

## **The Effect of Polyvinylpyrrolidone on the Formation of Copper Nanoplates in Wet-Chemical Reduction Method**

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### **ABSTRACT**

In this work, we report synthesis and characterization of copper nanoparticles in polymer matrix by wet-chemical reduction method using ascorbic acid as reducing agent, copper (II) sulfate as metal precursor and polyvinylpyrrolidone k-30 (PVP K-30) as surfactant agent. The reaction was carried out in a high-speed stirring mixture at room temperature under nitrogen atmosphere. Characterization of the samples was carried by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) analysis. The results indicated that, the molar ratio of precursor to surfactant plays a crucial role in the homogeneous growth of copper nanoparticles aggregates and the best condition for formation of homogeneous copper nanoparticles aggregates in polymer matrix was provided for a molar ratio of precursor to surfactant,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{PVP} = 70/1$  using ascorbic acid as reducing agent. The average particle size of zero valence Cu NPs calculated using Scherrer's formula was about 7.9 nm.

**Keyword:** Polyvinylpyrrolidone; Ascorbic acid; Copper nanoparticles; Wet chemistry method; Copper embedded in PVP matrix.

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### **1. INTRODUCTION**

The chemical and physical properties of metal nanoparticles differ from those of bulk metals because of surface or quantum size effects [1, 2]. They have been extensively investigated in the fields of catalysis [3-5], electronics [6, 7], magnetic devices [8, 9], photonics [10], optoelectronics [11], information storage [12, 13], biological labeling [14, 15], imaging [16], and sensing [17, 18].

Noting that, the intrinsic properties of metal nanoparticles are sensitive to their composition, size, shape, crystallinity and structure, many metals nanoparticles were successfully synthesized with controllable size. However, the challenge of shape-or-morphology-controlled synthesis of metal nanoparticles has been met with limited success. Therefore, intensive research motivation for

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shape-controlled synthesis of metal nanoparticles was undertaken based on the fact that in many cases it allows one to tune the properties with a greater versatility [19, 20]. Copper metal nanoparticles are mainly attractive due to their catalytic [21-23], optical, and electrical properties [24, 25]. While, due to the high reactivity of nanoparticles especially concerning oxidation, pure copper metal is not easy to synthesize. Since copper oxide forming at the surface of the metal particles change their structural properties. Thus, a protective coating has to be applied on the metallic particles to avoid oxidation [26]. Moreover, to stabilize the nanometric size of the nanoparticles, they have to be encapsulated by different organic or inorganic compounds [22, 24-31]. Herein, we report room temperature simple chemical reduction method for synthesis of copper nanoparticles using copper (II) sulfate as the metal precursor, ascorbic acid in an appropriate amount of NaOH as reducing agent and PVP as a surfactant.

## 2. EXPERIMENTAL

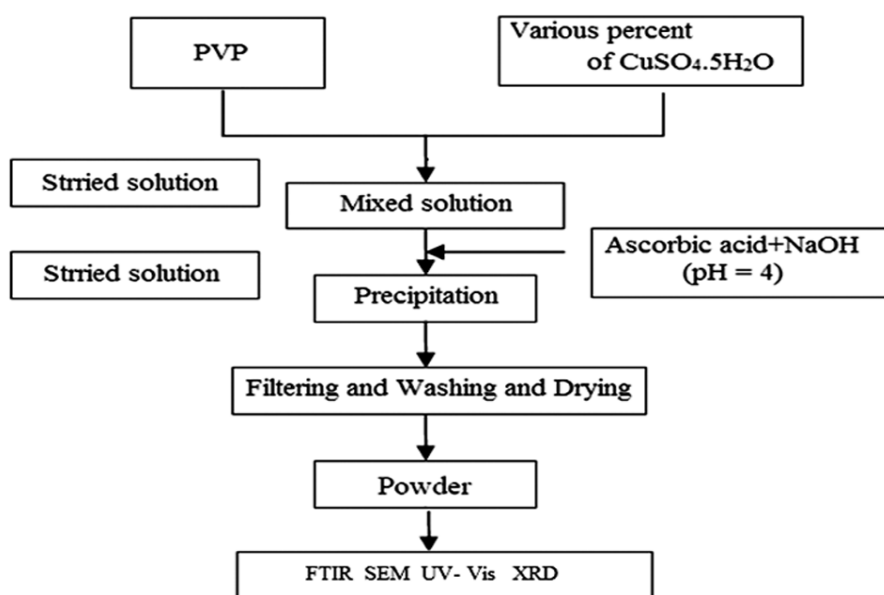
### 2.1. Materials

All chemicals were of analytical grade and

purchased and used without any further purification. Copper (II) sulfate pentahydrate salt ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) of 98% purity (Merck), was dissolved in deionized water. Polyvinylpyrrolidone K-30 (PVP-30) was purchased from TCI America. Ascorbic acid ( $\text{C}_6\text{H}_6\text{O}_6$ ) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich.

