

## Research Article

# Effect of Lithium Ions on Copper Nanoparticle Size, Shape, and Distribution

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Copper nanoparticles were synthesized using lithium ions to increase the aqueous electrical conductivity of the solution and precisely control the size, shape, and size distribution of the particles. In this study, the conventional approach of increasing particle size by the concentration of copper ions and PGPPE in a copper chloride solution was compared to increasing the concentration of lithium chloride when the copper chloride concentration was held constant. Particle size and shape were characterized by TEM, and the size distribution of the particles at different concentrations was obtained by particle size analysis. Increasing the concentration of copper ion in the solution greatly increased the aqueous electric conductivity and the size of the particles but led to a wide size distribution ranging from 150 nm to 400 nm and rough particle morphology. The addition of lithium ions increased the size of the particles, but maintains them in a range of 250 nm. In addition the particles exhibited spherical shape as determined by TEM. The addition of lithium ions to the solution has the potential to synthesize nanoparticles with optimal characteristics for printing applications by maintaining a narrow size range and spherical shape.

## 1. Introduction

Recently, there have been numerous studies regarding the manufacturing of nanosized metal particles on nanoink applications [1–4]. Metal inks containing nanoparticles can be used in the fabrication of a variety of printed electronics [5–7], such as flexible antennas [5], displays [8], and printed circuit boards [9]. Metal inks must comply with sufficient values of viscosity, conductivity, packing density, and postcuring conductivity to undergo a printing process [10]. Nanoink properties are closely related to the size, shape, size distribution, and colloidal suspension of the nanoparticles contained in the ink [11]. Uniform shape and size of nanoparticles are important for optimizing the packing factor and obtaining higher electrical conductivity values of ink-jetted patterns [10]. Furthermore, very small particle sizes compromise the colloidal stability of the particles contained in the ink since the particles have high

surface energy and tend to agglomerate [12]. Preferentially, particle sizes for various printing applications should range between 50 nm and 300 nm [13].

Several methods have successfully synthesized copper nanoparticles for printing applications, but all of these methods synthesize the particles within small ranges. For example particle size ranges from 4–10 nm with the sonochemical method [14], 20–28 nm using reverse micelles [15], 5–15 nm using microemulsions [16], and 45–50 nm with polyol method [17, 18]. Particularly, the wet or polyol method is relatively simpler than other methods and is effective in forming copper nanoparticles. Using the wet method, parameters such as particle size [19–22], shape [23, 24], and distribution [25–28] can be controlled relatively easily. In the wet method, the size of the reduced particles is mainly influenced by factors like the concentration of metal ions, pH, temperature, and reducing agent [1]. In previous

TABLE 1: Specifications of each solution with varying PGPPE concentrations.

	PGPPE ( $\times 10^{-3}$ mol of 50 mL)	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ( $\times 10^{-3}$ mol of 100 mL)	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ( $\times 10^{-3}$ mol of 50 mL)
1	6	0.3	1.5
2	8	0.3	1.5
3	10	0.3	1.5
4	12	0.3	1.5
5	14	0.3	1.5

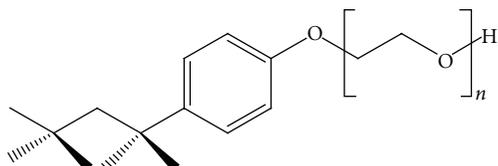


FIGURE 1: The molecular structure of PGPPE.

studies, the research team demonstrated that the aqueous electrical conductivity can be altered by the reducing agent and the concentration of metal ions in the solution, which can also influence the size of the nanoparticles [3]. One way to increase the copper particle size in solution by this means is to increase the copper ion concentration, causing reduced metal seeds to collide with one another and grow into larger metal nanoparticles. Surfactants may also be used to increase and/or decrease the aqueous electric conductivity and control the colloidal dispersion of the particles in solution and shape. However the use of surfactants decreases the electrical conductivity of the printed pattern and is expensive, making it necessary to minimize their use [29].

