

## Preparation of Cu Nanoparticles with a chemical reduction method

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### Abstract

In this research, Cu nanoparticles were prepared by chemical reduction method with  $\text{Na}_2\text{HPO}_4$  and  $\text{CuSO}_4$  in aqueous media using PVP and PVA as surfactant. Particle size and concentration of Cu nanoparticles were investigated by using scanning electron micrograph and energy dispersive X-ray microanalysis. The Results indicate that particle size and homogeneity of nanoparticles were dependent on the type and concentration of surfactant. Also, it was found that the range of particle size was between 7 - 58 nm. The surface analysis of the obtained product was determined by energy dispersive X-ray microanalysis (EDX), which has provided valuable information regarding the component's concentration of product, results were shown with one step filtration of solution, it was achieved 80 percent concentration of cu nanoparticle. In one case, SEM image reveals nanostructure of Cu particles with a cauliflower-like morphology. An individual cauliflower consists of several branches of width less than 100 nm and a length of few micrometers.

**Keywords:** Nanotechnology, nanoparticle, surfactant, morphology, particle size

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### Introduction

Over the past few years, considerable interest has been focused on metal nanoparticles due to their potential applications in diverse fields including catalysis, magnetic recording media, or microelectronics. Various methods are known which enable one to prepare these nanoparticles with controlled size and shape. These include metal vapour deposition, electrochemical reduction, radiolytic reduction, thermal decomposition, mechanical attrition and chemical reduction. Among these methods, the solution method is found to be simple and most versatile for metal nanoparticles [Schmit (1994); Suslick (1988); Livage et al (1998\_); Gates( 1995); Pileni (1997);Reetz et al (1994); Davis et al (1982) ].

Copper is one of the most widely used materials in the world. It has a great significance in all industries, particularly in the electrical sector due to low cost. Copper nanoparticles have been synthesized and

characterized by different methods. Stability and reactivity are the two important factors that impede the use and development of the metal cluster in a new generation of nano-electronic device. Different shapes and spherical copper nanoparticles can be synthesized by using reverse micelle as micro-reactor with protecting shells and dendrimer nano-reactors[Pileni et al(1998);Hulteen et al(1997)]. Also electrolytic techniques have been utilized to synthesize a variety of transition metal colloids (e.g. gold, silver, palladium, nickel and copper) of decahedral or isohedral shape by controlling the electrode potential [Lu et al 1997]. Chen and Sommers [Chen et al 2001] described that copper nanoparticles synthesized in one phase system with an alkanethiolate protecting monolayer. Gedanken et al. [Dhas et al 1998] reported that excellent surface resonance can be observed for copper nanoparticles when prepared by sonochemical method. In almost all of reports, it was observed that the copper nanoparticles contaminated with copper oxide. The high air-sensitivity of copper nanoparticles needs extremely careful and challenging approaches to avoid formation of its oxide in the end of product. In this research, synthesis of copper nanoparticles was studied by using chemical solution method. Carboxylic acids have been regularly used as surfactant for preparation of metal nanoparticles and also sodium citrate and myristic acid are excellent surfactant for preparation of silver nanoparticles [Charan et al( 2006); Khanna et al( 2007)]. Recently SFS used for preparation of silver and gold nanoparticles [Khanna et al( 2005a); Khanna et al( 2005b)] and in this work, poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) were used for synthesis of copper nanoparticles.

## **Materials and Method**

### **Instrumentation**

A magnetic mixer Model MK20, Digital scale Model FR200, scanning electron microscope (SEM) Model XL30 ,energy dispersive X-ray microanalysis (EDX) model and Centrifuge Model Z36HK were employed.

### **Reagents and Standard Solutions**

Material used in this work were copper sulfate  $\text{CuSO}_4$  (a= 99%), sodium hydroxide phosphate  $\text{Na}_2\text{HPO}_4$  (a=99%,  $M_w=140.96$ ), poly(vinyl pyrrolidone) (PVP,  $M_w=25,000$ ), poly (vinyl alcohol)( PVA , $M_w=72,000$ ). Distilled water was used through out this work.