### 2.2. Method

The detail of three-step preparation procedure of copper nanoparticles (Scheme 1) started by dissolving polyvinylpyrrolidone (0.001 M) in deionized water continued by adding appropriate amounts of copper (II) sulfate (0.05, 0.07, 0.2 M) and adding ascorbic acid dissolved in acidic media is presented in Table 1. The mixtures obtained were then stirred vigorously under  $\text{N}_2$  atmosphere. In these steps, the solution color was changed from blue to white, yellow and to olive green finally. When the solution color did not change, the reaction was ceased and precipitated product was recovered and stored for future experiments. The powders obtained were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, Fourier transform IR spectra (FTIR) and UV-Visible spectrophotometry



**Scheme 1:** Experimental dispositive in preparation of copper nanoparticles.

**Table1:** Experimental parameters in preparation of copper nanoparticles.

Morphology	CuSO <sub>4</sub> .5H <sub>2</sub> O (MolL <sup>-1</sup> )	Ascorbic acid (MolL <sup>-1</sup> )	CuSO <sub>4</sub> .5H <sub>2</sub> O /surfactant (molar ratio)	Type of surfactant (MolL <sup>-1</sup> )	Sediment color
Spherical + rodlike, Figure 1	0.05	0.2	50/1	PVP-K30 0.001	Drack brown
Flower-like Figure 2	0.07	0.2	70/1	PVP-K30 0.001	Gray
Mixture of Spherical and hexagonal Figure 3	0.2	0.2	200/1	PVP-K30 0.001	Black

(UV-Vis) analysis. The X-ray powder diffraction (XRD) was recorded on a D 5000-siemens equipped with Cu K $\alpha$  radiation ( $\lambda= 1.541\text{\AA}$ ) using a 30 KV operation voltage and 40 mA current. Scanning electron microscopy (SEM) images were obtained using a LEO 1430VP microscope. Infrared (IR) spectra were measured on a Perkin Elmer RXI Fourier transform infrared (FTIR) spectrometer and the UV-Vis spectra were measured on Shimadzu UV-1601PC spectrophotometer.

### 3. RESULTS AND DISCUSSION

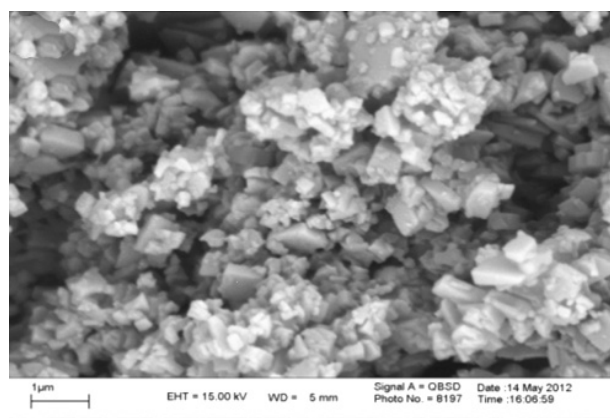
#### 3.1. SEM characterization

Figure 1 represents SEM image of copper nanoparticles prepared in a molar ratio of CuSO<sub>4</sub>.5H<sub>2</sub>O/PVP= 50/1 at the presence of ascorbic acid as reducing agent. This figure shows appearance of a mixed cubic and rod like morphology of the copper/PVP aggregates in CuSO<sub>4</sub>.5H<sub>2</sub>O/PVP molar ratio of 50/1. Figure 2 shows formation of a well homogeneous distribution of copper nanoparticles in flower like of copper nanoplates aggregates in a molar ratio of CuSO<sub>4</sub>.5H<sub>2</sub>O/surfactant= 70/1. Whereas, a mixed spherical and plates forms of copper nanoparticles

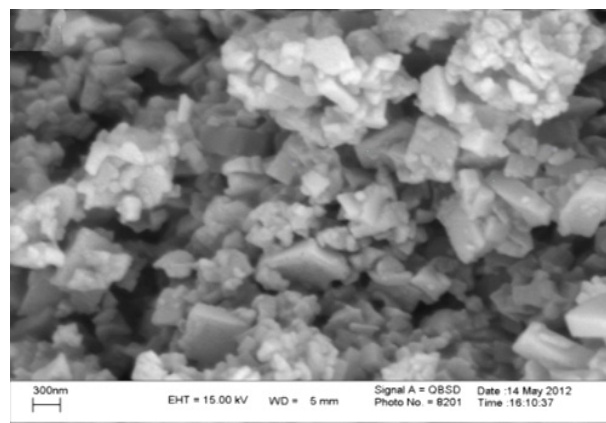
aggregates have been observed in a copper (II) sulfate/PVP molar ratio of 200/1 (Figure 3). These results is in contrast with the results published elsewhere that reveals a homogeneous distribution of Cu NPs agglomerates in nanocomposite films prepared with Cu NPs obtained from a Cu/PVP ratio of 7.2 and high Cu content by using SEM and X-ray energy dispersive spectroscopy of Cu-mapping [32].