In this study, a new wet approach to synthesize copper metal particles is investigated. The particle size, shape, and distribution of the particles in this experiment were compared to two conventional mechanisms: the addition of copper ions and surfactant. The effect of surfactants was observed by changing the concentration of PGPPE. Lithium ions were selected to increase the aqueous conductivity and control the size of copper nanoparticles because they are not reduced easily and can be widely distributed between particles due to their small size. In addition, lithium ions can be absorbed by copper and form an amphoteric colloid which prevents collisions between particles. The relationship between particle size and aqueous electrical conductivity was obtained for the three approaches. PSA and TEM were used to analyze the particle size distribution after the addition of copper and lithium ions.

## 2. Experimental

**2.1. Variation of Aqueous Electrical Conductivity by a Change in the Concentration of Surfactant.** Electrical properties of the aqueous solution were altered by changing the concentration of surfactants to increase the size of the copper particles. In this study, PGPPE (polyethylene glycol p-(1,1,3,3,3-tetramethylbutyl)-phenyl ether structure shown in Figure 1) was used as the surfactant.

Five diluted solutions of 50 mL containing PGPPE of varying concentrations (Table 1) were prepared and tested for their electrical conductivities. Then, 100 mL solutions containing  $0.3 \times 10^{-3}$  mol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were added to each solution, and electrical conductivity was measured again. A diluted solution of 50 mL containing  $1.5 \times 10^{-3}$  mol of hydrazine was slowly added to each solution while stirring at 300 RPM for five minutes. The solution was allowed to stabilize for another five minutes after stirring.

**2.2. Variation of Aqueous Electrical Conductivity by a Change In the Concentration of Copper Ions.** The electrical properties of the aqueous solutions were varied using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  as the main reaction reagent to identify its consequential effects on the size, shape, and distribution of copper particles. Five 100 mL solutions with copper chloride concentrations ranging from  $0.1 \times 10^{-3}$  to  $3 \times 10^{-3}$  as displayed in Table 2 were prepared. Then, 50 mL  $10 \times 10^{-3}$  mol PGPPE solutions were then added into each copper chloride solution. The electrical conductivity of the solutions was then measured. 50 mL hydrazine solutions with concentrations ranging from  $0.5 \times 10^{-3}$  to  $15 \times 10^{-3}$  as displayed in Table 2 were prepared and slowly added to the copper chloride solutions while stirring at 300 RPM for five minutes. The solution was allowed to stabilize for another five minutes after stirring.

**2.3. Variation of Aqueous Electrical Conductivity by the Addition of Lithium Ions.** In this portion of the experiment, the concentration of copper chloride, PGPPE, and reducing agent was fixed while the concentration of lithium chloride was varied. Five 100 mL solutions containing  $0.3 \times 10^{-3}$  mol of copper chloride and varying lithium chloride concentrations as specified in Table 3 were prepared. Then, a 50 mL solution containing  $10 \times 10^{-3}$  mol of PGPPE was added to each copper chloride solution and the electrical conductivity was measured. Diluted solutions of 50 mL containing  $1.5 \times 10^{-3}$  mol of hydrazine were slowly added to the solution containing copper chloride and lithium chloride while stirring at 300 RPM for five minutes. The solution was allowed to stabilize after stirring for another five minutes.

The three experiments were conducted at room temperature,  $25^\circ\text{C}$ . TEM images of representative samples for each solution were taken. For each solution, a 1 mL sample of the solution was diluted 20 times and measurements of the particle size and distribution were taken using a particle size analyzer (PSA, Malvern, Nano ZS90).

TABLE 2: Specifications of each solution with varying copper chloride concentrations.

	PGPPE ( $\times 10^{-3}$ mol of 50 mL)	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ( $\times 10^{-3}$ mol of 100 mL)	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ( $\times 10^{-3}$ mol of 50 mL)
1	10	0.1	0.5
2	10	0.3	1.5
3	10	0.6	3
4	10	1.2	6
5	10	3	15

TABLE 3: Specifications of each solution with varying lithium ion concentrations.

