

# Synthesis of Cu Nanoparticles for Preparation of Nanofluids

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## ABSTRACT

Copper nanoparticles have been prepared by reduction of Cu(II) ions in aqueous and non-aqueous solutions. The time at which elemental Cu was formed from starting 0.016M Cu solutions decreased from 10 hours to only 6 minutes when the concentration of hydrazine was increased from 0.059M up to 0.7M, respectively. The corresponding average crystallite size decreased from 30nm down to 16nm. The complete reduction of in ethylene glycol was achieved after 30 seconds when a NaOH/Cu mole ratio of 50 was used. The average crystallite size was estimated at 25 nm. In both approaches, the Cu-forming reaction involved the formation of intermediate Cu<sub>2</sub>O, which underwent dissolution and subsequent reduction into elemental Cu. UV-vis measurements evidenced the formation of nanosize Cu crystals. The surface plasmon resonance band was blue-shifted after intensive sonication suggesting a decrease in crystal size during the preparation of the nanofluid in ethylene glycol.

**Keywords:** copper nanocrystals, aqueous reduction, polyol reduction, nanofluids.

## 1. INTRODUCTION

Stable suspensions of nanometer solid particles in suitable solvents, so-called nanofluids, have shown enhanced thermal conductivity when compared with the fluid base. This feature enables these suspensions to be considered a promising material for efficient and effective thermal management in different systems, [1-4]. Nanofluids bearing metal nanoparticles, e. g. Ag or Cu, exhibit in general more remarkable thermal conductivity than those containing oxide nanoparticles [5-7]. The preparations of metal bearing nanofluids have been attempted by direct condensation of copper vapor in ethylene glycol [8]. Although the thermal conductivity measurements suggested an increase in the thermal conductivity of the nanofluid, the selected preparation route did not allow any possibility to restrict particle size at the nanoscale. The reasons behind the increase in thermal conductivity of nanofluids are still unclear; however, the big surface area in nanosize particles, the Brownian motion of suspended crystals and the establishment of fluid layers onto nanoparticles should be involved with this phenomenon. These enhanced thermal conductive nanofluids will find immediate applications in

cooling systems and in the design of smaller machines and components [8,9].

Despite of the technological importance of such a fluid, there is still a lack of systematic research on other possibilities to synthesize copper nanocrystals and the corresponding nanofluids where the tuning on crystal size could become possible. On this basis, the present work was focused on the optimization of the synthesis conditions of Cu nanoparticles and their subsequent stabilization in ethylene glycol. Copper nanoparticles have been synthesized through the reduction of Cu ions by hydrazine in water as well as by taking advantage of the reducing power of polyol solutions in excess of hydroxide ions. The preparation of the copper-bearing stable nanofluids has also been attempted by dispersing synthesized nanoparticles through intensive ultrasonication in ethylene glycol.

## 2. EXPERIMENTAL

### 2.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of Cu(II) sulfate pentahydrate salt, CuSO<sub>4</sub>·5H<sub>2</sub>O, with 98.0 – 102.0 % in purity (Alfa Aesar) and Cu(II) acetate salt, Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, (99%, Strem Chemicals), were dissolved in high purity water and ethylene glycol, respectively. Hydrazine, (N<sub>2</sub>H<sub>4</sub>), (+98%, Alfa Aesar) and ethylene glycol, (HOCH<sub>2</sub>CH<sub>2</sub>OH), (99%, Alfa Aesar) were used as reductant agents in aqueous and non-aqueous media, respectively. NaOH (+98%, Sigma - Aldrich) was also used to accelerate the reduction reaction in ethylene glycol.

### 2.2 Synthesis of Copper Nanoparticles

A. Aqueous reduction of Cu(II) ions: Required amounts of hydrazine and Cu(II) sulfate solutions were contacted with N<sub>2</sub>-purged water at room temperature conditions. Possible re-oxidation of Cu precipitates was avoided by conducting the reduction reaction in tightly closed reaction vessels. At the end of the contact time, the suspension was treated by centrifugation. Recovered solids were washed twice and stored in ethanol.

B. Polyol route: A Cu(II) acetate solution in ethylene glycol was added to a boiling ethylene glycol solution containing NaOH. The experimental set-up considered the

use of a condenser to recover volatilized solvent. The experiments were carried out at 500 rpm of stirring intensity using a mechanical stirrer. The reacting solutions were heated at different heating rates provided by a suitable control of the power of the mantle heater device. At the end of the reaction time, the polyol solution was allowed to cool down. Copper nanoparticles were recovered by centrifugation and washed in ethanol two times prior to their storage and characterization.

### 2.3 Nanofluid Preparation.

Cu nanoparticles produced by the above described methods were dispersed in ethylene glycol under intensive and prolonged ultrasonication cycles (up to 7 hours). Obtained suspensions were characterized by UV spectroscopy as a function of time to determine the suspension stability against sedimentation. The estimated volumetric fraction of Cu nanoparticles in ethylene glycol was 0.05%.