#### 3.2. XRD characterization

Figure 4 (a, b, c) shows typical XRD patterns for aggregated copper nanoparticles prepared in different ratio of precursor to surfactant. The peaks observed at  $2\theta= 43.52^\circ, 50.8^\circ$  have been corresponded to the (111), (200) lattice planes and are well indexed to face-centered cubic crystals with JCPDS card No. 4-836. This finding shows that, the best condition for crystallization of copper nanoplates may be provided by using appropriate molar ratio of precursor to surfactant, CuSO<sub>4</sub>.5H<sub>2</sub>O/PVP at the presence of ascorbic acid as reducing agent. Interesting point observed in this case was increasing intensity of the diffraction peak (111) in comparison with other peaks which indicates the growth direction of copper nanoplates is mainly dominated by the crystal facet (111). This

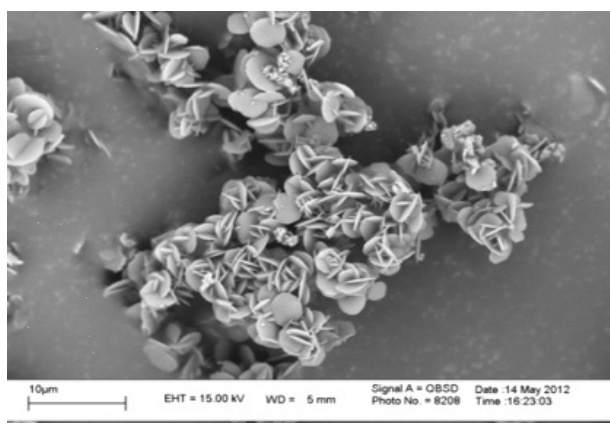


(a)

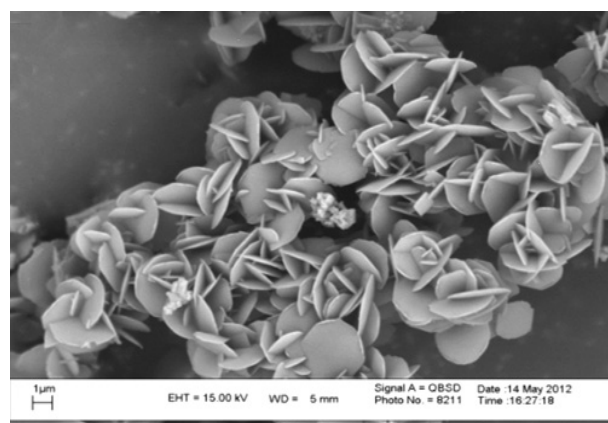


(b)

**Figure 1a, b:** Typical SEM images of copper nanoparticles aggregates prepared of copper sulfate/surfactant in a molar ratio of 50/1.

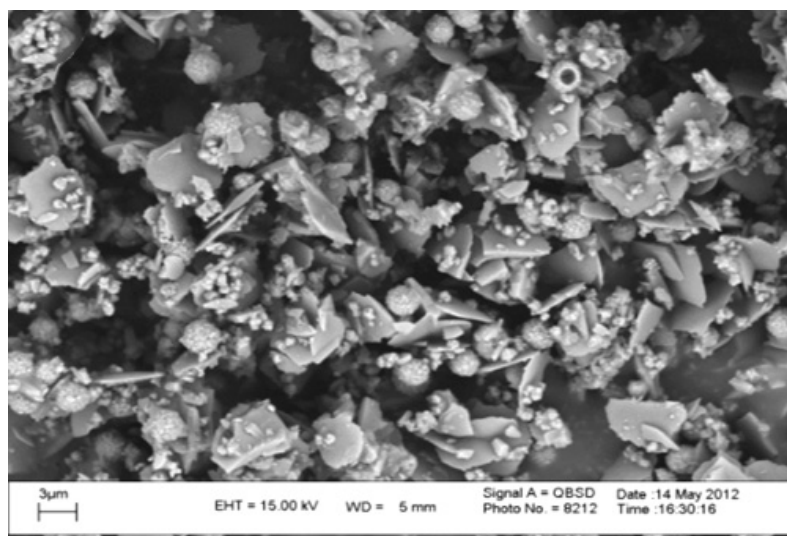


(a)



(b)

**Figure 2a, b:** Typical SEM images of homogenous distribution of copper nanoparticles aggregates prepared in a copper sulfate/PVP surfactant molar ratio= 70/1; 0.001 M.