	PGPPE ( $\times 10^{-3}$ mol of 50 mL)	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{LiCl}$ ( $\times 10^{-3}$ mol of 100 mL)		$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ( $\times 10^{-3}$ mol of 50 mL)
		$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{LiCl}$	
1	10	0.3	0.3	1.5
2	10	0.3	1.5	1.5
3	10	0.3	3	1.5
4	10	0.3	6	1.5

### 3. Results and Discussion

**3.1. Aqueous Electrical Conductivity as Function of the Concentration of Surfactant.** The electrical conductivity of the diluted solutions at various concentrations of PGPPE surfactant is shown in Figure 2. The aqueous electrical conductivity increased from 14 to 26 uS/cm as the concentration of surfactant increased. Figure 3 show the aqueous electrical conductivity and the average size of copper particles as function of surfactant concentration with a constant copper ion concentration. The aqueous electrical conductivity decreased 473 to 456 uS/cm by forming inverse micelles in aqueous solutions. PGPPE naturally forms a tangled, net-like structure in water, which inhibits the mobility of ions, and the average size of the copper particles from active ions increases from 159 nm to 173 nm. Surfactants offer the advantage of acting as emulsifiers and aid in the printing process, but the particle size does not increase significantly since the coalitions between copper particles were restricted by steric forces.

**3.2. Aqueous Electrical Conductivity as Function of the Concentration of Copper Ions.** Figure 4 shows the aqueous electrical conductivity and the average size of copper particles as function of copper ion concentration with a constant PGPPE concentration. The electric conductivity of the solution increased from 167 to 3905 uS/cm when the concentration of copper ion was increased. Adding copper ions increased the overall mobility of the solution and the coalition between particles, which aided the synthesis of large particles measuring approximately 300 nm.

**3.3. Aqueous Electrical Conductivity as Function of Addition of Lithium Ions.** Figure 5 shows the conductivity of the solutions and the sizes of the copper particles contained in solutions with lithium ions at various concentrations. The addition of lithium ions does not have a straightforward growing behavior as the addition of copper ions showed in experiment two. The electrical conductivity increased from 656 to 4080 uS/cm, and the copper particle sizes increased

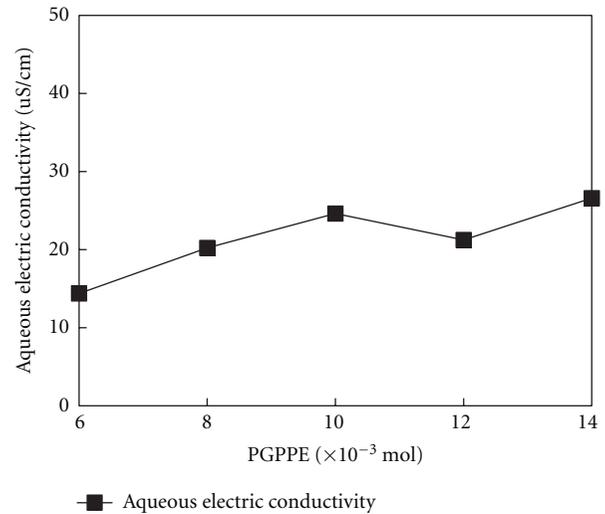


FIGURE 2: Aqueous electrical conductivity at different concentrations of surfactant without metal ions.

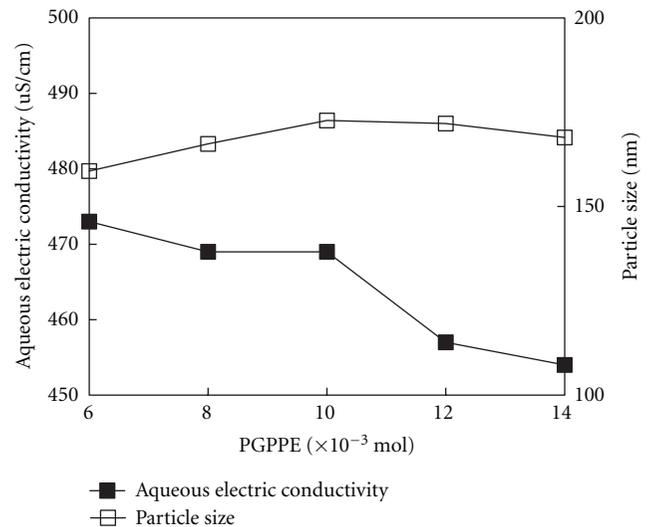


FIGURE 3: Aqueous electrical conductivity and average particle size of copper particles.