### **Cu nanoparticles Prepration**

The reaction was carried out in aqueous media at room temperature for 10 min. The conditions for nanoparticles formation are summarized in Table (1).

In a typical experiment, 0.01 mol/L,  $\text{Na}_2\text{HPO}_4$  was added slowly to a stirred aqueous solution (50 mL) containing 30 mL of  $\text{CuSO}_4$  (0.005 mol/L) and 20 mL of one of surfactants for 10 min. The solution was settled for one day and in order to separate copper nanoparticles centrifuge was employed. The resultant product was dried at 40 °C.

### **Results and discussion**

The morphology of nanoparticles was studied by using scanning electron microscope. As shown in Figs. 1-5, the size and homogeneity of particles are dependent on the type of surfactant. This result is presumably due to the amounts of anionic and nonionic surfactant adsorbed on the particles. Surface active agents influence the physical and chemical properties of the solution. The type of surfactant is known to influence the particle size, size distribution, morphology, and homogeneity of particles

[Eisazadeh et al (1994) ; Aldissi (1993); Talaie et al (1994); Eisazadeh et al (1995); Chattopadhyay et al (2001)]. As can be seen in the micrographs, the nanoparticles obtained using various surfactants (PVA, PVP) exhibits spherical particles. It is apparent that using surfactant decreases the tendency to form agglomerates, due to surfactant is prevented from gross aggregation of the particles. The nanoparticles obtained in aqueous media by using PVP, homogeneity increased and small spherical particles were obtained (Fig. 5).

It is well established that the size, morphology and structure of particles are dependent on concentration of surfactant in aqueous media. As can be seen in Figs.1-4, the amount of surfactants was affect on the particle size and homogeneity of particles. Also by increasing surfactant concentration, particle size decreased and homogeneity increased. The effect of surfactants volume was investigated and results were shown in figs. 1,2. SEM image (Fig. 1) reveals Nano structure of Cu particles with a cauliflower-like morphology. An individual cauliflower consists of several branches of width less than 100 nm and a length of few micrometers. The work reported in (Thi My et al., 2011). showed that Cauliflower-like Cu exhibited a higher specific capacitance than other sample and also showed good reversibility.

The surface analysis of the obtained product was determined by energy dispersive X-ray microanalysis (EDX), which has provided valuable information regarding the component's concentration of product. As can be seen, in Figs .6 and 7, concentration of Cu just with one step filtration is more than 80 percent. It is apparent, by using more step filtration increases the concentration of Cu nanoparticles.

## **Conclusions**

In this work Cu nanoparticles produced by reaction between  $\text{Na}_2\text{HPO}_4$  and  $\text{CuSO}_4$  in aqueous media by using PVP and PVA as surfactant. It was found that, the type of surfactant has a considerable effect on the morphology, homogeneity and particle size of resultant product which is probably due to the adsorption of surfactant. The SEM micrographs show that the type of surface active agent plays a major role on the surface morphology of products. As shown in Figs. 8 and 9 concentration of Cu nanoparticles with one step filtration was more than 80 percent .

