

Synthesis of Copper (II) Oxide Particle and Detection of Photoelectrochemically Generated Hydrogen

Yu Li

Chemical Engineering, University of California, Davis

NNIN REU Site: Nanotech @ UCSB, University of California, Santa Barbara, CA

NNIN REU Principal Investigator(s): Professor Martin Moskovits, Chemistry, University of California, Santa Barbara

NNIN REU Mentor(s): Nick Hight-Huf, Department of Chemistry, University of California, Santa Barbara

Contact: yugli@ucdavis.edu, mmoskovits@lsc.ucsb.edu, nhighthuf@chem.ucsb.edu

Abstract:

Nano-sized copper (II) oxide (CuO) particles (size ranging from 100-400 nm) were synthesized by ultrasonic spray pyrolysis (USP) starting from aqueous copper (II) nitrate with varying reaction conditions (reactor temperature 450K-1180K, residence time 2s-5s). The products were confirmed by Fourier transform infrared spectroscopy (FTIR) (1384 cm^{-1} assigned as $\text{Cu}^{2+}\text{-O}^{2-}$ stretching mode). Decreasing the reactor temperature resulted in an attenuation of x-ray diffraction (XRD) peak intensity (corresponding to apparent decreased crystallinity) coupled with an increase in mean particle size and deviation. The direct band gap was estimated to be $\sim 1.6\text{-}1.9$ eV from UV-Vis spectra.

Introduction:

Hydrogen has great potential as an environmentally friendly fuel since the byproduct of its combustion is water, yet the current method of hydrogen production is very inefficient and costly [1]. Solar energy is a large source of energy available for consumption, yet it is not utilized very efficiently [2]. The photoelectrochemical splitting of water as a method of hydrogen production using solar energy as a driving force to produce hydrogen is of great interest due to its ability to take advantage of abundant and renewable natural resources and convert them into highly deployable energy medium.

The focus of this research is on synthesizing nano-sized CuO nanoparticle that can absorb visible light to produce hydrogen from water. Objectives of this research project are to synthesize CuO nanoparticle and study their characterizations, also to test their hydrogen production performance.

Experimental Procedures:

Ultrasonic Spray Pyrolysis (USP). 0.1 M of $\text{Cu}(\text{NO}_3)_2$ solution was prepared by mixing 2.326 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ solid and 100 ml of DI water in a volumetric flask. The solution was stirred for 30 minutes. 50 ml of the $\text{Cu}(\text{NO}_3)_2$ solution was then nebulized (Sunpentown SU-2000) and carried into furnace (Linberg BlueM TF55035A) by air for heat treatment ranging from 450K-1180K. CuO nanoparticles were collected through a bubble trap of DI water after the furnace. CuO nanoparticles were cleaned in a sonicator. Reactor temperatures and air flow rates were varied to obtain different characterizations of CuO. Characters of CuO were studied by FTIR, XRD, TEM, SEM, and UV-Vis. Data explained in the "Result" section.

Improvement to Ultrasonic Spray Pyrolysis: Modifications to USP were attempted to decrease the particle size of CuO nanoparticle. Surfactants including soap and hexanol were

added to reduce the surface tension and reduce the size of the micronized droplets entering the tube furnace portion of the reactor. The $\text{Cu}(\text{NO}_3)_2$ solution was preheated before nebulization as an alternative method of reducing surface tension which according to literature [3] will reduce particle size of final products.

Photoelectrochemical Reaction: Only initial data was obtained from the hydrogen production analyser. Please refer to "Future Work" section for planned procedures for hydrogen production performance.

Results:

By the ultrasonic spray pyrolysis method, CuO was successfully synthesized at different reaction conditions (resident time between 2s-5s). CuO nanoparticles were confirmed by FTIR (NICOLET 4700 FT-IR) exhibiting a

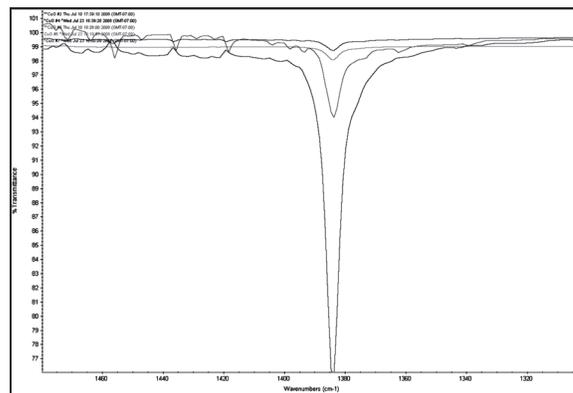


Figure 1: FT-IR, $\text{Cu}^{2+}\text{-O}^{2-}$ stretching mode peak at 1384 cm^{-1} . Confirmed the CuO nanoparticle actually was presented in final products.

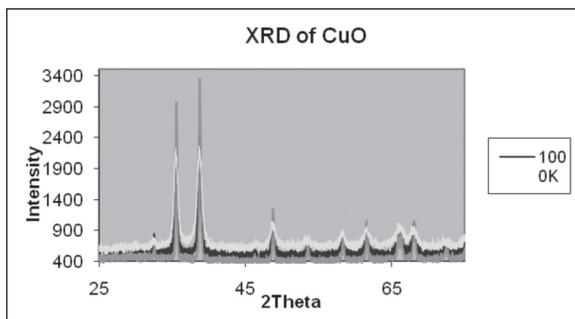


Figure 2: X-ray diffraction graph. Strong peaks showed the CuO hold crystalline structure. An increase in reactor temperature show an increase in peak intensity which suggest increase in crystallinity.