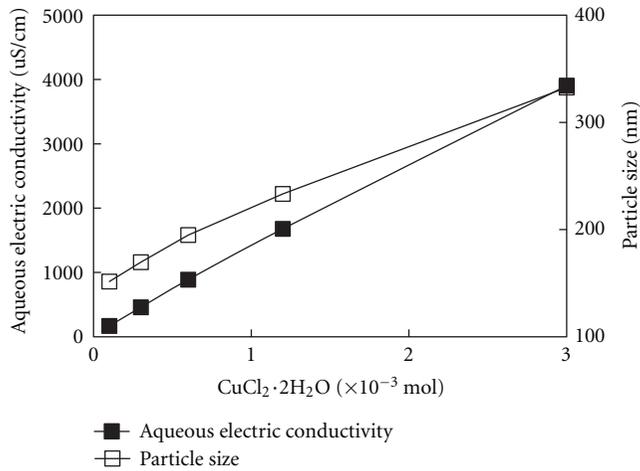


FIGURE 4: Aqueous electrical conductivity and average copper particle size at different copper ion concentrations.

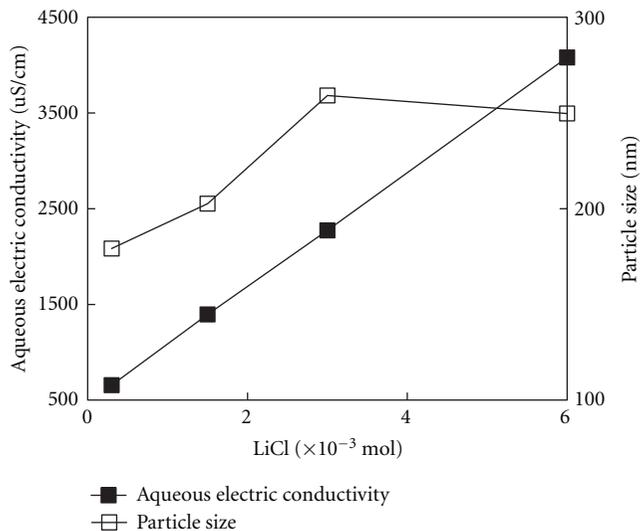


FIGURE 5: Aqueous electrical conductivity and average particle size at different lithium ion concentrations (copper ion concentration is held constant at  $0.3 \times 10^{-3}$  mol).

from 180 to 250 nm when the concentration of lithium ion was increased. Concentrations higher than  $3 \times 10^{-3}$  mol of lithium ions at constant of  $0.3 \times 10^{-3}$  mol of copper ions maintained size of the particles around 250 nm. Lithium ion in solution caused an increase in the copper particle size by increasing the activity of the solution, which as a result increased the frequency of the coalitions between particles. Once the copper ions were reduced, the copper particles attract the positively charged lithium ions which prevented coalition between particles by electrostatic repulsion. In this study a concentration of  $3 \times 10^{-3}$  mol lithium chloride is believed to be the point at which the copper particles start attracting the lithium ions. The electrostatic repulsion prevented the particles from colliding and forming clusters.