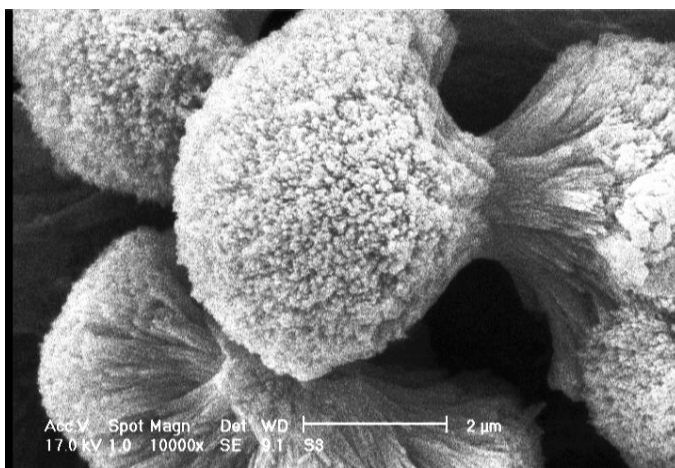


FIG. 1. Scanning electron micrograph of Cu nanoparticles formed in the presence of PVA as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01 \text{ mol/L}$ ,  $\text{CuSO}_4 = 0.005 \text{ mol/L}$ , PVA = 10 g/L, volume of solution = 50 mL, reaction time = 10 min at room temperature.

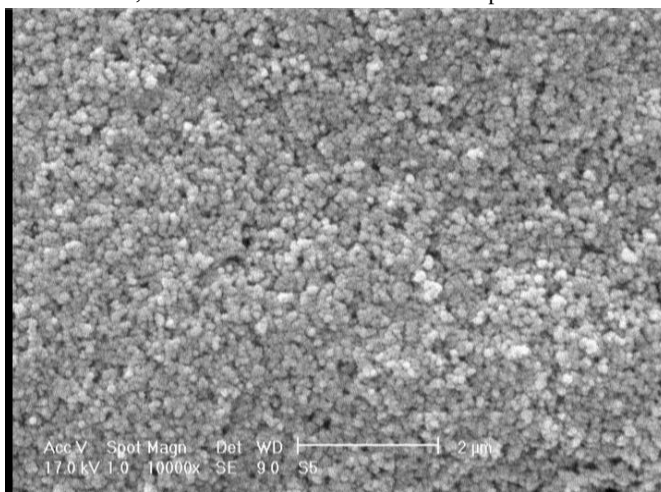


FIG. 2. Scanning electron micrograph of Cu nanoparticles formed in the presence of PVA as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01 \text{ mol/L}$ ,  $\text{CuSO}_4 = 0.005 \text{ mol/L}$ , PVA = 20 g/L, volume of solution = 50 mL, reaction time = 10 min at room temperature.

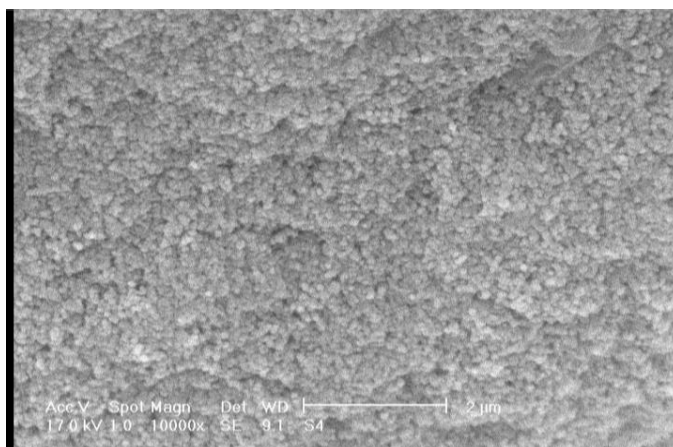


FIG. 3. Scanning electron micrograph of Cu nanoparticles formed in the presence of PVA as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01$  mol/L,  $\text{CuSO}_4 = 0.005$  mol/L, PVA = 30 g/L, volume of solution = 50 mL, reaction time = 10 min at room temperature.

