was made to try and increase the yield of the reaction, the concentration of the HCl etchant was also increased. It is possible for the HCl to have broken down into its base ions of H^+ and Cl^- during the reaction. If this did in fact happen, the free hydrogen ion had the option to either combine with a hydroxide ion or it could bind to a favored

particle facet, which in turn would cause etching. This means that it had some pull on the particle's final morphology. The extent of this interaction is uncertain. It was hypothesized that the degradation of the <111> facet was due to the HCl that is introduced by the NH_2OH-HCl post reduction of copper hydroxide. In an attempt to minimize the deformities, the amount of hydroxylamine was reduced. With the same experimental set up, the amount of NH_2OH-HCl was decreased to 17 mL from 20 mL. There was an immediate reduction of defects that were seen, specifically a reduction to facet deformation due to over etching. Figure 2 illustrates the decrease of defects in the particles observed. This added evidence to the hypothesis that the HCl component of the hydroxylamine did in fact, break down to its base components and interfaced with the cuprous oxide facets via etching.

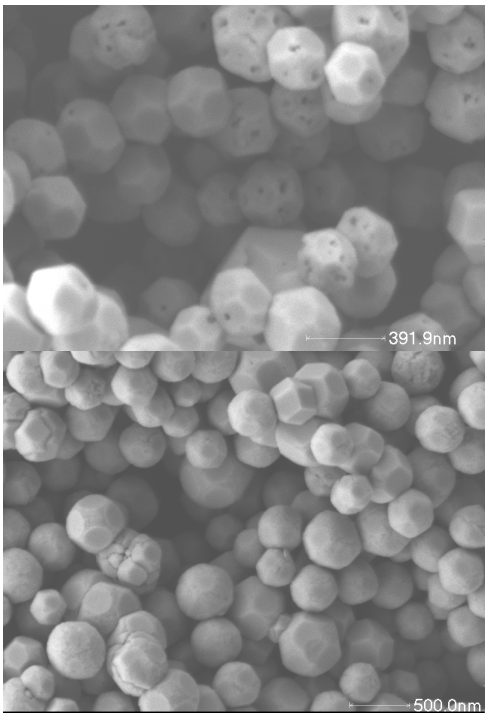


Figure 2: Cuprous oxide particles created with (top) 20 mL of hydroxylamine hydrochloride and (bottom) with 17 mL

3.2 Stir Rate as a shape controller

During an experiment in which a liter reaction volume was used, a mechanical stirring error yielded particles that were not only polydispersed but also the morphology control was completely lost. See figure 3. This gave insight that stirring rate played a vital role in the particle size and in the morphology. This hypothesis was supported by the work of Bai et al. Bai and coauthors observed that by simply increasing the stir rate from just 4 (rotations per second) r/s to 5.5 r/s yielded a morphology change from cubes to spheres [3]. The offered explanation for this occurrence was stirring rate affects the probability and the energy of the collisions between particles. Increasing the energy between particle collisions rounds out the edges of the particles. This explanation holds validity due to similar results being produced in a 250 mL reaction. See figure 4. The top SEM micrograph shows particles that were synthesized with a 500-RPM stir rate held constant throughout both reagent addition and post addition through the first half minute of aging. The bottom SEM micrograph represents