### 2.4 Characterization Techniques

Structural analysis of the powders was carried out by x-ray diffraction (XRD) using the Cu-K $\alpha$  radiation. The average crystallite size of produced powders was estimated by using the Scherrer's equation for the (111) and (200) peaks. UV-vis spectroscopy was used to determine optical properties of the Cu nanoparticles in different suspending media. Particle morphology was examined by high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM).

## 3. RESULTS AND DISCUSSION

### 3.1 Cu(II) Reduction in Hydrazine.

Figure 1 shows the XRD patterns for the solids produced after reduction of 0.0016M Cu(II) in 0.059M aqueous hydrazine solutions after different reaction times. The solids formed at earlier times consisted of partially reduced cuprous oxide (Cu<sub>2</sub>O). The drop in the intensity of the Cu<sub>2</sub>O peaks and the simultaneous increase and sharpening of the peaks corresponding to elemental copper, suggested that the final formation of elemental Cu from starting Cu(II) solutions took place through the formation of partially reduced Cu(I) oxide as an intermediate phase. This intermediate should have been redissolved at prolonged reaction times and finally reduced to the zero state. The average crystallite size for Cu nanoparticles varied from 25 nm to 30 nm when the reaction time was prolonged from 4 hours to 24 hours, respectively. In order to evaluate the effect of the initial concentration of Cu(II) species on the average crystallite of produced Cu nanoparticles, a 0.059M hydrazine solution was contacted with Cu(II) solutions in the range of concentrations between

0.016M and 0.064M. The reaction was interrupted when the complete reduction of Cu was realized. Figure 2 shows the XRD patterns for the solids produced at different initial Cu(II) concentration. Only peaks corresponding to elemental Cu were detected, suggesting the complete reduction of Cu(II) species. It was observed that the lowering of the Cu(II) concentration made the time required to form elemental Cu shorter. The reaction time was shortened from 34 hours to 12 hours when the Cu(II) concentration varied from 0.016M to 0.064M. The corresponding average crystallite sizes varied between 25nm and 27 nm.

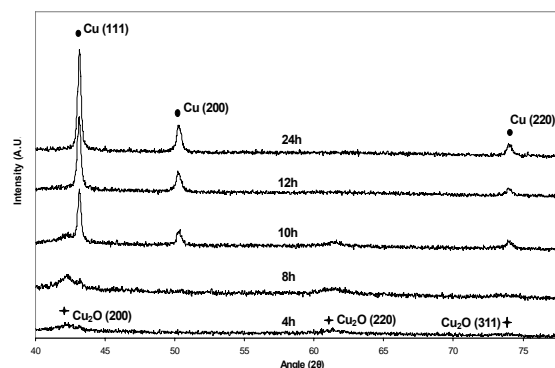


Figure 1: XRD patterns of powders synthesized at different reaction times. Reactants concentrations were 0.0016M Cu and 0.059M N<sub>2</sub>H<sub>4</sub>.

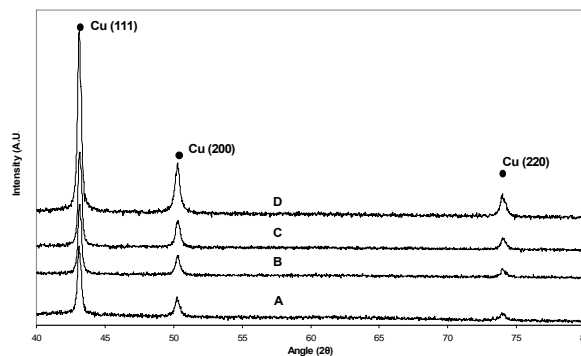


Figure 2: XRD patterns of powders synthesized at 0.059M N<sub>2</sub>H<sub>4</sub> and different Cu concentrations. A: 0.016M Cu; B: 0.032M Cu; C: 0.048M Cu and D: 0.064M Cu.

The effect of the hydrazine concentration on the kinetic of Cu(II) reduction and the corresponding crystal size was also evaluated. Figure 3 shows the XRD patterns of the solids produced from a 0.0016M Cu(II) solution and different concentrations of hydrazine. Once again, the reduction reaction was interrupted once the formation of elemental Cu was completed. As evident, the reduction of Cu(II) species required shorter times when the concentration of hydrazine was increased from 0.059M up to 0.70M. The corresponding reaction times and average crystallite size varied from 12hours to 30 minutes and from 30nm to 17nm, respectively. The nanoparticles were suspended in ethanol and characterized by UV-vis. The spectra, shown in figure 4,

displayed a surface plasmon (SP) resonance band at around 280nm that can be attributed to Cu nanoparticles [9].