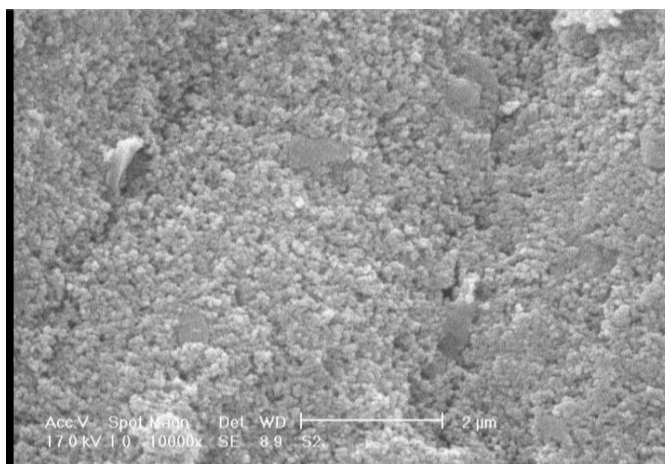


FIG. 4. Scanning electron micrograph of Cu nanoparticles formed in the presence of PVA as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01$  mol/L,  $\text{CuSO}_4 = 0.005$  mol/L, PVA = 40 g/L, volume of solution = 50 mL, reaction time = 10 min at room temperature.

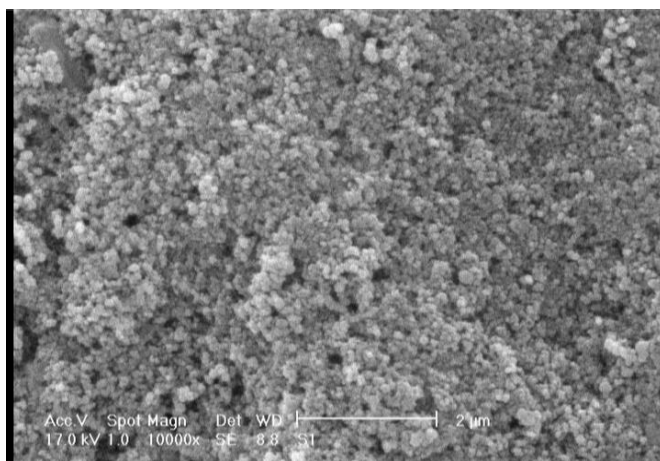


FIG. 5. Scanning electron micrograph of Cu nanoparticles formed in the presence of PVP as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01 \text{ mol/L}$ ,  $\text{CuSO}_4 = 0.005 \text{ mol/L}$ , PVP = 30 g/L, volume of solution = 50 mL, reaction time = 10 min at room temperature.

Table 1: Preparation conditions and type of surfactant on the sedimentation and particle size

| Type of surfactant       | Concentration of surfactant (g/L) | Volume of surfactant (mL) | volume of $\text{CuSO}_4$ = (0.05mol/L), (mL) | Sedimentation (mg/L) | Particle size range (nm) |
|--------------------------|-----------------------------------|---------------------------|-----------------------------------------------|----------------------|--------------------------|
| Poly (vinyl pyrrolidone) | 30                                | 20                        | 30                                            | —                    | 5-48                     |
| Poly (vinyl alcohol)     | 20                                | 10                        | 40                                            | Low                  | 10-58                    |
| Poly (vinyl alcohol)     | 20                                | 20                        | 30                                            | Low                  | 9-50                     |
| Poly (vinyl alcohol)     | 30                                | 20                        | 30                                            | —                    | 7-48                     |
| Poly (vinyl alcohol)     | 40                                | 20                        | 30                                            | —                    | 5-38                     |