### 3.4. Comparison of Copper Ion Effect and Lithium Ion Effect in Particle Shape and Size Distribution.

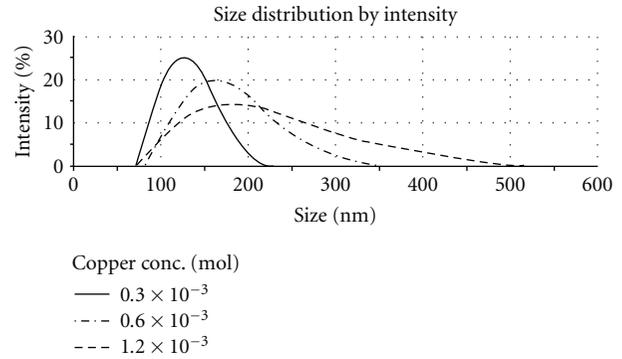


FIGURE 6: Particle size distributions at different copper ion concentrations.

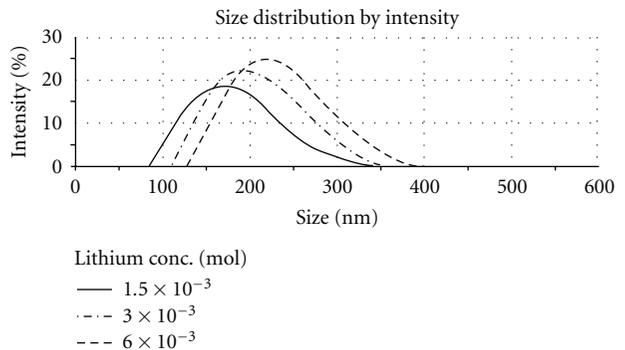


FIGURE 7: Particle size distributions at different lithium ion concentrations (copper ion concentration is held constant at  $0.3 \times 10^{-3}$  mol).

distribution and shape results of experiments 2 and 3 were compared using a PSA and TEM. Figure 6 shows the particle distribution at different copper concentrations while Figure 7 shows the particle distribution at different lithium concentrations. When the copper ion concentration increases without lithium ions, both the average particle size and particle size distribution increase significantly. Higher copper ion concentrations lead to less uniformly sized particles. However, when lithium ion concentrations increased at constant copper ion concentration ( $0.3 \times 10^{-3}$  mol), the average particle size increased but the particle distribution remained with narrow ranges. The addition of lithium ions to the solution increased the average particle size while maintaining a narrow particle size distribution, which is preferred for printing applications because wide distribution of particle size in nano inks can easily cause a clogging problem.

Figure 8 shows TEM images of the copper particle shapes at different copper ion concentrations while Figure 9 shows TEM images of particle shapes at different lithium ion concentrations. This study showed the effect of lithium ions on the synthesis of copper particles, where high concentrations of copper ion produced rough particle shapes. High concentration of copper ions caused copper particles to collide with one another and form larger clusters with rugged particle shapes, which can cause issues during

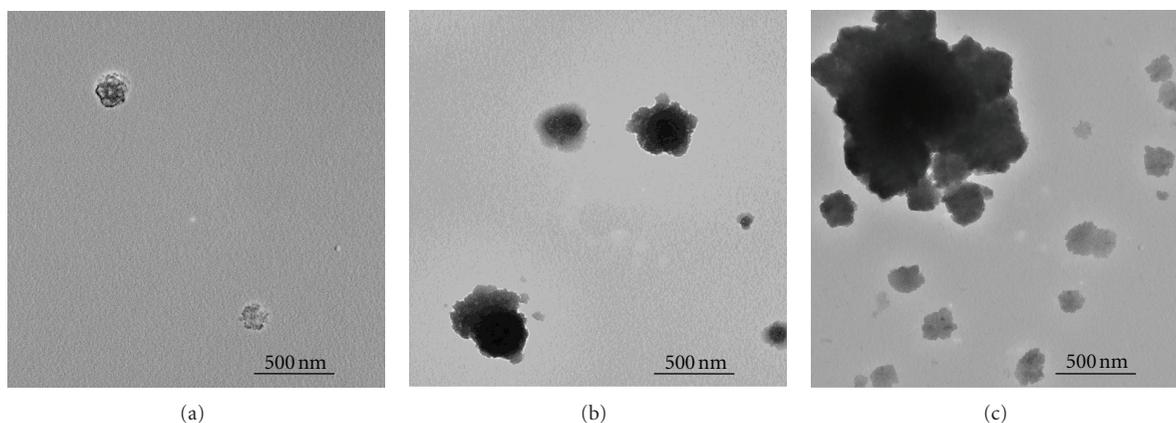


FIGURE 8: TEM images of copper particles at different copper ion concentrations (a):  $0.3 \times 10^{-3}$ , (b):  $0.6 \times 10^{-3}$ , (c):  $3.0 \times 10^{-3}$  mol of Cu ions).