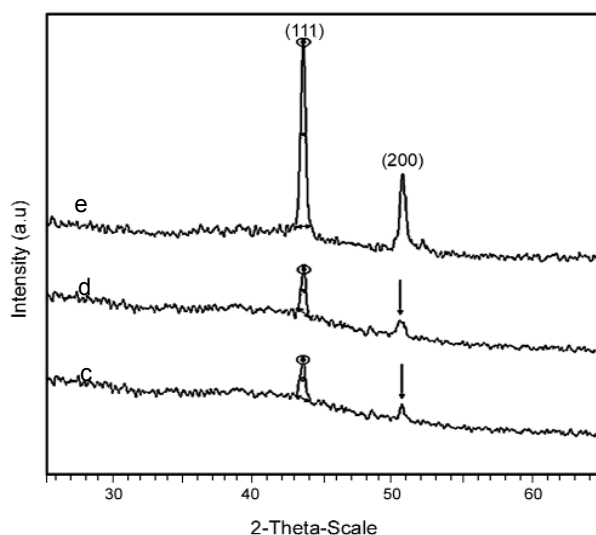


**Figure 3:** Typical SEM image of the copper nanoparticles aggregate prepared in a copper sulfate/surfactant molar ratio= 200/1.

phenomenon, as has been reported elsewhere [29, 30], can be related to the influence of PVP, as a surfactant on the morphology of the copper nanoparticle aggregates. Thus, the crystal growth direction is favorably oriented parallel to the (111) direction and the average particles size from the most intense peak estimated to be 7.9 nm for the sample with intense peak using Scherrer's formula:

$$D=0.9\lambda/\beta\cos\theta$$

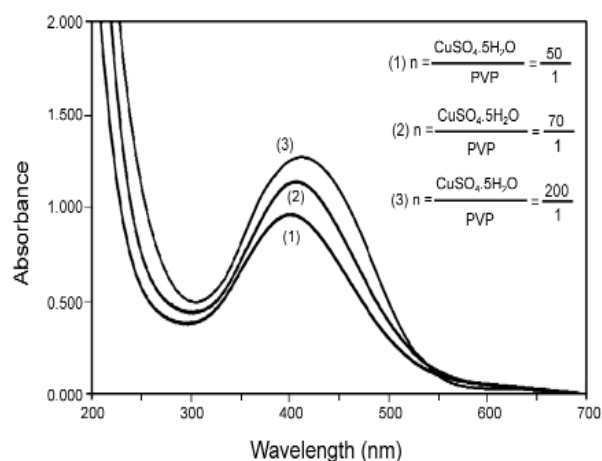
Where ' $\lambda$ ' is wave length of X-ray (0.1541 nm), ' $\beta$ ' is FWHM (full width at half maximum), ' $\theta$ ' is the diffraction angle and 'D' is particle diameter size.



**Figure 4:** XRD pattern of the prepared copper nanoparticles aggregates at a precursor to surfactant ratio of: a)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{PVP} = 50/1$ ; b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{PVP} = 70/1$ ; c)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{PVP} = 200/1$  in the presence of ascorbic acid as reducing agent.

### 3.3. UV-Vis characterization

Figure 5 represents UV-Visible spectra of copper nanoparticles suspensions of the copper/surfactant in a molar ratio of 50/1, 70/1 and 200/1. In these spectra, the strong absorption peaks observed at 400 nm, 406 nm, and 411 nm can be attributed to the oscillation of conduction band electrons of Cu, known as the surface surface plasmon resonance spectra of the copper conduction electrons band in the colloidal nanoparticles.



**Figure 5:** Spectra of copper nanoparticles with different molar ratio  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{PVP}$ .

## 4. CONCLUSIONS

In summary,

- ✓ The well-defined copper nanoparticles have been readily synthesized by wet chemistry method via reducing of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  by ascorbic acid in the presence of PVP-K30 as a surfactant in a  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{surfactant}$  molar ratio of 70/1.
- ✓ Ascorbic acid plays antioxidant role for colloidal copper, due to its ability to scavenge free radicals and reactive oxygen molecules
- ✓ Polyvinyl pyrrolidone works both as size controller and polymeric capping agent because it hinders the nuclei from aggregation through the polar groups, which strongly absorb the copper particles on the surface with coordination bonds
- ✓ The molar ratio of copper (II) sulfate/surfactant and the nature of surfactant can affect morphology and particle size of copper nanoparticles.

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