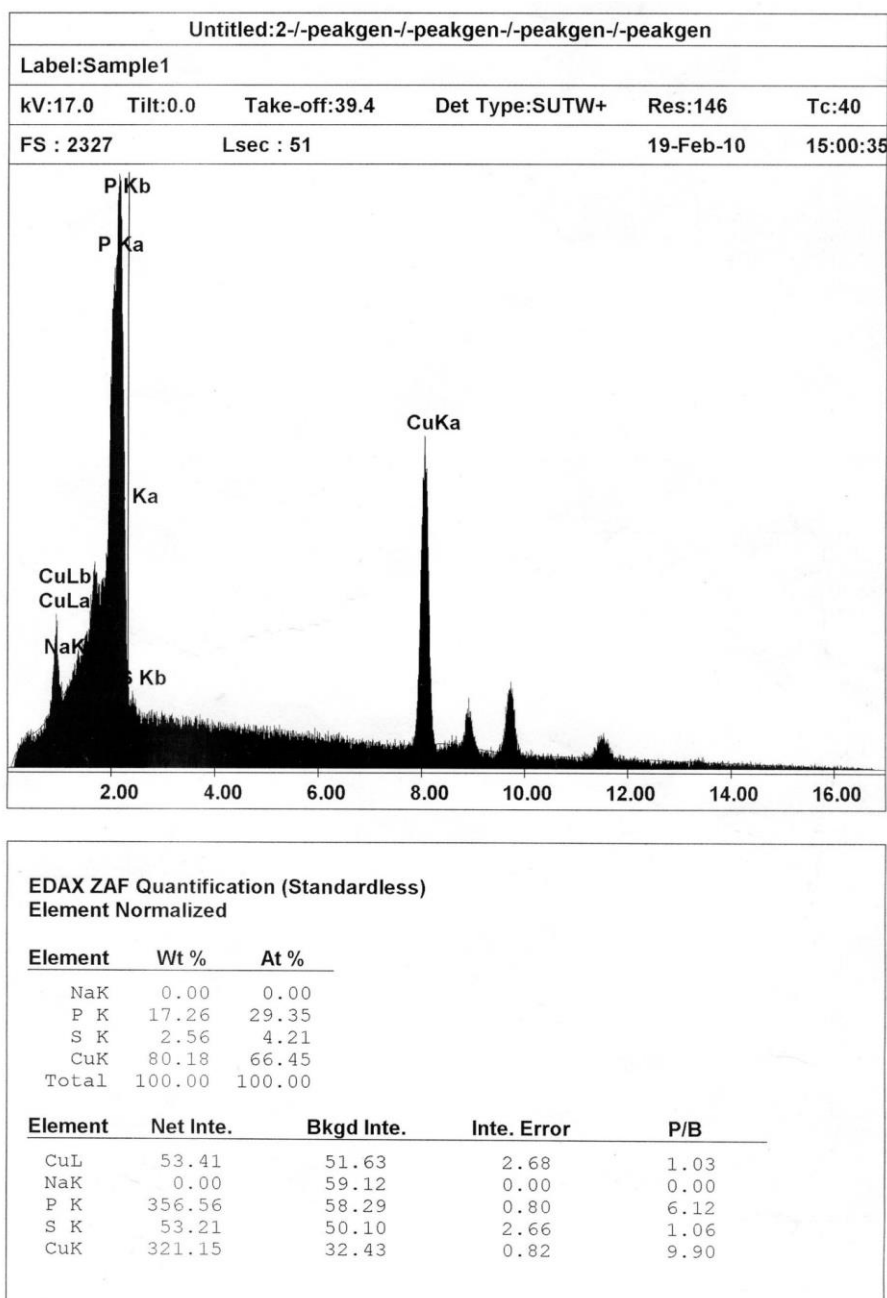


FIG. 6. Energy dispersive x-ray microanalysis (EDX) of Cu nanoparticles formed in the presence of PVA as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01 \text{ mol/L}$ ,  $\text{CuSO}_4 = 0.005 \text{ mol/L}$ ,  $\text{PVA} = 30 \text{ g/L}$ , volume of solution = 50 mL, reaction time = 10 min at room temperature.