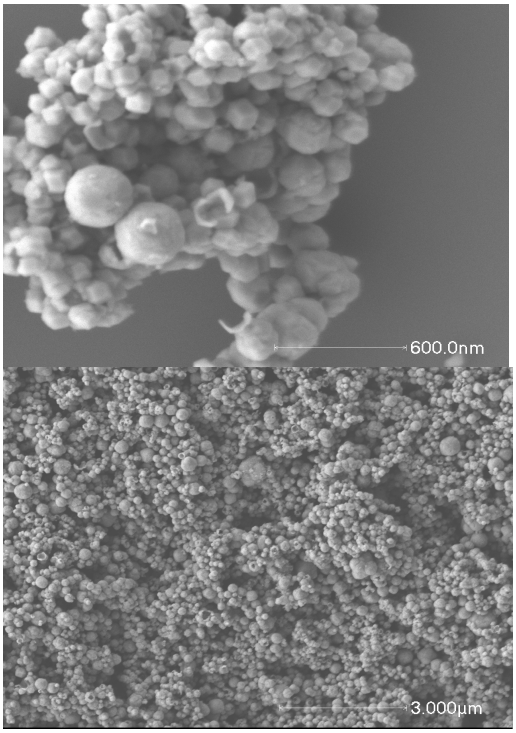


Figure 3: SEM micrograph of 1-liter synthesis during which stir bar had irregular stirring patterns. Top) Close up of a cluster of particles. Bottom) Overhead view.

particles that were spun at 2.5 on the stir plate, which is approximately 300 RPM, under the same conditions. Morphology uniformity was good for both the spheres and rhombic dodecahedras. It should be mentioned as supplied by Bai et al. that stirring too rigorously hinders the combination between different particles and in turn prevents crystal growth from there.

3.3 Reagent Addition Stir Timing

Copper hydroxide degradation was the cuprous oxide source for the nanoparticles. It was imperative to let as much copper hydroxide form from the NaOH/ $CuCl_2$ reaction as possible. The way to maximize this effect was to vary the time between the NaOH and NH_2OH-HCl. It was found that 40 seconds in-between the addition yielded the best results. Post addition of the NH_2OH-HCl was the Cu_2O formation stage. Three trials were undertaken at 30 seconds, 45 seconds, and 60 seconds. At 60 seconds, there were predominately spheres but also wires. Why there was a difference in particle size distribution is not understood yet. One hypothesis was that extended stir rates during the initial nucleation phase allowed for creation of more small seed particles. Shorter stir time allowed for larger seed particles to form. Further experimentation is needed to understand this occurrence.

4. Conclusion

The pervious work by Haung et. al was concentrated to ten times the initial concentration improving the yield of nanoparticles to a gram in a liter synthesis. In concentrating the reaction led to the increase of hydroxylamine hydrochloride, which caused extensive etching. When hydroxylamine hydrochloride was decreased, there was a decrease in the defects but also a change in the morphology. Stirring rate variation affected both shape and the size of particles. This was especially true post reagent addition during the seed particle formation phase. These results can be used to further the understanding of gram scale production. Future works would be involving a more comprehensive look of stir rate effects during the initial nucleation phase of the nanoparticles.