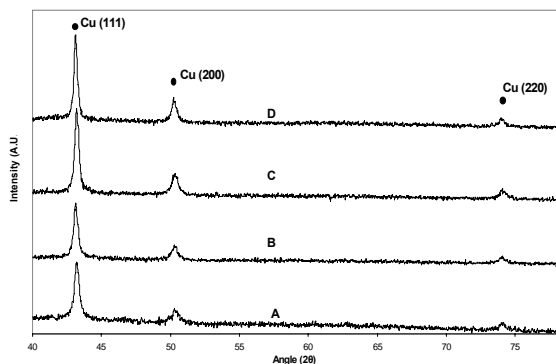


Figure 3: XRD patterns of Cu powders synthesized at different concentrations of hydrazine. A: 0.7M  $N_2H_4$ ; B: 0.24M  $N_2H_4$ ; C: 0.12M  $N_2H_4$  and D: 0.06M  $N_2H_4$ . The Cu concentration was 0.0016M.

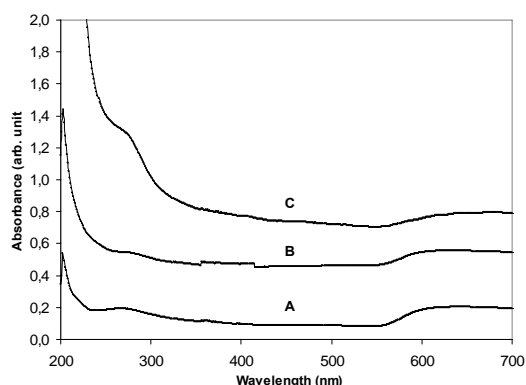


Figure 4: UV-vis absorption spectra of Cu nanoparticles suspended in ethanol. Copper was synthesized from 0.016M  $Cu_2SO_4$  and using 0.12M (A), 0.30M (B) and 0.65M (C) hydrazine solutions.

TEM and SEM images of figure 5 correspond to the Cu particles synthesized using 0.064M Cu and  $N_2H_4$  0.013 M . after 30 hours and 24 hours of reaction, respectively. Although strongly aggregated, the images evidenced the nanocrystalline nature of the particles.

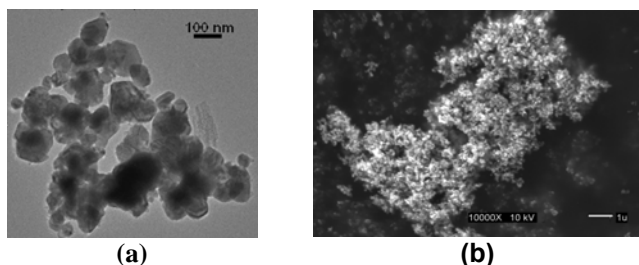


Figure 5: TEM (a) and SEM images of Cu nanoparticles synthesized using 0.013M  $N_2H_4$  and 0.064M  $CuSO_4$ .

### 3.2 Cu(II) Reduction in Ethylene glycol

XRD patterns in figure 6 correspond to the solids produced in ethylene glycol at different NaOH/Cu mole ratios,  $R'$ . The initial Cu(II) concentration was 0.0014M. The presence of NaOH accelerated the formation of elemental Cu; the reaction time was shortened from 1 hour to 30 s when the ' $R'$ ' values varied from 0, i.e. no NaOH, to 50. The corresponding average crystallite size decreased from 39nm to 21nm. The excess of NaOH would have enhanced the reducing conditions in the polyol media and/or accelerated the dissolution of any intermediate phase under strongly alkaline conditions. Under these conditions the enhancement of the nucleation rate, and hence the reduction in crystal size, could be expected.

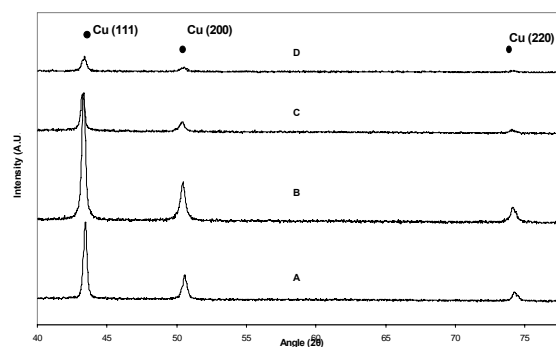


Figure 6: XRD patterns of Cu particles synthesized in ethylene glycol at NaOH/Cu mole ratio, ' $R'$ ', of 0 (B); 1 (C), 10 (D) and 50 (E). The initial Cu concentration was 0.0014M.

Figure 7 shows the UV-vis spectra of the Cu nanoparticles synthesized at different ' $R'$ ' values and suspended in ethanol.