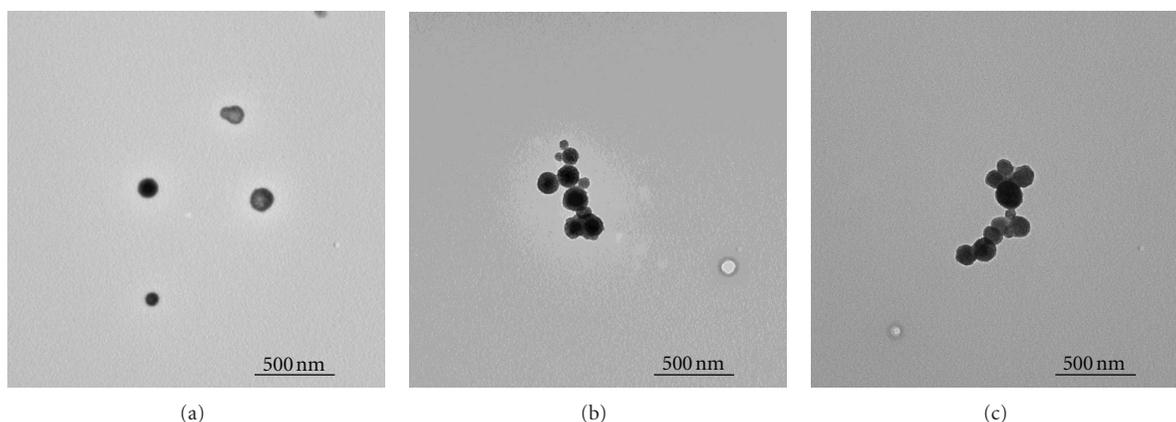


FIGURE 9: TEM images of copper particles at different lithium ion concentrations (a):  $1.0 \times 10^{-3}$ , (b):  $3.0 \times 10^{-3}$ , (c):  $6.0 \times 10^{-3}$  mol of Li ions, Cu ions conc.:  $0.3 \times 10^{-3}$  mol).

a printing process. The TEM images show that the addition of lithium ions is also a mechanism to control morphology, particle size, and size distribution of copper nanoparticles. As the copper was reduced, lithium ions were absorbed by the copper particles, forming a colloid in an aqueous phase. Each colloid particle had a positive charge, creating colloidal interparticle repulsion, which prevented the particles from abrupt growing. It is noted that narrowly distributed spherical copper particles in the range of 50 nm to 300 nm, preferable for printing processes, can be synthesized by the addition of lithium ions in the solution.

#### 4. Conclusion

In this study, the effects of surfactants, concentration of copper ions, and concentration of lithium ions on the size, shape, and size distribution of copper nanoparticles were investigated. Adding an optimized concentration of surfactant allows for the synthesis of nanoparticles while acting as a capping agent, but it can only increase the particle size up to 172 nm. An increase in the copper ion concentration is effective in increasing the size of particles. However, this increase results in a wide particle size

distribution, which made it difficult to synthesize particles with desired characteristics for metal inks to apply on direct printing technologies. Furthermore, at high copper ion concentrations, particles collide with one another, forming rugged clusters, which is a problem in the applications of nanoinks in printing applications. The addition of lithium ions can aid the formation of spherical copper particles, which aids packing factor and is favorable for printing processes. The capacity of lithium ions to maintain a narrow range of particles size distribution in 250 nm and spherical shapes makes it a suitable method to optimize copper particle parameters for printing applications.

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