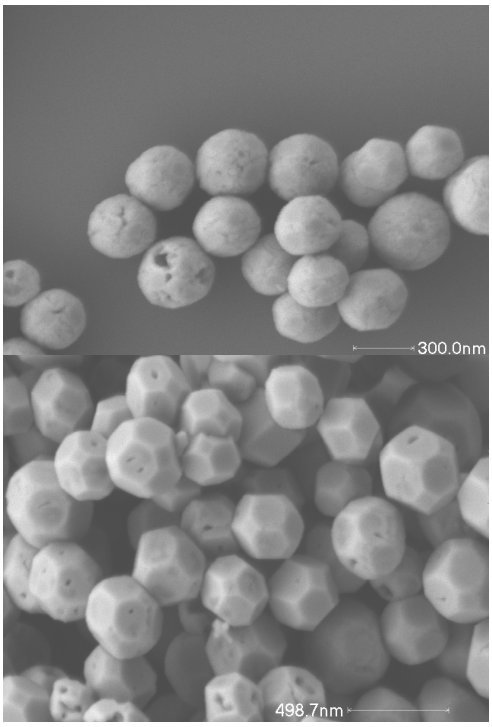


Figure 4: SEM micrograph Top) 500 RPM stir speed. Bottom) ~300 RPM stir speed

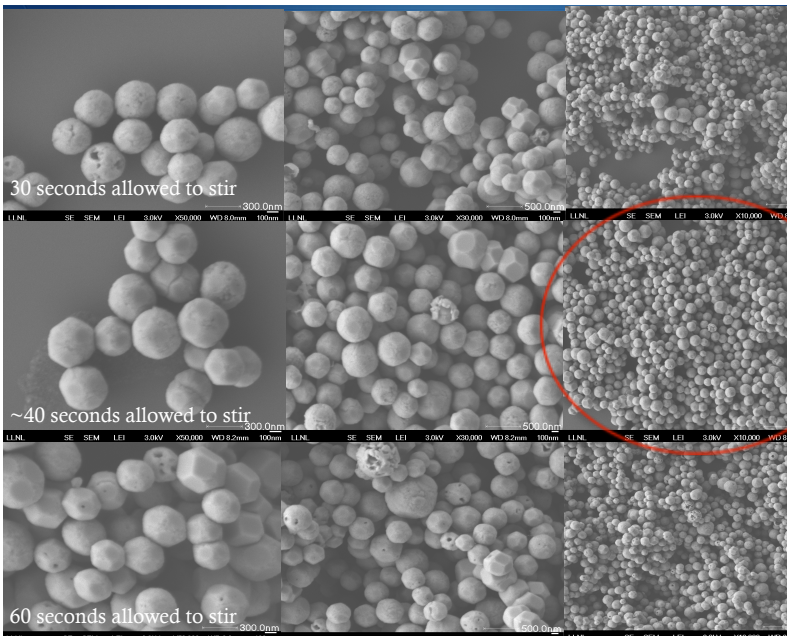


Figure 5: Post reagent stir time trails at 30, 40, and 60 seconds. The best results came from 40 seconds, which yielded the most monodispersed particles of the 3 trails

5. Acknowledgments

I would like to acknowledge the SULI program for its part in my sponsorship at Lawrence Livermore National Laboratory. Berry Goldman for heading the SULI program at the lab and for allowing me to come. Dr. Thomas Yong Han for his sponsorship, mentorship, and his patience. He provided a wonderful experience and look into bulk nanoparticle synthesis. Dr. Tammy Olson for her guidance. Pui Ching "Steve" Lan for his company in the lab and being my lab partner sometimes teacher during experiments. Steve provided SEM imaging as well. I thank everyone for his or her support. This experience was invaluable.

6. References

[1] Jin-Yi Ho and Michael H. Haung, " Synthesis of submicrometer-sized Cu_2O crystals with morphological evolution from cubic to hexapod structures and their comparative photocatalytic activity," in American Chemical Society, Vol 113, 2009, pp.14159-14164.

[2] Chun-Hong Kuo and Michael H. Huang, " Facile synthesis of Cu_2O Nanocrystals with systematic shape evolution from cubic to octahedral structures," in American Chemical Society, Vol 112, 2008, pp. 18355-18360.

[3] Yakui Bai, Tengfei Yang, Qing Gu, Guoan Cheng, Ruiting Zheng, " Shape control mechanism of cuprous oxide nanoparticles in aqueous colloidal solutions," in Powder Technology, Vol 227, 2012, pp.35-42.

[4] Dinesh Pratap Singh, Animesh Kumar Ojha, and Onkar Nath Srivastava, "Synthesis of different $Cu(OH)_2$ and CuO (nanowires, rectangles, seed-, belt-, and sheetlike) Nanostructures by Simple Wet Chemical Route," in The Journal of Physical Chemistry, Vol 113, 2009, pp. 3409-3418.

[5] Haolan Xu, Wenzhong Wang, and Wei Zhu, " Shape evolution and size-controllable synthesis of Cu_2O octahedra and their morphology-dependent photocatalytic properties," in The Journal of Physical Chemistry, Vol 110, 2006, pp. 13829-13834.

[6] Jiatao Zhang, Junfeng Lui, Qing Peng, un Wang, and Yadong Li, " Nearly monodispersed Cu_2O and CuO nanospheres: preparation and applications for sensitive gas sensors," in Chemistry of Materials, Vol 18, 2006, pp. 867-871.

[7] Wan-Chen Haung, Lian-Ming Lyu, Yu-Chen Yang, and Michael H. Huang, " Synthesis of Cu_2O nanocrystals from cubic to rhombic dodecahedral structures and their comparative photocatalytic acitivity," in The Journal of American Chemical Society, Vol 134, 2012, pp. 1261-1267