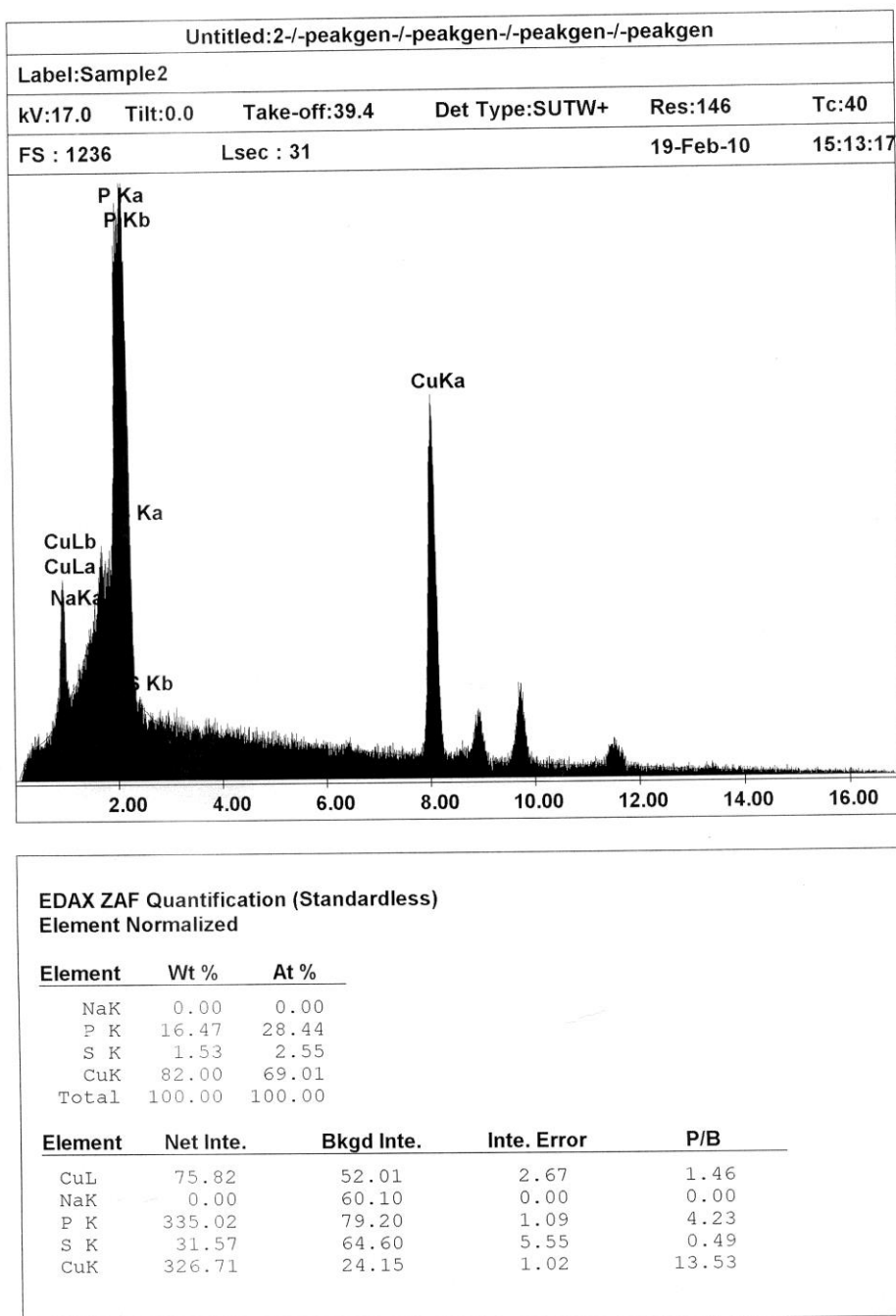


FIG. 7. Energy dispersive x-ray microanalysis (EDX) of Cu nanoparticles formed in the presence of PVP as surfactant in aqueous medium. Reaction conditions:  $\text{Na}_2\text{HPO}_4 = 0.01$  mol/L,  $\text{CuSO}_4 = 0.005$  mol/L, PVP = 30 g/L, volume of solution = 50 mL, reaction time = 10 min at room temperature.

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