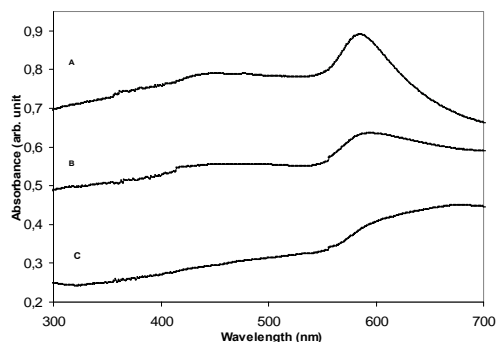


Figure 7: UV/VIS absorption spectrum of copper nanoparticles synthesized in ethylene glycol and suspended in ethanol. The ' $R'$ ' values were 0 (A), 1 (B) and 50 (C). Initial Cu concentration was 0.014M.

The spectra displayed a SP resonance band at around 590nm, which is also typical of Cu particles. Mott et al. observed the SP band at ~600nm [10] when ~100nm Cu nanoparticles were suspended in hexane. As known, the exact position of the SP may depend on several factors including particle size, shape, type of solvent and capping

agent, if any. Furthermore, the observed narrowing of the SP band in the solid produced at  $R=50$  suggests a less size polydispersity.

### 3.3 Nanofluid Stability

Copper nanoparticles synthesized in aqueous (hydrazine reduction) and non-aqueous (polyol reduction) media were suspended in ethylene glycol. Copper nanoparticles reduced by hydrazine were treated by 0.001M HCl solution in ethanol prior to their sonication. The volumetric % of the nanocrystals in the fluid was estimated at 0.05 %. In order to promote the nanofluid stability against sedimentation, the suspension was intensively ultrasonicated for 7 hours. The final suspension exhibited an orange tone and showed no evidence of settling of particles even after 96 hours. The UV-vis spectra were collected during 25 minutes at 5 minutes interval to determine the stability of the suspension.

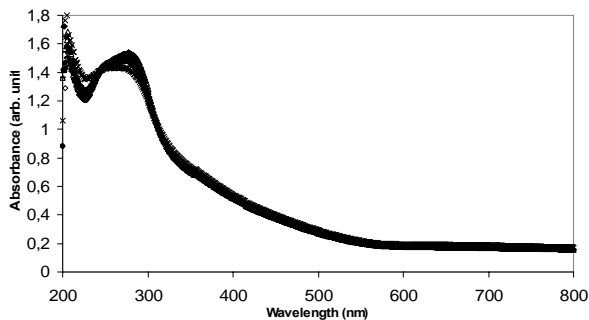


Figure 8: UV/VIS absorption spectra of Cu nanoparticles synthesized and suspended in ethylene glycol. The initial Cu concentration and 'R' were 0.0014M and 10, respectively.

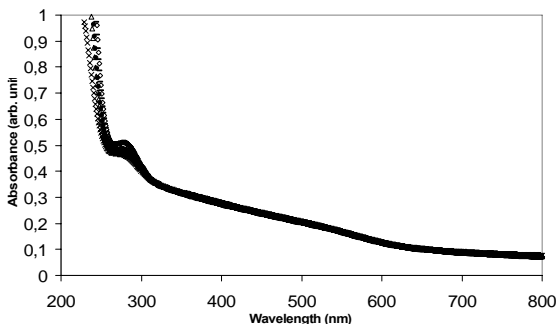


Figure 9: UV/VIS absorption spectra of Cu nanoparticles synthesized in 0.70M of hydrazine and suspended in ethylene glycol. The initial Cu concentration was 0.0016M.

As figures 8 and 9 show, the SP resonance band was centered on 280nm and no remarkable shifting was observed in the measurement period. This fact may suggest the stability of the suspension at least during the 25 minutes-period of data collection. Nevertheless, the position of the SP band was blue-shifted with respect to the SP position shown in figure 7. On the consideration that no dissolution of Cu nanoparticles could have taken place in

ethylene glycol media, this blue shift can be a consequence of the reduction in the nanoparticles size (fragmentation) by intensive ultrasonication. The position of the SP resonance band is in agreement with other reports where the size of Cu nanoparticles was in the 2-4nm range [11,12].

## 4. CONCLUDING REMARKS

We have successfully synthesized copper nanoparticles in aqueous and non-aqueous phase. The rate of the reduction reaction was strongly dependent on the concentration of hydrazine (aqueous route) and the NaOH/Cu mole ratio, 'R', in ethylene glycol media. Suitable hydrazine concentration and 'R' values were conducive to a dramatic shortening of the reaction time and, consequently, to a remarkable decrease in crystal size of Cu nanoparticles. Long-term stable nanofluids were prepared by intensive ultrasonication of Cu nanoparticles in ethylene glycol. Ultrasonication may have fragmented Cu crystals as suggested by blue-shifted SP resonance band.

## ACKNOWLEDGEMENTS

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