$\text{Cu}^{2+}\text{-O}^{2-}$ stretch mode peak at around 1384 cm^{-1} (Figure 1). X-ray diffraction graph (Figure 2) indicated all the CuO nanoparticle samples had strong crystalline structure. Intensity of the XRD peak at 1180K was higher than 1000K and 726K. It was suggestive that at higher reactor temperature, stronger crystalline structures were obtained. The particle sizes of CuO were investigated by scanning electron microscope (SEM) and transmission electron microscopy (TEM) in Figure 3. It is shown that sizes of CuO ranged from about 100-400 nm. The images also showed that there was a decreasing trend in particle size as reactor temperature increased. This trend makes sense as higher reactor temperatures resulted in lower residence times, lower resident times resulted in lower collision frequency, therefore reduced particle sizes.

Ultraviolet-visible spectra showed a display of absorbance corresponding to wavelength. According to the equation [4], $ah\nu = A(h\nu - E_g)^{n/2}$ —where a is absorbance, h is Planck's constant, ν is frequency, A is proportional constant, n is assumed to be 1, and E_g is the band gap—the band gap can be calculated after rearrangements and necessary calculations were done (Figure 4). It was found that the direct band gap of CuO samples deviate between 1.6eV to 1.9eV with no noticeable pattern.

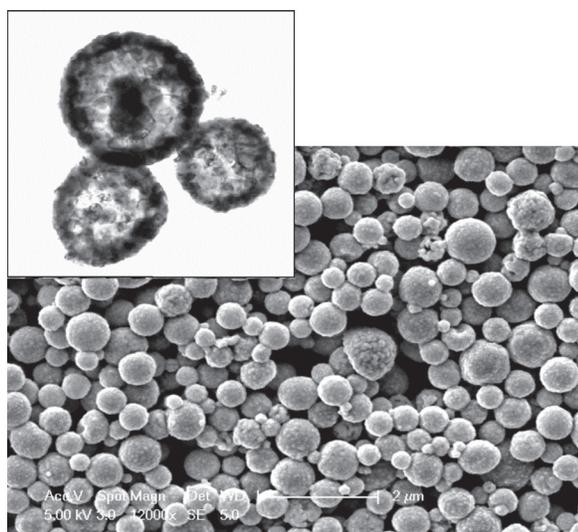


Figure 3: SEM and TEM image. CuO particle sizes were showed to be around 100 nm to 400 nm.

The efficiency rate of the hydrogen product is yet to be determined.

Conclusion:

Copper (II) oxide nanoparticle was fabricated by the ultrasonic spray pyrolysis method. CuO products were confirmed to be presented in the final products. CuO nanoparticles all showed strong crystalline structure. CuO particle sizes ranged from 100 nm to 400 nm according to TEM and SEM. Direct band gap of the CuO samples was measured to be about 1.6eV to 1.9eV by UV-Vis spectra.

Future Work:

Photoelectrochemical Reaction Testing. More investigation needs to be done on hydrogen evolution rate. Procedures for the investigation are planned as following: Mix 20 ml of DI water with 0.05g CuO sample in a test tube. Shine UV light on the test tube with a mercury lamp in a closed chamber. Collect any gas produced and analyzed the gas with a gas chromatography machine.

Acknowledgements:

I would like to thank the follow people who made this internship possible for me: my mentor Nick Hight-Huf, my coordinator Angela Berenstein, my principal investigators Professors Eric McFarland and Martin Maskovits, and the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program.

References:

- [1] Bellona, <http://www.interstatetraveler.us/Reference-Bibliography/Bellona-HydrogenReport.html>.
- [2] Eric McFarland, and Martin Maskovits, "High Efficiency Colloidal Photo Electro catalysts by Plasma Synthesized Fe_2O_3 Nanoparticles."
- [3] Department of Energy, <http://www.newton.dep.anl.gov/askasci/phy00/phy00627.htm>.
- [4] Diwakar Chauhan, V R Satsangi, Sahab Dass, and Rohit Shrivastav. "Preparation and Characterization of Nanostructured CuO Thin Films for Photoelectrochemical Splitting of Water." *Bulletin of Materials Science*. Vol. 29, No. 7. December 2006.

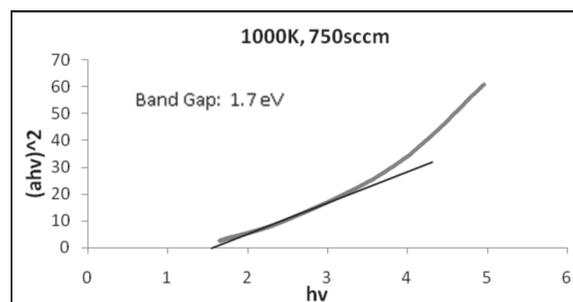


Figure 4: UV-Vis spectra after modification by $ah\nu = A(h\nu - E_g)^{n/2}$ (explained in result section). E_g , the direct band gap was obtained by the x intercept of the linear fit of the first part of spectra before it changes slope. Band gap for this sample was estimated to be 1.7eV. for all CuO samples, band gaps were between 1.6eV to 1.9eV.